

TECHNICAL PROGRAMME

**FIRST CATALYSIS SOCIETY
MEETING**

JANUARY 17-20, 2007

**METU NORTHERN CYPRUS
CAMPUS**

**GUZELYURT, NORTHERN
CYPRUS**

JANUARY 17, 2007:

**15:30-20:30 REGISTRATION, CULTURAL
AND CONVENTION CENTER**

**18:00-20:30 WELCOMING RECEPTION,
CULTURAL AND CONVENTION CENTER**

JANUARY 18, 2007 :

8:30-9:10 OPENING REMARKS

9:10-10:10 KEYNOTE LECTURE

Catalytic Processes for Clean Hydrogen Production from Hydrocarbons

Z. İlsen Önsan

10:10-10:30 COFFEE BREAK

10:30-12:30 CATALYSTS AND CATALYSIS FOR FUEL CELL SYSTEMS

10:30 A Mechanistic Approach to Elucidate Ethanol Electro-oxidation

Niyazi Alper Tapan

10:50 Thermodynamic Analysis of Hydrogen Production in an LPG Processor

Mustafa Karakaya, Ahmet K. Avci and Z. İlsen Önsan.

11:10 Synthesis and Characterization of Pt Based Electrocatalysts by Supercritical Carbon Dioxide Deposition Method

Ayşe Bayrakçeken, Alevtina Smirnova, Usanee Kitkamthorn, Mark Aindow, Lemi Türker, İnci Eroğlu, Can Erkey.

11:30 Alkaline Doped Pd/SnO₂: Low temperature CO Oxidation Catalysts and Sensor Materials

Burcu Mirkelamoğlu, Gürkan Karakaş

11:50 Low Temperature CO Oxidation Kinetics over Activated Carbon Supported Pt-Sn Catalysts

Fatma Soyal, Berrin Gülyüz, A. Erhan Aksoylu, Z. İlsen Önsan

12:10 Partial Regeneration of Ni-based Catalysts for Hydrogen Production via Methane Cracking

Reyyan Koç, Ashraf M. Lotfi, Erdoğan Alper, Eric Croiset, Ali Elkamel.

12:30-13:30 LUNCH BREAK

13:30-15:30 TRANSITION METAL CATALYSTS

13:30 Co-MCM-41 Type Catalytic Materials via Impregnation and Microwave Assisted Synthesis Methods

Aslı Nalbant, Yuda Yürüm.

13:50 Single-step Direct Synthesis of Cobalt Incorporated Mesoporous Silica SBA-15

Aysen Yilmaz, Ebubekir Sen, Semih Seyyidoglu, and Jie Fan.

14:10 Determination of Reaction Mechanism and Rate Parameters for Selective CO Oxidation over Pt-Co-Ce/Al₂O₃ Catalyst

Goktuğ Özyönüm, A. Nilgün Akın, Ramazan Yıldırım.

14:30 Deactivation of coprecipitated Co/Al₂O₃ catalyst

Meltem Yıldız, A. Nilgün Akın.

14:50 A Density Functional Study of C-H Bond Activation of Ethane by Pure and Fe and Al Doped silica

Mehmet Ferdi Fellah, Isık Onal.

15:10 Acidic Mesoporous Sulfated Zirconia Structures for Methane Coupling via Bromination

Volkan Degirmenci, Özlen Ferruh Erdem, Aysen Yilmaz, Deniz Uner, Dieter Michel

15:30-15:50 COFFEE BREAK

15:50-17:50 PANEL (TURKISH)

Kataliz Derneği'nin Misyonu Ne Olmalıdır?

19:00-21:00 POSTER SESSION, RECEPTION HOSTED BY ENGELHARD BASF

JANUARY 19th 2007:

8:30-9:30 KEYNOTE LECTURE

Alcohols as Alternates to Petroleum for Environmentally Clean Fuels and Petrochemicals

Timur Doğu

9:30-10:10 INDUSTRIAL LECTURE

Petrochemical industry as the primary consumer of catalysts

Nilüfer Yalçın

10:10-10:30 COFFEE BREAK

10:30-12:30 CATALYSIS FOR THE ENVIRONMENT

10:30 Reactions of Unsaturated Aliphatic Ester on Sulfided Catalysts for the Production of Second Generation Biofuels

O.I. Senol, T.-R. Viljava, A.O. Krause

10:50 Investigation Of Biodiesel Production From Canola Oil By Using Mg–Al Hydrotalcite Catalyst

Oğuzhan İlgen, İsmail Dinçer, Ertan Alptekin, Nezahat Boz, Mustafa Çanakçı, A. Nilgün Akın

11:10 Citral Hydrogenation over Ni, Pt, Ni-Sn and Pt-Sn Supported on Zeolites and MCM-41

Hilal Aykac, Selahattin Yılmaz, Levent Artok.

11:30 Catalytic Combustion of Ethyl Acetate

Tuğba Gürmen Özçelik, Süheyda Atalay, Erden Alpay

11:50 Synthesis and Characterization of Mesoporous Titania for Photocatalytic Antibacterial Surfaces

Alp Yürüm, Beril Erdural, Ufuk Bakir, Gurkan Karakaş

12:10 Mixed Metal Oxide Sorbents and Catalysts for H₂S Removal and Selective Oxidation of H₂S

Sena Yaşyerli, Zeynep Özaydın, Gülşen Doğu

JANUARY 20th 2007:

8:30-9:30 KEYNOTE LECTURE

Transition Metal Based Catalysts for the Synthesis of Carbon Nanostructures

Ahu Gümrah Dumanlı, Yuda Yürüm.

9:30-10:10 INDUSTRIAL LECTURE

Catalysis in modern inorganic synthesis processes

Ercan Önür, AKKİM, Yalova

10:10-10:30 COFFEE BREAK

10:30-12:30 OIL, GAS AND PETROCHEMICALS

10:30 A Novel Process for 2-Naphtol and Acetone Production

Tunçer H. Özdamar, Fatma Gül Boyacı, Güzide Çalık

10:50 Factors affecting catalyst activity in HDPE plant

Gediz Korkmaz

11:10 Catalytic Decarboxylation of Lignites

Ahu Gümrah Dumanlı, Yuda Yürüm

11:30 n-Butene Isomerisation over HZSM-5 and HZSM-22

Korhan Demirhan, Selahattin Yılmaz, Levent Artok

11:50 Use of Zeolite Catalysts in Petrochemical Industry

Özge Güvenir

12:10 Ziegler-Natta Catalysts in Slurry-Phase PP Production

A. Erdem Aygök

12:30-13:30 LUNCH BREAK

13:30-15:30 FUTURE TRENDS

13:30 Investigation of Bioprocess Parameters for Glucose Isomerase Production by *Bacillus Thermoantarcticus*

Işık Haykır, Pınar Çalık, İsmail Hakkı Boyacı

13:50 Propylene Epoxidation on Ag (111) surface: A Density Functional and ONIOM Study

Isik Onal, M.Ferdi Fellah, Evren Turkmenoglu.

14:10 Direct formation of H₂O₂ from H₂ and O₂

Meltem Yıldız, Ayse Nilgün Akın

14:30 Catalytic Wet Air Oxidation of Aniline by Nano-Structured CeO₂-supported Metal Oxide Catalyst

Gülin Aytimur, Süheyda Atalay

14:50 Palladium Loaded NaY Zeolite: A Highly Active Catalyst for Suzuki-Miyaura Reactions of Aryl Halides Under Aerobic Conditions.

Levent Artok, Gülay Durgun, Özge Aksın

15:10 Understanding Catalysis via Model Catalyst Design at the Molecular Level

Emrah Özensoy

15:40-16:00 COFFEE BREAK

16:00-17:40 GENERAL COUNCIL MEETING OF THE TURKISH CATALYSIS SOCIETY

17:40-18:00 CLOSING REMARKS

POSTERS

CATALYST PREPARATION

C-1 Palladium incorporated silicate structured mesoporous catalysts for ethanol reforming

Canan Sener, Timur Dogu, Gulsen Dogu

C-2 Acidity Characterization of Pb/SBA-15 Mesoporous Catalysts

Deniz Uner, Mehmet Akcay, Ozge Guner

C-3 Catalytic Degradation of Polypropylene with a Mesoporous Aluminosilicate Catalyst

Zeynep Obalı, Naime Aslı Sezgi, d Timur Doğu

C-4 Dielectric Behavior of the Catalysts Na-Zeolite Y

Ertugrul Izci, Alime Izci

C-5 Theoretical and Experimental Studies on CO Oxidation Over Pt-Pd Bimetallic Catalysts

E. Erunal, S. Kaya, R. Shaltaf, S. Ellialtioglu,

Deniz Uner.

C-6 Kinetics of Synthesis of Isobutyl Propionate Over Amberlyst 15

Alime Çıtak and Halit L. Hoşgün

C-7 TiO₂ Based Catalyst Preparation and Characterization for Photocatalytic C-C Bond Formation

Osman Karslioglu, Deniz Uner

C-8 Oxidation of Benzene to Maleic Anhydride in a Fixed Bed Reactor

Canan Uraz, Süheyda Atalay

C-9 Comparison of different heterogeneous catalysts in the esterification of butanol with acetic acid

Emine Sert, Ferhan S. Atalay

C-10 Characterization and activity studies of Co based catalysts

Çiğdem Güldür, Filiz Balıkçı

FUTURE TRENDS

F-1 Immobilized Lipase-Catalysed Resolution of (R,S) 1-Phenyl 1-Propanol in Packed Bed Reactor

Pınar Bakış, Emine Bayraktar, Ülkü Mehmetoğlu

ENVIRONMENTAL CATALYSIS

E-1 Morphological Characterization of Catalytic Soot Oxidation Foam Filter

Deniz Uner, Basar Caglar

E-2 TiO₂ Loaded Ordered Mesoporous SBA-15 Structures for CO₂ Reduction Reactions

Orçun Ergün, Aysen Yilmaz, Deniz Uner

E-3 Microcalorimetric Studies to Investigate the Effect of Sn Addition to Elucidate CO Poisoning on γ -Al₂O₃ Supported Pt-based Direct Ethanol Fuel Cell Catalysts

Hilal Demir, Deniz Uner

E-4 Determination of Optimum Conditions and the Kinetics of the Methanol Oxidation

A. Hilal Ulukardeşler, Süheyda Atalay, Ferhan S. Atalay.

OIL GAS AND PETROCHEMICALS

O-1 Ethanol Dehydration Over Solid Acid Catalysts Silicotungstic Acid, Tungstophosphoric Acid, Molybdophosphoric Acid and Nafion

Dilek, Varisli, Timur Doğu, Gülben Doğu

O-2 Thermodynamics of catalytic coal gasification of mixed metal oxides

A. Kanca, D. Uner

O-3 Modeling Homogeneous Partial Oxidation of Methane

Mukaddes, Can, Ayben, Yilmaz, Deniz Üner

O-4 Kinetics of Gas/Liquid Phase Synthesis of Octane Enhancing Additives on Acidic Resin Catalysts

N.Oktar, T.Doğu, G. Doğu, K. Murtezaoglu

ABSTRACTS

CATALYST PREPARATION

Co-MCM-41 Type Catalytic Materials via Impregnation and Microwave Assisted Synthesis Methods

Aslı Nalbant and Yuda Yürüm

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MCM-41 type catalytic materials with their hexagonal arrangement of unidimensional pores and large surface areas (greater than 1000 m² g⁻¹) fascinate the designers of new selective heterogeneous catalysts in the production of fine chemicals on large scale. Cobalt incorporated MCM-41 catalysts are attractive alternates which can be used in single wall carbon nanotube synthesis, oxidation of saturated and unsaturated hydrocarbons. Microwave assisted synthesis of mesoporous molecular sieves is a promising method due to several advantages over the conventional hydrothermal method. The advantages of microwave-induced heating include homogeneous heating throughout a reaction vessel, resulting in more homogeneous nucleation and shorter crystallization times. In this presentation, two different methods were compared. In the first method, MCM-41 type catalytic materials were synthesized with microwave radiation and then Co was impregnated into this material using different Si/Co ratios as 25, 50, 75 and 100. In the second method Co was added into the raw materials and then the mixture was treated in the microwave oven using different Si/Co ratios as 25, 50, 75 and 100. The products obtained were characterized by XRD, N₂ physisorption, SEM, EDS. The incorporation of metals into MCM-41 structure synthesized with microwave-induced heating and impregnation methods were compared. It is important to note that the synthesis of mesoporous material by microwave-induced heating reduced the synthesis time from days to hours. The products will be used as catalytic materials in the production of SWCT formation.

