DOI: 10.1002/adsc.200700187

Creation of a Monomeric Ruthenium Species on the Surface of Micro-Size Copper Hydrogen Phosphate: An Active Heterogeneous Catalyst for Selective Aerobic Oxidation of Alcohols

Junhua Liu,[a,b] Fang Wang,[a,b] Kunpeng Sun,[a] and Xianlun Xu[a,]*

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China
Fax: (+86)-931-827-7088; e-mail: xlxu@lzb.ac.cn
[b] Graduate School, Chinese Academy of Sciences, Beijing 100049, People's Republic of China

Received: April 16, 2007; Revised: August 17, 2007

Abstract: A new micro-size copper hydrogen phosphate (CHP) synthesized by the emulsion method combined with a monomeric ruthenium species was found to be a very effective catalyst for the selective oxidation of alcohols. Several kinds of alcohols were transformed into the corresponding aldehydes or ketones over the RuCHP catalyst by oxygen under very mild conditions. The results showed that the CHP material was perfect as a catalyst support due to its high ion-exchange ability and adsorption capacity.

Keywords: alcohols; aldehydes; copper hydrogen phosphate; ketones; oxidation; ruthenium

The aerobic oxidation of alcohols to aldehydes and ketones is a fundamental chemical transformation for the production of a large variety of important intermediates and fine chemical products.[1] However, most of these oxidants are toxic, hazardous, or are required in large excess. From an economical and environmental viewpoint, catalytic oxidations are particularly interesting. Recently, much attention has been paid to the development of metal catalysts employing O_2 (or air) or hydrogen peroxide as the ultimate stoichiometric oxidant. These attractive catalytic systems using cheap and readily available reactants display high atom efficiency and water is the only chemical by-product of the oxidation reactions.[2] Due to the disadvantages of homogeneous metal catalysts, current research has been focused on the development of efficient heterogeneous catalysts possessing superior activity as well as high reusability. Many reports on heterogeneous palladium catalysts have been published up to now,[3] and a few examples of solid-supported ruthenium catalysts are available.[4]

Various kinds of transition metal cations, which have a high potentiality for functioning as the catalytic active center, can be readily accommodated into some ores, such as hydrotalcite, apatite, hydroxyapatite and montmorillonite, based on their large cation exchange ability.[5] Also, use of hydroxyapatite as catalyst support is motivated by the following advantages:[6] (1) well-defined monomeric active species can be immobilized on the surface, on the basis of high ion-exchange ability and adsorption capacity; (2) the non-porous structure can help to overcome the problems of mass transfer limitation; (3) the weak acid-base properties prohibit side reactions induced by the support itself. What interests us is whether some kinds of metal phosphates have similar or better catalytic performances as the above samples; meanwhile, ores used as catalyst carriers were all prepared by conventional methods in those articles published so far,[5] and if the sizes of the phosphates material were measured in micro or nano size range, what about their catalytic performance. Thus, a micro-size copper hydrogen phosphate ($CuHPO_4$; CHP)[7] prepared by the emulsion method was reported in this article and if monomeric Ru cationic species could be uniformly fixed on the surface of it, then a Ru^{3+}-exchanged copper hydrogen phosphate (RuCHP) compound would be prepared. Although CHP has a lower surface area (only 7.09 $m^2 g^{-1}$) than the other metal phosphates (e.g., HAP), and there are no micropores or mesopores, the RuCHP catalyst showed unique catalytic performance for the oxidation of alcohols using molecular oxygen. To the best of our knowledge, this is the first report of the preparation of a new structural copper hydrogen phosphate by the emulsion method and utilization of the material as catalyst precusor for oxidation by ion-exchange with ruthenium. This method is fairly mild and easy to handle.

