

Short Communication

Influence of crystal size of HZSM-5 on hydrodeoxygenation of eugenol in aqueous phase



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ABSTRACT

Hydrodeoxygenation of eugenol to hydrocarbons in aqueous phase can be catalyzed by the combination of Pd/C and HZSM-5. In this paper, micro-, submicro- and nano-sized HZSM-5 samples were chosen as catalysts to investigate the influence of crystal size of HZSM-5 on the hydrolysis and dehydration. It was found that the formation rates of hydrocarbons were correlated with the total acidic sites of the submicro- and nano-sized HZSM-5 samples; while for the micro-sized sample, a much lower hydrocarbon formation rate was observed. Meanwhile, HZSM-5 with larger crystal size showed a lower hydrocarbon formation rate even with higher acid density.

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1. Introduction

With the depletion of fossil fuels, renewable resources such as biomass can be expected to play the role as sources of energy and chemicals in the foreseeable future [1]. Lignin is a main constituent of lignocellulosic biomass (15–30% by weight, 40% by energy) [1,2], and pyrolysis or hydrolysis of lignin can produce a large quantity of phenolic compounds [3]. Eugenol is an aromatic component in the products of lignin pyrolysis and in the volatile fraction of lignocellulosic bio-oils, and it is also the predominant lignin monomer in softwood which incorporates several key functional groups such as phenyl, hydroxyl, methoxyl and allyl [4].

Hydrodeoxygenation (HDO) has been considered to be the most effective method for bio-oil upgrading [5]. For the selective hydrogenation or oxidation of some bio-derived compounds, water is reported as a good reaction medium under moderate conditions [6–8], and a series of catalysts which combined of Pd/C and HZSM-5 have been developed for aqueous-phase hydrodeoxygenation of phenolic oil, such as Pd/C and liquid acid, base metal Raney Ni and solid acid [5,9,10]. Besides,

Pd/HZSM-5 and Ni/HZSM-5 catalysts are also prepared for one-pot aqueous-phase upgrading of the organic components in crude bio-oil [3,11]. Notably, the combination of Pd/C and HZSM-5 shows an extremely high selectivity in removing oxygen-containing groups in lignin-derived substituted phenolic monomers and dimers in water, which brings an efficient route for upgrading lignin-derived phenolic oil to transportation biofuels [12]. The catalytic function of the catalysts combined of Pd/C and HZSM-5 consists of the hydrogenation on metal catalysts and the deoxygenation on metal-deposited acidic supports [13]. Zhao reported that the rate-determining step in selective hydrodeoxygenation of lignin-derived phenolic monomers and dimers to cycloalkanes on Pd/C and HZSM-5 combined catalysts was the dehydration on HZSM-5 [12].

In general, the crystal size of HZSM-5 used in hydrodeoxygenation reactions is relatively large, usually in micro-scale size. For example, when using zeolite as catalyst in hydrodeoxygenation reactions, the rate-determining step tends to be the diffusion of reactant/product molecules within the micropores of zeolites [14]. With the decrease in crystal size, a significant increase in the catalytic stability can be obtained in the reactions catalyzed by ZSM-5 [14,15].

In this paper, the hydrodeoxygenation catalysts combined of Pd/C and HZSM-5 were prepared, and eugenol was selected as the reactant. Through changing the crystal size of zeolite, the catalytic effect of zeolite on the HDO reaction was investigated, and the catalytic mechanism was discussed.

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2. Experimental section

2.1. Catalyst synthesis and characterization

The micro-, submicro- and nano-sized HZSM-5 samples were respectively denoted as Z5-M, Z5-S and Z5-N for short description in this paper. Z5-M was purchased from the catalyst Plant of Nankai University (commercial code: NKF-5), and Z5-S and Z5-N were prepared by thermal treatment methods. The detailed processes for the preparation of Z5-S and Z5-N were introduced in the Supplementary material.

X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advance diffractometer using Cu K α radiation (wavelength λ = 1.5147 Å). The XRD crystallinity was defined according to Ref. [16]. Si and Al contents of the calcined zeolites were determined by X-ray fluorescence spectrometer (XRF, Axios PW4400, Panalytical) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, IRIS Intrepid II XSP, Thermo Fisher), respectively. Nitrogen adsorption-desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2020 sorptometer [17]. Scanning electron microscopy (SEM) analysis was conducted on a Hitach S-4800 electronic microscope working at 200 kV. The ammonia temperature-programmed desorption (NH₃-TPD) was tested on a Micromeritics Autochem 2920 instrument following the method of H. Xin [17].

