ELSEVIER

Contents lists available at ScienceDirect

Catalysis Communications



journal homepage: www.elsevier.com/locate/catcom

Short Communication

Fabrication of micellar heteropolyacid catalysts for clean production of monosaccharides from polysaccharides

Mingxing Cheng, Tian Shi, Shengtian Wang, Hongyu Guan *, Chunyan Fan, Xiaohong Wang *

Key Lab of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, PR China

A R T I C L E I N F O

Article history: Received 3 March 2011 Received in revised form 28 May 2011 Accepted 6 June 2011 Available online 13 June 2011

Keywords: Heteropolyacids Micellar catalysis Polysaccharides Hydrolysis Monosaccharides

1. Introduction

Heteropolyacids (HPAs) exhibit unmatched physical and chemical properties, which could act as reliable building blocks in the formation of new materials especially in a nanomaterial area [1]. HPAs with nanostructure could be assembled by surfactant encapsulation [2,3] as formation of vessels, quantum dots and micelles for special devices such as luminescence [4] and catalysis [5]. In the area of catalysis, the utilization of HPA micelles is the most often strategy to significantly accelerate the rate in a micellar medium [6,7]. Amphiphilic quaternary ammonium of HPAs with surfactant core and HPA surface can form supramolecular micellar assemblies ranging from the nanoscale to microscale in aqueous solution, which could possibly afford high local concentrations of the reactants near the catalysts. By now, amphiphilic HPA catalysts have been successfully used in various oxidation reactions [5,8-13] in emulsion or microemulsion system. However, few studies have been made to develop amphiphilic HPA micellar catalysts for the hydrolysis of polysaccharides into the reducing sugars. By now, Arai investigated the hydrolysis of sucrose in the presence of H₄SiW₁₂O₄₀ as a homogeneous catalyst [14]. And Shimizu et al. [15] studied the Lewis and Brønsted acidity of HPAs catalysts on the hydrolysis reactions for cellobiose and cellulose.

As a continuation of our work, we designed and synthesized micellar HPAs $[C_{16}H_{33}N(CH_3)_3]_xH_{3-x}PW_{12}O_{40}$ in catalyzing hydrolysis of polysaccharides into monosaccharide (glucose and fructose),

ABSTRACT

A micellar heteropolyacids (HPAs) catalyst had been prepared using surfactant cetyltrimethyl ammonium bromide (CTAB) and $H_3PW_{12}O_{40}$ as precursors. These micellar $[C_{16}H_{33}N(CH_3)_3]_xH_{3-x}PW_{12}O_{40}$ had been characterized to be micellar structure and the catalytic activity was evaluated by the hydrolysis of polysaccharides to the reducing sugars. The best catalytic activity was obtained over $[C_{16}H_{33}N(CH_3)_3]_xH_{2}O_{40}$ (abbreviated as $(C_{16}TA)H_2PW$), which showed 100% conversion and 99.6% selectivity within 60 min at 80 °C for hydrolysis of sucrose. And it was also active for the conversion of starch and cellulose. The leaching test showed that the HPA micellar catalysts have an excellent stability and can be used as heterogeneous catalysts for six times.

© 2011 Elsevier B.V. All rights reserved.

which is one of the key technologies for the full use of biomass, especially for the food industry [16,17], sustainable fuels and chemicals in the future [16,18,19]. Herein three main innovations are proposed: (1) The assembly of HPAs into a micellar system with Brønsted acidity, allowing the conversion of polysaccharides into monosaccharide; (2) Overcoming the shortage of local concentration in aqueous solution and promoting the reaction rate by HPA micellar catalyst; (3) Easily handling this catalyst.

2. Experimental

2.1. Material

Sucrose, starch and cellulose were all analytical reagents and purchased from J&K SCIENTIFIC LTD, which were used without further purification. Na₂WO₄, H₃PO₄(80%), diethyl ether and HCl(37%) were purchased from Sinopharm Chemical Reagent Co. Ltd. H₃PW₁₂O₄₀·23H₂O was prepared according to the literature method [20] and was calcinated at 300 °C for 6 h to obtain H₃PW₁₂O₄₀·6H₂O. 3,5-Dinitrosalicylic acid (DNS) reagent was prepared according Ref. [21], which is used to determine the amount of total reducing sugar.

