

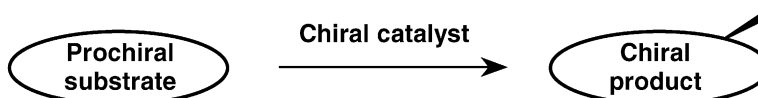
Contents

Articles

**Hans-Ulrich Blaser, Benoît Pugin,
Felix Spindler**

*Journal of Molecular Catalysis A: Chemical 231
(2005) 1*

Progress in enantioselective catalysis assessed
from an industrial point of view



Critical factors for industrial application:

- Enantioselectivity
- Catalyst activity and productivity
- Functional group tolerance
- Availability and diversity of catalysts
- Development time and effort

Important transformations:

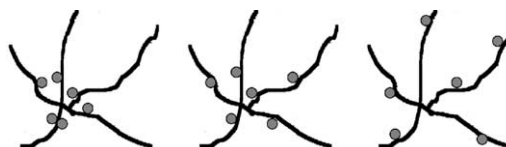
- Reduction of C=C, C=O and C=N groups
- Oxidation reactions
- Addition to C=C, C=O and C=N bonds
- Miscellaneous reactions

L. Holub, K. Jeřábek

*Journal of Molecular Catalysis A: Chemical 231
(2005) 21*

Influence of partial neutralization on catalytic
activity of ion exchange resin

Location of the active group within the polymer network may influence both the accessibility of the group and its intrinsic reactivity. Formally identical chemical content or overall concentration of the functional groups does not mean that the groups have also identical reactivity.

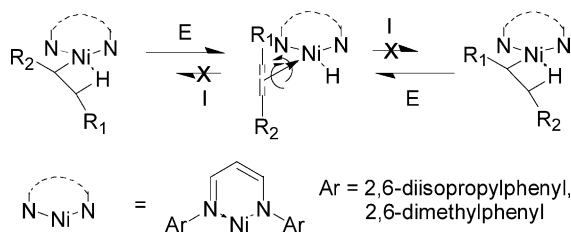


**Junkai Zhang, Haiyang Gao, Zhuofeng Ke,
Feng Bao, Fangming Zhu, Qing Wu**

*Journal of Molecular Catalysis A: Chemical 231
(2005) 27*

Investigation of 1-hexene isomerization and oli-
gomerization catalyzed with β -diketiminato Ni(II)
bromide complexes/methylaluminoxane system

β -Diketiminato Ni(II) complexes/MAO system catalyzed the isomerization and oligomerization of 1-hexene were investigated. The obtained products involve *trans*- and *cis*-2-hexenes and various dimer isomers. The “walking” of the Ni(II) atom from a secondary carbon to another one along the alkyl chain of the *m*-Ni-alkyl intermediates is blocked in the β -diketiminato Ni(II)/MAO catalyst system.

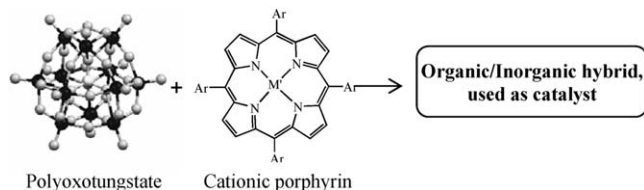


Isabel C.M.S. Santos, Susana L.H. Rebelo, M. Salete S. Balula, Rosália R.L. Martins, M. Manuela M.S. Pereira, Mário M.Q. Simões, M. Graça P.M.S. Neves, José A.S. Cavaleiro, Ana M.V. Cavaleiro

Journal of Molecular Catalysis A: Chemical 231 (2005) 35

Association of Keggin-type anions with cationic *meso*-substituted porphyrins: synthesis, characterization and oxidative catalytic studies

The preparation, characterization and catalytic application of new organic/inorganic hybrids with polyoxometalates and cationic porphyrins or metalloporphyrins are described. At 60°C, some of the new compounds catalysed the epoxidation with H₂O₂ of *cis*-cyclooctene, geraniol and (+)-3-carene with higher conversions than the corresponding metalloporphyrins alone. The polyoxometalates contributed, in general, to the stabilization of the metalloporphyrins in catalytic conditions.