oral

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Transition Metal Based Catalysts for the Synthesis of Carbon Nanostructures

Ahu Gümrah, Dumanliand Yuda Yürüm

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Carbon nanofibers (CNFs) and carbon nanotubes (CNTs) with their interesting structural, chemical, electronic and mechanical properties attracted the attention of many researchers all over the world. One of the methods that has been employed for CNF and CNT production is chemical vapor deposition (CVD). CVD is preferred due to its scalability and its potential low cost, as well as the structural perfection of the product. The most important factor in CVD is the control of the properties of metal catalyst. Our aim was to understand the structural and chemical effect of the catalyst on CVD process. Thus organometallic and oxide forms of Fe, Co, Ni, Cu and Zn were synthesized by different methods and the performance of these catalysts during the catalytic growth of carbon nanofiber and nanotubes was determined. The microstructure, surface properties, and thermal stability of the catalysts were investigated in order to relate these to the properties of the final carbon structure.

oral

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A density functional study of C-H bond activation of ethane by pure and Fe and Al doped silica

Mehmet Ferdi FELLAH and Isik ONAL

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C-H bond activation of light alkanes such as methane and ethane are very important step for partial oxidation reactions. Many papers on C-H bond activation methane and ethane have been published experimentally. Several steps of the dehydrogenation reaction of ethane by zeolite were studied by several authors using theoretical methods. Molecular dynamics simulation techniques have been used to study diffusion of the alkanes through the zeolite HZMS-5 framework. It was also used to determine the preferred adsorption sites of the alkanes in silicalite and HZMS-5. The mechanism of the reactions at the zeolite's acid site was investigated at the DFT (B3LYP) level of calculation using 6-31G** and 6-311G** basis sets (Furtado et.al(2001)). Density functional theory is used to determine transition states and the corresponding energy barriers of the reactions related to C-H bond activation of hydrogen exchange and dehydrogenation of ethane catalyzed by a protonated zeolite and the effects of cluster size and acidity on the reaction activation barriers were investigated by Blaszkowski et.al(1996). Ab initio methods were used to study the transition state structures and activation energies of ethane cracking, hydrogen exchange, and dehydrogenation reactions catalyzed by a zeolite model cluster Zheng et. al.(2005). In this study pure SiO₂ (low quartz) surface was modeled by a Si₂O₆H₄ cluster and Fe and Al were isomorphously substituted. All of the cluster atoms except for the active site and reactant and product molecules were kept fixed. The dangling orbitals of the oxygen atoms were saturated with H atoms. C-H bond activation was studied by means of density functional theory (DFT) calculations as implemented in SPARTAN (2002) at B3LYP level using 6-31G** as basis set. Transition state calculations were in general performed for determination of activation barriers. Relative energy profile which gives activation barrier was determined for pure and Fe and Al doped silica clusters by using coordinate driving calculation. The transition state activation barrier calculated for Fe doped cluster was found to be 37.6 kcal/mole. Approximate transition state activation barriers obtained were 66.1 and 84.1 kcal/mole for Al doped and pure silica clusters. The favorable effects of Fe and Al substitution on silica surface have been demonstrated theoretically for C-H bond activation of ethane. Activation barrier decreases with substitution of Fe and Al on silica surface. Activation barrier is substantially decreased from the approximate transition state value of 84.1 kcal/mole for pure silica cluster to 37.6 kcal/mole obtained for the transition state of Fe substituted silica. Fe substitution on silica surface has beneficial effect for C-H bond activation barrier of ethane.

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Kinetics of synthesis of isobutyl propionate over amberlyst 15

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The esterification of propionic acid with isobutanol in the presence of Amberlyst 15 as a catalyst was studied. Isobutyl propionate which synthesised in this reaction has fragrance of rum and is used in food industry. The experiments were carried out in a stirred batch reactor at temperatures from 318 K to 348 K. 1,4 dioxan was used as a solvent. The effects of amount of catalyst used, the reaction time, the stirring speed and the reaction temperature on the synthesis of isobutyl propionate were investigated.

It is observed that solid-liquid external mass transfer resistance was absence as a result of various stirring speed. It was also found that the reaction depended on temperature. Hence, a pseudo homogeneous model from experimental data for Amberlyst-15 was developed. The activation energy and equilibrium constant of this reaction were calculated to be 49.3 kJ/mol and 5.19, respectively. The expression of reaction rate as a function of temperature was determined for synthesis of isobutyl propionate.

poster

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Single-step Direct Synthesis of Cobalt Incorporated Mesoporous Silica SBA-15

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Highly ordered cobalt incorporated mesoporous silica SBA-15 (CoSBA-15) has been synthesized by single-step direct synthesis method. The degree of cobalt incorporation into mesoporous silica can be easily controlled by adjusting of Si/Co molar ratio in precursor solution. The mesoporous CoSBA-15 samples were characterized by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ sorption and infrared spectroscopy (FT-IR). The effect of cobalt salt adding sequence with respect to addition of triblock copolymers and siliceous sources was firstly investigated in this study. It is found that cobalt incorporation degree is highly dependent on the adding sequence of cobalt salt. Adding cobalt salt prior to addition of siliceous sources facilitate the incorporation of cobalt into SBA-15 materials. Inductively coupling plasma with optical emission spectroscopy (ICP-OES) elemental analyses proved that the maximum amount of Co in silica is 4.62% by weight obtained by adding CoCl₂ prior to adding of TEOS when Si/Co mol ratio of synthesis precursor solution is 1.5. When addition of Cobalt salt is after adding of TEOS, the maximum Cobalt loading amount is . It was found that most Co ions exist as isolated framework species when Si/Co > 5.

oral

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Theoretical and Experimental Studies on CO Oxidation Over Pt-Pd Bimetallic Catalysts

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Monte Carlo simulations for precious bimetallic catalysts [1-3] and Pd-Pt were performed as a function of cluster size and temperature in vacuo systems. Pd-Pt clusters bulk and surface compositions were predicted in a temperature range between 373 and 523 K with different atomic ratios and cluster sizes in order to compare the theoretical results with the experiments. The predictions indicated that Pd atoms segregated to the surface: at low Pd levels, Pd occupied preferentially 6 and 7 coordinated defect like sites. As the Pd concentration increased, first 8 coordinated (100) and then 9 coordinated (111) planes were populated. The experiments were based on CO oxidation reaction over γ -Al₂O₃ supported monometallic and bimetallic palladium-platinum catalysts at Pd:Pt atomic ratios: 1:3, 1:1, 3:1 was experimentally studied as well. The catalyst performance tests were done using a synthetic gas mixture consisting of CO, O₂, and N₂ in the temperature range 373 and 523 K. The results of Monte Carlo studies and reaction tests together were interpreted as CO oxidation primarily taking place at the defect like sites.

References:

1. Donnelly R.G., King T.S, Surf. Sci. 74, 89-108 (1978)
2. Strohl, J.K., King, T.S., J Catal 118 (1), 53-67 (1989)
3. Strohl, J.K., King, T.S., J Catal 116 (2), 540-555 (1989)

poster

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Determination of Reaction Mechanism and Rate Parameters for Selective CO Oxidation over Pt-Co-Ce/Al₂O₃ Catalyst

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Reaction mechanism and rate parameters for low temperature CO oxidation was studied in hydrogen-rich streams using a 1.4 wt% Pt-1.25 wt%Co-1.25 wt%Ce/Al₂O₃ catalyst prepared by incipient-to-wetness impregnation. Intrinsic kinetic data were obtained using a microflow reactors operating in differential mode by changing the CO and O₂ concentrations in feed and measuring the initial rates in 60 percent H₂ and He as balance. The experiments were carried out at 110 °C, both in the absence and the presence of 25 percent CO₂ and 10 percent H₂O.

The plausible elementary reactions constituting the CO oxidation mechanism were determined and various alternative reaction paths based on those elementary reactions were constructed. The mechanisms comprise of the single site monofunctional paths proceeding on the platinum sites, and dual site bifunctional paths proceeding on the platinum sites and the cobalt-ceria sites. The cobalt and the ceria sites were assumed to be the same for simplicity. H₂, CO₂ and H₂O in the feed stream were also not included in the reaction mechanisms, as their effect on the reaction rates were assumed to be through the rate parameters, but not through the mechanism.

Model equations were derived for each reaction paths using appropriate assumptions about the rate determining steps, the equilibrium and the surface coverage, and the experimental data were fitted using Levenberg-Marquardt regression scheme. The model discrimination was performed by the positive sign of kinetic parameters and fitness of regression. Three reaction paths (one monofunctional, and two bifunctional) were found to be plausible and no further discrimination was possible.

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Dielectric behavior of the catalysts Na- zeolite Y

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Alime Izci; Eskisehir Osmangazi University, Department of Chemical Engineering, Eskisehir, Turkey.

Zeolites are crystalline hydrated aluminosilicates of alkaline metals alkaline earth metals. The basic of zeolite structure is anionic frame of Si and Al T-atoms, which are tetrahedral, coordinated with oxygen atoms. The electrical properties of zeolites reveal enormous technical importance due to their manifold applications as solid catalysts. Zeolite Y was used this investigation. Zeolite Y is a synthetic zeolites and it exhibits the faujasite structure. The electrical conductivity and dielectric permittivity and loss factor of Na ion exchanged Zeolite Y was carried out in the 100 Hz – 1 MHz frequency region at room temperatures and different water contents by using HP4192A LF Impedance Analyzer. The results of this investigation were explained and given to be used for further studies in the some catalysis studies.

poster

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Alcohols as alternates to petroleum for environmentally clean fuels and petrochemicals

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Transportation and industry utilize about 57 % and 20 % of world total oil consumption, respectively. Fast increase of oil consumption in recent decades caused significant reduction in proven oil reserves, reaching to a reserve to production ratio value of about 40 years. Hydrocarbons produced from petroleum are essential for many products used in modern life. Also, new alternates are needed as motor vehicle fuels. Methanol and ethanol have very high potential to be used as fuels, as feedstock to produce number of petrochemicals and also to produce new transportation fuel alternates. Both of these alcohols have good burning characteristics and very high octane numbers. Dimethyl ether and diethyl ether, which can be produced by dehydration of methanol or ethanol over acidic catalysts have highly attractive properties to be used as alternates to diesel fuel and as fuel additives. Methanol and ethanol based tertiary ethers, such as MTBE, ETBE, TAME and TAEE are known to have highly attractive burning characteristics to be used as fuel additives for environmentally benign gasoline. Recent studies on selective oxidation and dehydration of ethanol over V and Mo based mesoporous catalysts showed very high ethylene yields, indicating the possibility of producing many petrochemicals from a non-petroleum feedstock, namely bio-ethanol. Acetaldehyde, diethyl ether, diethyl acetal etc. are some of the other products which can be produced by selective oxidation of ethanol. Steam reforming of ethanol over Pd, Ni and Cu based mesoporous catalysts is an attractive alternate to produce hydrogen, which can be used in fuel cells. Methanol is also one of the most important feedstocks for the chemical industry to produce different chemicals including formaldehyde, various polymers, paints etc. Considering the storage and clean production problems of hydrogen, significant research was devoted to direct methanol fuel cells as an alternate to be used in transportation. Another major advantage of methanol as a fuel alternate is the possibility of production of this alcohol starting from carbon dioxide, which is the main contributor to climate change due to green-house effect. Carbon dioxide is the cheapest carbon source and production of hydrocarbons starting from it is a major challenge in catalysis. Synthesis of methanol starting from CO₂ will complete a cycle in fuel synthesis and its use. All these processes for the production of different chemicals from alcohols and synthesis of these alcohols involve catalysis. Development of novel catalysts and environmentally clean new catalytic processes are some of the major issues on which significant research is in progress today. In this presentation a review of catalytic applications based on these alcohols will be reported.

