

## Contents

### Articles

**Craig L. Hill**

*Journal of Molecular Catalysis A: Chemical 262 (2007) 2*

Progress and challenges in polyoxometalate-based catalysis and catalytic materials chemistry

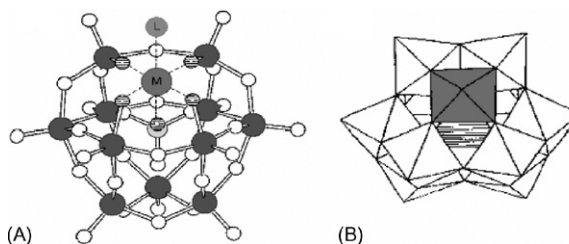
Classic challenges in polyoxometalate-based catalytic processes include quantifying the role of ion pairing on turnover rates, selectivity and system stability, knowing the actual reacting units, and systematically controlling competing processes.

**Oxana A. Kholdeeva, Raisa I. Maksimovskaya**

*Journal of Molecular Catalysis A: Chemical 262 (2007) 7*

Titanium- and zirconium-monosubstituted polyoxometalates as molecular models for studying mechanisms of oxidation catalysis

Recent developments in the synthesis of monosubstituted Keggin-type polyoxometalates  $[PM(L)W_{11}O_{39}]^{n-}$  ( $M = Ti(IV)$  and  $Zr(IV)$ ), studying their interaction with  $H_2O$  and  $H_2O_2$ , and application as molecular models of Ti- and Zr-single-site catalysts to probe mechanisms of  $H_2O_2$ -based selective oxidations are surveyed.

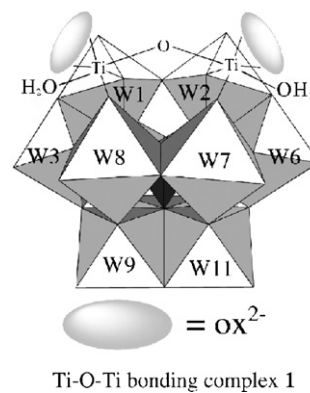


**Chika Nozaki Kato, Kunihiko Hayashi, Satoshi Negishi, Kenji Nomiya**

*Journal of Molecular Catalysis A: Chemical 262 (2007) 25*

A novel Ti–O–Ti bonding species constructed in a metal-oxide cluster  $[\{Ti(OH_2)(ox)\}_2(\mu-O)(\alpha-PW_{11}O_{39})]^{5-}$  as a precatalyst: Epoxidation of alkenes with hydrogen peroxide

A novel Ti–O–Ti bonding complex constructed in the monomeric, mono-lacunary  $\alpha$ -Keggin polyoxotungstate,  $[\{Ti(OH_2)(ox)\}_2(\mu-O)(\alpha-PW_{11}O_{39})]^{5-}$  (**1**) can act as a precatalyst for the epoxidation of cyclooctene, cyclohexene, and 1-octene with aqueous  $H_2O_2$  at 25 °C in a homogeneous system. The catalytic activities of complex **1** were considerably higher than those of dimeric mono-, di-, and tri-titanium(IV)-substituted Keggin polyoxotungstates.

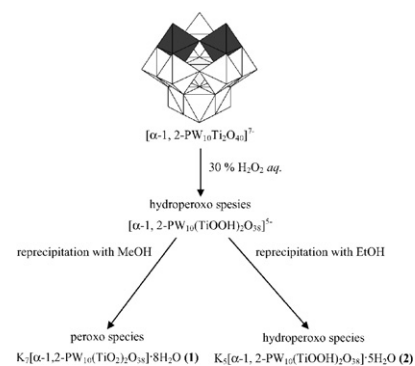


**Kunihiko Hayashi, Chika Nozaki Kato, Akira Shinohara, Yoshitaka Sakai, Kenji Nomiya**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 30