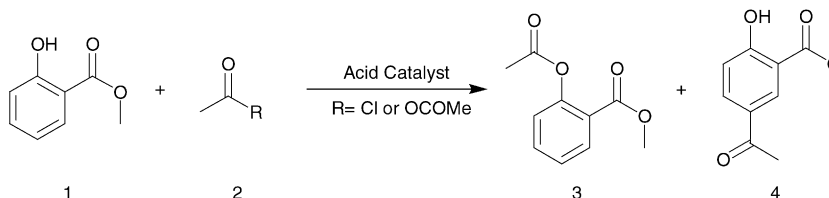


Mark J. Gronnow, Duncan J. Macquarrie, James H. Clark, Paul Ravenscroft

Journal of Molecular Catalysis A: Chemical 231 (2005) 47

A study into the use of microwaves and solid acid catalysts for Friedel-Crafts acylations

A range of solid acids has been used for the acetylation of methyl salicylate (see Scheme 1). A comparison between microwave and traditional heating has been also made. The microwave-solid acid combinations offer truly catalytic acylations with much reduced reaction times compared to those afforded by traditional alternatives albeit in reduced yields compared with aluminium chloride.

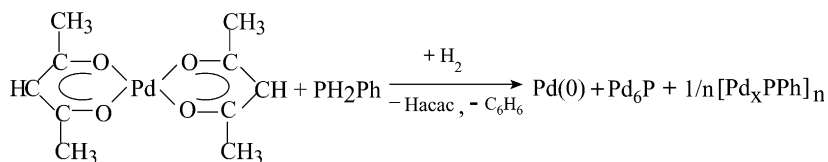


L.B. Belykh, T.V. Goremyka, L.N. Belonogova, F.K. Schmidt

Journal of Molecular Catalysis A: Chemical 231 (2005) 53

Highly active and selective catalysts of hydrogenation based on palladium bis-acetylacetonate and phenylphosphine

A new highly active catalyst for hydrogenation of unsaturated bonds, carbonyl and nitro groups based on Pd bis-acetylacetonate and phenylphosphine has been suggested. The conversion of Pd(acac)₂+*n*PH₂Ph in hydrogen leads to the formation of nanoscale particles containing Pd(0), Pd phosphide and Pd phosphinidene complexes. The associates of Pd phosphinidene complexes and Pd phosphide act as the carrier for Pd cluster.

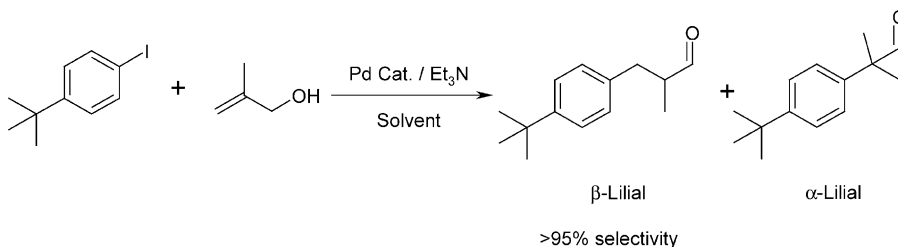


Stewart A. Forsyth, H.Q. Nimal Gunaratne, Christopher Hardacre, Angela McKeown, David W. Rooney, Kenneth R. Seddon

Journal of Molecular Catalysis A: Chemical 231 (2005) 61

Utilisation of ionic liquid solvents for the synthesis of Lily-of-the-Valley fragrance { β -Lilial[®]; 3-(4-*t*-butylphenyl)-2-methylpropanal}

The Heck reaction has been utilised in an ionic liquid to selectively form β -Lilial[®] which currently produced in the fine chemicals industry on the kiloton scale. The ionic liquid reaction shows higher rates of reaction than organic solvents and may be recycled easily.