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Catalytic degradation of polypropylene with a mesoporous aluminosilicate catalyst

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The amount of plastic wastes in the world has been increasing rapidly and the disposal of municipal and industrial plastic wastes has been becoming a major environmental problem in recent years. Landfilling, incineration and recycling are some of the disposal methods to utilize these wastes. Some drawbacks of the first two methods are the limitations in availability and cost of suitable and safe depots and the production of pollutants like light hydrocarbons, nitrous and sulphur oxides, and other toxins during incineration. Recycling of these waste polymers by chemical recovery is supposed to be an attractive approach to the solution of pollution problem caused by these wastes [1]. In this method, the waste plastics are thermally non-catalytically or catalytically degraded into gas and liquid products which can be utilized as fuels or valuable chemicals for petrochemical industry. Major advantages of the catalytic thermal degradation over the non-catalytic process are lower operating temperatures and higher yields of valuable chemicals. The most commonly used catalysts are zeolites (HZSM-5, HY, etc.), amorphous SiO₂-Al₂O₃ and in recent years, mesoporous aluminosilicate catalysts started to be used.

Zeolites are classified in microporous materials and reactions with bulky molecules not being handled due to pore size limitations is one important disadvantage that limits their applications. To overcome this situation, a continuous research was done to develop materials with constantly larger pores. Finally these researches led to the development of mesoporous materials and these materials are mainly made up of SiO₂ and have high surface areas and narrow pore size distributions, but to increase their acidity and catalytic activity in certain reactions such as polymer degradation, aluminum is incorporated within the silica framework.

In this study, several aluminosilicate catalysts from different aluminum sources, using different Al/Si ratios were synthesized in order to be tested in catalytic degradation of polypropylene. Tetraethyl orthosilicate (TEOS) was the silica source. These catalysts were synthesized by using hydrothermal synthesis route following a similar procedure described in our previous studies [2,3]. It was observed that these materials had high surface areas and exhibited isotherms of type IV but they gave poorer quality of XRD indicating a distortion of the long range ordering of the mesoporous structure and/or badly built hexagonal arrays. This is perhaps the result of the incorporation of aluminum into the silicate walls, causing structural irregularity. EDS results showed that the aluminum incorporated more effectively into the structure at low concentrations but not effectively at high concentrations. The activities of these catalysts in the degradation reaction of polypropylene was investigated by thermogravimetric analyses (TGA) and from these results a significant decrease was observed both in the degradation temperature of polypropylene and in the activation energy of degradation reaction.

References

- [1] Sezgi N.A., Wang, S.C., Smith, J.M., McCoy, B.J., *Ind.Eng.Chem.Res.*, 37 (1998), 2582-2591
- [2] Gucbilmez Y., Dogu, T., Balci, S. *Catalysis Today*, 100 (2005) 473-477
- [3] Obalı Z., Sezgi N.A., Doğu T., XX.National Chemistry Congress, September-2006, Kayseri/TURKEY

poster

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Deactivation of coprecipitated Co/Al₂O₃ catalyst

Meltem Yıldız and Ayşe Nilgün Akın

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CO hydrogenation product spectrum includes a great variety of products. The wide range of the conditions brings with it a wide range of products; paraffins, olefins, alcohols, etc. depending on the catalysts used and process conditions. Cobalt based catalyst systems seem to be especially suitable due to their high activity and selectivity, low water-gas shift activity and a comparatively low price. An extensive study was conducted on the development of coprecipitated cobalt-alumina catalysts for production of lower hydrocarbons by CO hydrogenation and 36 wt% Co/Al₂O₃ was found to exhibit optimum performance.

In this study the carbon deposits on coprecipitated 36 wt% Co/Al₂O₃ and their effects on CO hydrogenation were investigated concomitantly, since CO hydrogenation reaction used for the synthesis of hydrocarbons is subject to carbon deposition which may lead to blockage of the reactor and deactivation and disintegration of the catalysts. CO hydrogenation was performed in a differential fixed-bed reactor operated at atmospheric pressure. Deactivated catalysts have been characterized by total surface area measurements, temperature programmed oxidation and reduction (TPO, TPR) experiments. SEM (scanning electron microscopy) analyses have been performed on deactivated catalysts to obtain a better understanding of carbon deposition.

Experiments have been carried out to investigate the deactivation conditions of coprecipitated 36 % wt Co/Al₂O₃ catalyst used for the production of C1-C3 hydrocarbons by CO hydrogenation. For this aim, four different temperature (235-300 0C), three H₂/CO ratios (1-3), space times (5,5-17 mg.min/mL) and CO percentages in feed (10-33,33) have been chosen as variable parameters.

Activity of the catalyst increased by increasing temperature in the range of 235-275 0C and remained unchanged. For the reaction performed at 300 0C although 97 % conversion was observed, catalyst was completely deactivated in a very short time due to coke formation.

The effect of H₂/CO ratio in the feed on catalyst deactivation was investigated at 250 oC and three different feed ratios of 1 to 3. Increasing H₂/CO ratio increased the catalyst activity. Methane formed as the main product at higher H₂/CO. Although catalyst activity was not changed significantly for 9 hrs reaction period at all conditions, a maximum 6.8% carbon deposition was observed with increasing H₂/CO, and this caused a 2 % decrease in total surface area of the used catalyst.

Experiments performed at higher space times (W/F) have shown higher conversions, as expected. However, the catalyst activity decreased by time at higher space times. The percentage of CO in the feed gas was another variable studied for the deactivation conditions of coprecipitated Co/Al₂O₃ catalyst. Activity decreased by increasing CO% in the feed while selectivity to the C1-C3 hydrocarbons increased.

TPR experiments were performed on all used catalysts to investigate the effects of reaction conditions on the regeneration properties of the coprecipitated 36 wt% Co/Al₂O₃ catalysts by using thermogravimetric analysis (TGA). The results of TPR experiments were compared with the results of TPO experiments in order to obtain information for the regeneration conditions at both reducing and oxidizing atmospheres.

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Determination of optimum conditions and the kinetics of the methanol oxidation

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In this study, catalytic oxidation of methanol to formaldehyde was investigated in a laboratory scale fixed bed catalytic reactor. In order to obtain the optimum conditions, for the each catalyst prepared in laboratory, six different temperatures at a range of 250-375°C and three different space times (W/FA0) such as 50.63; 33.75 and 20.25 g/(mol/h) were tried. Experimental set-up mainly consisted of preheater, reactor and condenser. For this gas phase reaction, iron-molybdate catalysts supported by silica or alumina with a (Mo/Fe) ratio of 1.5, 3 and 5 were used. The analysis of liquid product was performed by using gas chromatograph.

To investigate the effect of each parameter both on the selectivity to formaldehyde and on the total conversion, the specified parameter was changed, as the others were being kept constant. It was found that, for all the catalysts and support types, as temperature was increased, total conversion increased whereas selectivity to formaldehyde decreased. As Mo/Fe ratio was increased, both total conversion and selectivity increased. With the same catalyst, at constant temperature, total conversion and selectivity increased as the space time was increased. Finally, silica support gave better results for conversion and selectivity than that of alumina support for all experiments.

After determining the optimum conditions for this reaction, the experiments aiming kinetic study was carried out. These experiments were performed on the catalyst favoring the formation of formaldehyde, which has a (Mo/Fe) ratio of 5 on silica support. First, the effects of external and internal diffusion were searched for. Seven reaction models derived by the mechanisms cited in the literature were tested to elaborate the kinetics of the reaction and the model on surface reaction controlling was found as the suitable reaction mechanism. Also, the kinetic parameters were computed by this model.

Keywords: formaldehyde, methanol oxidation, fixed bed catalytic reactor, iron-molybdate catalyst, kinetics of methanol oxidation

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A novel process for 2-naphthol and acetone production

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The novel process to produce simultaneously 2-naphthol and acetone with a high yield from naphthalene + propylene, through 2-isopropyl naphthalene (IPN) in the gas-liquid-liquid/catalytic alkylation reactor, 2-isopropyl naphthalene-hydroperoxide (2-IPNHP) in the liquid-liquid/catalytic oxidation reactor, and its decomposition in the liquid-phase acid catalysed decomposition reactor, achieved at low temperatures with the liquid catalysts, respectively, $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$, NaOHaq or $\text{Na}_2\text{O}_2\text{aq}$, and HClO_4 , was developed in our Laboratory [1-11]. The multi-phase catalytic reaction system with the liquid $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$ catalyst to produce IPN, the heterogeneous catalytic reaction system with NaOHaq or $\text{Na}_2\text{O}_2\text{aq}$ to produce 2-IPNHP, and the decomposition of 2-IPNHP in the presence of two different aprotic solvents of low dielectric constant, i.e. 2-isopropyl naphthalene (IPN) and acetone (AC), and the protogenic solvent acetic acid (ACOH), with two different oxyacid catalysts, i.e. HClO_4 and H_2SO_4 , will be presented and discussed thoroughly.

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Propylene epoxidation on Ag (111) surface: A density functional and ONIOM study

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There is a long history of experimental research for ethylene oxide formation due to its industrial importance. Considerable experimental effort has been devoted to understanding the mechanism of silver-catalyzed ethylene epoxidation as outlined in many reviews. The issues most often addressed have been the roles of oxygen and the promoters in the reaction. Fundamental experimental studies were carried out using primarily Ag 111 and Ag 110 single crystals which provided evidence for the key role of atomic rather than molecular oxygen in both the epoxidation and combustion reactions. In this DFT study of propylene epoxidation, preliminary calculations of atomic and molecular oxygen adsorption followed by reaction with propylene from the gas phase on a 22 Ag atom ONIOM cluster which simulates Ag (111) surface were carried out using DFT/B3LYP method with basis sets composed of Los Alamos LANL2DZ effective core pseudo-potentials (ECP) for silver and 3-21G** for carbon, oxygen and hydrogen as implemented in Gaussian 2003. A 22 Ag atom 2 layer ONIOM method is used to simulate Ag (111) surface where 4 Ag atoms are in high layer DFT region and the rest of the cluster (18 Ag atoms) is in low layer molecular mechanics region utilizing universal force field (UFF). Relative energy profiles as functions of a chosen reaction coordinate were calculated and two distinct pathways, one directly leading to propylene oxide, and the other forming a π -allyl radical were identified. Equilibrium geometry calculations were in general performed. Oxygen was both molecularly and atomically adsorbed onto the Ag cluster and optimized equilibrium geometries and relative energies of adsorption were calculated. The heat of adsorption values obtained in our study show reasonable agreement with the experimental values under low surface oxygen coverage conditions: -12.42 vs -9.2 kcal/mole for molecular and -51.15 vs -40.8 kcal/mole for atomic oxygen adsorption, respectively. Since it is generally accepted that atomic oxygen, rather than molecularly adsorbed oxygen reacts with ethylene, the calculations involving propylene adsorption and reaction are carried out involving an oxygen atom adsorbed on silver cluster. The next step along the reaction coordinate is the adsorption of propylene onto the oxygen-covered Ag surface. The final optimized equilibrium propylene oxide formation is found at a relative energy value of -11.70 kcal/mole. Approximate transition state energy barriers indicated a more favorable route for the case of π -allyl radical formation (5.03 kcal/mole) as opposed to propylene oxide formation (14.99 kcal/mole). DFT calculations, therefore, conclude that π -allyl radical formation is a more favorable route as opposed to direct propylene epoxidation on Ag (111) surface. Since π -allyl radical leads to combustion products which lower propylene oxide selectivity, this quantum mechanical result explains the long asked question by experimentalists of why Ag (111) surface is a good catalyst surface for ethylene epoxidation but less favorable for direct propylene oxide formation reaction.

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Acidity characterization of Pb/SBA-15 mesoporous catalysts

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SBA-15 samples are incorporated by Pb at different weight loadings to provide a controlled geometry in nanometer scale via using direct synthesis method. Surface acidity characterization of the synthesized Pb doped SBA-15 samples was done by measuring the in situ IR spectra of pyridine adsorbed on Pb doped SBA-15 samples at different weight loadings. Pyridine adsorption is a well-established technique to measure Brønsted- and Lewis-acid concentration. Pyridine is selective, stable and strongly adsorbed. The adsorption of pyridine results in the appearance of a band at 1540 cm^{-1} due to pyridinium ions (Hpy^+) formed on Brønsted-acid sites and another band at 1456 cm^{-1} attributed to a pyridine complex bonded to Lewis-acid sites (LPy). Samples showed both Lewis acidity and Brønsted acidity. The Brønsted-acid and Lewis-acid concentration for Pb/SBA-15 samples were calculated by integrating peak areas of the bands at 1540 and 1456 cm^{-1} , the result are presented in Table 1. The data indicate that the Brønsted-acid concentration and Lewis-acid concentration is dependent on Pb content. Brønsted-acid concentration decrease with the lead content and reaches a minimum for 15 wt%Pb loading, then increase. Similarly, Lewis acid concentration decrease with the addition of lead.

