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Zinc polyoxometalate on activated carbon: an efficient catalyst for selective oxidation of alcohols with hydrogen peroxide

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$[PW_{11}ZnO_{39}]^{5-}$ was immobilized on activated carbon and characterized using Fourier transform infrared, X-ray diffraction, Brunauer–Emmett–Teller and elemental analysis techniques. Effective oxidation of various alcohols with hydrogen peroxide was performed in the presence of this catalyst. Easy separation of the catalyst from the reaction mixture, cheapness, high activity and selectivity, stability as well as retained activity in subsequent catalytic cycles make this supported catalyst suitable for small-scale synthesis. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: catalysis; polyoxometalate; activated carbon; alcohol; oxidation; hydrogen peroxide

Introduction

Oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important and simple transformations in organic synthesis and industrial chemistry.[1,2] Alcohol oxidation is conventionally performed using dichromate and permanganate oxidants. Unfortunately, these oxidants are usually toxic, expensive and environmentally undesirable; and they also produce large amounts of wastes.[3,4] With economic and environmental concerns, the use of hydrogen peroxide as a safe, clean and cheap oxidant has been suggested to realize so-called green oxidation processes.[5]

Polyoxometalates (POMs) are a large family of metal–oxygen clusters of early transition metals. These compounds have stimulated many current research activities in a broad range of fields such as catalysis, materials science and medicine. Such a stimulation is because of diverse and highly modifiable sizes, shapes, charge densities, acidities and reversible redox potentials of POMs.[6,7] They also can act as efficient catalysts in the oxidation of various organic compounds.[8–13] The catalytic performances of different types of POMs such as phosphomolybdate, sandwich-type POMs, $[NaP_5W_{30}O_{110}]^{14-}$, $[IMo_6O_{24}]^{5-}$ and other POM catalysts have been demonstrated for oxidation of alcohols, sulfides and alkenes using a variety of oxygen sources.[14–24] Unfortunately, for many of these catalytic systems, the use of toxic solvents or difficult recovery and reusability of the catalysts have limited their applications in industrial and laboratorial synthesis. In order to be more effective in catalytic applications, POMs are usually incorporated on suitable materials for preparation of heterogeneous catalysts.

Heterogeneous catalytic processes show great advantages in terms of product separation and catalyst reusability. Therefore, they are more feasible for industrial applications.[3] Various supports such as silica,[25,26] alumina,[27] carbon,[28] titania,[29] zirconia,[30] MCM-41[31] and SBA-15[32] have been used in a range of catalytic applications. Activated carbon (AC) has been studied as a potential supporting material for heteropolyanions (HPA) in various redox reactions. These compounds are low-cost materials with porous structures, high surface area and pH stability.[33] ACs can be used to bind/support acidic HPAs, resulting in an extraordinary stability/regenerability towards HPA leaching from the AC support.[34] However, limited studies have been carried out using AC-supported HPAs for oxidative desulfurization. For example, phosphotungstic acid (HPW)/AC has been reported as an efficient catalyst for oxidative desulfurization with H_2O_2.[35]

To the authors' knowledge, few studies have been reported using transition metal-substituted POMs supported on AC for oxidation of alcohols. In the work reported here, for the first time, AC was used as a support for $[PW_{11}ZnO_{39}]^{5-}$ ($PW_{11}Zn$) and the resulting catalyst was employed in the oxidation of alcohols with hydrogen peroxide.