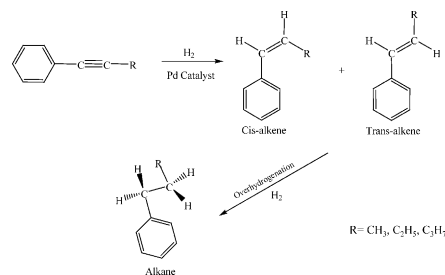


N. Marín-Astorga, G. Pecchi, J.L.G. Fierro, P. Reyes

Journal of Molecular Catalysis A: Chemical 231 (2005) 67

A comparative study of Pd supported on MCM-41 and SiO₂ in the liquid phase hydrogenation of phenyl alkyl acetylenes mixtures

The stereoselective hydrogenation of phenyl alkyl acetylenes at 298K and atmospheric pressure of hydrogen over Pd-supported catalysts has been studied. The catalysts were prepared by impregnation of MCM-41 and SiO₂ with Pd(acac)₂ precursor, with metal content close to 1wt.%. All the solids were characterised by nitrogen adsorption-desorption isotherms at 77K, TPR, H₂ and CO chemisorption, XRD and TEM measurements. Three competitive reaction systems 1-phenyl-1-pentyne/1-phenyl-1-propyne, 1-phenyl-1-pentyne/1-phenyl-1-butyne, 1-phenyl-1-butyne/1-phenyl-1-propyne have been examined. The results show that the competitive reaction results in an increase of the hydrogenation rate for phenyl alkyl acetylene with minor alkyl chain size in all studied systems. The reactions were found to be zero order concerning the alkyne concentration.

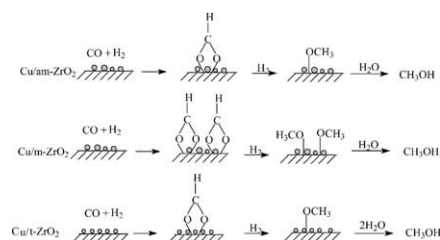


Zhong-Yi Ma, Cheng Yang, Wei Wei, Wen-Huai Li, Yu-Han Sun

Journal of Molecular Catalysis A: Chemical 231 (2005) 75

Catalytic performance of copper supported on zirconia polymorphs for CO hydrogenation

Cu/t-ZrO₂ catalyst showed the highest copper dispersion and the best catalytic performance for methanol synthesis from CO hydrogenation. The formate and methoxyl species were evidenced as intermediates and the formate-to-methoxyl mechanism was suggested for methanol synthesis on Cu/ZrO₂ catalyst.

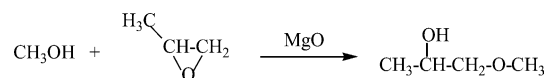


Wenyu Zhang, Hui Wang, Wei Wei, Yuhan Sun

Journal of Molecular Catalysis A: Chemical 231 (2005) 83

Solid base and their performance in synthesis of propylene glycol methyl ether

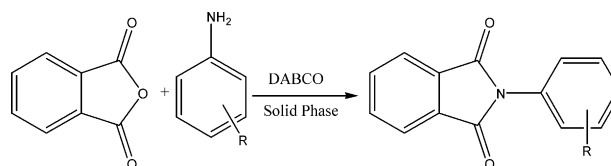
1-Methoxy-2-propanol can be efficiently synthesized over MgO from methanol and propylene oxide due to its base sites with moderate strength, which was illustrated by using CO₂-TPD and FTIR.



Majid M. Heravi, Rahim Hekmat Shoar, Leila Pedram

Journal of Molecular Catalysis A: Chemical 231 (2005) 89

Synthesis of *N*-arylphthalimides catalyzed by 1,4-diazabicyclo[2.2.2]octane [DABCO] in solventless system

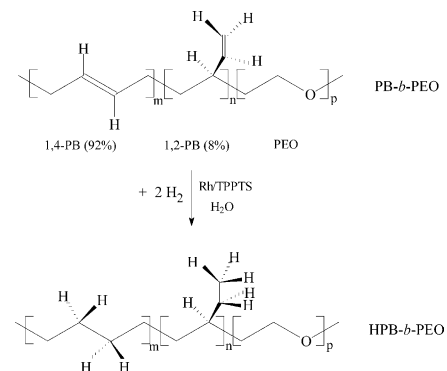


Vasilis Kotzabasakis, Eleni Georgopoulou, Marinos Pitsikalis, Nikos Hadjichristidis, Georgios Papadogianakis

Journal of Molecular Catalysis A: Chemical 231 (2005) 93

Catalytic conversions in aqueous media: a novel and efficient hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) catalyzed by Rh/TPPTS complexes in mixed micellar nanoreactors

Exceptionally high catalytic activities ($\text{TOF} > 840 \text{ h}^{-1}$) were achieved in the aqueous phase hydrogenation of polybutadiene-1,4-*block*-poly(ethylene oxide) catalyzed by water-soluble Rh/TPPTS complexes [TPPTS = $\text{P}(\text{C}_6\text{H}_4\text{-}m\text{-SO}_3\text{Na})_3$] in mixed micellar nanoreactors formed by dodecyltrimethylammonium chloride along with PB-*b*-PEO especially when *n*-hexane was added to the reaction system. This is the first example of a catalytic hydrogenation of an unsaturated polymer using water-soluble transition metal TPPTS complexes in aqueous media.