Figure 1 (**a**) shows the FT-IR spectra for the calcined copper hydrogen phosphate, the typical peaks for phosphate were found at *ca.* 615 cm^{-1} (P=O bend-

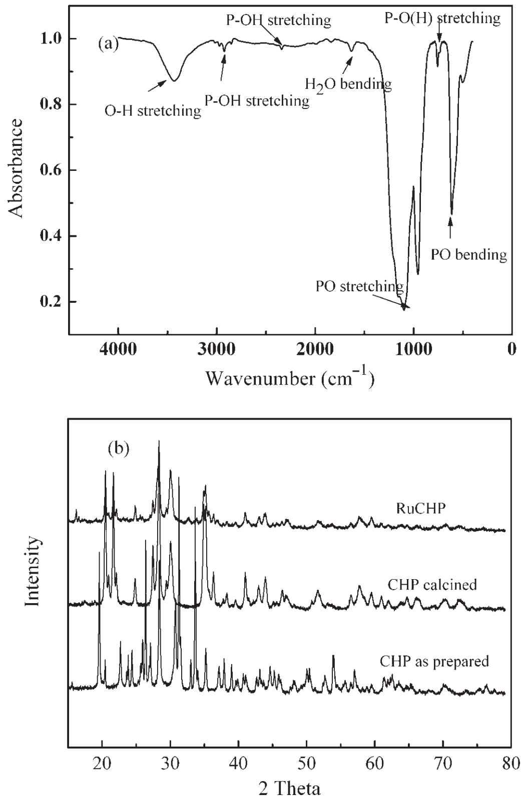


Figure 1. (**a**) FT-IR spectra of the CHP; (**b**) XRD of the CHP (as prepared, calcined) and RuCHP.

ing), 758 cm^{-1} [P–O(H) streching], 956 cm^{-1} (PO_4^{3-}, P–O streching), 1098 cm^{-1} (PO_4^{3-}, P–O streching), 3439 cm^{-1} (hydrogen bonded OH).[8] The XRD peak positions of RuCHP were similar to those of the parent CHP, while the strengths of the peaks of RuCHP were slightly weaker than those of CHP [Figure 1 (**b**)]. From the elemental analysis (XRF), the (Ru+Cu)/P ratio of the RuCHP was estimated to be 0.85 (Ru content: 6.1 wt%, 0.59 mmol g^{-1}), which was lower than that of Cu/P (1:1) in the parent CHP. Inductively coupled plasma (ICP) analysis revealed that copper was present in the filtrate after the ruthenium loading. XRF, EDS elemental analysis and ICP analysis all testified that ruthenium had exchanged with copper on the surface of CHP to give birth to RuCHP. The presence of chlorine was confirmed by XPS and XRF analyses, the atomic ratio of Ru to Cl was 1:1. The structural analysis results of RuCHP catalyst obtained from EXAFS spectra are shown in Table 1 and Figure 2. The Fourier-transformed (FT) spectrum of RuCHP was different from those of the reference samples $RuCl_3$, RuO_2, the lack of peaks above 3.0 Å indicated no Ru–Ru bond in this complex, while it was clearly visible in RuO_2, and $RuCl_3$,[9d] hence, monomeric Ru seems to be highly dispersed in CHP. Also, this conclusion was supported by fitting of the data (Table 1), scattering events occurring between 0.9 and 2.8 Å could be attributed to oxygen nearest neighbours, the inverse FT of main peaks was well fitted by the use of three Ru–O and single Ru–Cl shells. On the basis of the above data, a possible structure of this catalyst was proposed. The sheet morphologies of the CHP and RuCHP were observed by SEM, compared with the parent CHP, the crystal phase of the RuCHP had a slight breakage

Table 1. The structural parameters of the RuCHP catalyst.

Shell	Coordination number	Interatomic distance [Å]	$\Delta\sigma$[a] [Å^2]
Ru–O(1)	4.0	1.98	0.0068
Ru–O(2)	2.0	2.28	0.0077
Ru–O(3)	2.0	2.60	0.0095
Ru–Cl	1.0	2.32	0.0085

[a] Debye–Waller factor.

