

## Contents

### Articles

**Ezzat Rafiee, Mohammad Joshaghani,  
Fariba Tork, Akram Fakhri, Sara Eavani**

*Journal of Molecular Catalysis A: Chemical 283  
(2008) 1*

Esterification of mandelic acid catalyzed by heteropoly acid

The efficacy of various supported heteropoly acids in synthesis of mandelates from mandelic acid and various alcohols is investigated.

The results demonstrate that SiO<sub>2</sub> can be regarded as the best support for HPAs in comparison to other supports. The present procedure represents a clean, practical, simple, mild, and time-saving method for synthesis of mandelates with excellent yields and 100% selectivity.

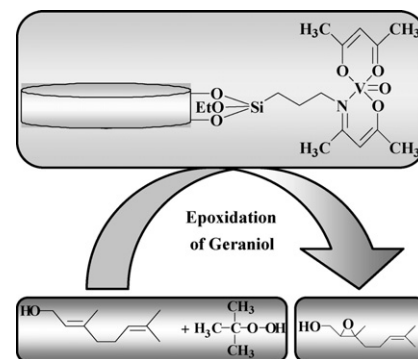


**Clara Pereira, Ana Rosa Silva,  
Ana Paula Carvalho, João Pires,  
Cristina Freire**

*Journal of Molecular Catalysis A: Chemical 283  
(2008) 5*

Vanadyl acetylacetonate anchored onto amine-functionalised clays and catalytic activity in the epoxidation of geraniol

Vanadyl(IV) acetylacetonate was immobilised onto two clays, laponite and K10-montmorillonite, functionalised with (3-aminopropyl)triethoxysilane. To assess the effectiveness of the immobilisation procedure, the complex was also directly anchored onto the two unmodified clays. The [VO(acac)<sub>2</sub>]-based materials were tested in the geraniol epoxidation. All catalysts were recycled and reused for 4 cycles.

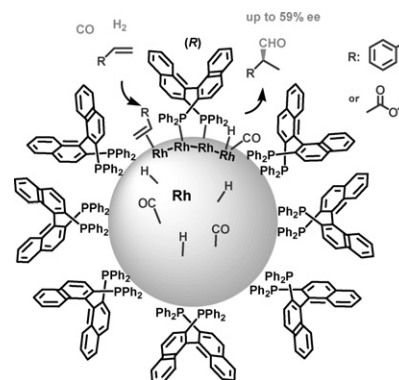


**Difei Han, Xiaohong Li, Huidong Zhang,  
Zhimin Liu, Gengshen Hu, Can Li**

*Journal of Molecular Catalysis A: Chemical 283  
(2008) 15*

Asymmetric hydroformylation of olefins catalyzed by rhodium nanoparticles chiral stabilized with (R)-BINAP ligand

The chirally stabilized rhodium nanoparticles and their supported catalysts exhibit high regioselectivity and chiral induction ability for the asymmetric hydroformylation of styrene and vinyl acetate.

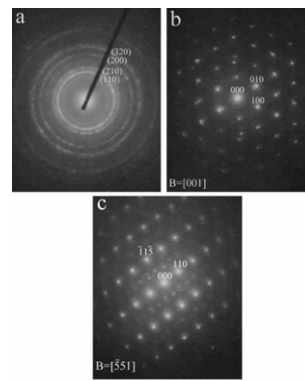


**Qinghe Yu, Chungeng Zhou, Xin Wang**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 23

Influence of plasma spraying parameter on microstructure and photocatalytic properties of nanostructured TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> coating

TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> coatings on transparent glasses were prepared by atmospheric plasma spraying (APS). As-sprayed TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> coatings consist of anatase TiO<sub>2</sub>, rutile TiO<sub>2</sub>, Fe<sub>3</sub>O<sub>4</sub> and FeTiO<sub>3</sub>. The grain size, rate of porosity and fractions of the anatase and FeTiO<sub>3</sub> phases in APS coatings were dependent on the process parameters. With an increase in plasma power, the content of anatase TiO<sub>2</sub> and the rate of porosity in the coatings were decreased while the content of the resultant FeTiO<sub>3</sub> phase and the grain size in the coating were increased. The coating condition of 500 A has the best photocatalytic efficiency and 600 A has the worst. The photocatalytic property of the APS TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> coatings was primarily dependent on synergistic effect of the fractions of FeTiO<sub>3</sub> and anatase phases.