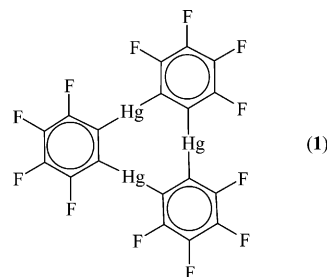


A.P. Zraisky, O.I. Kachurin, L.I. Velichko, I.A. Tikhonova, G.G. Furin, V.B. Shur

Journal of Molecular Catalysis A: Chemical 231 (2005) 103

Cyclic trimeric perfluoro-*o*-phenylenemercury: a highly efficient phase transfer catalyst for nitration of aromatic substrates with dilute nitric acid

A new remarkable property of perfluorinated polymeric macrocycle ($o\text{-C}_6\text{F}_4\text{Hg}$)₃ (**1**) is described. As has been shown previously, this macrocycle is capable of readily binding various anions and neutral Lewis bases to form complexes having unusual sandwich, pyramidal and bipyramidal structures. Now, the ability of **1** to catalyse the phase transfer nitration of aromatic substrates with dilute nitric acid in the presence of NaNO_2 as an initiator and NaCl as a promotor is reported.

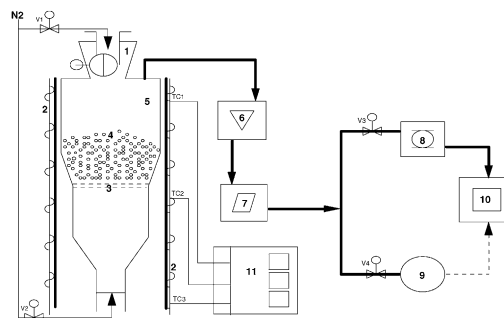


Y.-H. Lin, M.-H. Yang

Journal of Molecular Catalysis A: Chemical 231 (2005) 113

Catalytic reactions of post-consumer polymer waste over fluidised cracking catalysts for producing hydrocarbons

Diagram of a catalytic fluidised-bed reactor system: 1. Feeder; 2. Furnace; 3. Sintered distributor; 4. Fluidised catalyst; 5. Reactor; 6. Condenser; 7. de-ionised water trap; 8. 16-loop automated sample system; 9. Gas bag; 10. GC; 11. Digital controller for three-zone furnace.

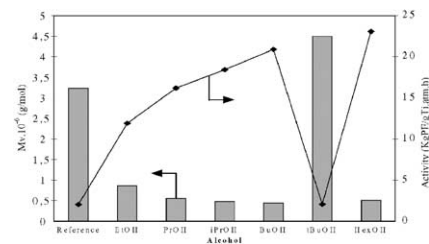


J. Chirinos, J. Fernández, D. Pérez, T. Rajmankina, A. Parada

Journal of Molecular Catalysis A: Chemical 231 (2005) 123

Effect of alkoxyxilanes formed in situ on the properties of Ziegler–Natta catalysts for olefin polymerisation

$\text{TiCl}_4/\text{MgCl}_2$ -alkoxyxilane-based catalysts for olefin polymerisation were prepared by supporting TiCl_4 on recrystallised MgCl_2 containing grafted alkoxyxilane. The alkoxyxilanes were generated in situ during the recrystallisation of MgCl_2 with SiCl_4 from alcoholic solutions. The effect of the nature of the alkoxyxilane on the catalytic performance and polymer properties was studied by using different alcohols as solvent. The results of the polymerisation of ethylene and propylene showed that the activities, molecular weights and isotacticities depended strongly on the structure of the alkoxyxilane (see figure), which possibly acts as an internal electron donor.