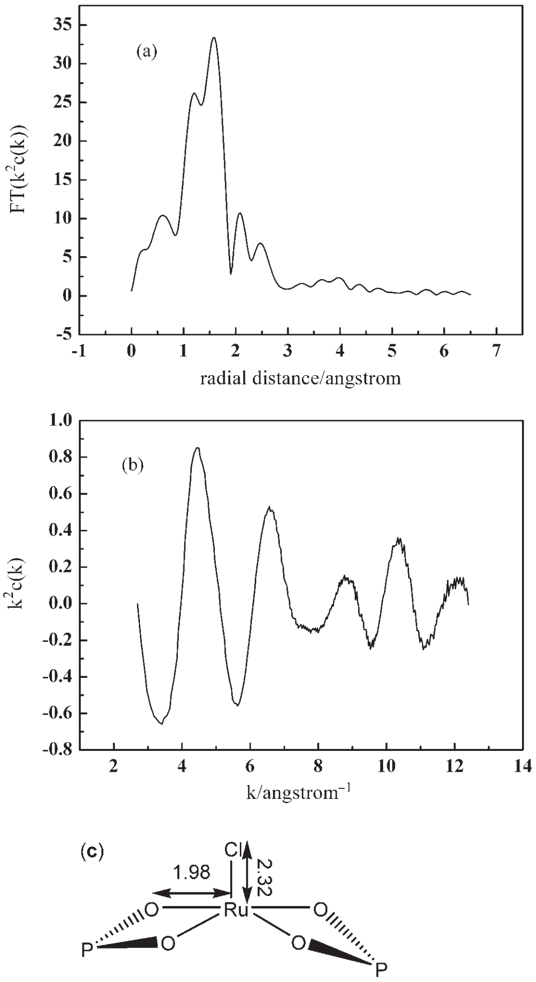


Figure 2. (**a**) Fourier transform (FT) magnitude of k^2-weighted EXAFS of RuCHP; (**b**) inverse FT of peaks with the $0.9 < R/Å < 3.0$ range of part (**a**); (**c**) a proposed structure of the RuCHP catalyst.

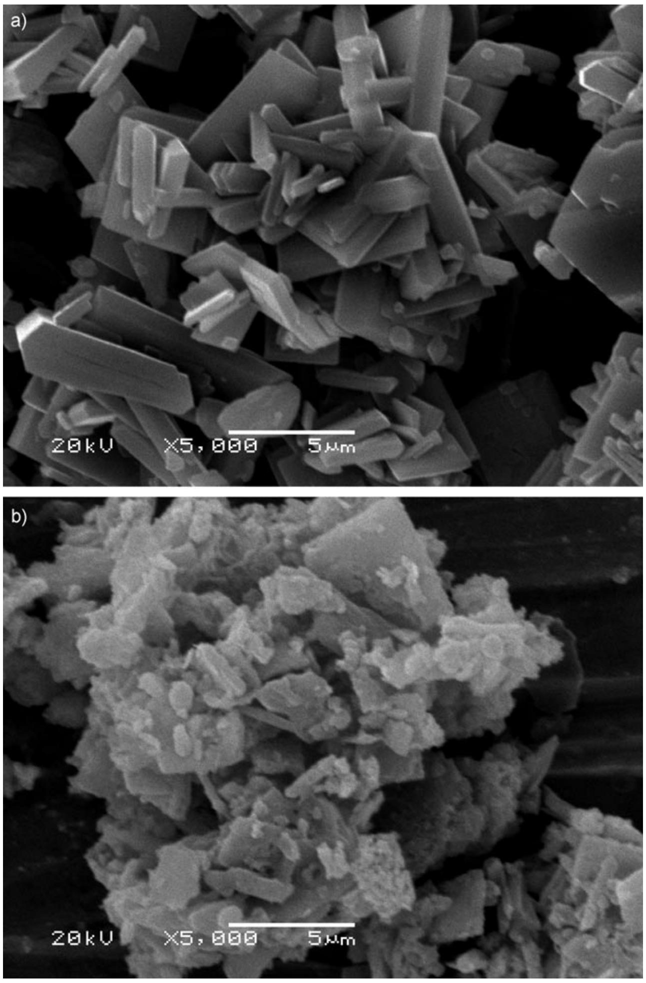


Figure 3. SEM images of the (*top*) CHP (calcined) and (*bottom*) RuCHP.

