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Facile one-pot synthesis of $V_xO_y@C$ catalysts using sucrose for the direct hydroxylation of benzene to phenol[†]

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$V_xO_y@C$ catalysts were prepared from sucrose and NH_4VO_3 by a one-pot hydrothermal method. They showed satisfactory catalytic performance for the hydroxylation of benzene to phenol in aceto-nitrile using oxygen as the oxidant.

Phenol is one of the most important industrial feedstocks that is widely used as the precursor for the production of phenol resins, fibers, dyestuffs, and medicine. From the viewpoints of economy and the environment, the direct hydroxylation of benzene to phenol in one step is very attractive compared to the traditional three-step cumene process. The oxidants for the direct hydroxylation of benzene are mostly focused on H_2O_2 ,¹⁻³ O_2 ,^{4,5} and N_2O .⁶⁻⁸ Among these oxidants, O_2 is the most economical and environmentally benign. With O₂ as the oxidant and a sacrificial reductant, the highest phenol yield of more than 20% could be achieved.^{9,10} Concentrated acetic acid aqueous solution⁹⁻¹² and acetonitrile^{13,14} are often employed as the solvents for the reaction. The reaction system with acetic acid as the solvent usually results in corrosion and pollution problems, although the yield of phenol is relatively higher. The reaction in acetonitrile can avoid corrosion, but the yield of the product is usually lower.

Catalysts using carbon as the supports have shown good performance for the direct hydroxylation of benzene to phenol, such as $Fe_3O_4/MWCNTs$,¹⁵ $VO_2/MWCNTs$,¹⁶ $Fe_3O_4/CMK-3^{17}$ and activated carbon-supported ferric sulfate.¹⁸ In addition, carbon treated with nitric acid shows catalytic activity itself. For example, the MWCNTs treated with concentrated HNO₃ can catalyze the hydroxylation of benzene with active oxygen which was generated on the defects of MWCNTs with dangling incomplete bonding,¹⁹ while the activated carbon treated with HNO₃ and hydrogen peroxide shows good catalytic activity for the hydroxylation of benzene.²⁰ Therefore, carbon has attractive potential as a catalytic material for the title reaction.

Utilization of renewable and abundant biomaterials is one of the most sustainable approaches for fabricating functional carbon materials. Hydrothermal carbonization of saccharides is an effective and green route to prepare carbon materials in catalysis, energy storage, CO₂ sequestration, and water purification.^{21,22} In addition, the reducibility of saccharides makes it possible to prepare metal-carbon catalytic materials via a one-pot saccharides hydrothermal process.²³⁻²⁵ There is no doubt that developing highly efficient, economic and simple catalytic systems for the direct hydroxylation of benzene to phenol is highly desirable. In the present work, a novel vanadium-carbon composite catalyst (designated as $V_x O_y @C$) was prepared from sucrose and NH₄VO₃ by a one-pot hydrothermal carbonization process for the first time. The as-prepared material exhibited satisfactory activity and selectivity for the direct hydroxylation of benzene to phenol with oxygen in acetonitrile.

In this approach, sucrose was used as the carbon source and reducing agent and NH₄VO₃ as the metal precursor. $V_x O_y$ (a) C could be prepared using different amounts of sucrose and NH₄VO₃. The amount of the catalyst powder obtained increased with an increased amount of NH4VO3 when the amount of sucrose was fixed (Fig. S1[†]). Little carbonaceous powder was formed without NH₄VO₃, indicating that NH₄VO₃ was the key to the formation of $V_x O_y$ (a)C. The vanadium content in the V_xO_y@C prepared from different amounts of NH₄VO₃ gradually increased with an increase in the amount of NH₄VO₃ used, which was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Table 2). This implied that the NH₄VO₃ was a reactant, which also acted as a catalyst.²⁶ During the carbonization, NH₄VO₃ was exhausted and the carbonization stopped. The functional groups on the carbonaceous material can stabilize the vanadium affording active and stable catalysts.²⁷

The hydrothermal temperature was important in the preparation of $V_x O_y$ C. The amount of the obtained catalysts increased with increasing hydrothermal temperature in the

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range of 120–180 °C (Fig. S1[†]), but the amount of the catalyst obtained reduced with a further increase in temperature. Saccharides usually carbonized at a relatively high temperature (160–190 °C).^{28–31} However, when some metal salts were added to the system, the carbonization temperature could be decreased. For example, glucose could be carbonized at 80 °C in the presence of iron nitrate, which was attributed to the ability of iron nitrate to catalyze the dehydration of glucose.²⁴ In this work, the sucrose and NH₄VO₃ system could carbonize above 120 °C.