Experimental

General and methods

All materials such as metal salts, alcohols, 30% hydrogen peroxide and solvents were of analytical grade, commercially available and used without further purification unless otherwise stated. $K_5[PW_{11}ZnO_{39}]\cdot 25H_2O$ was prepared according to the literature.[36–38]

Elemental analyses were performed using inductively coupled plasma atomic emission spectrometry with a PerkinElmer 7300

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DV elemental analyser. Fourier transform infrared (FT-IR) spectra were obtained with samples as potassium bromide pellets in the range 400–4000 cm^{-1} with a Nicolet Impact 400D instrument. Powder X-ray diffraction (XRD) data were obtained with a Bruker D8 Advance using Cu Kα radiation ($2\theta = 5$–70°). Brunauer–Emmett–Teller (BET) 'apparent' specific surface area of supported POM was determined from nitrogen adsorption measurements at 77 K using a Micromeritics Nanosord sens Iran Ltd Co NS 91 equipment. The oxidation products were quantitatively analysed using gas chromatography (GC) with a Shimadzu GC-16A instrument with a flame-ionization detector using a silicon DC-200 column. ^{1}H NMR spectra were obtained in chloroform with a Bruker 400 (296 K) and referenced to tetramethylsilane (0.0 ppm) as external standard.

Synthesis of $PW_{11}Zn@AC$ catalyst

An aqueous solution of $PW_{11}Zn$ was prepared by mixing Na_2HPO_4 (9.1 mmol), $Na_2WO_4{\cdot}2H_2O$ (100 mmol) and zinc nitrate (12 mmol) in 200 ml of water and adjusting the pH to 4.8.[23–25] AC (1 g) in 10 ml of water was added dropwise with stirring for 12 h. The solid was filtered and washed three times with water and then dried in vacuum at 100 °C for 4 h.

Typical procedure for oxidation of alcohols by H_2O_2

In a 25 ml round-bottomed flask equipped with a reflux condenser, a mixture of 0.2 g of $PW_{11}Zn@AC$ catalyst containing 5 μmol of $PW_{11}Zn$, 3 ml of acetonitrile and 1 mmol of alcohol was added. Then 1 ml of 30% H_2O_2 was added and the mixture was refluxed for an appropriate time (25 min to 4 h) with stirring. The progress of the reaction was monitored using GC with flame ionization detection and a silica pack column. At the end of the reaction, the catalyst was filtered out and 10 ml of 10% $NaHCO_3$ was added. The organic phase was extracted with chloroform and dried. Flash chromatography on a short column of silica gel with ethyl acetate–*n*-hexane as eluent gave pure products.

Recycling of the catalyst

A typical recycling experiment was carried out as follows. After the required reaction time, the round-bottom flask was cooled to room temperature. The $PW_{11}Zn@AC$ was separated from the reaction mixture by filtration. The catalyst was then thoroughly washed with CH_3CN and acetone followed by drying in vacuum at room temperature. It was then used in further oxidation reaction.

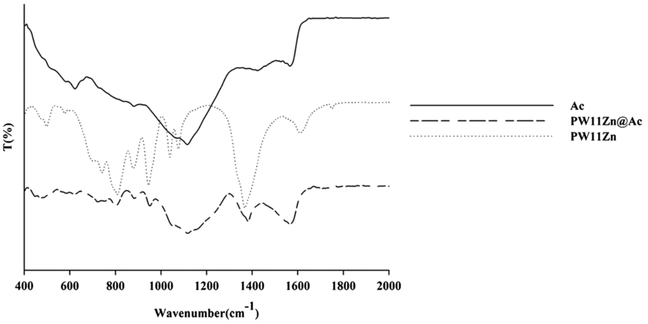


Figure 1. FT-IR spectra of AC, $PW_{11}Zn$ and $PW_{11}Zn@AC$.