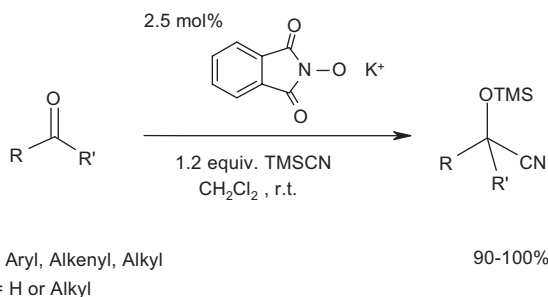
The selected area electron diffraction patterns (SAEDPs) of as-sprayed TiO<sub>2</sub>-Fe<sub>3</sub>O<sub>4</sub> coatings.

**Mohammad G. Dekamin, Shahrzad Javanshir, M. Reza Naimi-Jamal, Rahim Hekmatshoar, Javad Mokhtari**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 29

Potassium phthalimide-*N*-oxyl: An efficient catalyst for cyanosilylation of carbonyl compounds under mild conditions

Potassium phthalimide-*N*-oxyl was used as an effective, easy to handle and readily available Lewis basic organocatalyst for the facile addition of trimethylsilyl cyanide to various carbonyl compounds under mild conditions.

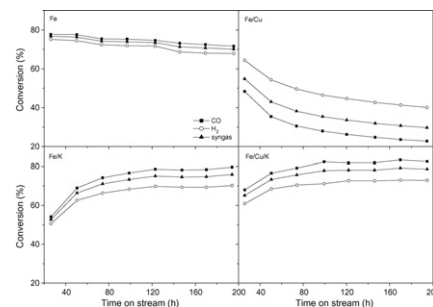


**Haijun Wan, Baoshan Wu, Chenghua Zhang, Hongwei Xiang, Yongwang Li**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 33

Promotional effects of Cu and K on precipitated iron-based catalysts for Fischer-Tropsch synthesis

The activity and stability of the catalysts. Reaction condition: 260 °C, 1.5 MPa, H<sub>2</sub>/CO = 0.67 and GHSV = 1000 h<sup>-1</sup>. The addition of Cu promoter into iron-based catalyst decreases the catalyst activity and accelerates the deactivation of iron-based catalyst. The addition of K and the co-promotional effects of Cu and K not only increase the catalyst activity, but also improve the catalyst stability.

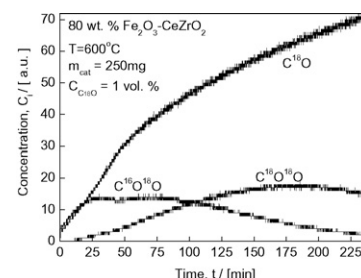


**Vladimir Galvita, Liisa K. Rihko-Struckmann, Kai Sundmacher**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 43

The CO adsorption on a Fe<sub>2</sub>O<sub>3</sub>-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst studied by TPD, isotope exchange and FTIR spectroscopy

The interaction of carbon monoxide with Fe<sub>2</sub>O<sub>3</sub>-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> was investigated by the adsorption investigation under isothermal CO/H<sub>2</sub> exposure and temperature-programmed desorption (TPD), as well as by in-situ diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), in order to understand the carbon monoxide formation during the cyclic water gas shift reaction. When the Fe<sub>2</sub>O<sub>3</sub>-Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> catalyst was exposed to a mixture of CO and H<sub>2</sub>, the majority of the surface species depicted by the DRIFT analysis were associated with carbonates. Investigations carried out using a H<sub>2</sub>O/He mixture showed that carbon oxides were produced during the interconversion of carbonate species on the catalyst surface with steam. The steady-state isotopic C<sub>18</sub>O experiments revealed that the Boudouard reaction occurred at temperatures higher than 350 °C (see following figure). The carbon deposits which were formed on the catalyst surface during the reduction step through the Boudouard reaction, led to CO formation during the successive re-oxidation step.