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Palladium incorporated silicate structured mesoporous catalysts for ethanol reforming

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As reported in the literature [1], Pd showed very high activity in hydrogen production by steam reforming of ethanol. Besides steam and dry reforming of ethanol and methane, palladium based supported catalysts have numerous other uses in catalytic reactions. Pd based composite materials also have applications in hydrogen purification and storage [2]. Discovery of mesoporous silicate structured MCM-41 type catalyst supports started a new avenue in catalysis research [3,4]. These materials have surface area values over 1000 m²/g and narrow pore size distributions. In the present study, Pd-Si mesoporous nanocomposite catalytic materials having different Pd/Si ratios were synthesized following an acidic direct hydrothermal synthesis route, for possible applications in steam reforming of ethanol and dry reforming of methane. The nanocomposite catalytic material were then characterized by XRD, XPS, EDS, nitrogen adsorption and SEM techniques. Unlike MCM-41, the XRD patterns indicated a rather wide d(100) band at a d value of 1.87. The materials with very high Pd/Si wt ratios over 1.3 were synthesized and these materials were found to have surface area values over 600 m²/g and rather narrow pore size distributions between 2-7 nm, with promising catalytic properties for reforming reactions.

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Ziegler-Natta Catalysts in Slurry-Phase PP Production

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Ziegler-Natta catalysts are used in PP production of PETKÝM. In this study, the brief information about the slurry phase PP production, the historical milestones in the development of Ziegler Natta catalysts, utilization of Z-N catalysts in PP slurry polymerization; important parameters directly effecting catalyst activity, catalyst poisons for 4 th generation catalysts, selection of most suitable type of solvent in PP polymerization, the reason for choosing heptane as polymerization medium; impurities in solvent heptane and feedstock material propylene and the problems frequently faced in PP slurry polymerization and remedies has been reviewed.

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TiO₂ Based Catalyst Preparation and Characterization for Photocatalytic C-C Bond Formation

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TiO₂, as thin film or nanocrystal, has appeared in many areas recently such as self-cleaning glasses, dye-sensitized solar cells and light induced superhydrophilic surfaces. Thin film coatings on glass substrates have a particular advantage over powders during photocatalytic tests such that less scattering takes place. With the fact that the substrate is transparent to visible light, incoming radiation is utilized the most efficiently on macroscopic scale.

Photocatalytic coupling of small C containing molecules is getting more attention everyday. Yulati et al. studied photocatalytic methane coupling in several papers [1-3]. In our study C-C bond formation with CO₂ in the gas phase will be studied using TiO₂ coated glass substrates as photocatalysts.

Two types of flat glass (ordinary and conducting indium tin oxide (ITO) glass) were coated for characterization by sol-gel method using titanium isopropoxide as Ti source, ethanol as solvent and acetic acid as modifier and water as hydrolyser. Characterization of these films was done with UV-VIS spectrometry and X-ray diffraction, yet no crystallinity was observed in the XRD spectrum. Differences were observed between the ITO and ordinary glass in light absorption characteristics. As catalyst, hollow borosilicate glass beads of 1-3 cm size were coated with the same procedure. Reaction tests are in progress.

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Characterization and activity studies of Co based catalysts

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Cobalt oxide supported catalysts were characterized and carbon monoxide oxidation properties of these catalysts were investigated. All Catalysts were prepared by co-precipitation technique. The catalysts were calcined at two different temperatures to see the effect of calcination temperature. Catalysts were characterized by various techniques. Phases present in the catalysts and average crystal sizes of the catalysts were determined by X-Ray Diffractometer system. Pore size distributions, pore volumes and BET surface areas of the catalysts were found by using N₂ adsorption/desorption isotherms. Shapes and distributions of the particles on the catalyst surface were determined by Scanning Electron Microscope (SEM). X-Ray photoelectron spectroscopy was used to determine the composition of the catalyst surface on the atomic level. The carbon monoxide oxidation studies were carried out to investigate the relation between the characteristic properties of the catalysts and the catalytic activity. All the Catalytic activity measurements were studied in temperatures between room temperature and 200oC, using a feed composition of 1% CO, 21% O₂ and remaining He. X-Ray studies showed that the catalysts calcined at 200oC have amorphous phase structure and catalysts calcined at 450 oC have crystal phase structure. The X-Ray Diffractometer analysis of 50/50 Co₃O₄/CeO₂ and 25/25/50 Ag₂O/Co₃O₄/CeO₂ catalysts showed the peaks which were due to presence of metallic Ag, Co₃O₄ and CeO₂ phases. It was concluded that Ag₂O is decomposed to metallic silver when the calcination temperature is increased from 200oC to 450C. Adsorption/desorption isotherms of the composite oxide catalyst fits the type IV isotherm. Characteristic feature of the isotherms in BDDT classification is the hysteresis loop. The average pore diameter of the catalysts varies in the mesopore diameter range (2 nm < pore diameter < 50 nm). The pore sizes and pore volumes of the catalysts were increased by increasing the molar ratio of cobalt oxide in the catalysts. All catalysts have multipoint BET surface areas above 120 m²/g and when calcinations temperature of the catalysts were increased from 200oC to 450oC, BET surface areas of the catalysts decreased by 70%, approximately. The highest values for surface areas were obtained from 100% Co₃O₄ and 50/50 Co₃O₄/CeO₂ catalyst calcined at 200oC. Surface areas of 100% Co₃O₄ and 50/50 Co₃O₄/CeO₂ calcined at 200oC were found to be 167.06m²/g and 158.67m²/g, respectively. SEM images of the catalysts showed that the catalysts have spherical particles with uniform distribution. X-Ray photoelectron studies of the catalysts calcined at 200oC showed that the Ag 3d 5/2 peak resulted from Ag₂O phase, the Co 2p 3/2 peak resulted from the Co₃O₄ phase and the Ce 3d 3/2 and Ce 3d 5/2 peaks resulted from the CeO₂ phase. Catalytic activities of the catalysts calcined at 200oC were higher than the catalysts calcined at 450oC. 50/50 Co₃O₄/CeO₂ calcined at 200oC has the light of temperature around 122 oC and gave the 100% CO conversion above 160oC

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Oxidation of Benzene to Maleic Anhydride in a Fixed Bed Reactor

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One of the main industrial routes to produce maleic anhydride (MAN) is the oxidation of benzene in gas phase. MAN is used in the manufacture of alkyd and polyester resins, surface coatings, plasticizers and agricultural chemicals. The predominant starting material is used to be benzene. A typical process using benzene as a feedstock involves passing a preheated vapor mixture of air and benzene over a catalyst disposed in a reactor. The reactor usually involves a multitube fixed bed reactor. The reaction is highly exothermic and the reactor is cooled by a molten salt mixture. Most widely used catalysts in the production of MAN include vanadium pentoxide, molybdenum trioxide and sodium oxide. In this study, gas phase catalytic oxidation of benzene was carried out in a laboratory scale fixed bed reactor on two different types of catalysts. These catalysts are prepared with two different compositions and supported by silica gel. The first prepared catalyst consists of %53.6 V₂O₅, %35.7 MoO₃ ve %10.7 Ni₂O₃. The composition of the second catalyst is %75 V₂O₅, %24 MoO₃, %1 Ni₂O₃. The effects of temperature, benzene flow rate, air flow rate and the catalyst composition were investigated on the reaction selectivity. Experiments were carried out at atmospheric pressure, at 300, 325, 350 and 375°C by changing the space-time (W/FBo) in the interval of 1*10⁶- 2.5*10⁶g.s/gmol, and the benzene/air mol ratio is between 0.0477-0.109. The conversions are calculated by evaluating the results of analysis by gas chromatography. It's found that conversion of benzene to MAN increases with increasing temperature. Although total conversion of benzene decreases, conversion of benzene to MAN increases. And the other result is: air flow rate increases with increasing conversion at constant temperature (T=350°C) and at nearly constant space time (1.33*10⁶ g.s/molB). The experiments performed over catalyst 2 are still going on by changing the reaction parameters. When the comparison of the catalysts is made, it can be said that both catalysts give same behaviours according to the conversion and selectivity values obtained from experimental results. MAN is produced with both catalysts. So, these two catalysts are suitable catalysts for the oxidation of benzene to MAN in a fixed bed reactor. As a result it can be concluded that both of the catalysts can be used for benzene oxidation to MAN in a fixed bed reactor.

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Comparison of different heterogeneous catalysts in the esterification of butanol with acetic acid

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n-Butyl acetate is an important solvent in the chemical industry. Primarily it is used in paint and coating manufacture and in the lacquer industry. Because of its lower impact on the environment, n-butyl acetate is able to replace the toxic and teratogenic ethoxy ethyl acetate that is often used as a solvent. Butyl acetate produced by the esterification of acetic acid with butanol in the presence of catalyst. Because of the first step of the esterification reactions is taking proton, acidic catalyst should be required. In the traditional methods, homogeneous catalysts such as sulfuric acid, hydrochloric acid were used.

The advantages for heterogeneous catalysis over those performed in the presence of mineral acids may be pointed in:

(i) Unlike the homogeneous catalysis, it does not include toxicity, corrosiveness, and difficulty in separation mixture and reusability.

(ii) The corrosive environment will be a minimal.

(iii) The catalyst can be easily filtered off and the product will be highly pure where the actual exclusion of the side reactions is expected.

Ion exchange resins, zeolites, supported or unsupported heteropolyacids and tungstophosphoric acid mainly used heterogeneous catalysts in esterification reactions.

In this study, Amberlyst 15 and alumina supported tungstophosphoric acid catalyst were used as catalysts. Experimental procedure was repeated for both catalysts and most efficient catalyst was found as Amberlyst 15 according to its high conversion and less deactivation. Also, effects of operating parameters such as temperature, mole ratios of reactants, speed of stirrer and catalyst loading were investigated.

The aim of this study is to compare the two different types of catalyst, to decide optimum operating conditions and to calculate the kinetic constants for the chosen catalyst.

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ENVIRONMENTAL CATALYSIS

A Mechanistic Approach to Elucidate Ethanol Electro-oxidation

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In order to elucidate the mechanism of ethanol oxidation, a cylindrical diffusion-surface reaction model has been developed on a platinum disc electrode. An ethanol electro-oxidation mechanism was proposed; in which electrochemical reactions proceed without adsorption of any electro-oxidation products (C2 type) on the surface. After simulation of the proposed mechanism, it was seen that the model can explain ethanol electro-oxidation behavior. The simulation of the mechanism indicated that the formation of acetaldehyde through oxidation of bulk ethanol is the rate determining step between 0.6 and 0.75 V vs. RHE. After 0.75 V vs. RHE, formation of surface acetate through bulk ethanol becomes the rate determining step. Oxidation model also shows that around 0.7 V vs. RHE, acetaldehyde coverage becomes the major surface species, and acetate formation starts around 0.7 V vs. RHE. In order to change ethanol oxidation mechanism, it is believed that C-C bond cleavage should be enhanced to remove major C2 type poisoning species like acetaldehyde.

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Synthesis and Characterization of Pt Based Electrocatalysts by Supercritical Carbon Dioxide Deposition Method

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Supercritical fluids have lately been receiving increasing attention in preparation of a wide variety of materials for fuel cells [1]. We have used the supercritical deposition technique to prepare carbon nanotube [2] and carbon aerogel [3,4] supported catalysts with small particle sizes and high dispersions and demonstrated that metal loading on the support could be controlled thermodynamically by adsorption isotherms [5,6]. In this study, we extended the supercritical carbon dioxide (scCO₂) deposition method to synthesize Pt based electrocatalysts on different carbon supports such as multi wall carbon nanotubes (MWCNTs) and two different types of carbon blacks (Vulcan XC 72R and BP2000). These catalysts were characterized by using XRD, TEM and cyclic voltammetry (CV). XRD and TEM results showed that the deposition method leads to Pt particles with average sizes as small as 1-2 nm dispersed uniformly on the carbon surfaces. CV results also showed that electrochemical surface area (ESA) of the synthesized Pt/Vulcan XC 72R and Pt/MWCNT catalysts are about three times larger than commercial ETEK catalyst at similar Pt loadings. Furthermore, ESAs of the catalysts were compared with another commercial catalyst of Tanaka Pt/C (46.5%).