Results and discussion

Characterization of the catalyst

The transition metal-substituted POM $K_5[PW_{11}ZnO_{39}]{\cdot}25H_2O$ and $PW_{11}Zn@AC$ were synthesized and characterized using the methods described elsewhere.[36–38] FT-IR spectra, which provide characteristic fingerprints for POM clusters (P–O, W–O and W–O–W stretch regions) in the range 500–1100 cm^{-1}, were used for structural confirmation. For AC, the band at 1500–1600 cm^{-1} is attributed to the C=O stretching vibrations of lactonic, quinonic or carboxylic groups. Also, the bands at 900–1300 cm^{-1} are assigned to C–O–C vibrations or C–O stretching of etheric, lactonic, carboxylic or phenolic groups.[39] In the regions 3037–3124 and 2844–2918 cm^{-1}, the bands correspond to aromatic and aliphatic groups.[40,41] Figure 1 shows the FT-IR spectra of $K_5[PW_{11}ZnO_{39}]{\cdot}25H_2O$, $PW_{11}Zn@AC$ and AC. In the FT-IR spectrum of $PW_{11}Zn@AC$, the peaks at 1070 and 960 cm^{-1} of $PW_{11}Zn$ are overlapped with C–O–C vibrations or C–O stretching of ether, lactonic, carboxylic or phenolic groups of AC. In addition, a broad intense band centred on 3450 cm^{-1} attributed to O–H stretching and a weak absorption at 1640 cm^{-1} (H_2O bending) indicate the presence of water in $PW_{11}Zn@AC$ and AC. Furthermore, the absorption peaks at 860–880 and 790–800 cm^{-1} are characteristic of Keggin structure and suggest the structure of the POM is preserved after incorporation on AC.

The XRD patterns of $PW_{11}Zn$, AC and also $PW_{11}Zn@AC$ were studied which are shown in Fig. S1. From the results, AC shows an amorphous structure with a broad band at 2θ about 10° to 30°. Unfortunately, the characteristic peaks for $PW_{11}Zn$ are located in the region of the AC broad band. However, in the XRD pattern of $PW_{11}Zn@AC$, a small band attributed to $PW_{11}Zn$ is observed. These results suggest that adsorbed $PW_{11}Zn$ is highly dispersed on the AC surface, and no crystalline phase is observed after dispersion of $PW_{11}Zn$ on AC. Similar results have also been reported by Alcañiz-Monge *et al.* where $H_3[PMo_{12}O_{40}]$ was supported on ACs.[42]

The elemental analysis results show that $PW_{11}Zn@AC$ samples contain 10 wt% of $PW_{11}Zn$. The molar ratio of P:Zn:W is also estimated to be 1:1:11. These results suggest that the Keggin structure is well preserved in the supported catalyst. Therefore, the elemental analysis and FT-IR spectra of $PW_{11}Zn$ and $PW_{11}Zn@AC$ confirm that the structure of $PW_{11}Zn$ is unchanged after impregnation of $PW_{11}Zn$ on AC. The BET surface area result for this catalyst shows that the surface area is 501 m^2 g^{-1}. The surface area for AC was previously reported to be 916 m^2 g^{-1}. So, it is demonstrated that the surface area of the catalyst after supporting of the POM is lower than that of AC. The reason is probably due to the presence of modifier species that are mainly fixed on the micropore entrances and walls, which block the access of N_2 molecules into the micropores to a certain extent.[43]

Catalytic studies

Following our previous studies on oxidative catalysis,[37,44,45] new heterogeneous catalysts based on transition metal-substituted POMs on AC were synthesized. The oxidation of benzyl alcohol with hydrogen peroxide under reflux conditions was chosen as a model reaction in order to test the catalytic activity of POM@AC catalysts. The catalytic activity of some other transition metal-substituted POMs was checked and the results show that $PW_{11}Zn@AC$ has the best catalytic activity. The oxidation reaction in the presence of $ZnCl_2$, AC and $H_3PW_{12}O_{40}$ as blank catalytic experiments was also performed, resulting in very low conversions (Table 4, entries 10–12).

Table 1. Effect of various solvents in the oxidation of benzyl alcohol with H_2O_2[a]

Entry	Solvent	Yield (%)[b]
1	CH_3CN	100
2	THF	65
3	$CHCl_3$	76
4	n-C_6H_{14}	5
5	$CH_3C(O)OC_2H_5$	54
6	H_2O	57
7	DMF	53
8	DMSO	56
9	CH_3OH	72
10	C_2H_5OH	67

[a] Reaction conditions: benzyl alcohol (1 mmol), catalyst (5 μmol), H_2O_2 (1 ml), solvent (3 ml) at reflux in 45 min.