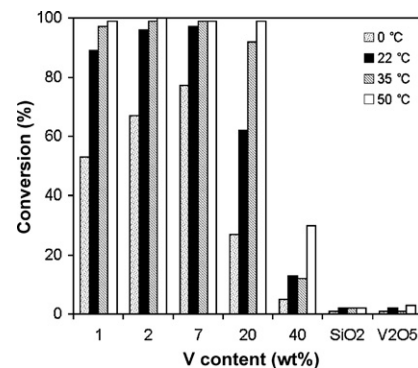


**Stephanie R. Livingston, Dharmesh Kumar, Christopher C. Landry**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 52

Oxidation of 2-chloroethyl ethyl sulfide using V-APMS

Vanadium-doped mesoporous silica was prepared by wet impregnation and characterized by XRD and  $N_2$  physisorption. The physical properties of the material were then correlated with results from the catalytic oxidation of 2-chloroethyl ethyl sulfide with peroxide. Isolated vanadium sites, obtained at low loadings, were important in producing the most active catalysts. Possible reaction schemes are discussed.

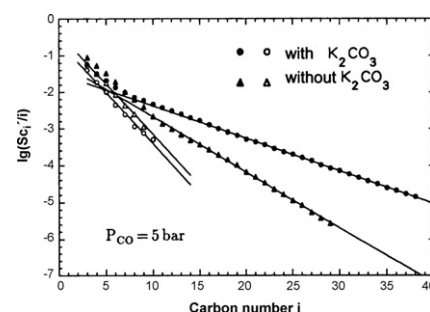


**J. Gaube, H.-F. Klein**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 60

Studies on the reaction mechanism of the Fischer–Tropsch synthesis on iron and cobalt

A novel mechanism of the Fischer–Tropsch synthesis is proposed based on the hypothesis that two incompatible mechanisms are involved resting exclusively on methylene and on carbon monoxide insertion, respectively. This hypothesis is supported by various co-feeding experiments with alkenes, alcohols and diazomethane and contributes to a sound interpretation of the promoter effect of alkali on iron and of the distribution of branched hydrocarbons.

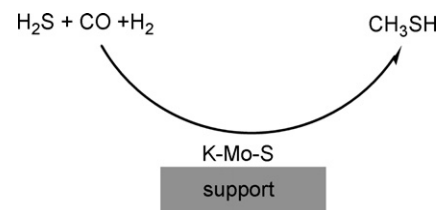


**Aiping Chen, Qi Wang, Qiaoling Li, Yingjuan Hao, Weiping Fang, Yiquan Yang**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 69

Direct synthesis of methanethiol from  $H_2S$ -rich syngas over sulfided Mo-based catalysts

One-step synthesis of  $CH_3SH$  from the reaction of  $H_2S$ -rich syngas ( $H_2S/CO/H_2$  mixtures) was investigated over the sulfided supported K–Mo catalysts. Compared to the  $CH_3OH-H_2S$  route for the synthesis of methanethiol, this method skips the step of the synthesis of  $CH_3OH$  from syngas.

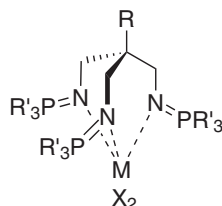


**Laurence Beaufort, Federica Benvenuti, Lionel Delaude, Alfred F. Noels**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 77

New tripodal iminophosphorane-based ethylene oligomerization catalysts. Part II. Catalytic behavior

Seven transition-metal complexes based on new tripodal iminophosphorane ligands were investigated as initiators for the oligomerization of ethylene in the presence of aluminum co-catalysts using high-throughput techniques. Structural modifications, either at the metal center or within the tripodal ligand, did not markedly affect the catalytic activity but had a significant impact on the oligomer distribution.



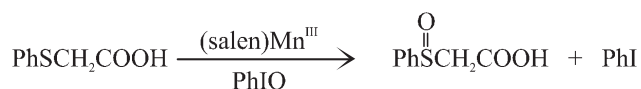
R = Me, Ph  
 R' = Cp, Ph  
 MX<sub>2</sub> = NiBr<sub>2</sub>, FeCl<sub>2</sub>,  
 PdCl<sub>2</sub>, Cu(OTf)<sub>2</sub>  
 Cp = cyclopentyl

**Arunachalam Chellamani, Paramasivan Sengu**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 83

Mechanistic study on the oxidation of (phenylthio)acetic acids by oxo(salen)manganese(V) complexes and the reactivity–selectivity principle.