2.2. Physical measurements

Elemental analysis was carried out using a Leeman Plasma Spec (I) ICP-ES and a PE 2400 CHN elemental analyzer. FTIR spectra (4000–400 cm⁻¹) were recorded in KBr discs on a Nicolet Magna 560 IR spectrometer. TEM image was measured on JOEL JEM-2100F microscope. The leaching concentrations of the catalysts during the reaction

^{*} Corresponding authors at: Northeast Normal University, 5268 Renmin Street, Changchun, Jilin Province, PR China. Tel.: +86 431 88930042; fax: +86 431 85099759. *E-mail address*: guanhy534@nenu.edu.cn (H. Guan).

^{1566-7367/\$ –} see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.catcom.2011.06.003

were also measured through analyzing the dissolved concentration of W in aqueous solution using a Leeman Plasma Spec (I) ICP-ES. The critical micellar concentration (CMC) of $(C_{16}TA)H_2PW$ was determined by conductivity versus concentration plot using conductome ter model DDS-11A.

The titration was used to evaluate the acidity characteristics of the solids [22]. 0.1 g of solid suspended in 20 mL sodium chloride solution (2.0 M) was stirred for 24 h. Then, the titration was carried out by a solution of sodium hydroxide (0.006 M) with the indicator phenolphthalein.

Sucrose's conversion was quantitative by thin-layer chromatography (TLC, DENSITOMETER CD 60) with tungsten lamp, and the scan wavelength was 418 nm. The concentration of monosaccharides was measured in the aqueous phase by high-performance liquid chromatography (HPLC), which conducted on a system equipped with a refractive index detector (Shimadzu LC-10A, HPX-87H column).

2.3. Preparation of $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$

A typical reaction procedure was as follows: 10 mL, 40 mM of hexadecyltrimethylammonium bromide (CTAB) aqueous solution was added into 10 mL, 40 mM of $H_3PW_{12}O_{40}$ · $6H_2O$ solution with stirring at room temperature [23]. The white precipitate formed immediately and was collected by filtration, then was dried at 100 °C for about 3 h. The resulting $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ was obtained with yield 46%. IR (1% KBr pellet, 4000–400 cm⁻¹): 1080, 980, 896, and 806 cm⁻¹. Anal. Calcd for $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$: W, 69.76; P, 0.98; C, 7.20; H, 1.39; N, 0.44%. Found: W, 69.37; P, 1.06; C, 7.43; H, 1.22; N, 0.39%.

The other catalysts $[C_{16}H_{33}N(CH_3)_3]_xH_3 - _xPW_{12}O_{40}$ were prepared in the same way except that the different molar ratio of CTAB and $H_3PW_{12}O_{40} \cdot 6H_2O$ was used.

 $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ was prepared according to Okuhara's method [24]. Before the reaction, the catalyst was calcined at 300 °C for 2 h.

2.4. Critical micelle concentration (CMC) determination

The CMC of $(C_{16}TA)H_2PW$ was determined at break points of nearly two straight-line portions of the specific conductivity versus concentration plot [25].

2.5. Catalytic procedure

For hydrolysis of sucrose, a mixture of sucrose (1.6 g) and catalyst (0.08 mmol) in distilled water (8 mL) were heated at 80 °C in a steal autoclave lined with Teflon under air for 60 min with agitation (300 rpm). After the reaction, the sample was centrifuged to separate the catalyst and the filtered solution was used for monosaccharides analysis by HPLC.

For hydrolysis of starch, a mixture of starch (0.1 g) and catalyst (0.07 mmol) in distilled water (7 mL) was heated at 120 °C in a steal autoclave lined with Teflon under air for 5 h with agitation (300 rpm). At the end of the reaction, the mixture was centrifuged to separate the catalyst and unreacted starch and the filtered solution was used for TRS and glucose analysis by HPLC. The conversion of starch can be determined by the mass change of the solid mixture.

