

## **CATL 1**

### **Plasma-CVD-coated glass beads as photocatalysts for water decontamination**

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Photocatalytically active titania (TiO<sub>2</sub>) films were deposited on 125 µm glass beads by means of low-temperature plasma-CVD in a vacuum fluidized bed, using titanium t-butoxide as precursor. The deposited amounts of titania were determined by digestion with (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> and the coatings were analyzed by XPS, ToF-SIMS, and HR-TEM. Glass particles coated with films of different thicknesses (10 - 100 nm) were tested as photocatalysts for water decontamination. The photocatalytic activity was evaluated in a fully irradiated, fluidized-bed photoreactor by monitoring the decomposition rate of oxalic acid in aqueous solution at 298 K. The as-deposited TiO<sub>2</sub> was amorphous and only after crystallization, induced by calcination at 450°C, the materials were catalytically active, with good abrasion resistance. The plasma-CVD films were about 50% as efficient as the reference material, P-25 immobilized on quartz sand.

## **CATL 2**

### **Fused hollow cathode cold atmospheric plasma source for gas treatment**

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A new type of the Cold Atmospheric Plasma source for catalytic plasma treatment of gas is presented. The Fused Hollow Cathode (FHC) source is based on simultaneous rf generation of hollow cathode discharges in an integrated, open structure, with flowing gas. The resulting Fused Hollow Cathode discharge is very stable, homogeneous, luminous, volume filling, without streamers. The power consumption is very low, of the order of tenths of Watt per cm<sup>2</sup> of the electrode structure area. Experimental results for the hollow electrode integrated open structure up to 20 cm<sup>2</sup> show the Fused Hollow Cathode performance with respect to varying process characteristics. The concept of the source is extremely suitable for scaling up for different gas throughputs. The Fused Hollow Cathode source represents a new non-equilibrium atmospheric plasma source for transformation of gas. Its design offers both - catalytic reactions in the bulk of plasma and at solid surfaces composing the open structure.

## **CATL 3**

### **Plasmachemical synthesis and/or regeneration of ultradispersed catalysts**

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Abstract text not available.

#### **CATL 4**

##### **Transformations on the alkali-halide crystals surface by the high energy irradiation and old air plasma influence**

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Physicochemical transformations on the alkali-halide crystals surface by the high-energy irradiation and cold air plasma influence were studied. The formation of the new compounds such as MeNO<sub>3</sub>, MeNO<sub>2</sub>, MeXO<sub>3</sub>, MeXO<sub>4</sub> was set up by the IR-spectroscopy.

#### **CATL 5**

##### **Microwave plasma torch production of supported metal particles**

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A low power, atmospheric pressure, microwave plasma torch was used to make alumina supported catalysts from aerosols. The aerosols consisted of mixtures of metal precursors and alumina, with metal weight content generally around 1 percent. These aerosols were passed through a variety (Argon, nitrogen, hydrogen or mixtures) of atmospheric pressure, low power (<1kW) plasmas at rates of the order of 5 liters/minute. The basis for this procedure was a simple hypothesis: in a mixture of metal particles and support materials metal atoms, generated during the passage of the input particles/salt precursors (<0.1 seconds in the 'hot zone') through the plasma torch, will coat the refractory support material. Metal particles will nucleate and grow on the surface of the refractory support in the cooler environment of the afterglow. To test the above hypothesis and potentially develop a novel technology, catalysts were initially created from inert gas/palladium particle-alumina particle aerosols which were passed through the center of atmospheric pressure, microwave generated, plasmas. Based on the results, variations were also tried. In particular, in later trials palladium salts were substituted for palladium metal particles. All the catalysts were found to be active for the test reaction, selective hydrogenation of 1-butene. Activity was found to be a strong function of the identity of the palladium precursor as well as the plasma and aerosol operating parameters. Also, the selectivity of all the plasma generated catalysts was better than that of catalysts produced using a conventional method. In fact, particles made by incipient wetness, but on plasma treated alumina, were also found to have the higher selectivity.