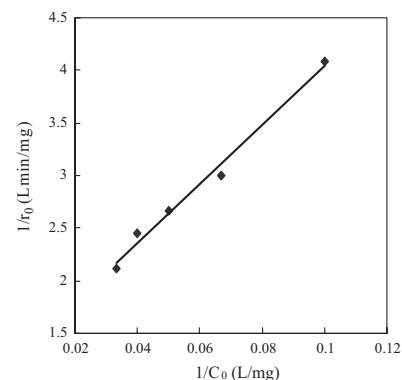
The oxygenation of several (*para*-substituted phenylthio)acetic acids with various substituted oxo(salen)manganese(V) complexes follows an overall second-order kinetics, first-order each in the oxidant and substrate. Substituent effect studies reveal the operation of a SET mechanism. This redox system falls under strong reactivity–selectivity principle.

**Zhong Junbo, Ma Di, Zhao Hong, Li Minjiao, Xie Bin, Li Jianzhang**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 93

Kinetic study on photocatalytic degradation of reactive orange 5 solution with phosphotungstic acid

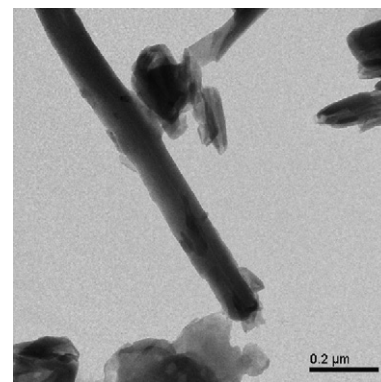
Figure shows plot of the reciprocal of the initial rate  $r_0^{-1}$  versus the reciprocal of the initial concentration  $C_0^{-1}$  for photocatalytic degradation of KGN. It is clear that a good fitting of the model to the experimental data may be observed thus confirming the L–H nature of the photocatalytic degradation reaction mechanism.

**Guilherme Sippel Machado, Kelly Aparecida Dias de Freitas Castro, Fernando Wypych, Shirley Nakagaki**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 99

Immobilization of metalloporphyrins into nanotubes of natural halloysite toward selective catalysts for oxidation reactions

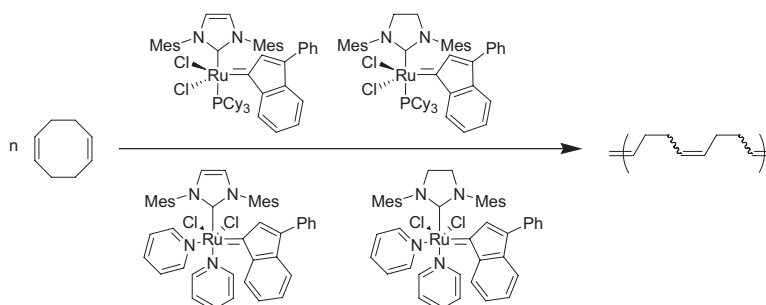
The process of metalloporphyrin immobilization into the nanotubes/nanoscrolls of natural halloysite is described. Immobilization of 100% was attained with an anionic iron(III) porphyrin via a pressurized system. The catalytic activities of the new materials were evaluated in the oxidation of cyclo-octene, cyclohexane and *n*-heptane. The results obtained in the present study show that these novel immobilized catalysts are a promising system for selective oxidation reactions.

**Pierre de Frémont, Hervé Clavier, Véronique Montembault, Laurent Fontaine, Steven P. Nolan**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 108

Ruthenium–indenylidene complexes in ring opening metathesis polymerization (ROMP) reactions

A series of well-defined ruthenium-based indenylidene catalysts are tested in ring opening polymerization metathesis (ROMP) with cycloocta-1,5-diene. The reactivity of the catalysts is examined by the polymerization kinetics.