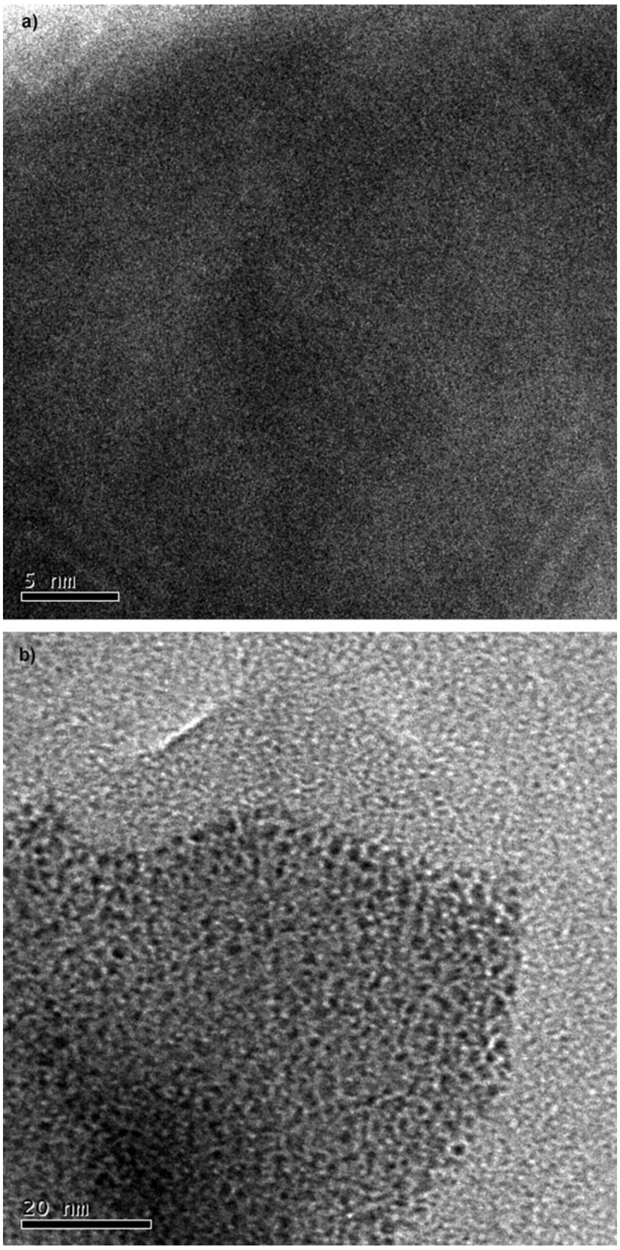
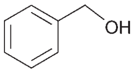
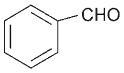
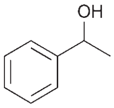
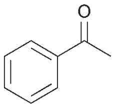
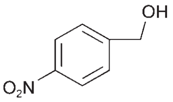
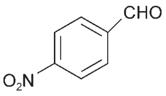
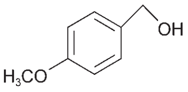
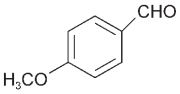
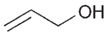
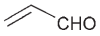
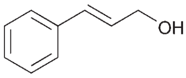
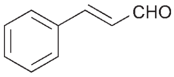
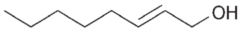
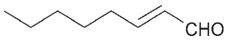
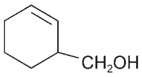
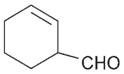
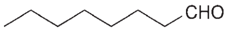
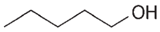
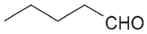
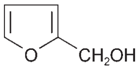
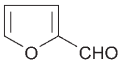
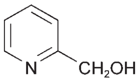
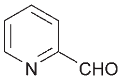
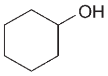
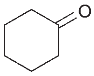
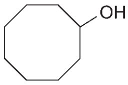
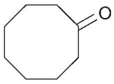


Figure 4. HRTEM images of the CHP (*top*) no Ru^{3+} particles; (*bottom*) with Ru^{3+} particles.