For hydrolysis of cellulose, a mixture of cellulose (0.1 g) and catalyst (0.07 mmol) in distilled water (7 mL) was heated at 170 °C in a steal autoclave lined with Teflon under air for 8 h with agitation (300 rpm). The reaction mixture was centrifuged to separate unreacted cellulose and catalyst. The clear solution was used for analysis. The conversion of cellulose was calculated according to Ref. [26].

2.6. Adsorption experiments

Adsorption experiments were carried out to determine the adsorption capacity of catalysts for polysaccharides. In the simultaneous adsorption experiments, 1.6 g of sucrose and 0.08 mmol of catalyst were mixed in a steal autoclave for 15 min at 80 °C in order to determine the adsorption effect by the IR spectroscopy.

2.7. Total reducing sugars (TRS) analysis [26]

A mixture that contained 2 mL of DNS regent and 1 mL of reaction sample was heated for 2 min in a boiling water bath, then cooled to room temperature by flowing water, and mixed with deionized water to 25 mL. The color intensity of the mixture was measured in a UV757CRT Model spectrophotometer at 540 nm. The concentration of total reducing sugars was calculated based on a standard curve obtained with glucose.

2.8. Yield and selectivity definitions

$$Conversion(\%) = \left(1 - \frac{A \text{ mass in product}}{A \text{ mass in the loaded sample}}\right) \times 100\%$$

$$Yield(\%) = \frac{\text{main product mass}}{\text{A mass in the loaded sample}} \times 100\%$$

$$Selectivity(\%) = \frac{Yield}{Conversion} \times 100\%$$

A stands for sucrose, cellulose or starch.

3. Results and discussion

3.1. Characterization of the micellar catalyst

From the results of elemental analysis (Table S1), the content of W, P, C, H and N of catalyst is agreed with the calculated values.

The IR spectra of $H_3PW_{12}O_{40}$ and $(C_{16}TA)H_2PW$ are shown in Fig. S1. The IR spectrum of H₃PW₁₂O₄₀ showed four characteristic peaks at 1080, 982, 888 and 803 cm^{-1} , reflecting the four different vibrations of oxygen atoms of the Keggin-type structure $PW_{12}O_{40}^{3-}$, which are attributed to the asymmetry vibrations P-O_a (internal oxygen connecting P and W), W– O_d (terminal oxygen bonding to W atom), W– O_b (edge-sharing oxygen connecting W) and W-O_c (corner-sharing oxygen connecting W₃O₁₃ units). The IR spectrum of (C₁₆TA)H₂PW was in good agreement with that of its parent $PW_{12}O_{40}^{3-}$, though the peaks were slightly shifted to 1080, 980, 896 and 806 cm⁻¹, showing that (C₁₆TA)H₂PW retains Keggin structure. The slight shift may be attributed to the influence of the $C_{16}TA$ on $PW_{12}O_{40}^{3-}$. And the spectrum of $(C_{16}TA)H_2PW$ exhibit two peaks at 2923 and 2851 cm⁻¹, which are the symmetric and asymmetric stretching vibrations of C-H₂ of C₁₆TA. Compared to the spectrum of CTAB [27], the peaks are shifted, which may also due to the influence of $PW_{12}O_{40}^{3-}$ on $C_{16}TA$.

As Table S1 shows $(C_{16}TA)_xH_{3-x}PW_{12}O_{40}$ exhibits different acidic capacity due to the different content of H⁺. And for these solid acid catalysts, the acidity of $(C_{16}TA)H_2PW_{12}O_{40}$ is the highest one about 1.8 mmol/g.

The critical micelle concentration (CMC) of $(C_{16}TA)H_2PW$ was determined by conductivity versus concentration plot given in Fig. S2. The CMC of $(C_{16}TA)H_2PW$ is 0.92 mM. This point confirms that $(C_{16}TA)H_2PW$ could form micelle in aqueous solution.

The cryo-TEM image of $(C_{16}TA)H_2PW$ also showed that it could form relatively uniform micellar droplets about 50–60 nm (Fig. 1).