The liquid phase of the hydrothermal reaction solution was analyzed using ¹³C NMR (Fig. S2†). The signals of glucose and fructose were observed, which demonstrated that sucrose was hydrolyzed to glucose and fructose.^{32,33} Furthermore, the signals of HMF (hydroxymethylfurfual) were also observed in the ¹³C NMR spectrum, suggesting that glucose and fructose were partially transformed to HMF under the hydrothermal conditions.^{34,35}

Fourier transform infrared (FT-IR) spectra of all the prepared catalyst samples were nearly identical (Fig. S3[†]). The O–H stretching bands at 3400 cm⁻¹ and 2930 cm⁻¹ indicated the presence of aliphatic hydrocarbons (–C–H).³⁶ The bands at 1710 cm⁻¹ and 1617 cm⁻¹ were attributed to C=O and C=C vibrations, respectively, indicating the aromatization of glucose during the hydrothermal treatment.²⁵ The bands in the range 1000–1300 cm⁻¹ were assigned to the C–OH stretching and OH bending vibrations, which showed the existence of residual hydroxy groups.^{30,37} Furthermore, the surface oxygen was characterized by XPS (Fig. S4[†]). Carbonyl groups, alcohol and/or ether groups, and carboxyl and/or ester groups were observed at 531.6, 532.5 and 533.5 eV,²⁰ respectively, which was consistent with the FT-IR spectra.

The mechanism of the hydrothermal process was proposed (Scheme 1) on the basis of the above characterizations and existing knowledge. NH_4VO_3 catalyzed the hydrolysis of sucrose to produce glucose and fructose, both of which were then partially transformed into HMF. Nuclei-oligomers were formed by the dehydration of glucose or polymerization of HMF in the initial stage. Simultaneously, NH_4VO_3 was partially transformed into the vanadium oxides, which were stabilized by the functional groups (OH and C=O) on the surface of the oligomers. With further polymerization and carbonization, the amorphous vanadium–carbon (XRD patterns in Fig. S5†) catalysts were formed. This was a hydrolysis–polymerization–carbonization process.

The XPS spectra of the V_xO_y @C catalysts showed the binding energy of V $2P_{3/2}$ in the range of 515.5–516.9 eV (Table S1[†]), indicating the existence of V⁴⁺ and V⁵⁺ in the catalysts.^{38,39} It was known that saccharides could act as reductants for many reactions.^{24,25} Therefore, the sucrose used in this work could reduce V⁵⁺ in NH₄VO₃ to V⁴⁺, which has been proved to be the active species for the hydroxylation of benzene.^{40,41} It can be observed from the SEM images (Fig. S6[†]) that the variation in the amount of NH₄VO₃ did not remarkably influence the morphology of the catalysts prepared at 120 °C. However, at 180 °C the particles of the catalysts were



Scheme 1 Schematic illustration of the synthesis of $V_x O_y @C$ by the hydrothermal process.

more uniform when less NH₄VO₃ was employed. NH₄VO₃ or vanadium oxides could not be observed in the XRD patterns (Fig. S5[†]), which was due to the high dispersion of the vanadium oxides. The BET surface area of the V_xO_y@C-0.195–120 determined by nitrogen sorption–desorption measurement was 33.1 m² g⁻¹ (Fig. S7[†]). The N content on V_xO_y@C-0.195–120 was about 1.5% according to the XPS analysis. This may be the adsorbed NH⁴⁺ on the surface which balanced the charge of the carboxyl groups.

The catalytic performances of the V_xO_y @C for the hydroxylation of benzene to phenol with molecular oxygen were investigated. Acetonitrile was used as the solvent and ascorbic acid as the sacrificial reductant, which proved to be essential for the hydroxylation reaction (Table 1, entry 6). In the reaction, phenol and hydroquinone were produced without observing the formation of catechol and benzoquinone. The yields of phenol were very low in water or without solvent (Table 1, entries 4, 5). It is known that the catalysts were hydrophilic. As shown in Fig. S8,[†] the catalyst V_xO_y @C-0.195–120 could be dispersed in the water phase in the mixture of water and benzene, but could not be stably dispersed in benzene. It could be well dispersed in the mixture of benzene and acetonitrile, suggesting that acetonitrile improved the dispersion of the catalyst in benzene.