## **CATL 6**

### **Reaction mechanism study of lean NO<sub>x</sub> reduction using plasma catalysis**

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Low temperature plasma devices combined with select catalysts have been shown to reduce 60% or more of the NO<sub>x</sub> in simulated lean-burn exhaust gases between 150-350°C. Despite a large interest in this field, very little has been reported about reaction mechanisms. This work elucidates reaction mechanisms for plasma catalytic NO<sub>x</sub> reduction using two catalysts, sodium Zeolite-Y and gamma alumina. With plasma and NaY extrudates, we have previously shown conversion of NO to N<sub>2</sub> and N<sub>2</sub>O in simulated exhaust gas. Using NO<sub>2</sub> as the feed gas at a catalyst temperature of 225°C, we were able to achieve 25% conversion of NO<sub>x</sub> to N<sub>2</sub> and N<sub>2</sub>O thermally. With plasma, 55% conversion of NO<sub>x</sub> to N<sub>2</sub> and N<sub>2</sub>O was achieved. Using a gamma alumina catalyst at 340°C, 60% conversion with plasma was observed using NO<sub>2</sub> as the feed gas. However, no thermal conversion was observed with the gamma alumina, suggesting a different mechanism than NaY. Reports in the literature suggest that the critical role of the plasma is simply to oxidize NO to NO<sub>2</sub>, however our results suggest that plasma-generated partially oxidized hydrocarbons are also important for optimum catalyst performance.

## **CATL 7**

### **Plasma decomposition of NO in the presence of TiO<sub>2</sub> photocatalysts**

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Plasma Assisted Catalytic Technology (PACT) chemical reactors have been newly developed. Synergetic effects between plasma excitation and catalytic activation may be expected in PACT which is a stable dielectric barrier discharge between the electrodes coated with catalytic metals at atmospheric pressure. We reported catalytic effects of metal electrodes for Pt, Rh, Pd, Au, Cu and Ni for the decomposition of NO(Rh>Fe), CO<sub>2</sub>(Rh>Pt=Cu>Pd>Au) and H<sub>2</sub>O(Au>Rh>Pd). Photocatalytic TiO<sub>2</sub> particles are dispersed on the surface of Ag electrodes in PACT by internal oxidation methods and photocatalytic effects of the plasma radiation in NO reactions were observed. The discharge can be formed between the 1 mm gap with a 2~8kV sin-wave (~10kHz). We found 100% decomposition (2NO → N<sub>2</sub>+O<sub>2</sub>) at an initial [NO] of 50ppm even in 20% O<sub>2</sub> which was only observed for precious metals in the presence of dispersed TiO<sub>2</sub> particles. The decomposition of NO depends upon the O<sub>2</sub> concentration. It is difficult to decompose NO efficiently at more than around 7% O<sub>2</sub> in N<sub>2</sub> with PACT reactors. A CCD camera system was used to clarify transitions of radicals. Radiation energy around 337 nm from the second positive band of N<sub>2</sub> may be effective in using TiO<sub>2</sub> as a photocatalyst.

## **CATL 8**

### **On the interaction between plasmas and catalyst for the utilization of greenhouse gases**

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Since gas discharge plasma is a mixture of electrons, highly excited atoms and molecules, ions, radicals, photons, etc, the chemistry is very complex. A very selective product from this plasma chemistry could become very expensive. To improve the selectivity of plasma synthesis a heterogeneous catalyst has been introduced into the plasma reactor. The experiment confirmed that the use of heterogeneous catalyst improves the selectivity of objective hydrocarbons. The use of heterogeneous catalyst, however, induces some difficulties in understanding of interactions between plasmas and catalyst. Moreover, the conventional parameters like pressure and gas temperature are not enough to describe such a catalytic plasma conversion. In this presentation, some aspects of interactions between plasmas and catalyst have been investigated, including effects of catalyst surface area, XPS analysis of plasma-used catalysts and charge analysis of a catalyst involved in the gas discharge reactions.

## **CATL 9**

### **Selective hydrogenation of acetylene to ethylene during the conversion of methane in a catalytic dc plasma reactor**

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Plasma reactors have been found to be an effective method for the conversion of methane at low temperatures. The use of NaOH Y zeolite stabilizes the streamer discharges that otherwise would not exist, and modifies reaction selectivities. Using NaOH Y zeolite, high methane conversions (68%) and high yields of C<sub>2</sub> hydrocarbons (primarily as acetylene) (47%), hydrogen (52%), and carbon monoxide (21%) have been obtained at room temperature in a catalytic dc plasma reactor. However, the industrial demand for acetylene is relatively low and its inherent safety issues make it non-transportable. Therefore, a desirable alternative is to control the product distribution towards ethylene by the use of selective hydrogenation catalysis. Palladium catalysts are commonly used for the selective hydrogenation of acetylene to ethylene. In this study, palladium metal was deposited on the Y zeolite using a CVD technique with metal loadings between 0.05 wt% and 1.0 wt%. The addition of palladium to the Y zeolite in the dc plasma reactor shifted the product selectivity from acetylene to ethylene and ethane with no change in methane conversion. However, the C<sub>2</sub> selectivities were affected by the amount of palladium loading. The 0.05% wt did not completely remove all of the acetylene, but did show a high selectivity towards ethylene with some ethane. On the other hand, the 1.0% wt. completely converted all of the acetylene, but over hydrogenated it to ethane.