[b] Yields refer to GC yields.

In the exploratory experiments, the effect of various solvents was examined using benzyl alcohol. The results (Table 1) show that the reaction in acetonitrile gives the highest conversion and selectivity towards aldehyde. Lower catalytic activities are observed using other solvents.

Various amounts of PW$_{11}$Zn@AC in the oxidation of benzyl alcohol were investigated by changing the catalyst amounts from 0.1 to 0.5 g. Results show that the conversion of benzyl alcohol is increased on increasing the catalyst amount. The maximal conversion (*ca* 100%) is achieved when 0.2 g of PW$_{11}$Zn@AC is used. Higher amounts of PW$_{11}$Zn@AC cause a decrease in aldehyde selectivity. The amount of hydrogen peroxide, as one of the factors influencing the oxidation of benzyl alcohol into benzaldehyde, was also investigated. The results are shown in Fig. 2. It can be seen that the conversion of benzyl alcohol is increased on increasing the molar ratio of H_2O_2 to benzyl alcohol. Complete conversion of benzyl alcohol is obtained using about 10 mmol of 30% H_2O_2. Higher amounts of H_2O_2 decrease the selectivity for benzaldehyde.

After obtaining the best conditions (0.2 g of PW$_{11}$Zn@AC catalyst, 10 mmol of H_2O_2 and CH_3CN as solvent), the reaction of other substrates was also studied (Table 2). The time courses of PW$_{11}$Zn, PW$_{11}$Zn@AC and AC under these reaction conditions are shown in Fig. 3.

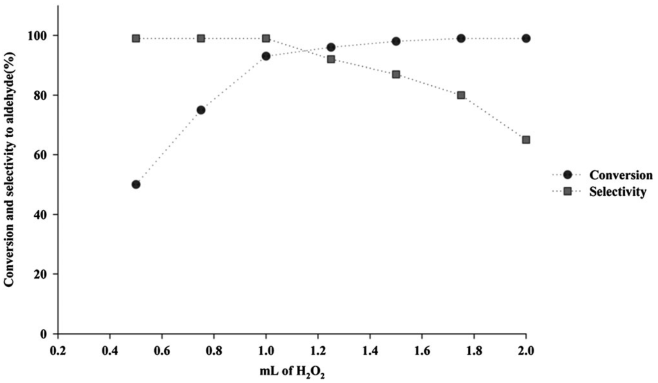
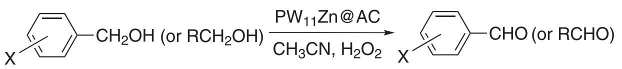


Figure 2. Effect of amount of hydrogen peroxide in the oxidation of benzyl alcohol with PW$_{11}$Zn@AC.

Table 2. Oxidation of various alcohols with hydrogen peroxide catalysed by PW$_{11}$Zn@AC[a]



Entry	Alcohol	Time (min)[b]	TOF (h^{-1})[c]
1	$C_6H_5CH_2OH$	45	267
2	2-$MeC_6H_4CH_2OH$	35	343
3	4-$MeC_6H_4CH_2OH$	25	480
4	2-$MeOC_6H_4CH_2OH$	35	343
5	4-$MeOC_6H_4CH_2OH$	25	480
6	3-$MeOC_6H_4CH_2OH$	70	171
7	2-$O_2NC_6H_4CH_2OH$	180	67
8	4-$O_2NC_6H_4CH_2OH$	240	50
9	4-$BrC_6H_4CH_2OH$	50	240
10	4-$FC_6H_4CH_2OH$	25	480
11	4-$ClC_6H_4CH_2OH$	35	343
12	2,4-$ClC_6H_3CH_2OH$	90	133
13	4-$HOC_6H_4CH_2OH$	50	240
14	3-Br-2-$HOC_6H_4CH_2OH$	25	480
15	$C_6H_{11}OH$	120	100
16	$C_6H_5CHCHCH_2OH$	70	171
17	n-$C_7H_{15}OH$	180	67
18	n-$C_6H_{13}OH$	180	67
19	CH_2CHCH_2OH	90	133