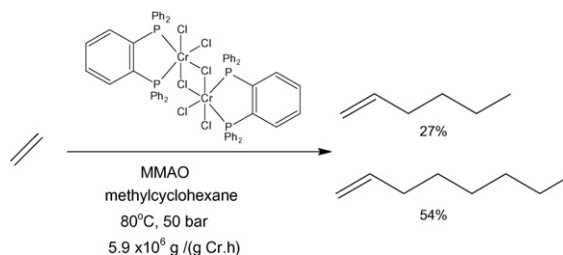


**Matthew J. Overett, Kevin Blann, Annette Bollmann, Raylene de Villiers, John T. Dixon, Esna Killian, Munaka C. Maumela, Hulisani Maumela, David S. McGuinness, David H. Morgan, Adam Rucklidge, Alexandra M.Z. Slawin**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 114

Carbon-bridged diphosphine ligands for chromium-catalysed ethylene tetramerisation and trimerisation reactions

The use of carbon-bridged diphosphine ligands in chromium-catalysed ethylene tri- and tetramerisation reactions was investigated. A catalyst with the bis(diphenylphosphino)benzene ligand was found to be among the most active selective oligomerisation catalysts yet reported. Various aspects of ligand design were found to independently affect the catalyst selectivity (1-octene:1-hexene ratio), including steric constraints around the catalytic centre, phosphine basicity, P–Cr–P bite angle and ligand bridge structure.

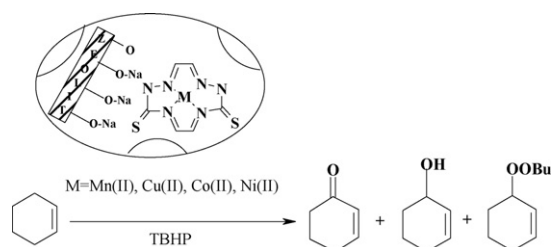


**Masoud Salavati-Niasari**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 120

Host (nanocage of zeolite–Y)/guest (manganese(II), cobalt(II), nickel(II) and copper(II) complexes of 12-membered macrocyclic Schiff-base ligand derived from thiosemicarbazide and glyoxal) nanocomposite materials: Synthesis, characterization and catalytic oxidation of cyclohexene

A series of Mn(II), Co(II), Ni(II) and Cu(II) complexes with 12-membered macrocyclic tetradentate ligand have been synthesized and characterized as homogeneous and encapsulated into the nanopores of zeolite–Y. The chelation of zeolite-exchanged metal(II) by N-containing ligand gives rise to a whole class of Host–Guest Nanocomposite Materials (HGNM) as heterogeneous liquid-phase oxidation, which exhibits similar catalytic performances than the homogeneous ones.

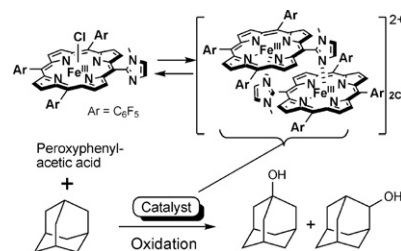


**Yuji Miyazaki, Akiharu Satake, Yoshiaki Kobuke**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 129

Oxidation of adamantane catalysed by imidazolyl-porphyrinatoiron(III) complexes and structural studies of 5-coordinating iron(III) porphyrin

Oxidation of adamantane with peroxyphenylacetic acid in the presence of chloro-5-(1-methyl-2-imidazolyl)-10,15,20-tri(pentafluorophenyl)porphyrinatoiron(III) (ImTPFP–Fe(III)Cl) gave adamantanol in 76% yield, whereas the yield was only 26% in the case of chloro-5,10,15,20-tetra(pentafluorophenyl) porphyrinatoiron(III). The apparent effect of the appended imidazolyl group is discussed in terms of a 5-coordinated dimer of ImTPFP–Fe(III)Cl, which was observed in the <sup>1</sup>H and <sup>19</sup>F NMR, and UV–vis spectra.