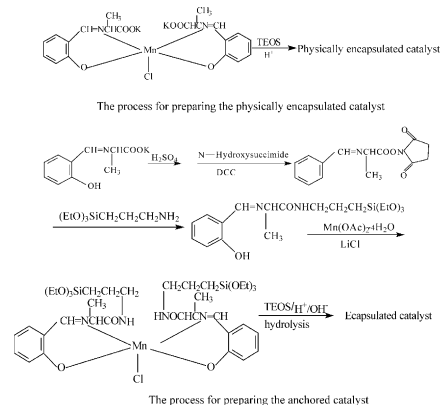


Jiquan Zhao, Jianping Han, Yuecheng Zhang

Journal of Molecular Catalysis A: Chemical 231 (2005) 129

Preparation of encapsulated and anchored alanine–salicylaldehyde Schiff base Mn(III) complexes by sol–gel method and their performance in aerobic epoxidation of cyclohexene

Two heterogenized catalysts entrapping alanine–salicylaldehyde Schiff base Mn(III) complex were prepared. They were characterized by FT-IR, XPS, N₂ adsorption and ICP and their catalytic performance for the aerobic epoxidation of cyclohexene were investigated.

**Zhongkui Zhao, Weihong Qiao, Guiru Wang, Zongshi Li, Lübo Cheng**

Journal of Molecular Catalysis A: Chemical 231 (2005) 137

Alkylation of α -methyl-naphthalene with long-chain alkenes catalyzed by butylpyridinium bromochloroaluminate ionic liquids

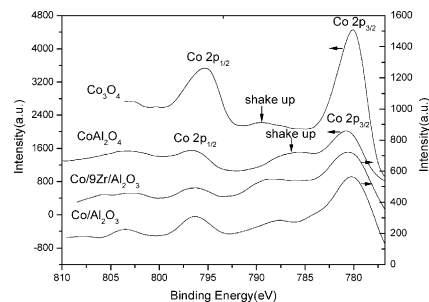
Alkylations of α -methyl-naphthalene with long-chain olefins (mixed olefins, $m+n = 7$ and 8 , mass ratio of C₁₁ to C₁₂ is 45/55) in the presence of novel ionic liquids have been investigated. The various reaction parameters are optimized. The BPyBr–AlCl₃ ionic liquids could be a practical catalyst for long-chain alkylation of α -methyl-naphthalene.

**Haifeng Xiong, Yuhua Zhang, Kongyong Liew, Jinlin Li**

Journal of Molecular Catalysis A: Chemical 231 (2005) 145

Catalytic performance of zirconium-modified Co/Al₂O₃ for Fischer–Tropsch synthesis

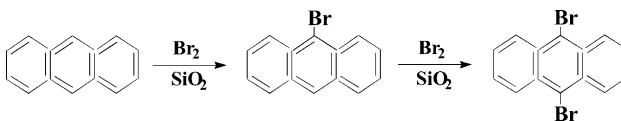
The addition of Zr inhibits the formation of CoAl₂O₄ and causes the increase of cobalt active site and reducibility for Co/Al₂O₃ catalyst, which enhances the activity and C₅₊ selectivity for Fischer–Tropsch synthesis. The olefin/paraffin ratio is found to increase.

**Jorma A. Seetula**

Journal of Molecular Catalysis A: Chemical 231 (2005) 153

Catalytic bromination of anthracene on silica gel

The kinetics of catalytic bromination of anthracene on silica gel has been investigated in situ under first-order conditions by means of spectroscopic methods. The relative rate of the 9-bromoanthracene and the 9,10-dibromoanthracene formations was determined.

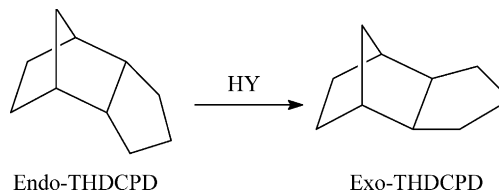


**Enhui Xing, Zhentao Mi, Chengwei Xin,
Li Wang, Xiangwen Zhang**

Journal of Molecular Catalysis A: Chemical 231
(2005) 161

Endo- to exo-isomerization of tetrahydrodicyclopentadiene catalyzed by commercially available zeolites

Isomerization of tetrahydrodicyclopentadiene was investigated. H-type Y zeolites were chosen to catalyze the conversion of endo-THDCPD to exo-THDCPD. The results show H-USY was active and selective enough for exo-THDCPD production.