## **CATL 10**

### **Plasma catalysis for natural gas conversion**

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The growing demand for inexpensive, ultra-clean and more efficient energy sources has undoubtedly been the major driving force in today's petroleum, energy, and automobile industries as well as government spending and policies. As a result, there is a rebirth of Gas-to-Liquids (GTL) technologies for converting the huge supply of stranded natural gas reserves into clean, high value liquid fuels, mostly through the traditional Fischer-Tropsch processes. However, research in alternative and less-proven methods, namely plasma catalysis, has emerged as potentially economical route of upgrading natural gas to other fuels. In this paper, we present a review, based on recent literature and our analysis, of the promises and limitations of various plasma-based techniques for the conversion of natural gas to other valuable products, such as higher hydrocarbons, methanol, syngas, or fuel hydrogen. Both thermal and non-thermal plasma sources (gliding arc, corona, dielectric barrier and microwave discharges) are discussed with technical as well as prevailing economic and environmental considerations.

## **CATL 11**

### **Analysis of a high frequency pulsed plasma for methane conversion**

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Methane conversion to more valuable chemicals has been received much more attention during past decades. A widely used process of acetylene production from methane is a pyrolysis that a high reaction temperature is maintained by preheating and partial oxidation. A large amount of carbon dioxide is emitted from the process. An arc plasma of methane to produce acetylene was developed many years ago. The extremely high reaction temperature enhanced by arc plasma and the deposit of carbon in the plasma space are the defects although this arc plasma has a relatively high energy efficiency. Last year, we developed a new pulsed plasma for methane conversion to acetylene and hydrogen. The energy efficiency increased dramatically with increasing pulse frequency. In this paper, the mechanism and future development of a high frequency pulsed plasma are discussed.

## **CATL 12**

### **New approach in the electron theory of catalysis: Electrodynamical & quantum mechanical model**

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A development of the comprehensive electron catalysis theory and a study of catalytic activity of the different materials (f.e., metal & semiconductors materials) is of a great importance, especially under construction of the fuel elements, electrochemical and plasma chemical generators etc. In our paper we propose a new approach in the electron theory of catalysis, based on the electrodynamical and quantum-chemical modeling of catalytic processes on the metallic and non-metallic materials [1]. On the example of the simple model reactions: the hydrogen ionization reaction and oxygen electrorestoring there are found the electron structure parameters ( the Fermi surface states density, the Fermi momentum and statical dielectrical permeability) which determine the catalytic activity of the metallic and semiconductive materials on relation to indicated reactions. The key moment of models is in adequate choice of the effective potential field of materials medium and obtaining the direct link between electron structure parameters of materials and catalytic activity properties with further numeral solution of equations of the Schrodinger type [2,3]. Some important catalytic activity predictions are made for some metal-porphirines ( in particular, phtalociamine etc.) and also biocatalysts [4]. It is carried out the model calculations for catalytic processes and considered some possibilities of improving the technological characteristics for the plasma chemical reactors processes. As an example, the model consideration of the excitation process for the vibration levels in the ammonia in its diluted mixture with argon is carried out.

## **CATL 13**

### **Oxidation of toluene in a low-pressure plasma catalytic fluidised-bed reactor**

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Abstract Plasma technology has been used for the study of the oxidation of toluene. Experiments have been performed in a low-pressure plasma catalytic fluidized-bed reactor supplied by an RF 13.56 MHz generator. On-line mass spectrometry and off-line gas chromatography were used for a qualitative and quantitative analysis of the products. The products of the oxidation of toluene, under the same operating conditions, depend on the catalyst used. The use of NiO-WO<sub>3</sub> on alumina catalyst leads to the total oxidation of toluene. The use of the zeolite YNa( faujasite) leads to the partial oxidation of toluene and the formation of cresols while the use of the zeolite ZM760 (mordenite) enhances the phenol formation and improves the liquid products formation. The influence of the parameters such as characteristics and the nature of the particles, the reaction time and the reaction mechanisms are discussed.