2.2. HDO of eugenol

A mixture of eugenol (385 μ L), H₂O (20 mL), Pd/C (5 wt.% Pd, 0.03 g) and HZSM-5 (0.5 g) were loaded into an autoclave. With a stirring rate of 680 rpm, the reactor was flushed with H₂ three times, and H₂ of 2 MPa was introduced to the reactor. Then, the temperature increased up to 240 °C. After quenching with ice to ambient temperature, the mixture in the reactor was sampled, and organic products were extracted by ethyl acetate. The organic and aqueous phases were both quantitatively analyzed by a gas chromatography-mass spectrometry (GC-MS; Agilent 7890A-Agilent 5975C; 30 m \times 250 μ m HP-5 capillary column).

3. Results and discussion

3.1. Catalyst characterization

The XRD patterns of Z5-M, Z5-S and Z5-N are shown in Fig. S1. It can be seen that there are obvious peaks at 2θ = 7–9° and 23–25° corresponding to the characteristic peaks of typical HZSM-5 phase, which indicates that the three samples all have typical characteristics of the MFI-type zeolite. Table 1 lists the relative crystallinity of each sample where Z5-M is used as a reference. Due to the broadening effect of small crystallographic domains on the peak of XRD patterns [18], the relative crystallinity of HZSM-5 sample decreases sharply from 100% to 50% in the order of Z5-M > Z5-S > Z5-N.

Fig. 1 shows the SEM images of these samples. As seen, Z5-M has a smooth surface and presents a typical coffin-like microstructure with

uniform crystallite size of 1.5–2.5 μ m; Z5-S also has a smooth surface, but the shape is irregular and the crystallite size is in the range of 0.6–1.0 μ m; whereas Z5-N presents a cauliflower-like morphology, and is aggregated by nano-crystal zeolite with crystallite size of 0.03–0.1 μ m.

Fig. 2 displays the nitrogen sorption isotherms of various ZSM-5 catalysts. The isotherm of Z5-M belongs to type I curve which is typical for microporous zeolite, and the sharp uptake at relative pressure P/P_0 < 0.05 confirms the presence of micropores. The isotherm shape of Z5-S is almost the same as that of Z5-M. Using the formulas based on the isotherms of Z5-S and Z5-M, similar BET surface area, mesopore volume and micropore volume can be obtained, as shown in Table 1. However, in the sorption isotherm of Z5-N, there is a hysteresis loop which differs from that of Z5-M or Z5-S, implying the presence of slit pores [19]. The presence of mesopore in Z5-N can also be verified by the BJH mesopore size distributions, as shown in Fig. S2. The BET surface area of Z5-N (438 m²/g) is similar to that of Z5-M (441 m²/g), but its mesopore volume is higher than those of Z5-M and Z5-S. Additionally, Z5-N and Z5-S have similar external surface area, which is higher than that of Z5-M.

The NH₃-TPD was commonly used to characterize the acidity of ZSM-5 zeolites [20]. As shown in Fig. S3, there are two ammonia desorption peaks for all catalysts, which correspond to two different types of acid site [21,22]. After the deconvolution and ammonia quantification [23], each profile can be deconvoluted by the Gauss curve fitting method into two separated peaks, where the amounts of weak and strong acid sites can be calculated and summarized in Fig. S4. It can be seen that the ratios of weak acid sites to strong acid sites are almost the same among these catalysts.

3.2. Catalytic performance

After four-hour hydrodeoxygenation reaction over Pd/C and HZSM-5 combined catalysts, the products were determined namely as methanol, 4-propyl-guaiacol, 2-methoxy-4-propyl-cyclohexanol, 4-propyl-cyclohexanone, 4-propyl-1, 2-dihydroxy-cyclohexane, 1-methyl-2-propyl-cyclohexane, propyl-cyclohexane. For comparison, the reaction of eugenol hydrodeoxygenation over Pd/C or HZSM-5 was carried out under the same reaction condition as that over the combined catalysts. As shown in Table S1, the reaction products over Pd/C were composed by a large proportion of 2-methoxy-4-propyl-cyclohexanol, few 2-methoxy-4-propyl-cyclohexanol and 4-propyl-cyclohexanol. The formation of 4-propyl-cyclohexanol was due to the hydrogenolysis over Pd/C. However, the eugenol was completely converted to 4-propyl-cyclohexane over HZSM-5, which was because that allyl group of eugenol can be hydrogenated without hydrogenation catalyst at this temperature. As mentioned above, Pd/C played the role as a hydrogenation catalyst, and only when the eugenol was hydrogenated, HZSM-5 can take effect on the deoxygenation of phenols. So, both of Pd/C and HZSM-5 were indispensable components for eugenol hydrodeoxygenation. According to Refs [24,25], the main reaction pathways of eugenol hydrodeoxygenation can be deduced as Fig. 3 shows. Generally, the products can be divided into three categories,

Table 1
Physico-chemical properties and chemical composition of ZSM-5 zeolites.