Isolation, characterization, and reactivity of the reaction products of the dimeric, Ti–O–Ti bridged anhydride form of the 1,2-di-titanium(IV)-substituted  $\alpha$ -Keggin polyoxometalate with aqueous 30%  $\text{H}_2\text{O}_2$

The isolation and characterization of the monomeric bis[peroxotitanium(IV)]-substituted  $\alpha$ -Keggin polyoxometalate (POM)  $\text{K}_7[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiO}_2)_2\text{O}_{38}] \cdot 8\text{H}_2\text{O}$  (**1**) and the monomeric bis[hydroperoxotitanium(IV)]-substituted  $\alpha$ -Keggin POM  $\text{K}_5[\alpha\text{-}1,2\text{-PW}_{10}(\text{TiOOH})_2\text{O}_{38}] \cdot 5\text{H}_2\text{O}$  (**2**) are described. Complex **1** did not show any activity for 2-propanol oxidation in the absence of 30%  $\text{H}_2\text{O}_2$  whereas complex **2** showed an effective activity for the oxidation reaction.

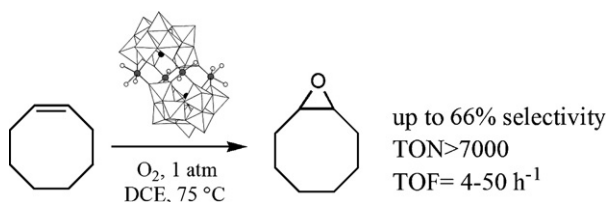


**Marcella Bonchio, Mauro Carraro, Anna Farinazzo, Andrea Sartorel, Gianfranco Scorrano, Ulrich Kortz**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 36

Aerobic oxidation of *cis*-cyclooctene by iron-substituted polyoxotungstates: Evidence for a metal initiated auto-oxidation mechanism

Catalytic aerobic epoxidation is a key process for new sustainable systems in the field of hydrocarbon functionalization. The screening of selected Fe-POM catalysts for the aerobic epoxidation has been performed using *cis*-cyclooctene as model substrate.

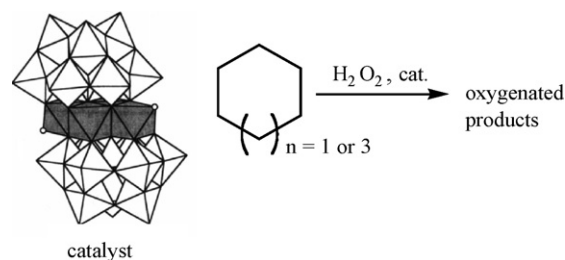


**Isabel C.M.S. Santos, José A.F. Gamelas, M. Saletto S. Balula, Mário M.Q. Simões, M. Graça P.M.S. Neves, José A.S. Cavaleiro, Ana M.V. Cavaleiro**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 41

Sandwich-type tungstophosphates in the catalytic oxidation of cycloalkanes with hydrogen peroxide

Sandwich-type tungstophosphates of general formula  $\text{B-}\alpha\text{-}[\text{M}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{n-}$ ,  $\text{M} = \text{Co}^{\text{II}}$ ,  $\text{Mn}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$ , were used for the catalytic oxidation of cyclohexane and cyclooctane with hydrogen peroxide in acetonitrile. The conversion of the cycloalkanes was always higher than 68% after 12 h of reaction.

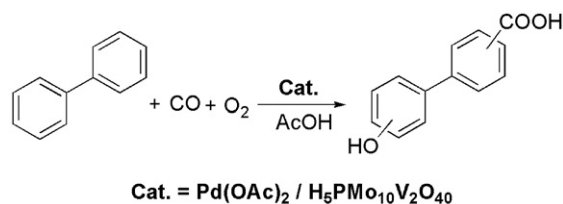


**Shingo Yamada, Satoshi Sakaguchi, Yasutaka Ishii**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 48

Carboxylation and hydroxylation of biphenyl by the Pd/molybdovanadophosphoric acid/dioxygen system

Concomitant introduction of COOH and OH groups to biphenyl was achieved by allowing biphenyl to react with CO and  $\text{O}_2$  using the Pd/molybdovanadophosphoric acid catalytic system. The reaction was found to proceed through the formation of biphenylcarboxylic acid followed by hydroxylation of the resulting carboxylic acid.