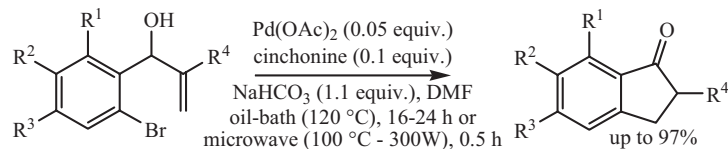


**Anna Maria Zawisza, Benjamin Ganchegui, Iván González, Sandrine Bouquillon, Anna Roglans, Françoise Hémin, Jacques Muzart**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 140

Heck-type reactions of allylic alcohols. Part IV: (2-Substituted)-1-indanones via 5-endo-trig cyclizations.

Under microwave irradiation, the Pd-catalyzed 5-endo-trig cyclizations depicted on the scheme proceed not only more quickly than under thermal heating, but also with higher yields.

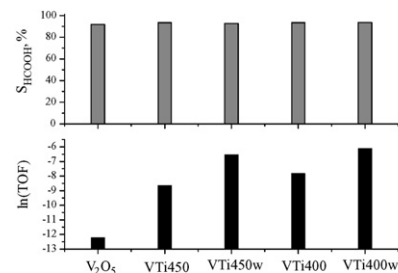


**G.Ya. Popova, T.V. Andrushkevich,  
E.V. Semionova, Yu.A. Chesalov, L.S. Dovitova,  
V.A. Rogov, V.N. Parmon**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 146

Heterogeneous selective oxidation of formaldehyde to formic acid on V/Ti oxide catalysts: The role of vanadia species

The activity of supported V/Ti oxide catalysts is determined by the nature of vanadium oxide species. The monolayer vanadium–titania catalysts are highly active in the formaldehyde oxidation to formic acid. According to the TPR data, these vanadium species contain a more weakly bonded oxygen as compared to oxygen in bulk  $V_2O_5$ . The bulk  $V_2O_5$  is highly selective, but low active in respect to the oxidation of formaldehyde to formic acid as compared with the supported V/Ti oxide catalysts. The presence of bulk amorphous or crystalline  $V_2O_5$  in the V/Ti oxide catalysts leads to a partial blocking of the active sites and hence decreases the catalyst activity in the oxidation of formaldehyde to formic acid.



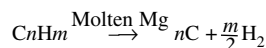
Comparison of the selectivity to formic acid ( $S_{HCOOH}$ ) and activity  $\ln(TOF)$  for the  $V_2O_5$  and V/Ti oxide catalysts at the temperature of the reaction 120°C. The conversion of formaldehyde is 78±2% for V/Ti catalysts and 8.9% for  $V_2O_5$ .

**K. Wang, W.S. Li, X.P. Zhou**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 153

Hydrogen generation by direct decomposition of hydrocarbons over molten magnesium

Hydrogen and carbon were prepared by hydrocarbon direct decomposition.

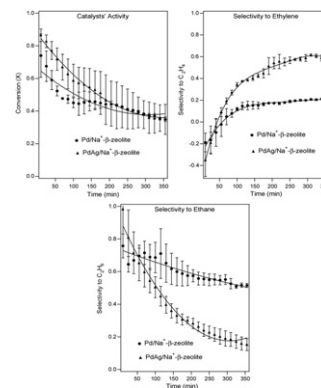


**Wei Huang, Raul F. Lobo, Jingguang G. Chen**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 158

Characterization of  $Na^+$ - $\beta$ -zeolite supported Pd and PdAg bimetallic catalysts using EXAFS, TEM and flow reactor

Alloying Pd with Ag reduced the acetylene hydrogenation activity but increased the selectivity. The apparent activation energy of acetylene hydrogenation on Pd/ $Na^+$ - $\beta$ -zeolite and PdAg/ $Na^+$ - $\beta$ -zeolite were estimated to be 8 kcal/mol and 15.2 kcal/mol. The formation of PdAg bimetallic particles on the  $Na^+$ - $\beta$ -zeolite support was confirmed by TEM, EXAFS, and CO adsorption using FTIR spectroscopy.



**Denys Baskakov, Wolfgang A. Herrmann**

*Journal of Molecular Catalysis A: Chemical* 283 (2008) 166

Water-soluble metal complexes and catalysts. Part XI. Novel ligands from tris(hydroxymethyl) phosphane and amino acids: Synthesis and catalytic studies in two-phase hydroformylation