[a] Reaction conditions: alcohol (1 mmol), catalyst (5 μmol), 30% H_2O_2 (1 ml), CH_3CN (3 ml) at reflux.

[b] Yields are quantitative and refer to GC yields.

[c] Turnover frequency.

Various organic substrates containing electron-donating groups, such as *p*-methoxybenzyl alcohol and *p*-methylbenzyl alcohol, are converted into the corresponding aldehydes with 99% selectivity (Table 2, entries 2–6). Nitrobenzyl alcohols, which have an electron-withdrawing group, are oxidized into the corresponding aldehydes in longer times compared to other substrates with electron-donating groups (Table 2, entries 7 and 8). In previous studies, it was mentioned that electron-rich arenes with electron-donating substituents show shorter oxidation times whereas times for electron-withdrawing groups are longer.[51] Halogen-containing substrates in *para* position take part in the oxidation reaction giving high yields (Table 2, entries 9–11). The oxidation of *p*-hydroxybenzyl alcohol was also carried out with high selectivity and without oxidation of hydroxyl group. The corresponding aldehyde is the only reaction product (Table 2, entry 13). In view of the fact that the oxidation of aliphatic alcohols is much more difficult than that of benzylic ones, other interesting results are obtained by conversion of aliphatic alcohols. In this regard, the oxidation of cyclohexanol, 1-hexanol and 1-heptanol into the corresponding ketones takes place in slightly longer times (Table 2, entries 15, 17 and 18). The oxidation of cinnamyl alcohol and 1-propenol gives corresponding aldehydes without any oxidation of C=C double bond (Table 2, entries 16 and 19).

It was postulated that the oxidation mechanism for POM catalysts involves oxo- and peroxometal intermediates by transition metal-substituted and addenda atoms.[52,53] For Zn-substituted POMs, it was found that the favoured reaction path is heterolytic cleavage of O–O bond.[44]

The stability of the catalyst, very low leaching of the active component, heterogeneity of the catalyst under reaction conditions and catalyst recyclability are important points that should be addressed in the oxidation processes over the PW$_{11}$Zn@AC catalyst. It is found that $PW_{11}Zn@AC$ does not lose its catalytic activity/selectivity during at least five catalytic cycles in the oxidation of benzyl alcohol with hydrogen peroxide (Table 3). Moreover, according to the FT-IR data, the structure of $PW_{11}Zn$ in the supported catalyst is retained during the oxidation reaction (Fig. 4).

In order to show the applicability and efficiency of our catalytic system, results are compared with some of the recently reported methods for the oxidation of benzyl alcohol by hydrogen peroxide. As is evident from Table 4, the proposed system yields superior results in comparison to most of the other methods. Additionally, our catalytic system has very good reusability for this reaction.