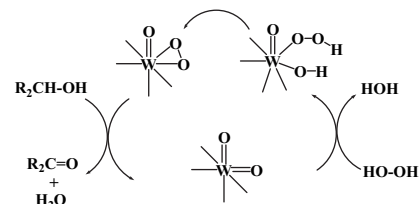


**Rohit H. Ingle, N.K. Kala Raj, P. Manikandan**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 52

[SbW<sub>9</sub>O<sub>33</sub>]-based polyoxometalate combined with a phase transfer catalyst: A highly effective catalyst system for selective oxidation of alcohols with H<sub>2</sub>O<sub>2</sub>, and spectroscopic investigation

Na<sub>9</sub>[SbW<sub>9</sub>O<sub>33</sub>] in conjunction with methyltricapryl ammonium chloride is efficient for selective oxidation of variety of alcohols with aq. H<sub>2</sub>O<sub>2</sub> to yield corresponding carbonyls even in the absence of organic solvents. In case of allylic alcohols, the catalyst is highly selective for the alcohol oxidation reaction and least selective for epoxidation reaction. IR studies support the formation of W-peroxo intermediate species and the stability of the catalyst.

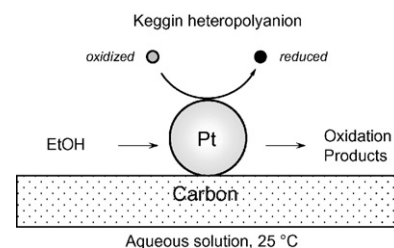


**Yurii V. Geletii, Andrei Gueletii, Ira A. Weinstock**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 59

Electron capture and transport by heteropolyanions: Multi-functional electrolytes for biomass-based fuel cells

Keggin heteropolyanions,  $\alpha$ -H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (H<sub>3</sub>1) and H<sub>5</sub>PV<sub>2</sub>Mo<sub>10</sub>O<sub>40</sub> (H<sub>5</sub>2), are evaluated for use as an alternative to H<sub>2</sub> in the storage and transfer of electrons in biomass-based electrochemical energy-conversion devices. These cluster-anions are reversibly reduced as they efficiently “capture” electrons by rapid oxidation of intermediates formed during Pt(0)-catalyzed anaerobic oxidations of EtOH and other alcohols.



**Guixian Li, Yong Ding, Jianming Wang, Xiaolai Wang, Jishuan Suo**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 67

New progress of Keggin and Wells–Dawson type polyoxometalates catalyze acid and oxidative reactions

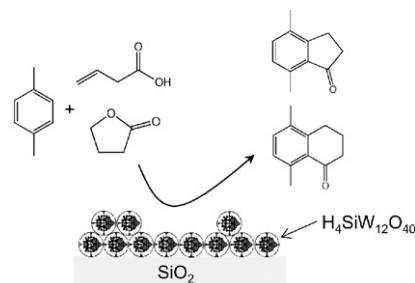
This review summarizes some recent research progress in catalytic application of Keggin and Wells–Dawson type polyoxometalates. Particular attention is given to most developments of our recent studies on the use of POMs as heterogeneous and homogeneous catalysts for the selective oxidation and acid-catalyzed reactions. With the development of the synthetic chemistry of POMs, more and more POMs with novel structures will be produced and POMs catalysis will find much wider practical applications.