Fig. 1. The cryo-TEM image of (C₁₆TA)H₂PW micellar catalyst.

3.2. Catalytic activity

The micellar HPA catalysts were used in hydrolysis of sucrose (Fig. 2), and the hydrolysis products are glucose and fructose. It can be seen that these micellar HPA catalysts exhibit some certain catalytic performance in this hydrolysis reaction. The active range of this series is $(C_{16}TA)H_2PW \sim [C_{16}H_{33}N(CH_3)_3]_{0.5}H_{2.5}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{1.5}H_{1.5}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2}HPW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2.5}H_{0.5}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2}PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]_{2}PW_{12}O_{40}$.



Fig. 2. Hydrolysis of sucrose by $(C_{16}TA)_xH_{3-x}PW_{12}O_{40}$. Reaction conditions: 0.1 g of sucrose, 0.08 mmol of catalyst and 10 mL of water for 60 min at 80 °C.

Table T	
The hydrolysis of sucrose by different catalysts	Reaction conditions: 80 °C 60 min_catalyst 0.08 mmol

corresponding to the strength of their Brønsted acidity (Table S1). This point shows that the certain Brønsted acidity must be kept for an acid catalyst in order to promote the hydrolysis of sugar. The fact that $[C_{16}H_{33}N(CH_3)_3]_{0.5}H_{2.5}PW_{12}O_{40}$ is less active than $(C_{16}TA)H_2PW$ might be attributed to the effect of the amount of the carbonic chain. There are less hydrophobic tails in $[C_{16}H_{33}N(CH_3)_3]_{0.5}H_{2.5}PW_{12}O_{40}$ than $(C_{16}TA)H_2PW$ and $[C_{16}TA)H_2PW$, but the acidic difference between $(C_{16}TA)H_2PW$ and $[C_{16}H_{33}N(CH_3)_3]_{0.5}H_{2.5}PW_{12}O_4$ is less. Therefore, $(C_{16}TA)H_2PW$ exhibits higher activity attributed to its higher acidity and large amount of carbonic chain.

From Table 1, micellar HPA catalysts show higher selectivity than H₃PW₁₂O₄₀. H₃PW₁₂O₄₀ is a homogeneous acid catalyst, which is favorable for the conversion of sucrose, but the selectivity of monosaccharides is low owing to its high acid strength and the ratio of glucose with fructose is 1:0.7. $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ is a heterogeneous acid catalyst, which exhibits high selectivity and low conversion. The high activity of (C16TA)H2PW is attributed to the accumulation of sucrose around the catalyst. (C16TA)H2PW with a guaternary ammonium-hydrophobic tail and a HPA hydrophilic head group, exhibits amphiphilic properties and acts as both catalyst and surfactant to assemble micelle in an aqueous solution. The IR spectrum of adsorption of sucrose on (C₁₆TA)H₂PW (Fig. S1) confirms the assembly of sucrose on the HPA head region. The spectrum of $(C_{16}TA)$ H₂PW-adsorbed sucrose gives four characteristic peaks at 1080 cm⁻¹ 978 cm⁻¹, 895 cm⁻¹, and 807 cm⁻¹ corresponding to $PW_{12}O_{40}^{3-}$ structural vibrations. Compared to the peaks of $PW_{12}O_{40}^{3-}$, the vibration bands of W–O_d, W–O_b and W–O_c shift from 978 to 982, 895 to 888, 807 to 803 cm⁻¹, respectively. This result indicates that some interaction occurs between the OH group from sucrose and the HPA molecules. In addition, the peaks at 1486 and 1474 cm^{-1} are attributed to the C–O vibration of sucrose, indicating the assembly of sucrose on the catalyst. Therefore, sucrose is accumulated through interactions with the micelle surface or through insertion into the micelle itself compared to the surrounding water phase.