When water was the solvent, the water around the catalyst formed a stagnant film which depressed the adsorption of benzene and lowered the activity. When acetonitrile was

Table 1 Catalytic performances of $V_x O_y @C-0.195-120$ for the hydroxylation of benzene to phenol^a

Entry	Solvent	Time [h]	Phenol selectivity ^b [%]	Phenol yield [%]
1	Acetonitrile	5	95.9	9.1
2	Acetonitrile	10	93.8	9.2
3	Acetonitrile	24	93.8	12.2
4	_	10	100	0.5
5	Water	10	100	0.8
6	Acetonitrile ^c	10	100	0.03

^{*a*} Catalyst V_xO_y@C-0.195–120, 25 mg; ascorbic acid, 0.8 g; acetonitrile, 2.0 g; benzene, 1.0 mL; O₂ pressure, 3.0 MPa; temperature, 80 °C. ^{*b*} Hydroquinone was detected. ^{*c*} Without ascorbic acid.

 $\mbox{Table 2}$ Catalytic performances of the $V_x O_y @C$ for the hydroxylation of benzene to phenol^a

Entry	Catalysts	V% (ICP)	Phenol selectivity [%]	Phenol yield [%]
1	V _x O _v @C-0.293-120	5.85	91.0	8.4
2	$V_r O_v (a) C - 0.195 - 120$	4.38	92.1	9.2
3	$V_r O_v (a) C - 0.098 - 120$	3.62	93.3	9.4
4	$V_r O_v (a) C - 0.050 - 120$	3.09	90.3	9.7
5	$V_x O_y (a) C - 0.025 - 120$		91.3	9.5
6	$V_r O_v (a) C - 0.195 - 150$	3.73	93.5	9.5
7	$V_r O_v (a) C - 0.195 - 180$	3.80	92.4	9.4
8	$V_x O_y (0, 0, 195-210)$	4.55	90.8	9.2

 a Reaction conditions: catalyst, 25 mg; ascorbic acid, 0.8 g; acetonitrile, 2.0 g; benzene, 1.0 mL; O₂ pressure, 3.0 MPa; temperature, 80 °C, time, 10 h.

employed as the solvent, the substrate benzene was miscible with acetonitrile, and the catalyst could be well dispersed. The excellent dispersion of the catalyst in the mixture of acetonitrile and benzene favored the adsorption of benzene affording a high yield of phenol in acetonitrile (Table 1, entries 1–3).

The yield of phenol first increased with reaction temperature and then decreased with a threshold of 80 °C (Fig. S9[†]). The decrease of the oxygen solubility with an increase of temperature was one of the main reasons for this phenomenon.⁴² The self-oxidation of ascorbic acid as the sacrificial reductant prolonged the reaction,^{43,44} which caused the decline in the yield of phenol. The influence of oxygen pressure was investigated (Fig. S10[†]). The yield of phenol had a maximum at an oxygen pressure of 3.0 MPa. In the low pressure range, the yield enhancement with increasing pressure could be attributed to the larger solubility of oxygen at the higher oxygen pressure.⁴² However, too much oxygen might cause the overoxidation of phenol, which resulted in a decrease in the yield of phenol. When the reaction time was prolonged, the yield of phenol was increased to 12.2% (Table 1, entries 1-3), which was higher than that reported in the literature with acetonitrile as the solvent and oxygen as the oxidant.^{14,45}

The performance of the catalysts prepared under different conditions were evaluated (Table 2). The catalysts prepared at 120 °C with different amounts of NH₄VO₃ gave similar phenol yields (Table 2, entries 1-4), although V content in the catalysts decreased gradually with the decrease of the amount of NH₄VO₃ used for preparing the catalysts. This, however, is understandable considering that the binding energy of V 2P_{3/2} decreased with the decreased V content (Table S1[†]), indicating that ratio of V^{4+}/V^{5+} increased in the catalysts, and V^{4+} has been proved to be more active for activating oxygen.^{40,41} When the hydrothermal temperature for preparing the catalysts was increased, the reaction efficiency of sucrose and NH₄VO₃ was improved, therefore, the vanadium content in the catalysts was increased. However, the carbonization was enhanced with the increase of the hydrothermal temperature and more active sites were embedded in the carbonaceous powder. The competition of the opposite effects led to the result that the yield of phenol did not vary considerably with the hydrothermal temperature (Table 2, entries 5–8).