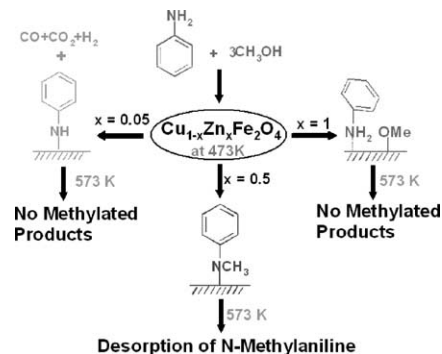


**Munusamy Vijayaraj,
Balasundaram Murugan,
Shubhangi Umbarkar,
Sooryakant G. Hegde,
Chinnakonda S. Gopinath**

Journal of Molecular Catalysis A: Chemical 231
(2005) 169

An insight into the mechanism of selective mono-*N*-methylation of aniline on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$: a DRIFTS study

Mechanistic details of selective mono-*N*-methylation of aniline on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ are successfully explained by in situ IR studies. Perpendicular orientation of aromatic ring of aniline, methyl group availability, an optimum metal-ion distribution on catalyst surface and stability of methyl groups on Zn lead selectively to *N*-methylaniline on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Desorption limited kinetics is evident from the *N*-methylaniline formation at low temperature.

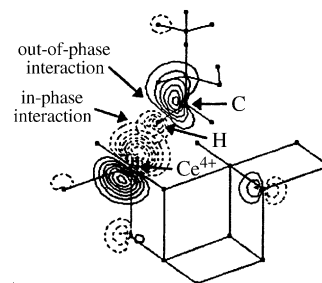


**Naoki Ichikawa, Satoshi Sato, Ryoji Takahashi,
Toshiaki Sodesawa**

Journal of Molecular Catalysis A: Chemical 231
(2005) 181

PIO study on 1,3-butanediol dehydration over CeO_2 (111) surface

Quantum calculation was executed to observe the orbital interactions between 1,3-butanediol molecule and CeO_2 (111) surface. Out-of-phase interaction between H and C atoms in the 2-position methylene group was induced by the in-phase interaction between the H atom and a surface Ce cation.

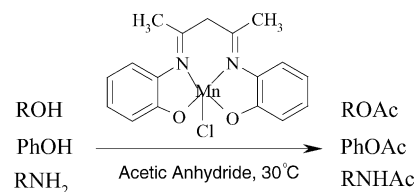


**Masoud Salavati-Niasari,
Samansa Hydarzadeh, Ahmad Amiri,
Shahpour Salavati**

Journal of Molecular Catalysis A: Chemical 231
(2005) 191

Manganese(III) bis(2-hydroxyanil)acetylacetonato complex as effective catalyst for acylation of alcohols, amines and phenols with acetic anhydride

Acylation of alcohols, amines and phenols with acetic anhydride in an efficient manner using [bis(2-hydroxyanil)acetylacetonato]manganese(III)chloride, $[\text{Mn}(\text{haacac})\text{Cl}]$, as a catalyst. Using this method acylation of a primary NH_2 group in the presence of secondary NH and primary OH have been achieved with high selectivity.

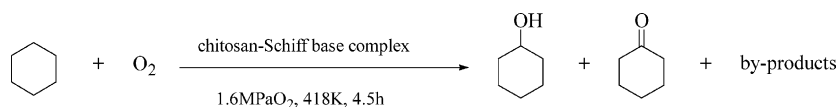


Jinhui Tong, Zhen Li, Chungu Xia

Journal of Molecular Catalysis A: Chemical 231 (2005) 197

Highly efficient catalysts of chitosan-Schiff base Co(II) and Pd(II) complexes for aerobic oxidation of cyclohexane in the absence of reductants and solvents

Three chitosan-Schiff base Co(II) and Pd(II) complexes were prepared and characterized. The complexes have shown high catalytic activities for cyclohexane oxidation with molecular oxygen without any solvents and reductants. When chitosan-salicylaldehyde Schiff base Co(II) complex was used as catalyst, 9100 turnover numbers and 96% selectivity were obtained. The complexes can be reused several times and are also efficient for the oxidation of bulky cyclic alkanes and linear alkanes.