#### **CATL 14**

##### **Roles of catalysts in nonthermal plasma chemical processing of hazardous air pollutants**

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Nonthermal plasma affords very unique reaction media where low concentrations of hazardous air pollutants (HAPs) can be efficiently decomposed at short residence times due to large magnitudes of excited electrons. Only with nonthermal plasma, however, it is very difficult to control the abundances of active oxygen species such as ozone, oxygen atoms, etc. derived from gaseous oxygen and humidity in situ. Perovskite oxides, which are known to act as catalysts for partial oxidation of hydrocarbons at higher temperatures, are inherently used as ferroelectric materials in packed-bed reactors, and other types of metal catalysts can be used as electrode modifiers and a component in nonthermal plasma-catalyst hybrid reactors. This paper will discuss the roles of catalysts such as barium titanate used in packed-bed reactors and metal catalysts hybridized with silent discharge reactors from the viewpoint of their involvement in the oxidation of nitrogen, CO, and VOCs.

#### **CATL 15**

##### **TOF: Validation of the concept in heterogeneous catalysis**

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Values of TOF reported for reactions on metallic catalysts have been validated by surface science work on single crystals in a number of cases. The best example of a TOF on a non-metallic catalyst is that of Haag: it deals with cracking of alkanes on ZSM5 over more than 3 orders of magnitude of specific rates and single acidic sites. In the future, as single site catalysts become the rule rather than the exception, rates will be routinely reported in reciprocal seconds, i.e., as a TOF. Two advantages of such reporting are the transparency of the single time unit and its reproducibility from lab to lab on samples that are well characterized by reported protocols.

## **CATL 16**

### **Electrostatic model for QM calculations of hydrocarbons in zeolites**

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Conversions of hydrocarbons on zeolites belong to the technologically most important classes of heterogeneous catalytic reactions. Experimentally, it is often difficult to obtain information about interaction of hydrocarbon molecules with active sites (AS) of zeolites and therefore computer simulations could be a possible alternative in these cases. The molecular cluster approach is the most widely used model for accurate description of interaction of hydrocarbons with AS at the quantum mechanics (QM) level. But the crystal environment of zeolite couldn't be taken in account with this model due to fast increasing of calculation time with extending of zeolite cluster. Since hydrocarbons interaction with atoms of AS is comparatively weak it is possible to presuppose that changes in properties of adsorbed molecules (e.g. vibrational bands shifting) are determined with electrostatic influence of zeolite framework and the electronic contribution to such interactions is small. QM calculations of vibrational frequencies of methane molecule proved this presupposition: spectra of methane calculated using model where all atoms of AS were replaced with point charges are in good agreement with cluster model calculations but computational time is in 10–20 times less (B3LYP/6-31g\*\*++). Beside this, increasing of atoms number in framework doesn't increase amount of CPU time, so electrostatic model can treat all unit cell of zeolite (approximately 300 atoms or more) (Fig. 1) and predict siting of hydrocarbons molecules in pores of different types of zeolites on the ground of experimental IR bands shifting.

## **CATL 17**

### **Computational studies of olefin epoxidation**

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The results of density functional calculations that aim at establishing the mechanism for the epoxidation of ethylene on silver surfaces will be presented. We examined the binding of ethylene to O atoms on silver, along with the role that cesium (a known promoter to the silver catalyzed epoxidation of olefins) plays in forming bound ethylene-oxygen species. Transition state calculations, for the formation of the epoxide and aldehyde products from ethylene, will also be presented. These calculations form the basis of our interpretation as to why silver is a facile surface for olefin epoxidation.

## **CATL 18**

### **Noble metal catalysed selective oxidation of alcohols in supercritical carbon dioxide**

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It has been known that noble metals can catalyse oxidation of organic molecules with gaseous oxygen in liquid phase. However, the use of organic solvents is strictly prohibited due to the risk of forming explosive peroxides. Water is the solvent of industrial consideration. Unfortunately, there are prevailing problems in selectivity, catalyst deactivation and metal leaching when the reaction is operated in water. Here we demonstrate, for the first time, that an extremely good selectivity to carbonyl compounds (>99%) at high yields is achieved through the oxidation of a range of alcohols by molecular oxygen using carbon-supported noble metal catalysts in supercritical CO<sub>2</sub>. On the other hand, a much lower selectivity to carbonyl compounds in aqueous solution is obtained with a significant quantity of the alcohol being over-oxidized to acid. Hence, the work suggests clearly that the active noble metal sites can undertake different mechanisms under different reaction media.