**Yuichi Kamiya, Yasunobu Ooka, Chisato Obara, Ryuichiro Ohnishi, Toshio Fujita, Youhei Kurata, Katsuyuki Tsuji, Tetsuo Nakajyo, Toshio Okuhara**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 77

Alkylation–acylation of *p*-xylene with  $\gamma$ -butyrolactone or vinylacetic acid catalyzed by heteropolyacid supported on silica

Friedel–Crafts-type reaction of *p*-xylene with  $\gamma$ -butyrolactone or vinylacetic acid over solid acids were investigated. H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> supported on SiO<sub>2</sub> was found to be the most active and selective catalyst for these reactions.

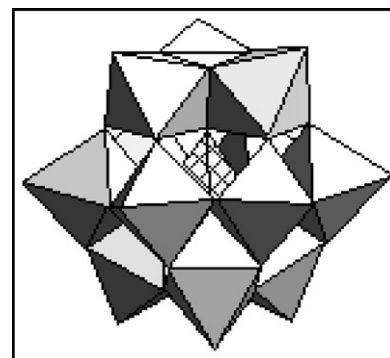


**I.V. Kozhevnikov**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 86

Sustainable heterogeneous acid catalysis by heteropoly acids

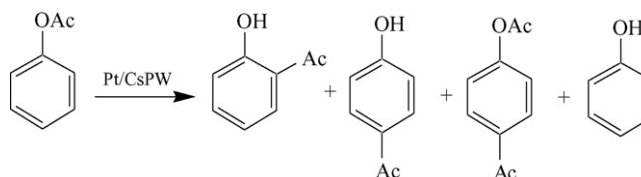
Heterogeneous acid catalysis by heteropoly acids offers substantial economic and green benefits. This paper describes approaches that could help overcome the deactivation of HPA catalysts: developing novel HPA catalysts possessing high thermal stability; enhancing coke combustion; coke inhibition on HPA catalysts; reactions in supercritical fluids; and cascade reactions using multifunctional HPA catalysis.

**Mehdi Musawir, Elena F. Kozhevnikova, Ivan V. Kozhevnikov**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 93

Fries rearrangement of phenyl acetate catalysed by platinum-doped heteropoly salt: Catalyst regeneration and reuse

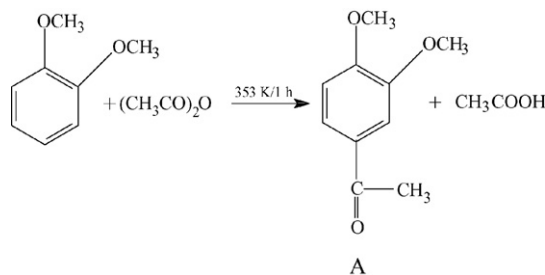
The acidic cesium heteropoly salt  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  (CsPW) is an active solid acid catalyst for the Fries rearrangement of phenyl acetate. Doping CsPW with Pt metal (0.3 wt%) allows full regeneration of catalyst activity and selectivity by coke combustion at 350 °C and ambient pressure, which occurs without structural damage to the catalyst.

**Dhanashri P. Sawant, A. Vinu, F. Lefebvre, S.B. Halligudi**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 98

Tungstophosphoric acid supported over zirconia in mesoporous channels of MCM-41 as catalyst in veratrole acetylation

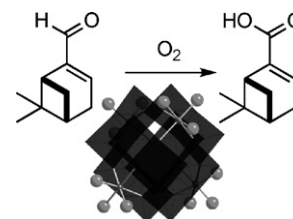
Tungstophosphoric acid (TPA) over zirconia dispersed uniformly in mesoporous silica (MS) channels of MCM-41 and MCM-48 were synthesized and tested for their catalytic activities in veratrole acetylation to acetoveratrone with acetic anhydride. Among the catalysts, 15 wt.%TPA/22.4 wt.%ZrO<sub>2</sub>/MCM-41 calcined at 1123 K was found to be most active than others in the acetylation reaction.