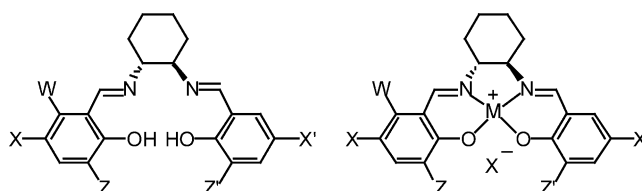


Marie F. Renehan, Hans-Jörg Schanz, Eoghan M. McGarrigle, Cormac T. Dalton, Adrian M. Daly, Declan G. Gilheany

Journal of Molecular Catalysis A: Chemical 231 (2005) 205

Unsymmetrical chiral salen Schiff base ligands. Synthesis and use in metal-based asymmetric epoxidation reactions

A set of chiral non-racemic unsymmetrical salen ligands and complexes derived from two dissimilar salicylaldehydes was synthesised and used in asymmetric epoxidation reactions. The results were compared to the same reactions run with the symmetrical analogues.

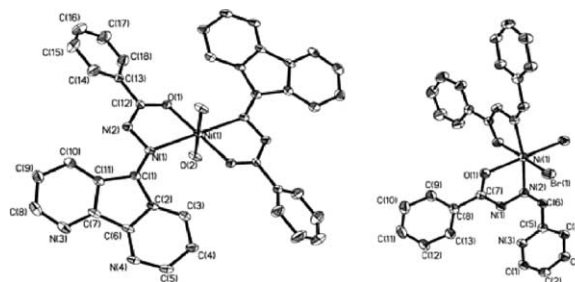


Junxian Hou, Wen-Hua Sun, Dongheng Zhang, Liyi Chen, Wei Li, Dongfeng Zhao, Haibin Song

Journal of Molecular Catalysis A: Chemical 231 (2005) 221

Preparation and characterization of acylhydrazone nickel(II) complexes and their catalytic behavior in vinyl polymerization of norbornene and oligomerization of ethylene

The acylhydrazone nickel(II) complexes bearing the derivatives of 4,5-diazafluorene-9-one-benzoylhydrazone or 2-pyridinecarboxaldehyde-benzoylhydrazone show considerable activities for ethylene oligomerization at ambient pressure and good activities for vinyl polymerisation of norbornene when activated with methylaluminoxane.

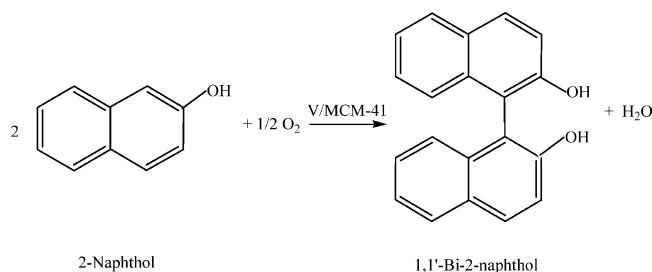


Takahiro Ikeda, Naohisa Misawa, Yuichi Ichihashi, Satoru Nishiyama, Shigeru Tsuruya

Journal of Molecular Catalysis A: Chemical 231 (2005) 235

Liquid-phase oxidative coupling of 2-naphthol by vanadium catalysts supported on MCM-41

1,1'-Bi-2-naphthol was produced by the liquid-phase oxidative coupling reaction of 2-naphthol using vanadium impregnated MCM-41 (V/MCM-41) catalyst, of which active vanadium sites were suggested to be the tetrahedral V⁵⁺ species based on the correlation between the yield of 1,1'-bi-2-naphthol and the intensity of the tetrahedral V⁵⁺ species estimated by the diffuse reflectance (DR) spectra of the V/MCM-41 catalysts.