Catalyst	Si/Al ^a	XRD crystallinity, %	BET surface area ^b , m ² g ⁻¹	External surface area ^c , m ² g ⁻¹	Mesopore volume cm ³ g ⁻¹	Micropore volume ^d , cm ³ g ⁻¹	Weak acid/strong acid ^e	NH ₃ chemisorbed ^e , mmol g ⁻¹
Z5-M	58	100	441	33	0.04	0.18	1.14	1.65
Z5-S	98	74	434	58	0.08	0.17	0.98	0.59
Z5-N	25	50	438	60	0.20	0.16	1.14	2.51

^a XRF and ICP-OES.

^b BET method.

^c t-plot method.

^d BJH method (adsorption branch).

^e NH₃-TPD.

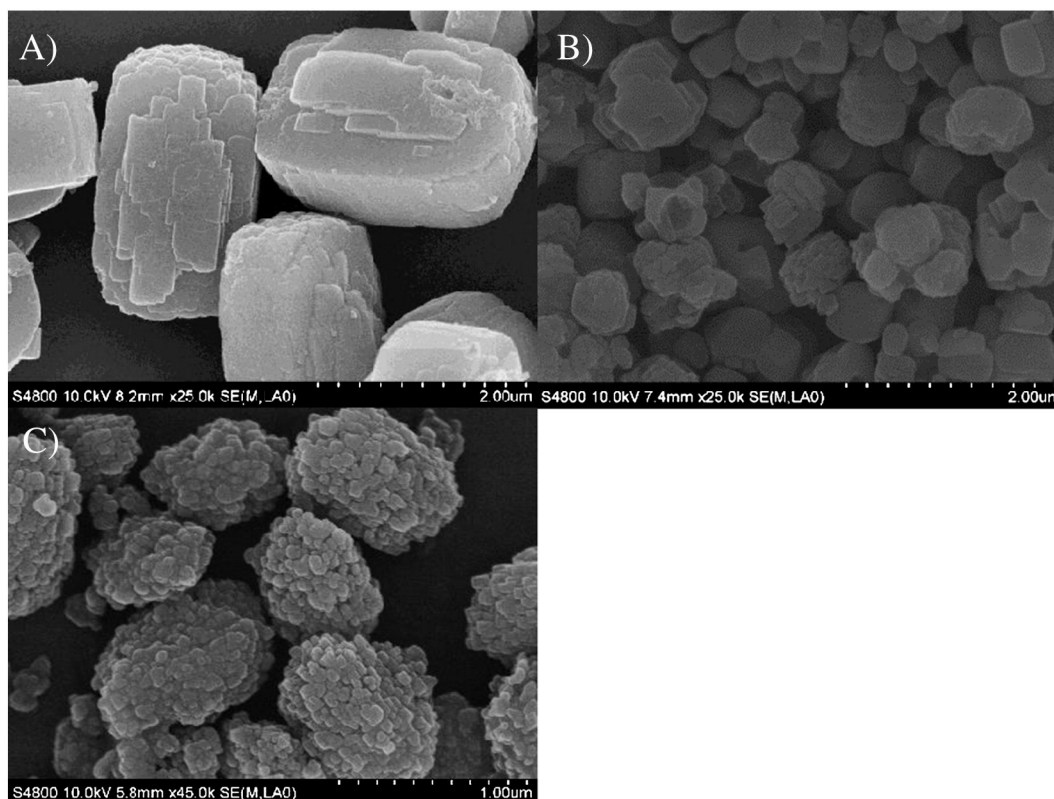


Fig. 1. Scanning electron micrographs of ZSM-5 catalysts. (A) Z5-M, (B) Z5-S, and (C) Z5-N.

including 4-propyl guaiacol, oxygenated hydrocarbons and hydrocarbons. Considering that the turnover frequency of the acid-catalyzed reaction is at least two orders of magnitude lower than the rate of metal-catalyzed hydrogenation [24], thus the acid-catalyzed reactions are the rate-determining step in the reaction network. Moreover, the HZSM-5 with smaller crystallite size possesses larger pore volume, more secondary pores and shorter channels, which can obviously reduce diffusion path length obviously [26]. In this work, in order to evaluate the reactivity of these ZSM-5 catalysts, the reaction of eugenol hydrodeoxygenation was performed at 240 °C and under the H_2 pressure of 2 MPa. As shown in Fig. 4, the conversion rate of eugenol

over Z5-M catalyst is lower than that over the other two samples, and the selectivity of hydrocarbons also has the same trend.