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Morphological Characterization of Catalytic Soot Oxidation Foam Filter

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In this study, Pb-Co mixed metal oxide soot oxidation catalysts were coated on a SiC foam filter via incipient wetness impregnation. The slurry was prepared such that the Pb/Co weight ratio was 2 and it was stirred continuously during coating. The coating was accomplished by three consecutive impregnation-drying-calcinations cycles. After each cycle surface structure and composition were analyzed by Scanning Electron Microscope (SEM). SEM analysis was performed on three different regions in the filter which are (i)high porosity (10 ppi-pores per inch square) region, (ii)low porosity(80 ppi) region inside the filter and (iii)low porosity(80ppi) region outside the filter. EDX analysis revealed that surface composition of Pb is high on the high porosity region and surface composition of Co is high on low porosity region inside the filter. Also large crystals were observed on the surface with a weight ratio Pb/Co equal to 2/1. It was shown that temperature and homogeneity influences the quality of the coating. After the final coating, paraffin soot was deposited on the surface by using a candle. Then soot oxidation treatment was done in a laboratory oven at 400oC. The soot deposition and oxidation steps were repeated two more times. After each deposition and oxidation step structural change was monitored by SEM analysis. SEM pictures after the final oxidation revealed that in zones with higher Co amounts, surface structures were not visible due to soot accumulation. On the other hand zones with higher Pb amounts did not show any soot indicating the role of Pb in oxidation, but the Pb composition of the surface decreased due to the evaporative loss of Pb. After each step in the study, XRD analyses were also performed to determine the crystalline phases on the surfaces. Silicon dioxide phase was detected before the coating, after the coating and after the soot oxidation treatment.

poster

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Thermodynamic analysis of hydrogen production in an lpg processor

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Supply of a continuous hydrogen feed is crucial to the operation of the PEM fuel cell (PEMFC), which can practically be used in vehicular and small-scale combined-heat-and-power (CHP) applications. Catalytic fuel processors that convert readily available fossil fuels to hydrogen for use in the fuel cell provide a solution to the challenge of pollution prevention. The designated processor is the assembly of an indirect partial oxidation (total oxidation + steam reforming) reactor, water-gas shift (WGS) and preferential oxidation (PROX) reactors, and process units such as heat exchangers and pumps. The present work encompasses the calculation of the equilibrium of hydrogen production in the indirect partial oxidation and water-gas shift reactors from liquefied petroleum gas (LPG) which is commercially available at different compositions. The thermodynamic analysis is carried out by the Gibbs free energy minimization method, which relies on the fact that, in a closed system at constant temperature and pressure, the Gibbs free energy attains a minimum. Independent of the reaction scheme, the equilibrium composition is determined solely by the inlet stream composition, temperature and pressure. In order to determine the operating conditions that result in the highest hydrogen yield, a parametric study is conducted by varying, one at a time, the butane-to-propane and water-to-fuel molar ratios in the feed to the processor and the feed temperature. The results indicate that the maximum hydrogen production (ca. 10 moles H₂/mole LPG fed) is achieved with a butane-to-propane ratio of 3:1, water-to-fuel ratio of 3:1 and temperature of ca. 940 K.

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TiO₂ loaded ordered mesoporous SBA-15 structures for CO₂ reduction reactions

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Different amounts of titanium dioxide loaded mesoporous silica SBA-15 structures have been synthesized by a sol-gel method using the self organizing polymer pluronic 123, TEOS and adding titanium(IV) isopropoxide into the solution in the preheating and precalcination stage. X-ray diffraction, X-ray photoelectron spectroscopy and BET analyses have been performed on the samples. Low angle XRD spectroscopy demonstrated long range order of mesoporous SBA-15 structure is preserved under Ti loading. Formation of rutile and anatase crystals is observed at the composition of Ti/Si=0.20 molar ratio while no crystal phase is observed for lower Ti/Si ratios. Ratio of characteristic anatase XRD peak intensities to rutile peak intensities increase with Ti loading, which suggests that anatase formation dominates at higher Ti loadings. XPS Ti2p peaks further support the XRD data for the anatase crystal formation for Ti/Si=0.20 and higher loadings. XPS O1s peaks indicate the incorporation of titanium is through the Si-O-Ti bonds. Photocatalytic CO₂ reduction experiments are in progress.

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Microcalorimetric Studies to Investigate the Effect of Sn Addition to Elucidate CO Poisoning on γ -Al₂O₃ Supported Pt –based Direct Ethanol Fuel Cell Catalysts

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Direct use of alcohols such as ethanol and methanol in fuel cells are currently being investigated in broad extent. Ethanol is non-toxic and has higher hydrogen content when it is compared with methanol. Pt is the best known electro oxidation catalyst used in the fuel cells. However, pure Pt is poisoned by the strongly adsorbed intermediates especially CO. Current solution to the problem is to develop Pt alloys resistant to CO poisoning. The most suitable alloy catalyst for the Direct Ethanol Fuel Cell reported in the literature is the Pt-Sn alloy. But, how Sn modifies the electronic and geometric structure of the catalyst and how does the mechanism of ethanol electro-oxidation changes in the presence of Sn is still debated. In order to answer some of these questions, microcalorimetric measurements of carbon monoxide, hydrogen, oxygen, and ethanol were performed on pure and Sn containing and 5%Pt/Al₂O₃ model catalysts. Microcalorimetric measurements were performed at 323 K by using a Tian-Calvet type heat flow calorimeter (Setaram C-80) connected to a gas handling system and a volumetric adsorption apparatus employing Baratron capacitance manometers in the range of 10⁻⁴-10 Torr for precise pressure measurement. The catalysts were prepared by incipient wetness impregnation of PtCl₂(NH₃).2H₂O and SnCl₂.2H₂O salts. The amount of Sn was adjusted to obtain Pt:Sn ratios varying between 1:0 to 15:1. The results showed that when Sn addition increases the CO, O₂, and H₂ saturation coverages decreased. It is concluded that Sn covers the stronger sites on Pt and blocks the active surface of Pt. The initial heats are nearly the same for all Pt-Sn catalysts. This may be attributed to the fact that when Sn was added the electronic configuration did not change significantly for all catalysts. Ethanol microcalorimetry data indicated significant amounts of adsorption on the Al₂O₃ support.

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Partial Regeneration of Ni-based Catalysts for Hydrogen Production via Methane Cracking

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Methane cracking has the potential to produce high purity, carbon monoxide-free hydrogen suitable for application in PEM fuel cells. The two products of reaction are molecular hydrogen and solid carbon. The carbon appears in the form of carbon filaments whose growth is hindered by carbon encapsulation leading to total deactivation of the catalyst. Several attempts have been made to regenerate the catalyst, mainly by gasifying the carbon filament in air or steam. Our work on 5-wt% Ni/Al₂O₃ indicated that after complete gasification of the carbon the catalyst has lost nearly all its activity toward methane cracking. However, if the gasification proceeds to only a certain extent, it is possible to recover significant activity of the catalyst. This technique, also known as, partial regeneration, is a promising strategy to overcome the challenge of catalyst deactivation in catalytic decomposition of methane. Optimization of the partial regeneration method is presented here, in particular the extent to which the gasification should take place. Activity of the catalyst and the extent of gasification have been monitored through thermogravimetric analysis. Most experiments have been performed at atmospheric pressure and 773 K, but a few results are also reported for 873 K.

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Alkaline Doped Pd/SnO₂: Low temperature CO Oxidation Catalysts and Sensor Materials

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The development of catalytic technologies for monitoring and eliminating pollutants in motor vehicle and chemical process exhaust gases are key issues in environmental abatement efforts. In these circumstances, low temperature oxidation of CO, especially during engine cold start period is of critical importance for the performance of catalytic converters. In addition, low temperature CO oxidation catalysts find applications in closed cycle recycling of CO₂ in sealed CO₂ lasers, CO gas sensors and selective CO oxidation in H₂ rich streams. Tin dioxide is a CO oxidation catalyst, oxidizing chemisorbed CO through a mechanism of lattice oxygen abstraction above 300°C. Furthermore, palladium oxide-tin dioxide system catalyzes the reaction between CO and O₂ even at sub-ambient temperatures.

Improvements in the catalytic activity of PdO/SnO₂-based catalysts were obtained by the promotion of this catalyst by trace amounts of alkali-metals (Li, Na or K), which are well-known promoters of oxidation reactions and; spectroscopic and dynamic techniques were used to elucidate the fundamentals of the mechanism of low temperature CO oxidation activity of PdO/SnO₂-based catalysts. Catalysts were investigated with XRD, XPS, DRIFTS to investigate the changes in the crystal and surface structure of the catalysts and, the interactions of palladium and tin with each the alkaline promoter and oxygen. The effect of the structural variations in the catalysts on oxygen storage capacity of the catalysts, the reactivity and mobility of surface oxide and hydroxide species and the mechanisms of CO oxidation with these catalysts were investigated with temperature programmed techniques, such as temperature programmed reduction and reaction spectroscopies, together with surface titration experiments. Lithium and sodium were observed to increase oxygen storage capacity of the catalysts furthermore, lithium has lead to formation of a new crystallographic phase which was supposedly formed through the interaction of lithium with surface hydroxides and stabilized hydroxy species at the surface suppressing the CO oxidation activity of the catalysts. Sodium addition was observed to result in surface segregation of palladium atoms and promoted the reduction of surface oxides/hydroxides resulting in enhanced CO oxidation activity. Finally, potassium promoted the incorporation of palladium atoms to tin dioxide network decreasing the amount of active centers at the surface and leading to poor CO activity.

The spectroscopic and dynamic characterization data on alkali-metal promoted PdO/SnO₂-based catalysts has shown that alkaline addition altered the chemical and catalytic properties of these materials; as well as the catalyst morphology. Therefore, alkali-metal promotion of PdO/SnO₂ result in a family of catalysts, each exhibiting different reduction behavior and reactivity towards different reducing agents and; hold promising outcomes for various applications.

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Catalytic Combustion Of Ethyl Acetate

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Ethyl acetate is one of the organic compounds which are used in printing units. The gas stream carrying ethyl acetate must be treated before discharge to atmosphere. In this study, the catalytic combustion of ethyl acetate has been investigated over prepared metal oxide catalysts.

CeO, Co₂O₃, Mn₂O₃, Cr₂O₃ and CeO - Co₂O₃ catalysts were prepared on monolith support and they were tested. Catalysts were prepared in consecutive two steps. In the first step, monolith support was corroded in acidic solution. In the second step, corroded monolith support was coated with the chosen metal oxide. Activity of these prepared catalysts was predetermined by light-off experiments.

Experimental setup includes mainly a vaporizer, a preheater, a monolith reactor, a condenser and an absorber. In the experiments, the reactor temperature was changed between 100 -350 °C, at 1 atm pressure and 500% of excess air were used.

Before the catalyst testing experiments, homogeneous gas phase combustion reaction of ethyl acetate was searched for. According to experimental results, 45% of ethyl acetate was converted, at maximum reactor temperature tested, which was 350 °C.

All prepared catalysts were tested to find the best catalyst for complete combustion of ethyl acetate. According to the results, all catalysts tested gave higher conversion than that of homogeneous experiments. However, with none of these prepared catalysts, complete combustion could not be achieved. Any satisfactory result could be obtained by the catalyst, Mn₂O₃ and Cr₂O₃. At low reactor temperature, conversion obtained with Co₂O₃ catalyst was higher than CeO catalyst, however the temperature beyond 200°C, CeO catalyst presented higher conversion than that of Co₂O₃ catalyst. On the mixed metal oxide catalyst, the synergetic effect of CeO and Co₂O₃ could not be seen. The maximum conversion obtained with CeO catalyst at 350°C the reactor temperature, was 74%.

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Synthesis and Characterization of Mesoporous Titania for Photocatalytic Antibacterial Surfaces

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For human health, microbial contamination on any surface is a potential risk and these surfaces may require regular and thorough disinfection. For disinfection, chemicals utilized are either ineffective in long-term or environmentally not benign. Alternatively, semiconductor photo-catalysis, particularly TiO₂ (anatase), is a potential option, since it is not hazardous to environment and can be applied to any surface easily. The anatase phase creates electron-hole pairs under UV radiation and these pairs participate in oxidation reactions that attack any organic material thus creating a medium with antimicrobial properties. The focus of the efforts that has been done was to increase the surface area and decrease the particle size for obtaining more advanced materials. One of the most popular approaches is to synthesize anatase with sol-gel process and then hydrothermally treating it.