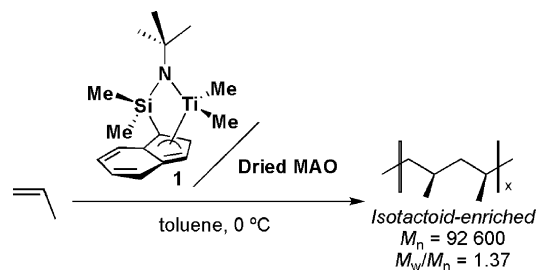


Kei Nishii, Tomiki Ikeda, Munetaka Akita, Takeshi Shiono

Journal of Molecular Catalysis A: Chemical 231 (2005) 241

Polymerization of propylene with $[t\text{-BuNSiMe}_2\text{Ind]TiMe}_2$ -MAO catalyst systems

Propylene polymerization was conducted with *ansa*-indenylamidodimethyltitanium complex ($[t\text{-BuNSiMe}_2\text{Ind]TiMe}_2$: **1**) in toluene or heptane in the presence of dried methylaluminoxane (MAO) or dried modified MAO (MMAO), which was prepared from the toluene solutions of MAO or MMAO by removing free trialkylaluminium contained. When dried MAO was used in toluene, **1** effected quasi-living polymerization of propylene, and gave poly(propylene) with isotactic triad of 40%.

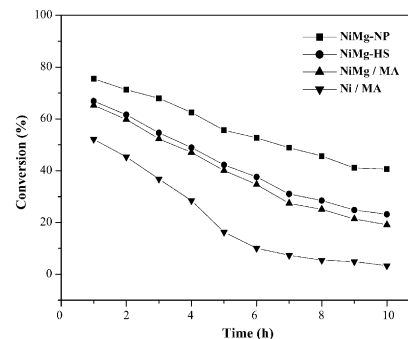


Pil Kim, Younghun Kim, Heesoo Kim, In Kyu Song, Jongheop Yi

Journal of Molecular Catalysis A: Chemical 231 (2005) 247

Preparation, characterization, and catalytic activity of NiMg catalysts supported on mesoporous alumina for hydrodechlorination of *o*-dichlorobenzene

Chemical templates containing binary metal components were used for the preparation of porous NiMg-NP (a NiMg- Al_2O_3 catalyst templated by a NH_4OH -treated precipitate) and NiMg-HS (a NiMg- Al_2O_3 catalyst templated by a HCl-treated solution). Ni and NiMg catalysts supported on mesoporous alumina (MA) were also prepared by an impregnation method. These catalysts were characterized and applied to the hydrodechlorination of *o*-dichlorobenzene.

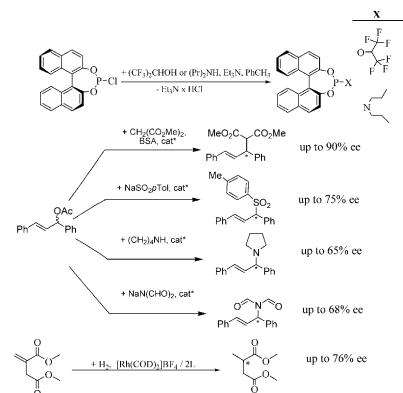


K.N. Gavrilov, S.E. Lyubimov, S.V. Zheglov, E.B. Benetsky, V.A. Davankov

Journal of Molecular Catalysis A: Chemical 231 (2005) 255

Enantioselective Pd-catalysed allylation with BINOL-derived monodentate phosphite and phosphoramidite ligands

P-monodentate phosphite (**1**) and phosphoramidite (**2**) ligands have been synthesised from (*S*)-BINOL. The phosphoramidite **2** showed higher enantioselectivity than its phosphite analogue **1** and provided good enantioselectivity in the Pd-catalysed allylic substitution of 1,3-diphenylallyl acetate with dimethyl malonate (up to 90% ee), sodium *para*-toluene sulfinate (up to 75% ee), pyrrolidine (up to 65% ee) and sodium diformylamide (up to 68% ee), as well as in the Rh-catalysed hydrogenation of dimethyl itaconate (up to 76% ee).



Bülent Alıcı, smail Özdemir, Kaan Karaaslan, Engin Çetinkaya, Bekir Çetinkaya

Journal of Molecular Catalysis A: Chemical 231 (2005) 261

Synthesis and catalytic properties of 1-alkylperimidineruthenium(II) complexes

The synthesis and characterization of the new complexes $\text{RuCl}_2(\text{N-alkylperimidine})(p\text{-cymene})$ are presented. New in situ generated ruthenium (perimidine) complexes are active catalysts to perform the cycloisomerization of 1,6-diallyltyrosylamide.