Our previous paper has reported that the total amount of acid sites of ZSM-5 were responsible for the changes of hydrocarbons selectivity during the reaction of eugenol hydrodeoxygenation over Pd/C and ZSM-5 [25]. Fig. 5 presents the relationship between the hydrocarbons formation rate and the total amount of acid sites over each ZSM-5 catalyst. For Z5-N, in the reaction of hydrodeoxygenation of eugenol, a slight increase of acid sites causes a significant increase in selectivity of hydrocarbons compared with Z5-M catalyst. Besides, for Z5-S and Z5-N catalysts, the relationship between the hydrocarbon formation rate and the total amount of acid sites can be described as a linear correlation through the origin of coordinates. The results indicate that the acid sites have a significant effect on deoxygenation activities over Z5-S and Z5-N catalysts, and that the reactions presumably do not show diffusion-limited features. Meanwhile, for Z5-M and Z5-S, higher hydrocarbon selectivity is obtained when using Z5-S as catalyst, which indicates that diffusion limitation has a significant influence on the hydrodeoxygenation reaction using Z5-M as catalyst. That is to say, the effective acid sites of Z5-M may not be fully utilized.

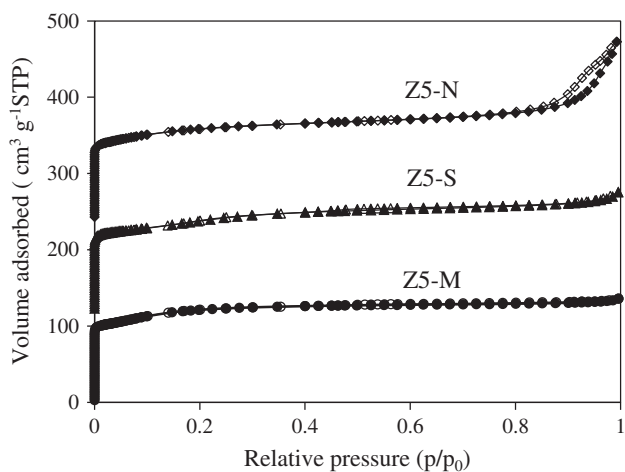


Fig. 2. Nitrogen adsorption-desorption isotherms of ZSM-5 catalysts at 77 K (Z5-S, and Z5-N are offset vertically by 120 and 240 $cm^3 g^{-1}$ STP, respectively).

4. Conclusions

The catalytic activities of three HZSM-5 samples with different crystal sizes were investigated in the reactions of eugenol hydrodeoxygenation using the combination of Pd/C and HZSM-5 as catalysts. It was found that the reaction activities of Z5-N and Z5-S showed the general regularity with the effect of acid sites. However, higher amount of acid sites provided by Z5-M had a lower hydrocarbon selectivity compared with Z5-S, which indicated that diffusion limitation caused by longer pore path had a significant influence on the hydrodeoxygenation reaction when using Z5-M as catalyst. With decreasing crystal size of HZSM-5 samples, the diffusion resistance was restricted, so that the crystal size