**Dorit Sloboda-Rozner, Karine Neimann, Ronny Neumann**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 109

Aerobic oxidation of aldehydes catalyzed by  $\epsilon$ -Keggin type polyoxometalates [Mo<sub>12</sub>V<sub>3</sub>O<sub>39</sub>( $\mu_2$ -OH)<sub>10</sub>H<sub>2</sub>{X<sup>II</sup>(H<sub>2</sub>O)<sub>3</sub>}<sub>4</sub>] (X = Ni, Co, Mn and Cu) as heterogeneous catalysts

Polyoxometalates of the  $\epsilon$ -Keggin structure [Mo<sub>12</sub>V<sub>3</sub>O<sub>39</sub>( $\mu_2$ -OH)<sub>10</sub>H<sub>2</sub>{X<sup>II</sup>(H<sub>2</sub>O)<sub>3</sub>}<sub>4</sub>] (X = Ni, Co, Mn and Cu), have been synthesized and used as heterogeneous catalysts for the aerobic oxidation of aldehydes to carboxylic acids.



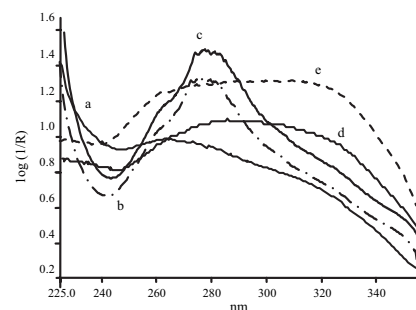


**Qian Deng, Wenhui Zhou, Xiaomei Li, Zhenshan Peng, Shaoliang Jiang, Ming Yue, Tiejun Cai**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 149

Microwave radiation solid-phase synthesis of phosphotungstate nanoparticle catalysts and photocatalytic degradation of formaldehyde

Photocatalysts  $M_3PW_{12}O_{40}$  ( $M = NH_4^+, Cs^+, Ag^+, Cu^{2+}$ ) have been prepared by microwave radiation solid-phase synthesis method and photocatalytic performance of the catalysts is studied using simulated polluted air containing formaldehyde and methyl alcohol. In the order of  $(NH_4)_3PW_{12}O_{40}$ ,  $Cs_3PW_{12}O_{40}$ ,  $Ag_3PW_{12}O_{40}$ , and  $Cu_3(PW_{12}O_{40})_2$ , the activity of photocatalysts increase, which is accordance with the increase of the red shift and absorption intensity of diffuse reflectance UV-vis. Among the photocatalysts  $M_3PW_{12}O_{40}$ ,  $Cu_3(PW_{12}O_{40})_2$  is the most efficient catalysis which has stronger absorption of UV-vis at 350 nm.

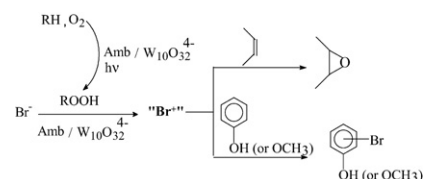


**Alessandra Molinari, Graziano Varani, Eleonora Polo, Silvia Vaccari, Andrea Maldotti**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 156

Photocatalytic and catalytic activity of heterogenized  $W_{10}O_{32}^{4-}$  in the bromide-assisted bromination of arenes and alkenes in the presence of oxygen

Photochemical excitation ( $\lambda > 300$  nm) of  $(nBu_4N)_4W_{10}O_{32}$  heterogenized with Amberlite IRA-900 causes the reductive activation of  $O_2$  to alkyl hydroperoxides, which induce the formation in situ of reactive  $Br^+$  from bromide ions. Thus, it is achieved the transformation of phenol and anisole into their monobrominated derivatives and of alkenes into their corresponding epoxides at room temperature and atmospheric pressure.