In the present study, mesoporous nanostructured anatase and trititanate particles were prepared while the source materials were both commercial TiO₂ (anatase) and sol-gel-type TiO₂. Initially materials were processed with a hydrothermal treatment under alkaline condition and then in a medium with neutral condition for various time intervals. Scanning Electron Microscope (SEM) images and X-Ray Diffraction (XRD) patterns revealed that alkaline treatment of commercial anatase yields nanofibers while on the other hand, sol-gel type counterpart converted to nanoplates with both samples having trititanate structure. Additional hydrothermal treatment of these materials with distilled water results with crystal growth, formation of nano structured bipyramidal crystalline particles and conversion back to anatase structure.

Photocatalytic antimicrobial activities of the samples were determined against *Escherichia coli* under UV irradiation. Antimicrobial activities of the samples treated in an alkaline medium have been improved when compared with the source samples. Whereas, a limited activity and a time lag in bacterial inactivation were observed for samples hydrothermally treated in distilled water. Nevertheless exposing these samples to UV irradiation in aqueous conditions before bacterial inactivation enhanced the photocatalytic activity.

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Investigation Of Biodiesel Production From Canola Oil By Using Mg–Al Hydrotalcite Catalyst

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Biodiesel, monoalkyl esters of fatty acids derived from vegetable oils or animal fats, is known as a clean and renewable fuel. Biodiesel is usually produced by the transesterification of vegetable oils or animal fats with methanol or ethanol. Biodiesel is a promising alternative fuel to diesel regarding the limited resources of fossil fuel and the environmental concerns. Transesterification can be performed using homogeneous basic catalysts including Na or K hydroxides, carbonates or alkoxides. Base catalysis is preferred to acid catalyzed routes using sulfuric or sulfuric acids, which are more corrosive with lower activities. In this conventional method, a large amount of waste water was produced to separate and clean the catalyst and the products. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalyst should be introduced. Many types of heterogeneous catalysts, such as alkaline earth metal oxides, various alkaline metal compounds supported on alumina or zeolite can catalyze transesterification reactions. The Mg-Al hydrotalcites are solids with interesting basic properties that have shown good activity in transesterification reactions.

In this study, the transesterification of canola oil with methanol has been studied in a heterogeneous system, using Mg–Al hydrotalcite as solid base catalyst. Hydrotalcite was prepared by co-precipitation of magnesium and aluminum hydroxides from their nitrate solutions by using aqueous solution of sodium carbonate as precipitating agent. The effects of methanol/canola oil molar ratio, type of alcohol and co-solvent, reaction temperature, particle size and mass ratio of catalyst to oil on biodiesel production were investigated. Our results showed that methanol is the best alcohol for this reaction conditions and using n-hexane and isopropyl alcohol as co-solvents decreased the product yield. The highest triglyceride conversion of 71.9 % was achieved after 9 hour of reaction time at 60 oC, with a 6:1 molar ratio of methanol to canola oil and 3 wt.% catalyst of 125-150 µm particle size.

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Low Temperature CO Oxidation Kinetics over Activated Carbon Supported Pt-Sn Catalysts

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The kinetics of low temperature CO oxidation was studied in the absence and presence of H₂ using a 1wt%Pt-0.25wt%SnO_x catalyst supported on HNO₃-oxidized activated carbon (AC). Intrinsic kinetic data were obtained in the initial rates region at 383 K and atmospheric pressure in 4 mm-ID stainless steel fixed-bed down-flow micro-reactors located in a tube furnace controlled to ± 0.5 K. The micro-reactor was operated in the differential mode using different sets of CO and O₂ concentrations each at different space times and catalyst loadings. Molar reactant concentrations in the feed were varied between 1-10% CO and 1-4% O₂ in experiments conducted in the absence of hydrogen. In preferential CO oxidation experiments, the H₂ concentrations used were between 5-60%. Flow rates of pure helium used as inert, of hydrogen as well as of CO/He and O₂/He mixtures were all controlled by calibrated mass flow controllers. An on-line temperature-controlled and programmable gas chromatograph having a thermal conductivity detector and a concentric CTR I column operating at 300°C was used for the analysis of reactant and product gases.

The 1wt%Pt-0.25wt%SnO_x/AC catalyst used in the kinetic studies was prepared by sequential impregnation of aqueous tin chloride and hexachloroplatinic acid precursors. The commercial activated carbon employed as support material (NORIT-ROX) was pretreated with HCl to remove its ash and sulfur content, washed with water to remove the HCl and then further oxidized in an HNO₃ solution followed by rinsing prior to the impregnation procedure.

The aim of the present work was to investigate the CO and O₂ dependence of low temperature CO oxidation rates over 1wt%Pt-0.25wt%SnO_x/AC while also demonstrating the unique properties of AC supports. A power-function rate expression with positive dependence on carbon monoxide and negative dependence on oxygen was obtained at 383 K for low temperature CO oxidation. The effect of the presence of H₂ in the feed on CO oxidation rates was also investigated since preferential CO oxidation is a promising method for H₂ clean-up in fuel processor/fuel cell systems.

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Reactions of unsaturated aliphatic ester on sulfided catalysts for the production of second generation biofuels

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Environmental concerns and depleting oil reserves have increased the importance of utilization of biofuels as traffic fuels. Wood, vegetable oils and animal fats are considered as the resource for the second generation biofuels whose production involve the conversion of the raw material to liquid (bio-oil) followed by an upgrading process, which aims to reduce the high oxygen content of bio-oil. Oxygen can be present in various forms of oxygenates in bio-oils [1]. When vegetable oils and animal fats are used for example, oxygen is found in the form of saturated and unsaturated fatty acid methyl or ethyl esters with 14-22 carbon atoms. Hydrodeoxygenation (HDO) on conventional sulfided catalysts is an alternative approach to produce hydrocarbons from bio-oils in the presence of hydrogen [2]. Since the catalysts are active in their sulfided form, a sulfiding agent is typically added to the HDO feed in order to maintain the sulfided level of the catalysts [2].

In our laboratory, we have intensively studied the HDO of different aromatic and aliphatic oxygenates on sulfided catalysts [3,4]. The HDO performances of different oxygenates have been observed to vary depending on several factors such as the molecular structure of oxygenate, the type of catalyst, and the presence and the amount of sulfiding agents. The present study focuses on the effect of saturation of the carbon chain on the HDO of aliphatic esters. For this purpose, the HDO of an unsaturated aliphatic ethyl ester was studied in the absence and presence of H₂S on sulfided NiMo/ γ -Al₂O₃ and CoMo/ γ -Al₂O₃ catalysts. The results were compared to those of a saturated ethyl ester obtained under similar conditions. In the HDO of the unsaturated ester, the hydrogenation of double bond is followed by the formation of hydrocarbons from the corresponding saturated ester. Thus, the saturated ester was the primary product and hence the presence of the double bond led to an increase in the hydrogen consumption, which is undesired in industrial context. The effects of H₂S on the reactions of the unsaturated and saturated esters were found to be similar. Yet, the HDO conversions and the product distributions were affected by H₂S differently. The presence of H₂S suppressed the HDO conversion of the unsaturated ester in contrast to that of the saturated ester. The reduction of the hydrogenation activity of the catalysts in the presence of H₂S explained the variations in the HDO conversions and the product distributions.

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Citral Hydrogenation over Ni, Pt, Ni-Sn and Pt-Sn supported on Zeolites and MCM-41

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Liquid phase hydrogenation of citral was studied over Ni, Pt, Ni-Sn and Pt-Sn catalysts. Na-Y, MCM-41, Mordenite were used as catalyst supports. MCM-41 was synthesised hydrothermally. Monometallic and bimetallic catalysts were prepared by impregnation and coimpregnation methods. The catalytic tests were carried in liquid phase at 80°C under 6 bar pressure with a stirring speed of 600 rpm in a semi-batch reactor.

The catalysts Ni and Pt contents were around 8.5 wt. % and 5.0 wt.%, respectively while Sn content of the bimetallic catalysts was about 0.46 %. The activity of the catalysts and product distribution were affected by type of active metal and type of support. The major product over monometallic and bimetallic catalysts was citronellal. Ni/MCM-41 catalyst gave the highest selectivity to unsaturated alcohols (SUOL, citronellol, geraniol and nerol), 5.1 mole % among the monometallic catalysts with an overall conversion of 89.0 %. The most selective monometallic Pt catalyst to unsaturated alcohols was Pt/Na-Y, 24.7 %. Pt catalysts showed higher SUOL compared to Ni catalysts. Ni catalysts were more active than Pt catalysts.

Addition of Sn affected catalysts activity and selectivity differently. Sn loading decreased the activity of Ni/Na-Y and Ni/Na-Mor while it the unsaturated alcohol formation. The most increase was observed over Ni-Sn/Mordenite; SUOL increased from 0 to 9.3 mole %. An increase up to 15 % in geraniol and nerol formation was observed over Ni-Sn/Na-Y Ni-Sn/Na-Mor. However SUOL decreased over MCM-41 while its activity increased. Sn loading to Pt catalysts increased SUOL over Pt-Sn/MCM-41 and Pt-Sn/Clino. The most increase was observed over the later; 10.0 mole % to 18.75 %. However, SUOL decreased over Pt-Sn/Na-Y.

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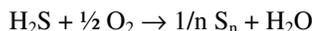
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Mixed Metal Oxide Sorbents and Catalysts for H₂S Removal and Selective Oxidation of H₂S

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Among the methods for the removal of H₂S, high temperature removal has many advantages such as sorbent regeneration, high temperature application. In our previous studies [1-3], a number of sorbents (Cu, V, Mo, Mn, Fe oxides and/or mixed oxides) were developed for high temperature desulphurization. These sorbents were synthesized by the complexation method. Characterization results showed that mixed metal oxides such as Cu₂V₂O₇, CuMoO₄, CeVO₄ can be obtained in a highly porous structure using the complexation method. Reaction mechanisms proposed were tested by using the concentrations of H₂S, SO₂ and H₂O in the effluent stream of the fixed-bed reactor. The deactivation model developed was applied to predict sorption rate parameters. Among the mixed oxides studied in our group, Mn-Cu mixed oxide sorbent showed higher reactivity, higher retention capacity and good regenerability properties. In addition to these mixed metal oxides, new mesoporous supported (copper incorporated MCM-41) sorbents were developed and used for H₂S sorption [4].

The Claus Process is the most commonly used process to recover sulfur from process gasses. In the first step of conventional Claus Process for sulfur recovery from process gases, H₂S is partially converted to SO₂ by thermal oxidation at high temperatures and in the second step, unconverted H₂S is reacted with SO₂ in a catalytic converter to produce elemental sulfur. Efficiency of this process is strongly affected by the equilibrium limitations of the second step. However, a single step selective oxidation of H₂S to elemental sulfur is practically irreversible and does not have thermodynamic limitations.



In our studies, catalytic activities of Cu-based [5] (Cu-V and Cu-V-Mo) and Ce-based [6] (CeO₂, Ce-V) mixed metal oxide catalysts were investigated for selective oxidation of H₂S to elemental sulfur. Both Cu-based and Ce-based mixed oxide catalysts gave high activity and selectivity for H₂S oxidation. Oxidation state of vanadium in Cu-V catalyst has an important role on selective oxidation to elemental sulfur. Partially reduced catalyst (Cu-V) containing V⁺² and V⁺⁴ in the forms of Cu₃VS₄ and VO₂ showed high activity in selective oxidation. Vanadium has remained +5 oxidation state in Ce-V catalyst (CeVO₄).

In this presentation, a review of our studies on high temperature H₂S removal and selective catalytic oxidation of H₂S to elemental sulfur will be given.

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Investigation of biodiesel production from canola oil by using Mg–Al hydrotalcite catalyst

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Biodiesel, monoalkyl esters of fatty acids derived from vegetable oils or animal fats, is known as a clean and renewable fuel. Biodiesel is usually produced by the transesterification of vegetable oils or animal fats with methanol or ethanol. Biodiesel is a promising alternative fuel to diesel regarding the limited resources of fossil fuel and the environmental concerns. Transesterification can be performed using homogeneous basic catalysts including Na or K hydroxides, carbonates or alkoxides. Base catalysis is preferred to acid catalyzed routes using sulfuric or sulfuric acids, which are more corrosive with lower activities. In this conventional method, a large amount of waste water was produced to separate and clean the catalyst and the products. Therefore, for the development of an environmentally benign process and the reduction of the production cost, a new process using heterogeneous catalyst should be introduced. Many types of heterogeneous catalysts, such as alkaline earth metal oxides, various alkaline metal compounds supported on alumina or zeolite can catalyze transesterification reactions. The Mg-Al hydrotalcites are solids with interesting basic properties that have shown good activity in transesterification reactions.