(Figure 3), HRTEM testified that it had no micropores or mesopores, also, no Ru^{3+} particles were found in a great extent of the CHP surface [Figure.4 (*top*)], but adsorption of Ru^{3+} ions (and Cl^- ions) also was found [Figure 4 (*bottom*)], this means that the Cu^{2+} ion exchange with Ru^{3+} is not absolute. In fact, the nature of the interaction between phosphates and metal ions in aqueous solution is composed by three steps: surface adsorption, ion exchange between Cu^{2+} and metal ions involving diffusion into the solid and dissolution of CHP and precipitation of a new phase (or phases), these processes often act together.[9d]

The catalytic activity of the copper hydrogen phosphate-supported ruthenium catalyst was examined for the catalytic aerobic oxidation of alcohols at 80 °C under O_2 bubbling conditions; representative results are shown in Table 2. All the benzylic and allylic alcohols showed high reactivity for the oxidative dehydrogenation (entries 1, 3–10), they were converted to the corresponding aldehydes or ketones in 100 % conversions and 92–99 % yields. In an enlarged activity experiment the oxidation of benzyl alcohol was also performed to give a 92 % yield of benzaldehyde; a TON as high as 1040 could be achieved (entry 3). Although a long reaction time was demanded, primary aliphatic alcohols were smoothly oxidized to aldehydes in high yields (entries 11 and 12). Moreover, this catalyst system was applicable for the oxidation of heterocyclic alcohols, for example, furan-2-methanol and pyridine-2-methanol gave the corresponding aldehydes in high yields (entries 13 and 14), it was worthy to mention that cyclohexanol and cyclooctanol were effectively oxidized to the corresponding cycloalkanones in 18 h (entries 15 and 16). Also, bubbling oxygen was

Table 2. Oxidation of alcohols with hydrogen peroxide catalyzed by RuCHP with molecular oxygen.[a]

Entry	Time (h)	Substrate	Product	Conversion [%][b]	Yield [%][b]
1	4			100	>99
2[c]	10			2	2
3[d]	48			92	92
4	5			100	>99
5	5			100	>99
6	5			100	>99
7	1			100	98
8	1			100	96
9	2			96	92
10	4			97	93
11	12			95	95
12	10			97	97
13	14			100	>99
14	18			100	>99
15	18			92	92
16	18			97	97

[a] Alcohol (10 mmol), RuCHP (0.2 g), toluene (5 mL), 80 °C, O_2 bubbling.
[b] Determined by GC.
[c] Ar atmosphere.
[d] An enlarged activity experiment: alcohol (20 mmol), RuCHP (0.03 g), toluene (10 mL).

necessary for the oxidation of alcohols under air conditions in place of pure O_2, the above oxidations proceeded smoothly but slowly, a 72 % yield of benzaldehyde was obtained (the conditions were the same as entry 1, Table 2), while the reaction almost could not proceed in the presence of an argon atmosphere (entry 2). Furthermore, the recycled catalyst could be used for oxidation of benzyl alcohol without changes in conversion and selectivity values, it gave a 98 % yield for the second use and a 97 % yield for the third use. It was confirmed by induced coupled plasma techniques (ICP) that the Ru content of recycled RuCHP catalyst was the same as that of the fresh one and no Ru was detected in the filtrate. Also, the catalyst was filtered off after *ca.* 50 % conversion at the reaction temperature, but further treatment of the filtrate under similar reaction conditions did not afford to any products. The oxidation of cinnamyl alcohol to cinnamyl aldehyde by CHP without ruthenium was carried under the same conditions as entry 8, but only a trace of product was obtained, it was concluded that CHP itself had a slight oxidation function.

During the reaction courses, we noticed that: (1) when the actual oxygen concentration was monitored, controlled by the rate of oxygen supply to the catalyst surface, it had a strong influence on the overall reaction rate; (2) one mole of H_2O was produced for every mole of benzaldehyde formation; (3) XPS revealed that no reduction of Ru^{3+} species to Ru^{2+} or Ru(0) took place after oxidation of benzyl alcohol;

(4) CHP itself could not effect the oxidation reaction by oxygen. On the basis of literature data[4b,9] and the above experimental measurements, a possible catalytic cycle for this reaction system using RuCHP was proposed: the oxidation was initiated by a ligand exchange between an alcohol and a Cl species of the RuCHP to give a Ru alcoholate species, which then underwent β-hydride elimination to produce the carbonyl compound and a hydrido-ruthenium species, subsequent the catalyst was regenerated by molecular oxygen to close the catalytic cycle.