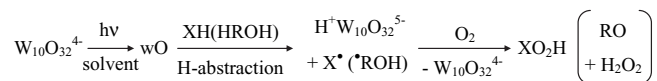


**Charles Tanielian, Fabien Cougnon, Rachid Seghrouchni**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 164

Acetone, a substrate and a new solvent in decatungstate photocatalysis

It is shown that, in addition to acetonitrile (AN) and water, acetone (AC) may be used as solvent in decatungstate photocatalysis even if its reactivity towards the transient  $wO$  is  $\sim 3-4$  times higher than that of AC. Additionally, a significant solvent effect is observed in the decatungstate photocatalyzed oxygenation of propan-2-ol: the reactivity of  $wO$  is slightly lower in AC than in AN (factor 1.8), but much more important in water.

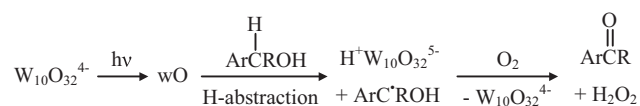


**Charles Tanielian, Ioannis N. Lykakis, Rachid Seghrouchni, Fabien Cougnon, Michael Orfanopoulos**

*Journal of Molecular Catalysis A: Chemical* 262 (2007) 170

Mechanism of decatungstate photocatalyzed oxygenation of aromatic alcohols. Part I. Continuous photolysis and laser flash photolysis studies

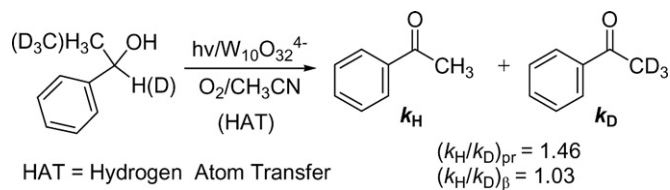
The decatungstate photocatalyzed oxygenation of aromatic alcohols results in quantitative formation of peroxides and of the corresponding arylketones, which themselves may react under the experimental conditions. Determination of kinetic parameters characterizing the various intermediates and determined by  $O_2$  consumption under continuous photolysis and laser flash photolysis, permits us to conclude that aromatic alcohols react by hydrogen-atom abstraction.



**Ioannis N. Lykakis, Charles Tanielian,  
Rachid Seghrouchni, Michael Orfanopoulos**

*Journal of Molecular Catalysis A: Chemical* 262  
(2007) 176

Mechanism of decatungstate photocatalyzed  
oxygenation of aromatic alcohols. Part II. Kinetic  
isotope effects studies

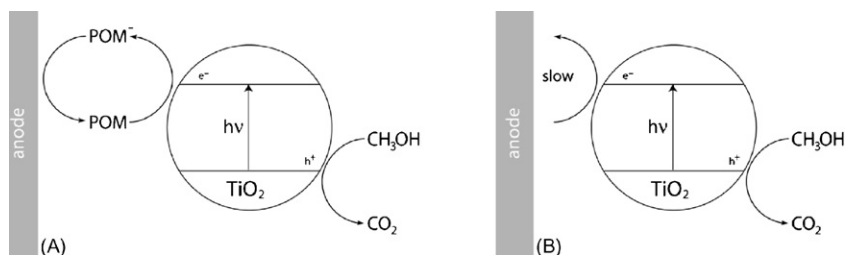


**Chaokang Gu, Curtis Shannon**

*Journal of Molecular Catalysis A: Chemical* 262  
(2007) 185

Investigation of the photocatalytic activity of  
TiO<sub>2</sub>-polyoxometalate systems for the oxidation of  
methanol

TiO<sub>2</sub> and phosphotungstate display a remarkable synergy when used together to catalyze the photoelectrochemical oxidation of methanol (A). The 50-fold increase in photocurrent we observe compared to a conventional TiO<sub>2</sub> photocatalyst (B) arises due to the improved separation of photogenerated electron-hole pairs in the presence of phosphotungstate.