## **CATL 19**

### **TiO<sub>2</sub> - SiO<sub>2</sub> Xerogel photocatalyst for decontamination of indoor air**

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The application of TiO<sub>2</sub> for photocatalytic destruction of organics in air and water is a focus of significant research. A new photocatalyst, through the combination of SiO<sub>2</sub> and TiO<sub>2</sub>, has been synthesized that improves many of the problems faced by commercial photocatalysts such as P25. The resulting composite material has high surface area and good structural strength. This presentation presents the characterization of this material by atomic absorption, x-ray diffraction (XRD), transmission electron microscopy (TEM), and BET surface area analysis. The BET surface area was found to be about 500 m<sup>2</sup>/g. The XRD showed the TiO<sub>2</sub> to be anatase crystals with an average crystal size of 6 nm. TEM clearly shows the structure of the xerogel. The atomic absorption analysis revealed the composition of the xerogel. Finally, the photocatalytic activity under ultra-violet illumination was tested. It was found that the xerogel catalyzed the complete oxidation of ethylene faster than P25.

## **CATL 20**

### **In situ determination of catalyst oxidation and reduction kinetics in the selective oxidation of butane with VPO**

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We have utilized a novel, flow-through microbalance to measure oxygen uptake and release from VPO catalysts in the selective oxidation of butane to maleic anhydride. In addition to oxidation and reduction transients, this method permits determination of catalyst oxygen content during steady-state operation, as well as the capacity of the catalyst to deliver oxygen under cyclic redox operating conditions. Comparison of the kinetics and energetics of the individual catalyst reduction and oxidation steps with those obtained for steady-state and cyclic operation serves to distinguish the rate determining processes in butane oxidation under different reaction conditions.

## **CATL 21**

### **High selective supported Ni catalyst for hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol**

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Liquid hydrogenation of furfuryl alcohol was carried out at an autoclave using Ni-supported catalyst. Experimental results verified that best catalyst preparation method and procedure for the production of tetrahydrofurfuryl alcohol (THFA). Nickel supported catalysts with Ni contents 60-20wt% are the most active for the hydrogenation of furfuryl alcohol. The multiple impregnation method used in this study can improve obviously the activity and selectivity of the supported nickel catalyst. Under mild conditions (catalyst concentration 1wt%, 170 C, 5-6MPa, 4-4.5hrs, and agitation 1000rpm), furfuryl alcohol was hydrogenated into THFA with a good yield (95-96%), a high selectivity (>95%) and total conversion. More than 90% of THFA fraction with purity higher than 99% was obtained through the vacuum distillation of the product in a packed column with theoretical plate number 30-40 at vacuum of 730-740mmHg. It appears that furfuryl alcohol hydrogenation could be scaled up using the Ni-supported catalyst for the industrial production of THFA.

## **CATL 22**

### **Role of vanadia species in V/Ti oxide catalysts for toluene partial oxidation**

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Partial oxidation of toluene on V/Ti oxide catalysts is a reaction of industrial interest. In spite of the detailed study of the nature of surface vanadia species, there is an evident lack of the information concerning their reactivity. The present work demonstrates an application of the transient response techniques in combination with "in situ" DRIFT and FT-Raman spectroscopy for the discrimination of the reactivity of different vanadia species. Catalysts consisting of 0.35-3.7 monolayers of vanadia on titania were studied. In anaerobic conditions, conversion of toluene to benzaldehyde (BA) with selectivity close to 100% was found. BA is formed mainly by nucleophilic (O<sup>2-</sup>) oxygen in isolated monomeric vanadia species, while electrophilic oxygen (O<sup>-</sup>) present in polymeric and bulk vanadia species is responsible for the formation of carbon oxides. An addition of potassium was observed to increase the yield of BA.

## **CATL 23**

### **Semi-transparent titanium dioxide aerogels: Catalyst characterization and photocatalytic oxidation**

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Aerogels as a new form of photocatalysts could significantly improve the available technology for photocatalytic degradation of air contaminants. In this study a pure low density and an ultra-low density titanium dioxide aerogel have been synthesized and characterized with respect to surface area, particle size distribution, x-ray diffraction, and UV light penetration. In addition, photocatalytic tests have been carried out on ethylene in air. The same tests have been carried out on the presently most effective photocatalyst Degussa P25. The effectiveness of the aerogels in removing ethylene has been shown to be better in comparison to that of the Degussa. The superiority of the aerogel is mainly attributed to the larger fraction of interior surface, the high porosity resulting in a higher accessibility of reaction sites, and the deeper UV light penetration into the material. The reaction rate constants for ethylene oxidation were determined assuming a Langmuir-Hinshelwood type rate expression.