It is known that the length of quaternary ammonium cations $[(C_nH_{2n+1})N(CH_3)_3]_5$ plays a vital role not only in the formation of the micellar system but also the catalytic activity. The hydrophobic chain must possess a certain length (>C10) to enable successful micelle formation [28]. Therefore, the effect of carbon chain length on the catalytic activity had been checked in Fig. 3. With the enhancement of the length from C8 to C18, the conversion increases significantly, from 56.5% for $(O_8TA)H_2PW_{12}O_{40}([(C_8H_{17})N(CH_3)_3]H_2PW_{12}O_{40})$ to 97.5% for (O₁₈TA)H₂PW₁₂O₄₀([(C₁₈H₁₇)N(CH₃)₃]H₂PW₁₂O₄₀), respectively. The catalytic difference between $(C_{16}TA)H_2PW$ and $(O_{18}TA)$ H₂PW₁₂O₄₀ is less. This result confirms that the length of the carbonic chain of cations plays an important role in the formation of micelle as well as the hydrolysis reaction. $(O_8TA)H_2PW_{12}O_{40}$, with a short carbon chain comprising less than C10, has difficulty forming a micelle and only acts as a heterogeneous catalyst, resulting in low conversion (56.5%). The surfactant-HPAs act as both a catalyst and a surfactant to assemble micelles in water.

Catalyst	Amount of sucrose/g	Amount of water/mL	Conversion of sucrose/%	Yield of mon-/%	Glu:Fru	Selectivity/%	TOF/g mmol $^{-1}$ h $^{-1}$
H ₃ PW ₁₂ O ₄₀	1.6	8	100	87.5	1:0.7	87.5	18.2
Cs _{2.5} H _{0.5} PW	1.6	8	94.3	88.2	1:1	93.5	18.4
(C16 TA)H2PW	1.6	10	92.7	89.8	1:1	96.9	18.5
(C16 TA)H2PW	1.6	8	100	99.6	1:1	99.6	20.0
(C ₁₆ TA) H ₂ PW	1.6	7	100	92.1	1:1	92.1	20.0
$(C_{16}TA) H_2PW$	1.6	6	100	88.7	1:1	88.7	20.0
$(C_{16}TA) H_2PW$	1.6	5	100	77.6	1:0.9	77.6	20.0
(C16 TA)H2PW	1.6	4	100	63.1	1:0.8	63.1	20.0
(C16 TA)H2PW	1.8	10	88.3	79.4	1:1	89.9	19.9
(C16 TA)H2PW	2.0	10	84.0	70.7	1:1	84.2	21.0
(C16TA) H2PW	3.0	10	76.8	64.2	1:1	83.6	28.8

From Table 1, it can be seen that the usage of sucrose influenced the conversion and yield of monosaccharides, while the yield of monosaccharides decreased as increasing the usage of sucrose. It can be seen that the amount of water influenced the selectivity of monosaccharides (Fig. S3). It is known that water is not only the solvent, but also is a reactant. In hydrolysis reaction, a large amount of water is favorable for the promotion of the reaction in kinetics and equilibrium but decreases the acidic strength leading to low activity of acid catalysts [29]. Using the same amount of sucrose and different amount of catalyst, water content influences the conversion and the yield. In lower usage of catalyst, decreasing the amount of water could enhance the conversion and yield of monosaccharides. This is due to the lower acidic sites for lower usage of catalyst, therefore, lower amount of water provides the higher acidic strength. In higher amount of catalyst, 8 mL of water is suitable for the hydrolysis of sucrose into sugars with high conversion and high selectivity. At the situation of same amount of catalyst and different usage of sucrose, the conversion and yield increase first and then decrease, which achieve highest at 8 mL of water.

The temperature influenced the yield of monosaccharides from hydrolysis of sucrose (Fig. 4.). It can be seen that the reaction temperature had a large effect on the sucrose conversion and monosaccharides yield. When reaction temperature was 70 °C, the conversion of sucrose was 66.1% and the yield of monosaccharide was 63.5%; and when the temperature increased to 80 °C, the sucrose conversion reached about 100% for 60 min. So the temperature played a positive role for sucrose conversion. Enhancement of temperature from 70 °C to 90 °C could increase monosaccharides selectivity, while could reach the highest 99.8% at 90 °C. However, higher temperatures (120 °C) gave rise to byproducts leading to low monosaccharides selectivity (95.2%). Therefore, 80 °C was selected as the reaction temperature. In addition, the stirring rate also influences the activity (Fig. S4). At the lower stirring rate (100 rpm), the conversion of sucrose and yield were only 95.7% and 91.2%, respectively. Speeded up the stirring rate, the conversion and yield increased, but the effect shows no significance for 300 and 500 rpm.