The effect of the vanadium precursors used for preparing the catalysts was also investigated. Vanadium(IV) oxide bis(2,4pentanedionate) and vanadium(III) chloride were employed to synthesize the $V_x O_y$ (a)C-A and $V_x O_y$ (a)C-Cl catalysts, respectively. The vanadium content (Table S2,[†] 4.19 wt%) and vanadium species (Table S2,⁺ 516.7 eV) of the $V_x O_y$ (a)C-A detected from the XPS data were similar to those of the V_xO_v@C-0.195–120 (Table 2, entry 2, 4.38 wt%; Table S1,[†] entry 2, 516.9 eV). Therefore, the yield of phenol over the $V_x O_y$ (a)C-A (Table $S2,^{\dagger}$ 8.9%) was similar to that over the V_xO_v@C-0.195–120 (Table 2, entry 2, 9.2%). The vanadium content of the $V_r O_v$ (a)C-Cl was only 0.91 wt% (Table S2⁺), which was the main reason that $V_x O_y$ @C-Cl gave a low yield of phenol (Table S2,[†] 5.9%). The precursors might affect the process of forming the catalysts and, subsequently, influenced the activity of the catalysts.

In conclusion, $V_x O_y @C$ can be prepared using sucrose as the carbon source by a facile one-pot hydrothermal method, which can catalyze the direct hydroxylation of benzene to phenol with molecular oxygen in acetonitrile efficiently.

Experimental

Preparation of the catalysts

The $V_r O_v (a) C$ catalyst was prepared by a hydrothermal method. Typically, sucrose (3.40 g) and the desired amount of NH₄VO₃ (for example 0.195 g) was dissolved in distilled water (30 mL). The solution was stirred for several minutes, and transferred into a 50 mL Teflon-lined stainless steel autoclave, which was then sealed and heated at 120 °C for 12 h. The resulting products were filtered, washed several times with distilled water and finally dried at 100 °C overnight. The obtained catalyst was denoted as V_xO_y@C-0.195-120. V_xO_y@C prepared under different conditions is denoted as $V_x O_y @C-c-t$, in which c represents the amount of NH₄VO₃ used (with the unit of g), and t is the hydrothermal temperature (with the unit of °C). The catalysts prepared from vanadium precursors of vanadium(IV) oxide bis(2,4-pentanedionate) and vanadium(m) chloride were denoted as $V_x O_y$ @C-A and $V_x O_y$ @C-Cl, respectively. The amounts of the two vanadium precursors used were 0.441 g and 0.265 g, respectively, which were equal to the moles of NH_4VO_3 for preparing the V_xO_y@C-0.195-120.

Characterization of the catalysts

The catalysts were characterized by scan electron microscopy (SEM), powder X-ray diffraction (XRD), FT-IR and X-ray photoelectron spectroscopy (XPS) techniques. The SEM examination was conducted on a Hitachi-s4300 electron microscope operated at 15 kV. The samples were spray-coated with a thin layer of platinum before observation. The XRD was performed on a X'PERT SW X-ray diffractometer operated at 30 kV and 100 mA with Cu K α radiation. The XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg K α radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. FT-IR spectra were recorded on a Bruker Tensor 27 spectrometer with a resolution of 2 cm⁻¹ and consisted of 32 scans. Brunauer–Emmett–Teller (BET) surface areas and pore volumes were measured on a Micromeritics ASAP 2020 sorptometer by using nitrogen adsorption at 77 K. The loading content of V in the catalysts was determined using ICP-AES (VISTAMPX).