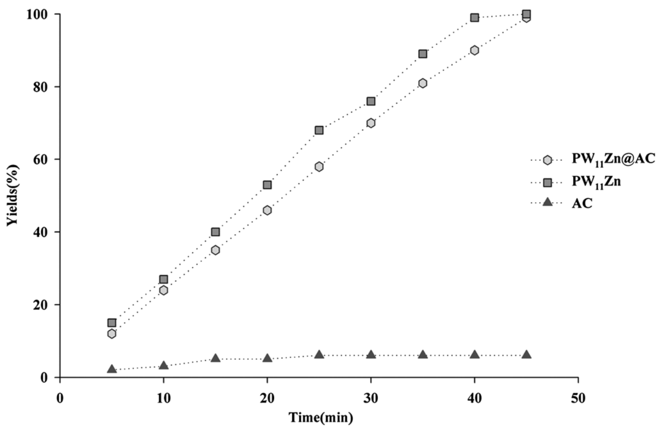


Figure 3. Conversion–time curves for oxidation of benzyl alcohol with $PW_{11}Zn$, $PW_{11}Zn@AC$ and AC. Reaction conditions: benzyl alcohol (1 mmol), $PW_{11}Zn$ and $PW_{11}Zn@AC$ (5 μmol) or AC (2 g), 30% H_2O_2 (10 ml) at reflux in acetonitrile (3 ml).

Table 3. Reusability of $PW_{11}Zn@AC$ in the oxidation of benzyl alcohol[a]

Run	Yield (%)[b]
1	99
2	99
3	99
4	98
5	98

[a] Reaction conditions: benzyl alcohol (1 mmol), catalyst (5 μmol), H_2O_2 (1 ml), 45 min, CH_3CN (3 ml) at reflux.
[b] Yields refer to GC yields.

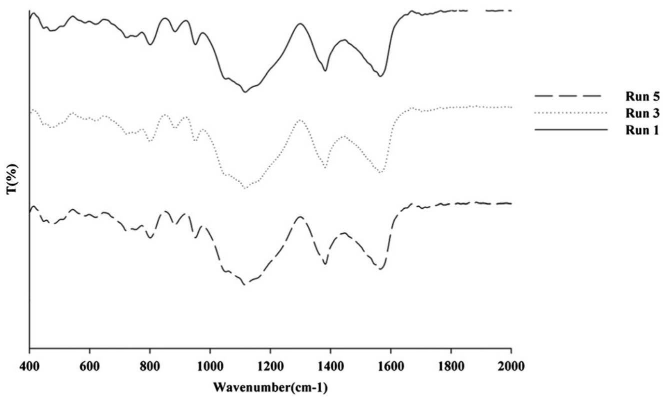


Figure 4. FT-IR spectra of $PW_{11}Zn@AC$ recovered in runs 1, 3 and 5.

Table 4. Comparison of results for the oxidation of benzyl alcohol by H_2O_2 in the presence of various POM catalysts

Entry	Catalyst	Time (h)	Conversion (%)	Ref.
1	$Cs_{1.5}H_{1.5}PMo_{12}O_{40}/SiO_2$	5	69.1	[46]
2	$Na_6[SiW_{11}ZnO_{40}]\cdot 12H_2O$	2	100	[47]
3	$Na_9[SbW_9O_{33}]$	2	94	[48]
4	$H_3PMo_{12}O_{40}$	5	84	[15]
5	$[Zn_4(H_2O)_2(PW_9O_{34})_2]^{10-}$	8	94	[49]
6	$[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$	1.15	100	[44]
7	HPW-IL-SBA-15/5 m	6	93	[50]
8	$(TBA)_4[PW_{11}FeO_{39}]/SiO_2$	2	80	[45]
9	$PW_{11}Zn@AC$	0.75	100	—
10	$ZnCl_2$	0.75	13	—
11	AC	0.75	8	—
12	$H_3PW_{12}O_{40}$	0.75	21	—

Conclusions

A novel and efficient procedure for the oxidation of various alcohols with hydrogen peroxide has been developed using $PW_{11}Zn@AC$ as a cheap, effective and recyclable catalyst. This catalytic system has been applied for the oxidation of various alcohols into the corresponding carbonyl compounds with good to excellent yields. The $PW_{11}Zn@AC$ catalyst could be reused for at least five runs with consistent activity and selectivity.