In conclusion, a simple and convenient route for the synthesis of micro-size copper hydrogen phosphate by a non-ionic surfactant emulsion method was achieved. Then an RuCHP catalyst with monomeric Ru species was prepared by ion-exchange. This catalyst could act as an effective heterogeneous catalyst for the oxidation of various alcohols (benzylic, allylic and cycloaliphatic alcohols). The catalyst was recyclable and no Ru leaching was observed during the oxidations. The present simple and mild method to prepare micro-size copper hydrogen phosphate can be applied to other metal compound systems, some other samples measured in the micro- or nano-size range have been prepared in our group. Also, this simple design strategy for CHP-bound transition metal catalysts can be further applied to other systems, we anticipate that these novel catalysts also will exhibit outstanding catalytic performances in a wide range of functional transformations in organic synthesis, it will be reported in our subsequent papers.

Experimental Section

Preparation of Micro-Size Copper Hydrogen Phosphate ($CuHPO_4$) by a Surfactant Emulsion Method[10]

Aqueous solutions of copper nitrate and phosphoric acid were made by dissolving 6.04 g $Cu(NO_3)_2{\cdot}3H_2O$ (0.025 M) and 1.8 mL 85% H_3PO_4 in 8 mL deionized water. 4 g surfactant poly(oxyethylene)$_{10}$nonylphenol ether (NP-10,5% by weight) were added to cyclohexane (80 mL) to make the organic phase; Aqueous solution and organic phase were mixed according to the volume ratio 1:10, the pH of the emulsion was adjusted to 7 by adding concentrated ammonium hydroxide with continuous stirring, and the emulsion was aged at 25 °C for 24 h. The mixture was centrifuged and washed with absolute ethanol and water. After drying overnight in a vacuum oven at 80 °C, the product was calcined at 500 °C for 6 h to obtain grey CHP precursor powders. The CHP (1.0 g) was stirred with 75 mL of a 2.0×10^{-2} M aqueous $RuCl_3$ solution at 25 °C for 24 h. The obtained slurry was filtered, washed with deionized water, and dried overnight in a vacuum oven at 80 °C yielding the RuCHP as a dark brown powder.

Oxidation Reactions of Alcohols with Oxygen

All reactions were performed in a round-bottom one-neck glass flask equipped with a reflux condenser, a magnetic stirrer and a gas inlet allowing us to bubble a flow of oxygen into the reaction mixture (25 mL min^{-1}). A typical procedure was as follows: a mixture of benzyl alcohol (10 mmol), RuCHP (0.2 g) in a solvent (5 mL toluene) was charged in the reactor and saturated with oxygen at room temperature for 5 min. Then the reactor was placed into the oil bath preheated to 80 °C to start the reaction, the resulting mixture was stirred under bubbling oxygen for 4 h. The products were identified by GC using the authentic samples of aldehydes or ketones.

Acknowledgements

The authors would like to thank Professor B .X. Lin (Peking University) for the determining the fabric of the CHP, Professor K. Q. Lu (Institute of Physics, Chinese Academy of Sciences) for the EXAFS measurements and Professor S. Q. Wei (National Synchrotron Radiation Laboratory, University of Science & Technology of China) for the EXAFS data analysis.

References

[1] R. A. Sheldon; J. K. Kochi, *Metal-catalyzed Oxidations of Organic Compounds*, Academic Press, New York, **1994**.

[2] a) S. Velusamy, T. Punniyamurthy, *Org. Lett.* **2004**, *6*, 217; b) M. S. Kwon, N. Kim, C. M. Park, J. S. Lee, K. Y. Kang, J. Park, *Org. Lett.* **2005**, *7*, 1077; c) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, *127*, 9374; d) B. Guan, D. Xing, G. Cai, X. Wan, N. Yu, Z. Fang, L. Yang, Z. Shi, *J. Am. Chem. Soc.* **2005**, *127*, 18004; e) S. Gauthier, R. Scopelliti, K. Severin, *Organometallics* **2004**, *23*, 3769; f) B. Karimi, A. Zamani, J. H. Clark, *Organometallics* **2005**, *24*, 4695; g) M. V. Vasylyev, R. Neumann, *J. Am. Chem. Soc.* **2004**, *126*, 884; h) H. R. Mardani, H. Golchoubian, *Tetrahedron Lett.* **2006**, *47*, 2349; i) S. Velusamy, A. Srinivasan, T. Punniyamurthy, *Tetrahedron Lett.* **2006**, *47*, 923.