In this study, the transesterification of canola oil with methanol has been studied in a heterogeneous system, using Mg–Al hydrotalcite as solid base catalyst. Hydrotalcite was prepared by co-precipitation of magnesium and aluminum hydroxides from their nitrate solutions by using aqueous solution of sodium carbonate as precipitating agent. The effects of methanol/canola oil molar ratio, type of alcohol and co-solvent, reaction temperature, particle size and mass ratio of catalyst to oil on biodiesel production were investigated. Our results showed that methanol is the best alcohol for this reaction conditions and using n-hexane and isopropyl alcohol as co-solvents decreased the product yield. The highest triglyceride conversion of 71.9 % was achieved after 9 hour of reaction time at 60 oC, with a 6:1 molar ratio of methanol to canola oil and 3 wt.% catalyst of 125-150 µm particle size.

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OIL GAS AND PETROCHEMICALS

Catalytic Decarboxylation of Lignites

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The aim of this study was to investigate the catalytic effect of different metal ions on decarboxylation of lignites and relate this effect to the d-electron configurations of the ions. The catalytic effect of the transition metal ions on the decarboxylation of Beypazari lignite was investigated in terms of the change in the calorific values of the decarboxylated lignite samples. The selected transition metal ions for this study were Cr²⁺, Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺ and Zn²⁺. The optimum temperature and concentration of the metal ions for the decarboxylation experiments were determined according to the increases in calorific values of the coal. Catalytic activity of Zn²⁺ was relatively higher than those of Cr²⁺, Mn²⁺ and Co²⁺ ions in decarboxylation reactions. Activation energies of the decarboxylation reactions from different metal ions were calculated by kinetic methods and the results were correlated with the calorific measurements.

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Modeling Homogeneous Partial Oxidation of Methane

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In the last several decades, considerable effort has been directed toward the conversion of methane to value-added products such as transportable liquid hydrocarbons and oxygenates. The production of syngas is a very important process to the petrochemical industry because syngas is the building block for many chemicals including methanol, higher hydrocarbons through Fischer-Tropsch chemistry, and acetic acid. CH₄ partial oxidation is a mild exothermic process and theoretically yields a synthetic gas with a H₂/CO ratio of 2. To understand the kinetic behaviour of the CH₄ partial oxidation, a kinetic analysis is performed using the CHEMKIN package incorporating the GRI 30 mechanism. The model is considered is a plug flow reaction system is a length of 30 cm. Reactor diameter is 1 inch and flow rate is 300 cm³/sec. Simulations were performed over a temperature range of 800-3000 K with a 100 K interval. Temperature has a significant effect on product yields. Maximum H₂ mole fraction is obtained at 2200 K (mole fraction is 0.66). Formation of other hydrocarbons such as C₂H₂, C₂H₄, C₂H₆, C₃H₈ can also be found partial oxidation of CH₄, although in extremely small quantities. When the temperature was below 1200 K at 1 atm or higher than 2000 K pressure effect on the production of synthesis gas was almost negligible. Only within the temperature range of 1200 K-2000 K, the pressure effect becomes important. As the pressure increases, H₂ yields decrease. When O₂/CH₄ is less than 0.5, the equilibrium products involve CO and H₂ with no CO₂ and H₂O formation. However, as the O₂/CH₄ is increased from 0.5, partial oxidation and full combustion co-exist and products involve a mixture of CO, H₂, CO₂ and H₂O. The optimum operating conditions for homogeneous CH₄ partial oxidation reforming are determined as 2200 K and 1 atm.

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n-Butene Isomerisation over HZSM-5 and HZSM-22

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n-Butene isomerisation was studied over different HZSM5 and HZSM22 zeolites in a packed bed reactor. Na-ZSM-5 zeolites were synthesised for different synthesis time (3, 6, 12, 24, 48, 72, 96 h), SiO₂/Al₂O₃ ratios (20.1, 35.8 and 75.5) and TPABr amount (SiO₂/TPABr ratio of 3.3, 5.5, 12.5) at 150 oC in teflon lined autoclaves. for SiO₂/Al₂O₃ of Na-ZSM-22 zeolites were synthesised for both rotational and static mode of preparation at 150 oC for 4 days. Na-ZSM5 synthesised at 96 h and Na-ZSM-22 were converted to H form and tested in the reaction.

XRD analysis showed that lowest cristalinity was obtained for the starting gel having the highest aluminum content (SiO₂/Al₂O₃ = 20.1) . The microparticles had spherical shape. Their surface areas was determined by nitrogen adsorption method and it was found that the surface area increased with SiO₂/Al₂O₃ ratio: BET surface areas of 222.3, 294.84 and 366.7 m²/g for SiO₂/Al₂O₃ ratios of 20.1, 35.8 and 75.5 were determined, respectively. Their mean pore size were measured as 6.3 Å. It was found that for SiO₂/TPABr ratio of 12.5, amorphous material was obtained. Higher cristallinity was obtained when the ratio was 3.3. As the TPABr content increased the phase purity, particle size and the surface area of zeolites increased. HZSM-22 synthesized by two different routes showed two different morphologic and crystallographic phases (rotational: morphology: needles and spherical particles, static sponge-like and plate-like shapes). Only the rotational mode gave characteristic XRD peaks given in the literature.

The results obtained for HZSM-5 synthesised with different SiO₂/Al₂O₃ ratio at 440 oC and WHSV of 22 h⁻¹ for a reaction time of 2h showed that Selectivity to isobutene increased by increasing SiO₂/Al₂O₃; it was 1, 52. and 56 % for SiO₂/Al₂O₃ of 20.1, 35.8 and 75.5, respectively. Selectivity to isobutene increased as the acidity of the zeolites decreased with increasing SiO₂/Al₂O₃ ratio while acid site strength increased. Long time on stream (22 h) tests for these catalysts showed that selectivity increased slightly with time and there was no deactivation. Selectivity was higher at a lower temperature: at 375 oC it was 79 % and at 440 oC it was 60 %. Selectivity to isobutene increased from 68 to 79 by increasing WHSV from 11 to 22 h⁻¹ at 375 oC respectively. So short contact time was better.

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Use of Zeolite Catalysts in Petrochemical Industry

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Zeolites are crystalline hydrated aluminosilicates with well defined channels and cavities. They are relatively easy to synthesize and offer control over the pore size as well as its pore architecture. Due to the shape selectivity of their well defined pore architecture and modification ease of the pores, they are extensively used as catalysts.

In petrochemical industry they have wide range of applications covering a range of different commercial processes such as xylene isomerization, toluene disproportionation, hydrogenation and dehydrogenation of hydrocarbons.

As being the unique petrochemical company of Turkey, many zeolite catalysts have been used in Petkim. Use of zeolite catalysts in petrochemical industry and in Petkim has been reviewed.

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Factors affecting catalyst activity in HDPE plant

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Petkim HDPE plant is a slurry type process, which based on the exothermic polymerization reaction of ethylene in hexane using MgCl₂ supported TiCl₄ and Triethylaluminum (TEA) catalyst pair. The activity of the catalyst pair plays an important role in the productivity of the HDPE plant. The aim of this study is making an overview to the mechanism of the catalytic reaction of ethylene and demonstrating the potential sources of deactivation for the catalyst pair.

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Petrochemical industry as the primary consumer of catalysts

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Catalyst is a substance that selectively accelerates chemical reaction, when present in only small amounts relative to the feedstock are being processed, is of major importance to the chemical companies. Petrochemical industry is an important branch of industry for catalyst manufacturers, because there are number of processes in the production chain of petrochemical industry such as hydrogenation, dehydrogenation, isomerization, alkylation, oxidation, cracking and number of polymerization processes. In this study, the petrochemical industry, Petkim as sole producer of petrochemicals in Turkey, type of catalysts used in this industry and the importance of catalysts for industry has been reviewed.

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Ethanol Dehydration Over Solid Acid Catalysts Silicotungstic Acid, Tungstophosphoric Acid, Molybdophosphoric Acid and Nafion

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Solid heteropoly acid catalysts, such as tungstophosphoric acid (TPA), molybdophosphoric acid (MPA), silicotungstic acid (STA) and acidic resin catalysts, such as nafion, Amberlyst 15 etc. show high activities in dehydration reactions [1]. Diethyl-ether (DEE), which is a valuable chemical and a future motor vehicle fuel alternate [2], is expected to be produced by the dehydration reaction of ethanol. Another product of such a dehydration process is ethylene, which is one of the main feedstocks of petrochemical industry. Production of ethylene and other petrochemicals from a nonpetroleum feedstock is a major challenge in catalysis. In the present study, dehydration of ethanol was investigated using heteropolyacid catalysts such as TPA, MPA, STA and also using nafion (N). Dehydration of ethanol in a fixed bed vapor phase flow reactor.

Among the catalysts used for the ethanol dehydration reaction, silicotungstic acid catalyst showed the highest activity in the temperature range between 140-250 oC [3,4]. Activities of the four solid acid catalysts used follow, STA>TPA>N>MPA. Selectivity of diethyl-ether, which is the main product of dehydration at lower temperatures, decreased with an increase of temperature, especially over 200 oC. On the other hand, significant increase in ethylene selectivity was observed with an increase in temperature over 240 oC. For instance with a feed stream containing 48 % ethanol in helium and using 0.8 g of TPA catalyst in the reactor, ethanol conversion, ethylene selectivity and DEE selectivity values of 0.94, 0.73 and 0.27 were obtained at 250 oC. However, the corresponding values at 180 oC are 0.58, 0.22 and 0.78 , respectively. Results of this work showed that very high DEE and ethylene yield values can be obtained as a result of dehydration of ethanol over STA, TPA and nafion.

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Acidic Mesoporous Sulfated Zirconia Structures for methane coupling via bromination

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Owing to the environmental restrictions throughout the world, non-polluting and atom-efficient catalytic technologies are much important now. The use of highly corrosive, hazardous and polluting mineral acids, such as HF and H₂SO₄ is commonly employed in the today's petrochemical and refinery industries.

In the effort to replace those acids, zirconium oxide, or zirconia, when modified with sulfate ions, forms a highly acidic or superacidic catalyst that exhibits superior catalytic activity that can activate C-C and C-H bonds of alkanes at relatively mild conditions. Thus, S-ZrO₂ and modified S-ZrO₂ form an important class of catalysts.

The commercial zirconia has a rather low surface area of 50 m²/g or even less. Inclusion of sulfated zirconia in the mesoporous silicas provides a proper catalyst for many industrially important acid catalyzed reactions. The combination of silica and zirconia, not only increases the surface area of zirconia, but also improves the acidity by providing a fine distribution of acid sites in the silica framework.

In this study we report a liquid like acidity of the high surface area sulfated zirconia in the mesoporous silica (SBA-15) structure. SBA-15 type mesoporous materials have higher stability than other mesoporous silicas due to their thicker walls, which enables the introduction of other metals into the framework. The sulfated zirconia incorporated SBA-15 type catalysts were prepared at different zirconia loadings (5-30 mol%ZrO₂). Zirconia was introduced in the form of ZrOCl₂ • 8H₂O during the preparation of SBA-15 and calcined at 500°C. Subsequent sulfation introduced superacidic character to the material. Catalysts were characterized by XRD, BET, and TEM. Besides, the effect of the inclusion of sulfated zirconia to SBA-15 on the acidic properties was investigated by means of ¹H MAS NMR.

BET results indicate that the preparation of 5mol% ZrO₂ loading with high surface area (313m²/g) was accomplished. XRD results showed the formation of ZrO₂ crystals after 25mol% loading. In other words, the ZrO₂ crystals are finely distributed in the mesoporous silica framework up to this loading. TEM images revealed that even at 15mol% ZrO₂ loading the mesoporous hexagonal structure of SBA-15 prevailed.

A sharp ¹H resonance line at 10.6ppm was observed in the ¹H MAS NMR investigations. This signal is close to the acid signal observed in liquid superacids. This seems to support the idea that sulfated zirconia is not only an oxidant but also a good proton donor, a controversial subject in catalysis. The relative intensity of this line exhibited a maximum with zirconia loading at 25 mol% ZrO₂, which coincided with the appearance of the crystalline zirconia phases in the XRD results. Further increase in zirconia content resulted in a decrease in the intensity of the acid line at 10.6 ppm. Thus, there is an optimum for ZrO₂ loading between 15 and 25%.