Catalytic tests

The hydroxylation of benzene was performed in a Teflon-lined stainless-steel reactor (20 mL) that was equipped with a pressure gauge, thermocouple, gas-inlet valve, magnetic stirrer, and an electric heater with a controller. In a typical experiment, 0.025 g of catalyst, 0.80 g of ascorbic acid, and 1.0 mL of benzene were added to 2.0 g of acetonitrile successively. After the system was charged with 3.0 MPa of O₂ at room temperature, the hydroxylation reaction was conducted at 80 °C for the desired time under vigorous stirring. After the reaction, toluene was added into the product mixture as an internal standard for product analysis. The mixture was analyzed using a gas chromatograph (GC) of Agilent 6820 equipped with a flame ionization detector (FID). The products of phenol and hydroquinone were detected using GC in this reaction system. The yield of phenol was calculated as: (mole of formed phenol)/(mole of initial benzene) × 100%.

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Notes and references

- L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari and R. Ungarelli, *Angew. Chem., Int. Ed.*, 2003, 115, 5087–5090.
- D. Bianchi, R. Bortolo, R. Tassinari, M. Ricci and R. Vignola, *Angew. Chem., Int. Ed.*, 2000, **112**, 4491–4493.
- 3 P. Borah, X. Ma, K. T. Nguyen and Y. Zhao, *Angew. Chem.*, *Int. Ed.*, 2012, **51**, 7756–7761.
- 4 R. Bal, M. Tada, T. Sasaki and Y. Iwasawa, *Angew. Chem.*, *Int. Ed.*, 2005, **45**, 448–452.
- 5 A. Kubacka, Z. Wang, B. Sulikowski and V. Cortés Corberán, *J. Catal.*, 2007, **250**, 184–189.
- 6 J. B. Taboada, E. J. M. Hensen, I. W. C. E. Arends, G. Mul and A. R. Overweg, *Catal. Today*, 2005, **110**, 221–227.
- 7 A. S. Kharitonov, V. I. Sobolev and G. I. Panov, *Russ. Chem. Rev.*, 1992, **61**, 1130.
- 8 H. Xia, K. Sun, Z. Feng, W. X. Li and C. Li, *J. Phys. Chem. C*, 2008, **112**, 9001–9005.