Acknowledgments

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References

[1] S. Furukawa, A. Tamura, T. Shishido, K. Teramura, T. Tanaka, *Appl. Catal. B* **2011**, *110*, 216.
[2] M. Hudlick, *Oxidations in Organic Chemistry*, American Chemical Society, Washington, DC, **1990**.
[3] X. Wang, G. Wu, N. Guan, L. Li, *Appl. Catal. B* **2012**, *115–116*, 7.
[4] S. V. Ley, A. Madin, in *Comprehensive Organic Synthesis*, Vol. *3* (Eds: B. M. Trost, I. Fleming, S. V. Ley), Pergamon, Oxford, **1991**, pp. 251–289.
[5] G. Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636.
[6] I. M. Mbomekalle, B. Keita, L. Nadjo, P. Berthet, K. I. Hardcastle, C. L. Hill, T. M. Anderson, *Inorg. Chem.* **2003**, *42*, 1163.
[7] K. Sugahara, S. Kuzuya, T. Hirano, K. Kamata, N. Mizuno, *Inorg. Chem.* **2012**, *51*, 7932.
[8] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, *Science* **2003**, *300*, 964.
[9] X. Xue, W. Zhao, B. Ma, Y. Ding, *Catal. Commun.* **2012**, *29*, 73.
[10] S. Pathan, A. Patel, *Appl. Catal. A* **2013**, *459*, 59.
[11] N. Mizuno, K. Yamaguchi, K. Kamata, *Coord. Chem. Rev.* **2005**, *249*, 1944.
[12] N. Mizuno, M. Misono, *Chem. Rev.* **1998**, *98*, 199.
[13] M. Misono, *Chem. Commun.* **2001**, 1141.
[14] C. Yang, Q. Jin, H. Zhang, J. Liao, J. Zhu, B. Yu, J. Deng, *Green Chem.* **2009**, *11*, 1401.
[15] P. Tundo, G. P. Romanelli, P. G. Vazquez, F. Arico, *Catal. Commun.* **2010**, *11*, 1181.
[16] G. Absillis, T. N. Parac-Vogt, *Inorg. Chem.* **2012**, *51*, 9902.
[17] K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara, N. Mizuno, *Nat. Chem.* **2010**, *2*, 478.