## **CATL 25**

### **Relationship of chemisorption- and isotopic tracing-based TOF's to true site activities for reactions on metal catalysts**

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Turnover frequency (TOF) is, without a doubt, one of the most important concepts in heterogeneous catalysis. TOF represents the rate at which a product is formed on an active site and provides a standardized measure used for elucidating the effects of catalyst composition and reaction conditions. While the definition of TOF is rather simple and easy to understand, obtaining an accurate measure of TOF for solid catalysts continues to be the greatest challenge in the 21st century. Traditionally, TOF is based on an assumption that the number of active sites on a solid catalyst can be determined by adsorption characteristics. For supported metal catalysts, the number of exposed metal atoms, measured by chemisorption of CO or H<sub>2</sub>, has been used to approximate the number of active sites. Even though the TOF based on chemisorption, TOFChem, has been an essential part of supported metal catalysis, the potential gross over-estimation of the active sites using the number of exposed metal atoms has been well acknowledged. We consider that the approximation of the number of active sites using the number of the most active surface intermediates determined via steady-state isotopic transient kinetic analysis (SSITKA) is the most viable means to date to better estimate the site activity. The values of TOF based on the number of active surface intermediates, TOFITK, have been compared with those of TOFChem for structure-sensitive and insensitive reactions on a variety of supported metal catalysts. The advantages and limitations of using TOFITK to approximate the site activity are discussed.

## **CATL 26**

### **FCC catalysts for enhanced LCO and LPG production**

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The pore distribution and acidity of zeolite and kaolinite were investigated to elucidate the coordinative effect of active components and support of catalysts on the enhanced liquefied petroleum gas and light cycle oil production in a fluid catalytic cracking process. The amount of weak acidity in macro pores was directly related to the conversion of heavy feedstock. The decrease of strong acidity in FAU zeolite (Y) inhibited the conversion of light cycle oil, while the addition of MFI zeolite (ZRP-4) in catalyst formulation selectively cracked the gasoline fraction into liquefied petroleum gas. VGO cracking reaction network, mechanism and its dependence on the catalytic materials were discussed.

## **CATL 27**

### **Atomic insight into hydrodesulfurization**

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We have dosed and imaged Ni atoms on single crystal MoS<sub>2</sub> at 4 K using a low temperature ultrahigh vacuum scanning tunneling microscope. This system was used to study fundamental aspects of the mechanism of hydrodesulfurization. STM images have shown that Ni atoms remains highly mobile at 77 K and still can be easily manipulated by the STM tip at 4 K. Spectroscopic imaging has shown that adsorbed Ni clusters display empty orbitals that are well suited to bind reactant molecules. STM studies on the adsorption and chemical changes of thiophenes on single crystal metal surfaces will also be presented.

## **CATL 28**

### **XPS study of carbided molybdena-alumina catalyst for the hydrodesulfurization of thiophene**

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The relationship between the molybdenum species of carbided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts and the HDS activity of the catalysts was studied by XPS. The HDS of thiophene was carried out in a fixed-bed microreactor at 623 K and atmospheric pressure. The 4.8% MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst was carbided by a temperature-programmed reaction with 20% CH<sub>4</sub>/H<sub>2</sub>. The 873 K carbided catalyst held the highest TOF (Based on CO adsorption). From XPS analysis, the 873 K carbided molybdenum catalyst was significantly difficult to sulfide the molybdenum species on the surface of the carbided catalyst. Furthermore, the molybdenum oxidation states of the carbided Mo/Al<sub>2</sub>O<sub>3</sub> catalysts decreased with increasing carbiding temperature, and Mo<sup>3+</sup> ion is predominant on the surface of the 873 K carbided catalyst and was the most active for the HDS of thiophene.

## **CATL 29**

### **Active sites in sulfated zirconia catalysts**

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One of the early claims for the sulfated zirconia was that it was a superacid. Acid sites have been of great interest because of the wide range of reactions that they catalyze. Much attention has been devoted to characterizing the Brønsted and Lewis acid sites. Many workers have reported a linear relationship between the number of Brønsted acid sites and the catalytic cracking. Thus, this is an excellent example of the ability to determine the number of acid sites and relate it to turnover frequencies (TOF). Attempts to do this with the sulfated zirconia show that a simple structure of the acid sites is inadequate for the sulfated zirconia catalyst.