- 9 L. N. Zhao, Y. L. Dong, X. L. Zhan, Y. Cheng, Y. J. Zhu, F. L. Yuan and H. G. Fu, *Catal. Lett.*, 2012, **142**, 619–626.
- 10 Y. Y. Gu, X. H. Zhao, G. R. Zhang, H. M. Ding and Y. K. Shan, *Appl. Catal.*, A, 2007, 328, 150–155.
- 11 H. Kanzaki, T. Kitamura, R. Hamada, S. Nishiyama and S. Tsuruya, *J. Mol. Catal. A: Chem.*, 2004, **208**, 203–211.
- 12 Y. Ichihashi, T. Taniguchi, H. Amano, T. Atsumi, S. Nishiyama and S. Tsuruya, *Top. Catal.*, 2008, 47, 98–100.
- 13 C. J. Zhou, J. Wang, Y. Leng and H. Q. Ge, *Catal. Lett.*, 2010, **135**, 120–125.
- 14 J. Q. Chen, S. Gao, J. Li and Y. Lv, *Chin. J. Catal.*, 2011, 32, 1446–1451.
- 15 S. Q. Song, H. X. Yang, R. C. Rao, H. D. Liu and A. M. Zhang, *Appl. Catal.*, A, 2010, 375, 265–271.
- 16 S. Q. Song, S. J. Jiang, R. C. Rao, H. X. Yang and A. M. Zhang, *Appl. Catal.*, A, 2011, 401, 215–219.
- 17 P. Arab, A. Baeiei, A. Koolivand and G. Mohammadi Ziarani, *Chin. J. Catal.*, 2011, **32**, 258–263.
- 18 Y. K. Zhong, G. Y. Li, L. F. Zhu, Y. Yan, G. Wu and C. W. Hu, *J. Mol. Catal. A: Chem.*, 2007, 272, 169–173.
- 19 S. Q. Song, H. X. Yang, R. C. Rao, H. D. Liu and A. M. Zhang, *Catal. Commun.*, 2010, **11**, 783–787.
- 20 J. Q. Xu, H. H. Liu, R. G. Yang, G. Y. Li and C. W. Hu, *Chin. J. Catal.*, 2012, 33, 1622–1630.
- 21 L. Yu, C. Falco, J. Weber, R. J. White, J. Y. Howe and M.-M. Titirici, *Langmuir*, 2012, 28, 12373–12383.
- 22 M.-M. Titirici, R. J. White, C. Falco and M. Sevilla, *Energy Environ. Sci.*, 2012, 5, 6796–6822.
- 23 M. Y. Xing, D. Y. Qi, J. L. Zhang and F. Chen, *Chem.-Eur. J.*, 2011, 17, 11432-11436.
- 24 G. B. Yu, B. Sun, Y. Pei, S. H. Xie, S. R. Yan, M. H. Qiao, K. N. Fan, X. X. Zhang and B. N. Zong, *J. Am. Chem. Soc.*, 2009, **132**, 935–937.
- 25 P. Makowski, R. D. Cakan, M. Antonietti, F. Goettmann and M. M. Titirici, *Chem. Commun.*, 2008, 999–1001.
- 26 N. Hoffmann, E. Löffler, N. A. Breuer and M. Muhler, *ChemSusChem*, 2008, **1**, 393–396.
- 27 G. D. Ding, W. T. Wang, T. Jiang, B. X. Han, H. L. Fan and G. Y. Yang, *ChemCatChem*, 2013, 5, 192–200.
- 28 X. M. Sun and Y. D. Li, Angew. Chem., Int. Ed., 2004, 43, 3827-3831.
- 29 Q. Wang, H. Li, L. Q. Chen and X. J. Huang, *Carbon*, 2001, 39, 2211–2214.
- 30 X. M. Sun and Y. D. Li, Angew. Chem., Int. Ed., 2004, 43, 597-601.
- 31 N. Baccile, G. Laurent, F. Babonneau, F. Fayon, M. M. Titirici and M. Antonietti, J. Phys. Chem. C, 2009, 113, 9644–9654.
- 32 J. Zhang and E. Weitz, ACS Catal., 2012, 2, 1211–1218.
- 33 F. Jiang, Q. J. Zhu, D. Ma, X. M. Liu and X. W. Han, J. Mol. Catal. A: Chem., 2011, 334, 8–12.
- 34 C. Yao, Y. Shin, L. Q. Wang, C. F. Windisch, W. D. Samuels,
 B. W. Arey, C. Wang, W. M. Risen and G. J. Exarhos, *J. Phys. Chem. C*, 2007, 111, 15141–15145.
- 35 H. Mehdi, V. Fábos, R. Tuba, A. Bodor, L. T. Mika and I. T. Horváth, *Top. Catal.*, 2008, 48, 49–54.

- 36 Y. Shin, L. Q. Wang, I. T. Bae, B. W. Arey and G. J. Exarhos, J. Phys. Chem. C, 2008, 112, 14236–14240.
- 37 M. Sevilla and A. Fuertes, *Carbon*, 2009, 47, 2281–2289.
- 38 X. H. Gao and J. Xu, Catal. Lett., 2006, 111, 203-205.
- 39 E. Hryha, E. Rutqvist and L. Nyborg, *Surf. Interface Anal.*, 2012, 44, 1022–1025.
- 40 Y.-k. Masumoto, R. Hamada, K. Yokota, S. Nishiyama and S. Tsuruya, *J. Mol. Catal. A: Chem.*, 2002, **184**, 215–222.
- 41 X. H. Gao, X. C. Lv and J. Xu, Chin. J. Chem., 2009, 27, 2155–2158.
- 42 S.-t. Yamaguchi, S. Sumimoto, Y. Ichihashi, S. Nishiyama and S. Tsuruya, *Ind. Eng. Chem. Res.*, 2005, **44**, 1–7.
- 43 T. Miyahara, H. Kanzaki, R. Hamada, S. Kuroiwa, S. Nishiyama and S. Tsuruya, *J. Mol. Catal. A: Chem.*, 2001, 176, 141–150.
- 44 M.-a. Ishida, Y. Masumoto, R. Hamada, S. Nishiyama, S. Tsuruya and M. Masai, *J. Chem. Soc., Perkin Trans.* 2, 1999, 847–854.
- 45 H. Yang, J. Q. Chen, J. Li, Y. Lv and S. Gao, *Appl. Catal.*, *A*, 2012, **415-416**, 22–28.