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FUTURE TRENDS

Investigation of bioprocess parameters for glucose isomerase production by *Bacillus thermoantarcticus*

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D-Glucose/xylose isomerase (D-xylose ketol isomerase; EC 5.3.1.5) commonly referred to as glucose isomerase (GI), catalyzes the reversible isomerization of D-glucose and D-xylose respectively to D-fructose and D-xylulose, is one of the highest tonnage value enzymes. Isomerization of glucose to fructose is of commercial importance in the production of high-fructose corn syrup (HFCS).

The aim of this study is to design a production medium for glucose isomerase production by *Bacillus thermoantarcticus*. For the fermentation medium design, a statistical approach called Response Surface Methodology (RSM) is used. Before arranging an experimental design with RSM, approximate ranges of the factors: xylan, (NH₄)₂SO₄ and yeast extract were determined by varying one factor at a time while keeping the others constant. The effects of variables were investigated with small-scale batch laboratory experiments that were conducted in orbital shakers under agitation and heating rate control, using air-filtered 150 ml Erlenmeyer-flasks having 33 ml working volume capacities. The highest volumetric activity was obtained as 1630 U dm⁻³ in the medium containing 10.64 kg m⁻³ birchwood xylan, 5.92 kg m⁻³ (NH₄)₂SO₄, 5.66 kg m⁻³ yeast extract, and the salt solution at 55°C and pH= 6.0. By using the designed medium, fermentation and oxygen transfer characteristics of the bioprocess were investigated in V = 3.0 dm³ bioreactor systems with a VR = 1.65 dm³ working volume, at 55°C, at Q_o/VR=0.5 vvm, N=750 min⁻¹. In order to find the rate limiting step of the glucose isomerase production process by *B. thermoantarcticus*, the maximum possible oxygen utilisation rate (OD = $\frac{Q_o}{V} \cdot \frac{C_{X/YX/O}}$) and the maximum possible mass transfer rate (OTR_{max} = KLaCO*), a kind of Damköhler number, Da, defined as maximum possible oxygen utilisation rate per maximum mass transfer rate were calculated to compare the mass transfer and biochemical reaction rates.

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Direct formation of H₂O₂ from H₂ and O₂

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Hydrogen peroxide is an important oxidizing agent that plays an important role in “green chemistry” with water being the only byproduct. H₂O₂ has an increasing utilization as pulp bleach in the pulp and paper industry, as an oxidant in waste water treatment, and as a source of oxygen for epoxidation reactions. H₂O₂ is also an effective reagent in the removal of residual aromatic sulphur compounds from fuels. Currently, the commercial production of H₂O₂ is a circuitous process that involves the catalytic hydrogenation of an anthroquinone and by treatment of hydroquinone with O₂ to produce H₂O₂. Despite of its production on a multi-million scale, there are drawbacks to the commercial process such as the cost of the quinone component and the loss of this compound by oxidation. Furthermore the commercial production is not environmentally friendly.

As a potentially less expensive and environmentally friendly route to H₂O₂, its direct formation from H₂ and O₂ has been actively investigated over the past two decades. The direct oxidation of hydrogen normally is carried out in a three-phase system that includes a solid catalyst, a liquid phase and the reagent gases. Researches have focused on the catalyst type and the role of the liquid, which may include an acid and a halogenide.

In this study Au containing SiO₂, Al₂O₃, CeO₂ and CuOx catalysts were prepared with coprecipitation or impregnation methods from aqueous solutions of precursors. NaOH was used as the precipitation reagent in the preparation of coprecipitated catalysts. The catalysts prepared have been characterized by techniques of XRD.

Direct combination of hydrogen and oxygen to form hydrogen peroxide in liquid media with prepared catalysts were carried out in a slurry reactor at atmospheric pressure and room temperature. The O₂/H₂ ratio of 2/1, with 50 ml/min flow rate, was used in these experiments. Catalyst activity measurements were tested by iodimetric titration method by using KMnO₄.

Results are discussed based on effects of support material, catalyst preparation method, reaction time and medium (type of halogenide and acid) on hydrogen peroxide yield in direct oxidation of hydrogen to produce hydrogen peroxide. Our results show that catalytic performance of Au based catalyst was greatly dependent on the kind of support material, precipitation conditions and liquid media used in the reaction. The highest yield in the study was obtained with coprecipitated Au/CeO₂ catalyst in a reaction mixture of 0.25 N H₃PO₄ , 0.1 M NaBr and absolute ethanol.

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Catalytic wet air oxidation of aniline by nano-structured CeO₂-supported metal oxide catalyst

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In recent years, the fast progress in technology and the developments in science, made the environment protection inevitable. Wastewaters and the disposal of these without treatment are very harmful for human and animal health. In order to treat especially the nitrogen containing wastes coming from chemistry, petrochemistry and food industry, the new advanced treatment technologies are investigated.

One of the most important techniques for treatment of wastes in liquid phase is Catalytic Wet Air oxidation, CWAO, process. The process can treat any kind of organic aqueous waste, even toxic, produced by various branches of industrial activity. CWAO is one of the available treatment technologies, which consists of the total oxidation of the organic species present in the effluent to CO₂, N₂ and H₂O at moderate temperatures and pressures (125–220 °C, 5–50 bar), using oxygen or air as oxidant [1,2].

Another point is that nanoscience and nanotechnology is some how take very important role in our lives. It is inevitable to make researches on this innovation which is investigated all over the world.

In this connection, the main objective of this study was to investigate the applicability of wet air oxidation of aqueous solutions with nitrogen containing pollutants by nano-structured catalyst.

In the study, as CeO₂ supported metal oxide catalyst, Co₃O₄/CeO₂ was prepared. Co₃O₄/CeO₂ particles were prepared by the sol gel method as reported in literature [3,4,5]. The procedure is mainly divided into two sections. First, CeO₂ support was prepared by sol-gel technology and then it was impregnated with Co₃O₄ by incipient wetness impregnation method. The catalyst prepared was investigated using a Scanning Electron Microscopy and their phases were analyzed with powder X-ray diffraction. The activity of this catalyst was tested by CWAO of model solution of aniline and the appropriate operating conditions were investigated. The experiments were conducted in a 500 mL, stainless steel bubble reactor. Air is distributed throughout the reactor by the help of a sparger. It is also important to be aware of the selectivity of inorganic nitrogen (aniline) into ammonia, nitrite, nitrate and nitrogen gas to evaluate the efficiency of process.

The experiments were performed at constant operating conditions of, pH:7, pressure: 5atm, air flow rate: 1.36 L/min for 300 mL of aqueous solution and reaction time :2 hours. The parameters tested were initial aniline concentration (1, 4 g/L), catalyst loading (0.5, 2g/L) and temperature (100, 125, 150oC) Noncatalytic oxidation experiments were also performed to investigate the effect of catalyst presence. Also, to get more information on the path of the reaction, only an experimental set is performed with 4 g/L initial aniline concentration and 0.5 g/L catalyst loading the experiments are repeated at 100, 125,150 and 175oC at 4 atm of pressure.

As a result, at high aniline initial concentration (4g/L), higher removals were obtained with respect to removals obtained with low aniline initial concentration. In the experiments performed with high concentration of aniline, the effect of catalyst loading was not investigated as expected. The optimum operating conditions were found to be 0.5 g/L catalyst loading and a temperature of 150oC. At low aniline initial concentration, effect of catalyst loading was more considerable. The optimum operating conditions were 0.5 g/L catalyst loading and a temperature of 150oC or 2 g/L catalyst loading and a temperature of 125oC.

Keywords: Catalytic Wet Air Oxidation, nano-structured catalyst, aniline

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Immobilized Lipase-Catalysed Resolution of (R,S) 1-Phenyl 1-Propanol in Packed Bed Reactor

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Enzymes in organic solvents are finding increasing applications in organic synthesis. Lipases have been established as valuable catalysts in organic synthesis in order to perform regio- and stereo- selective transformations. Recently, the preparation of enantiomerically enriched compounds has become a major research area in industries, especially pharmaceutical and fine chemical industry. Lipases have been used in the resolution of racemic mixtures for the preparation of optically pure compounds. Derivatives of enantiomerically pure 1-phenyl 1-propanol, belonging to family of secondary alcohols is a cancer drug. The aim of this work is to establish an enzymatic transesterification process for the continuous production of the (S)-enantiomer 1-phenyl 1-propanol in a packed bed reactor. The enzymatic reaction studied is the stereoselective transesterification of racemic 1-phenyl 1-propanol by immobilized *Candida antarctica* lipase (Novozym 435).

The experiments were achieved using a glass column with a water jacket for temperature control. Immobilized biocatalyst (Novozyme 435) and molecular sieve were packed into the column. For continuous operation of the packed bed reactor, a reaction mixture [(R,S)1-phenyl 1-propanol, 167 mM and 334 mM acyl donor in isooctane] was pumped into the enzyme column at varying flow rates. Columns with different ratios of L/D (height to diameter) (5-10) were used. The conversion of (R,S)1-phenyl 1-propanol and enantiomeric excess of (S)1-phenyl 1-propanol was measured by HPLC using chiral column (Chiral cell OB).

The enantiomeric excess and conversion of the substrate were evaluated as a function of a few critical parameters, such as flow rate of reaction mixture, L/D ratio of enzyme column, the ratio of molecular sieve to enzyme. The maximum enantiomeric excess (ee) was obtained as 99 % between the residence time (2.36 -1.06 min. ee value was decreased (70 %) at the residence time below 1.06 min. It was not observed any effect of L/D on the enantiomeric excess and conversion. The enantiomeric excess increased from 95 % to 99 % with increasing the ratio of molecular sieve to enzyme (w/w) from 1/1 to 3/2 and later it decreased from 99 % to 86 %.

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Palladium Loaded NaY Zeolite: A Highly Active Catalyst for Suzuki-Miyaura Reactions of Aryl Halides Under Aerobic Conditions.

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A Palladium loaded NaY zeolite which was prepared through introduction of Pd(NH₃)₄²⁺ onto NaY zeolite by ion-exchange method was found to be highly active catalyst for Suzuki-Miyaura cross-coupling of aryl halides and arylboronic acids under aerobic conditions. Depending on the halide type, different experimental protocols had to be applied. In an N, N-dimethyl acetamide/water mixture (1/1), in the presence of Na₂CO₃ as a base and at 100 oC, aryl bromides coupled with phenylboronic acid to yield > 90% desired products with TOFs up to 4 x 10⁵ h⁻¹. Even multi-substituted, electron rich aryl bromides with sensitive functional groups could successfully couple.

The catalyst managed its activity effectively, also, in pure water solvent. Water soluble aryl bromides, such as bromobenzoic acids and bromophenols, promptly reacted with phenylboronic acid with Pd concentration of 0.001 mol% with TOF values of 4 x 10⁵ h⁻¹. Other water immiscible substrates required relatively higher Pd concentrations, typically 0.01 mol%, for effective coupling.

The catalyst can also activate the electron poor chloroarenes toward Suzuki-Miyaura reaction under aerobic conditions. However, the reaction required the use of ethoxides as bases, water free aprotic solvent and the employment of higher temperatures (120-140 oC). It is an interesting finding that the presence of 3-4 g of moist NaY zeolite/10 mL solvent medium was crucial for the activity of aryl chlorides.

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Understanding Catalysis via Model Catalyst Design at the Molecular Level

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Traditionally, many surface science techniques that have been used in the past as in situ methods for the investigation of heterogeneous catalytic reactions required ultra high vacuum (UHV) conditions, as well as relatively simple but atomically well-defined model catalysts such as single crystals. The difficulties in correlating UHV surface science experiments on well-defined model catalysts, with the high pressure (atmospheric or higher) results on sophisticated technical catalysts such as metal particles deposited on a high surface area metal oxide substrate have led to the genesis of two commonly used terms in surface science: the pressure gap and the materials gap. However, recent developments in the spectroscopic instrumentation and the model catalyst design have provided new opportunities for investigating the catalytic surfaces under conditions that are more similar to the realistic catalytic reaction conditions and thus created means to narrow the pressure and the materials gap such as the polarization modulation infrared reflection absorption spectroscopy (PM-IRAS). In this presentation, our recent results about various NO_x abatement related model heterogeneous catalytic systems will be investigated. Furthermore, a few illustrative examples highlighting crucial fundamental phenomena on the reasons of catalytic activity, catalyst poisoning and catalytic aging will also be discussed.

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