[3] a) D. R. Jensen, M. S. Sigman, *Org. Lett.* **2003**, *5, 63; b) T. Iwasawa, M. Tokunaga, Y. Obora, Y. Tsuji, J. Am. Chem. Soc.* **2004**, *126*, 6554; c) S. K. Mandal, D. R. Jensen, J. S. Pugsley, M. S. Sigman, *J. Org. Chem.* **2003**, *68*, 4600; d) M. S. Sigman, D. R. Jensen, *Acc. Chem. Res.* **2006**, *39*, 221; e) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037; f) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley. A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight, G. J. Hutchings, *Science* **2006**, *311*, 362; g) M. Caravati, D. M. Meier, J.-D. Grunwaldt, A. Baiker, *J. Catal.* **2006**, *240*, 126; h) J. Muzart, *Tetrahedron* **2003**, *59*, 5789; i) Z. Hou, N. Theyssen, A. Brinkmann, W. Leitner, *Angew. Chem. Int. Ed.* **2005**, *44*, 1346.

[4] a) K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2002**, *41*, 4538; b) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2000**, *122*, 7144; c) S. Kobayashi, H. Miyamura, R. Akiyama, T. Ishida, *J. Am. Chem. Soc.* **2005**, *127*, 9251; d) B.-Z. Zhan, M. A. White, T.-K. Sham, J. A. Pincock, R. J. Doucet, K. V. R. Rao, K. N. Robertson, T. S. Cameron, *J. Am. Chem. Soc.* **2003**, *125*, 2195.

[5] Pertinent references, see: a) S. Sugiyama, T. Minami, H. Hayashi, M. Tanaka, N. Shigemoto, J. B. Moffat, *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 293; b) K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 5662; c) K. Mori, K. Yamaguchi, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2002**, *124*, 11572; d) T. Mitsudome, T. Umetani, N. Nosaka, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *Angew. Chem. Int. Ed.* **2006**, *45*, 481.

[6] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657.

[7] SEM testified that CHP was a pure phase, on the basis of XRD (JCPDS 44–004), elemental analysis, FT-IR, TGA data and mass spectrum studies, compound CHP is formulated as $CuHPO_4$.

[8] a) D. Hoegaerts, B. F. Sels, D. E. De Vos, F. Verpoort, P. A. Jacobs, *Catal. Today* **2000**, *60*, 209; b) M. Öner, Ö. Doğan, *Prog. Crys. Grow. Chara. Mater.* **2005**, *50*, 39; c) G. C. Koumoulidis, A. P. Katsoulidis, A. K. Ladavos, P. J. Pomonis, C. C. Trapalis, A. T. Sdoukos, T. C. Vaimakis, *J. Coll. Interf. Sci.* **2003**, *259*, 254.

[9] Similar mechanisms were reported as follows: a) A. Dijksman, A. Marino-González, A. M. i Payeras, I. W. C. E. Arends, R. A. Sheldon, *J. Am. Chem. Soc.* **2001**, *123*, 6826; b) Z. Opre, J.-D. Grunwaldt, M. Maciejewski, D. Ferri, T. Mallat, A. Baiker, *J. Catal.* **2005**, *230*, 406; c) L. W. Chung, Y. D. Wu, B. M. Trost, Z. T. Ball, *J. Am. Chem. Soc.* **2003**, *125*, 11578; d) Z. Opre, J.-D. Grunwaldt, T. Mallat, A. Baiker, *J. Mol. Catal. A: Chem.* **2005**, *242*, 224.

[10] Pertinent articles, see: a) K. Onuma, A. Ito, *Chem. Mater.* **1998**, *10*, 3346; b) L. M. Rodriguez-Lorenzo, M. Vallet-Regi, *Chem. Mater.* **2000**, *12,* 2460; c) G. K. Lim, J. Wang, S. C. Ng, L. M. Gan, *Langmuir,* **1999**, *15,* 7472; d) S. Bose, S. K. Saha, *Chem. Mater.* **2003**, *15*, 4464.