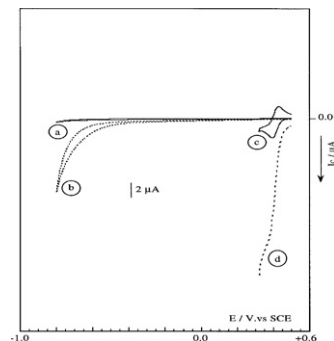


**Bineta Keita, Louis Nadjo**

*Journal of Molecular Catalysis A: Chemical* 262  
(2007) 190

Polyoxometalate-based homogeneous catalysis of  
electrode reactions: Recent achievements

This short focused review shows the usefulness of the broad family of Polyoxometalates (POMs) in selected electrocatalytic processes. Reduction and oxidation capabilities exist as well, with these robust and versatile catalysts. Quantitative transformations were demonstrated in several examples, including hydrogen production, NO<sub>x</sub> reduction, coenzyme oxidation. Several parameters must be taken into account in the design and study of these processes.



**In Kyu Song, Mahmoud S. Kaba,  
Kenji Nomiya, Richard G. Finke,  
Mark A. Barteau**

*Journal of Molecular Catalysis A: Chemical* 262  
(2007) 216

Scanning tunneling microscopy (STM) and tunneling spectroscopy (TS) studies of polyoxometalates (POMs) of the Wells-Dawson structural class

Wells-Dawson structure polyoxometalates self-assembled into well-ordered arrays on graphite. Tunneling spectroscopy showed negative differential resistance behavior. Framework substitutions and increases in the number of charge-compensating protons had negligible effects on array periodicities. For salts of trisubstituted POMs, Q[P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>] (Q = Na<sub>9</sub>, Cs<sub>9</sub>, (Bu<sub>4</sub>N)<sub>9</sub>, (Bu<sub>4</sub>N)<sub>5</sub>Na<sub>3</sub>(Re(CO)<sub>3</sub>), periodicities were greater than the anion dimensions, reflecting the size of these counter cations. Large scan-area (90 nm × 90 nm) image of (Bu<sub>4</sub>N)<sub>5</sub>Na<sub>3</sub>(Re(CO)<sub>3</sub>)[P<sub>2</sub>W<sub>15</sub>Nb<sub>3</sub>O<sub>62</sub>] array on HOPG.

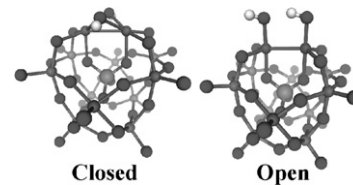


**David Quiñero, Keiji Morokuma,  
Yurii V. Geletii, Craig L. Hill,  
Djamaladdin G. Musaev**

*Journal of Molecular Catalysis A: Chemical* 262  
(2007) 227

A density functional study of geometry and electronic structures of  $[(\text{SiO}_4)(\text{M}^{\text{III}})_2(\text{OH})_2\text{W}_{10}\text{O}_{32}]^{4-}$ ,  $\text{M} = \text{Mo}, \text{Ru}$  and  $\text{Rh}$

The effects of redox-active M-atoms ( $\text{M} = \text{Mo}, \text{Ru}$  and  $\text{Rh}$ ) of the di-d-transition-metal-substituted  $\gamma$ -Keggin polyoxometalates  $[(\text{SiO}_4)(\text{M}^{\text{III}})_2(\text{OH})_2\text{W}_{10}\text{O}_{32}]^{4-}$ , on the geometry and electronic structure of these species were evaluated at the density functional level. It was shown that open isomers may coexist with closed isomers only for  $\text{M} = \text{Mo}$ .



**Jorge A. Fernández, Xavier López,  
Josep M. Poblet**

*Journal of Molecular Catalysis A: Chemical* 262  
(2007) 236

A DFT study on the effect of metal, anion charge, heteroatom and structure upon the relative basicities of polyoxoanions

DFT calculations carried out for a series of polyoxotungstates show that the protonation energy of a given oxygen site depends on the number and nature of metal centers directly bonded to an oxygen site, the charge of the anion and the bonding angle in bridging sites.