Heterogeneous or homogeneous one for the micellar HPA catalyst? Therefore, the heterogeneous nature of the catalytic reaction had been confirmed. For this purpose, a test had been performed as following: the $(C_{16}TA)H_2PW$ is stirred in water at 80 °C (without saccharide) within 60 min, and then the solid is separated from the aqueous phase by an ultrafiltration membrane. To this liquid phase, the saccharide is added and the reaction is done for further 60 min at 80 °C. The conversion and yield are 2.5 and 2.3%, respectively. Compared to the results of that without any catalyst (1.1% conversion and 0.7% yield, respectively), this conversion and yield are almost the same, indicating there is a little catalyst residual in the liquid phase. From



Fig. 3. Hydrolysis of sucrose by $[(C_nH_{2n+1})N(CH_3)_3]H_2PW$ catalysts. Reaction conditions: 0.1 g of sucrose, 0.08 mmol of catalyst and 10 mL of water for 60 min at 80 °C



Fig. 4. Hydrolysis of sucrose by (C16TA)H2PW at different temperatures. Reaction conditions: 1.6 g of sucrose, 0.08 mmol of catalyst and 8 mL of water for 60 min.

this result, (C₁₆TA)H₂PW is confirmed as a heterogeneous one and the leaching amount of (C₁₆TA)H₂PW is little.

The regeneration of $(C_{16}TA)H_2PW$ is of practical and economic importance. It can be easily achieved by the centrifugation of the white solid from the reaction system. This residue was reused without any treatment. The regenerated reagent is as reactive as the freshly prepared catalyst. The catalytic activity of the hydrolysis of sucrose is maintained efficiently after six repeated experiments, showing only a slight decrease (Fig. 5) and the total amount of $(C_{16}TA)H_2PW$ leaching through six runs of the reaction reaches 143 ppm.

The hydrolysis of starch and cellulose by this micellar HPA catalyst (C16TA)H2PW was done in order to evaluate its catalytic activity. It can be seen that the micellar $(C_{16}TA)H_2PW$ catalyst (0.07 mmol) could catalyze the hydrolysis of starch (0.1 g) at 120 °C for 5 h with 96.1% conversion, 82.4% yield of glucose and TOF 0.274 g mmol $^{-1}$ h $^{-1}$. In addition, this micellar HPA catalyst (0.07 mmol) achieved the conversion of cellulose (0.1 g) into glucose with 44.1% conversion, 89.1% selectivity of glucose and TOF 0.079 g mmol $^{-1}$ h $^{-1}$ at 170 °C for 8 h.

4. Conclusions

The micellar acid catalyst had been synthesized by using surfactant cetyltrimethyl ammonium bromide (CTAB) and H₃PW₁₂O₄₀ as precursors. The hydrolysis of polysaccharides such as sucrose, starch and cellulose had been achieved by a micellar HPA catalyst $(C_{16}TA)H_2PW$. (C₁₆TA)H₂PW exhibited remarkable catalytic performance for the hydrolysis of polysaccharides. Moreover, this catalyst can be recycled by centrifuge and can be reused at least six times. This heterogeneous



1486

Fig. 5. The life span of catalyst for sucrose hydrolysis. Reaction conditions: 1.6 g of sucrose, 0.08 mmol of catalyst and 8 mL of water for 60 min at 80 °C.

micellar HPA catalyst is a clean, facile, economical and an environmentally benign process toward the production of monosaccharides from polysaccharides.

Supplementary materials related to this article can be found online at doi:10.1016/j.catcom.2011.06.003.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20871026, 51078066). And it was supported by analysis and testing foundation of Northeast Normal University and the projects of Jilin Provincial Science and Technology Department (201105001).