[18] M. Bonchio, A. Sartorel, P. Mirò, M. Carraro, S. Berardi, O. Bortolini, A. Bagno, C. Bo, *Chem. Eur. J.* **2014**, *20*, 10932.
[19] M. Carraro, B. Bassil, A. Sorarù, S. Berardi, A. Suchopar, U. Kortz, M. Bonchio, *Chem. Commun.* **2013**, *49*, 7914.
[20] C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem. Rev.* **1995**, *43*, 407.
[21] X. Zhang, K. Sasaki, C. L. Hill, *J. Am. Chem. Soc.* **1996**, *118*, 4809.
[22] S. J. Zhang, S. Gao, Z. W. Xi, J. Xu, *Catal. Commun.* **2007**, *8*, 531.
[23] A. Khenkin, R. Neumann, *Adv. Synth. Catal.* **2002**, *344*, 1017.
[24] N. M. Okun, T. M. Anderson, C. L. Hill, *J. Am. Chem. Soc.* **2003**, *125*, 3194.
[25] W. Kuang, A. Rives, M. Fournier, R. Hubaut, *Appl. Catal. A* **2003**, *250*, 221.
[26] X. M. Yan, G. S. Su, L. Xiong, J. Fuel, *Chem. Technol.* **2009**, *37*, 318.
[27] A. Griboval, P. Blanchard, E. Payen, M. Fournier, I. L. Dubois, J. R. Bernard, *Appl. Catal. A* **2001**, *217*, 173.
[28] I. V. Kozhevnikov, *Catal. Lett.* **1994**, *27*, 187.
[29] S. Damyanova, J. L. G. Fierro, *Chem. Mater.* **1998**, *10*, 871.
[30] S. Damyanova, L. M. Gómez, M. A. Bañares, J. L. G. Fierro, *Chem. Mater.* **2000**, *12*, 501.
[31] P. A. Jalil, M. A. Al-Daous, A. R. A. Al-Arfaj, A. M. Al-Amer, J. Beltramini, S. A. I. Barri, *Appl. Catal. A* **2001**, *207*, 159.
[32] F. Marme, G. Coudurier, J. C. Védrine, *Micropor. Mesopor. Mater.* **1998**, *22*, 151.
[33] S. Sumimoto, C. Tanaka, S. T. Yamaguchi, Y. Ichihashi, S. Nishiyama, S. Tsuruya, *Ind. Eng. Chem. Res.* **2006**, *45*, 7444.
[34] I. V. Kozhevnikov, *Chem. Rev.* **1998**, *98*, 171.
[35] J. Xiao, L. Wu, Y. Wu, B. Liu, L. Dai, Z. Li, Q. Xia, H. Xi, *Appl. Energy* **2014**, *113*, 78.
[36] H. Hamidi, E. Shams, B. Yadollahi, F. K. Esfahani, *Electrochim. Acta* **2009**, *54*, 3495.
[37] H. Danafar, B. Yadollahi, *Catal. Commun.* **2009**, *10*, 842.
[38] B. J. S. Johnson, A. Stein, *Inorg. Chem.* **2001**, *40*, 801.
[39] C. Sepúlveda, R. García, P. Reyes, I. T. Ghampson, J. L. G. Fierro, D. Laurenti, M. Vrinat, N. Escalon, *Appl. Catal. A* **2014**, *475*, 427.
[40] J. Figueiredo, M. Pereira, M. Freitas, J. Orfao, *Carbon* **1999**, *37*, 1379.
[41] G. Ramirez, R. Cuevas, *Appl. Catal. B* **1990**, *57*, 223.
[42] J. Alcañiz-Monge, G. Trautwein, S. Parres-Esclapez, J. A. Maciá-Agulló, *Micropor. Mesopor. Mater.* **2008**, *115*, 440.
[43] X.-L. Lio, J.-X. Guo, Y.-H. Chu, D.-M. Luo, H.-Q. Yin, M.-C. Sun, R. Yavuz, *Fuel* **2014**, *123*, 93.
[44] Z. Nadealian, V. Mirkhani, B. Yadollahi, M. Moghadam, S. Tangestaninejad, I. Mohammadpoor-Baltork, *J. Coord. Chem.* **2012**, *65*, 1071.
[45] M. R. Farsani, B. Yadollahi, *J. Mol. Catal. A* **2014**, *392*, 8.
[46] G. Peng, Y. Wang, C. Hu, E. Wang, S. Feng, Y. Zhou, H. Ding, Y. Liu, *Appl. Catal. A* **2001**, *218*, 91.
[47] J. Wang, L. Yan, G. Li, X. Wang, Y. Ding, J. Suo, *Tetrahedron Lett.* **2005**, *46*, 7023.
[48] R. H. Ingle, N. K. Kala Raj, P. Manikandan, *J. Mol. Catal. A* **2007**, *262*, 52.
[49] Y. Ding, W. Zhao, B. Ma, W. Qiu, *Can. J. Chem.* **2011**, *89*, 13.
[50] H. Zhao, L. Zeng, Y. Li, C. Liu, B. Hou, D. Wu, N. Feng, A. Zheng, X. Xie, S. Su, N. Yu, *Micropor. Mesopor. Mater.* **2013**, *172*, 67.
[51] K. P. Peterson, R. C. Larock, *J. Org. Chem.* **1998**, *63*, 3185.
[52] N. K. Kala Raj, A. V. Ramaswamy, P. Manikandan, *J. Mol. Catal. A* **2005**, *227*, 37.
[53] Y. Liu, K. Murata, M. Inaba, *Catal. Commun.* **2005**, *6*, 679.

Supporting information

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