References

- [1] A. Müller, F. Petters, M.T. Pope, D. Gatteschi, Chem. Rev. 98 (1998) 239.
- [2] D. Volkmer, A.D. Chesne, D.G. Kurth, H. Schnablegger, P. Lehmann, M.J. Koop, A. Müller, J. Am. Chem. Soc. 122 (2000) 1995.
- W.F. Bu, H.L. Fan, L.X. Wu, X.L. Hou, C.W. Hu, G. Zhang, X. Zhang, Langmuir 18 [3] (2002) 6398.
- M. Green, J. Harries, G. Wakefield, R. Taylor, J. Am. Chem. Soc. 127 (2005) 12812. [4]
- [5] S. Zhao, X.H. Wang, M.X. Huo, Appl. Catal., B: Environ. 97 (2010) 127.
- [6] T. Dwars, E. Paetzold, G. Oehme, Angew. Chem. 117 (2005) 7338.
- [7] S. Zhao, C.L. Sun, L. Wang, X.B. Xu, X.H. Wang, Dalton Trans. 39 (2010) 5087.

- [8] R. Neumann, A.M. Khenkin, J. Org. Chem. 59 (1994) 7577.
- [9] A. Lambert, P. Plucinski, I.V. Kozhevnikov, Chem. Commun. 6 (2003) 714.
- [10] M.L. Guo, Green Chem. 6 (2004) 271.
- [11] J. Kaur, I.V. Kozhevnikov, Catal. Commun. 5 (2004) 709.
- [12] C. Li, Z.X. Jiang, J.B. Gao, Y.X. Yang, S.J. Wang, F.P. Tian, F.X. Sun, X.P. Sun, P.L. Ying, C.R. Han, Chem. Eur. J. 10 (2004) 2277.
- [13] H.Y. Lu, J.B. Gao, Z.X. Jiang, F. Jing, Y.X. Yang, G. Wang, C. Li, J. Catal. 239 (2006) 369.
 [14] K. Arai, Y. Ogiwara, Makromol. Chem., Rapid Commun. 4 (1983) 181.
- [15] K. Shimizu, H. Furukawa, N. Kobayashi, Y. Itayab, A. Satsuma, Green Chem. 11 (2009) 1627.
- [16] A. Tanriseven, S. Doğan, Process. Biochem. 36 (2001) 1081.
- A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411. [17]
- [18] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew. Chem. Int. Ed. 46 (2007) 7164.
- [19] L.D. Schmidt, P.I. Dauenhauer, Nature 447 (2007) 914. [20] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, Inorg. Chem. 22
- (1983) 207 [21] G.L. Miller, Anal. Chem. 31 (1959) 426.
- [22] L.N. Zhou, K. Liu, W.M. Hua, Y.H. Ying, Z. Gao, Chin. J. Catal. 30 (2009) 196.
- [23] M.M.Q. Simões, C.M.M. Conceição, J.A.F. Gamelas, P.M.D.N. Domingues, A.M.V. Cavaleiro, J.A.S. Cavaleiro, A.J.V. Ferrer-Correia, R.A.W. Johnstone, J. Mol. Catal. A: Chem. 144 (1999) 461.
- T. Okuhara, et al., Chem. Mater. 12 (2000) 2230. [24]
- [25] P. Mukherjee, K.J. Mysels, NSRDS-NBS, 1971, p. 36.
- [26] J. Tian, J.H. Wang, S. Zhao, C.Y. Jiang, X. Zhang, X.H. Wang, Cellulose 17 (2010) 587.
- [27] Z.E.A. Abdalla, B. Li, A. Tufail, Colloids and Surf. A: Physcochem. Eng. Aspects 341 (2009) 86.
- T. Dwars, E. Paetzold, G. Oehme, Angew. Chem. Int. Ed. 44 (2005) 7174. [28]
- [29] D. Yamaguchi, M. Kitano, S. Suganuma, K. Nakajima, H. Kato, M. Hara, J. Phys. Chem. C. 113 (2009) 3181.