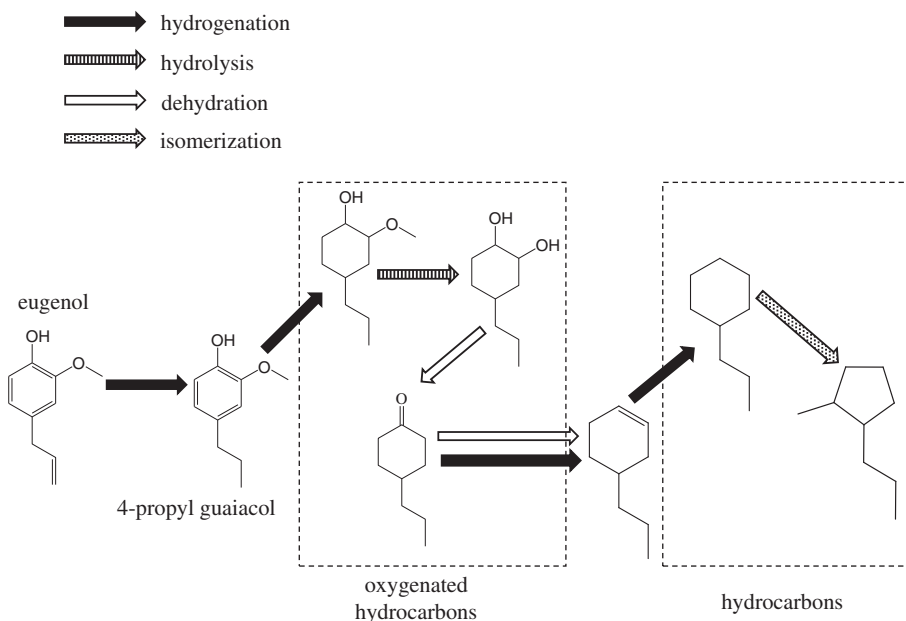


Fig. 3. Schematic reaction pathways of eugenol hydrodeoxygenation using Pd/C and HZSM-5 as catalysts at 240 °C and 2 MPa.

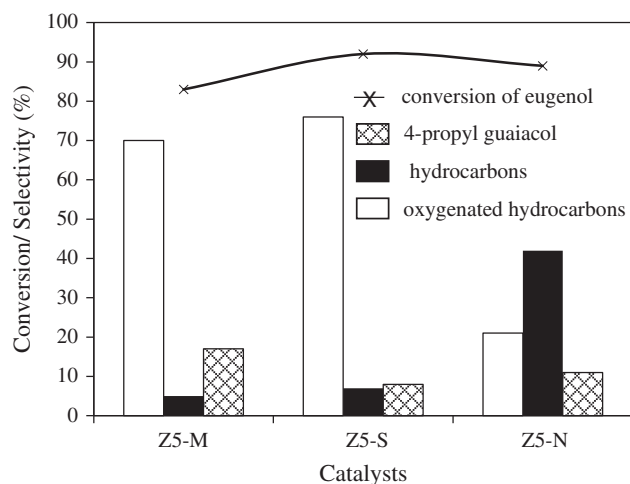


Fig. 4. The conversion of eugenol and selectivity of oxygenated hydrocarbons, hydrocarbons, and 4-propyl guaiacol over Pd/C and HZSM-5 catalysts.

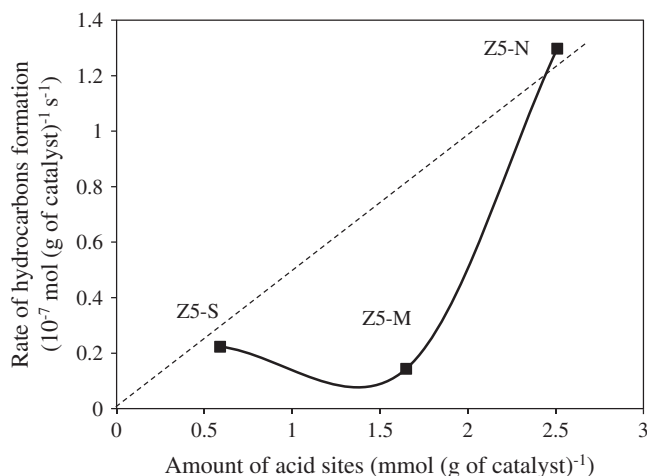


Fig. 5. Relationship between the hydrocarbons formation rate and the total amount of acid sites for different ZSM-5 catalysts.

of HZSM-5 had a considerable influence on the hydrodeoxygenation of bio-oil.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2014.07.014>. These data include MOL files and InChIKeys of the most important compounds described in this article.

References

- [1] J. Zakzeski, P.C.A. Bruijninx, A.L. Jongerius, B.M. Weckhuysen, *Chem. Rev.* 110 (2010) 3552–3599.
- [2] N. Yan, Y. Yuan, R. Dykeman, Y. Kou, P.J. Dyson, *Angew. Chem. Int. Ed.* 49 (2010) 5549–5553.
- [3] C. Zhao, D.M. Camaioni, J.A. Lercher, *J. Catal.* 288 (2012) 92–103.
- [4] C.G. Nolte, J.J. Schauer, G.R. Cass, B.R.T. Simoneit, *Environ. Sci. Technol.* 35 (2001) 1912–1919.
- [5] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, *Angew. Chem. Int. Ed.* 48 (2009) 3987–3990.
- [6] R.D. Cortright, R.R. Davda, J.A. Dumesic, *Nature* 418 (2002) 964–967.
- [7] C. Zhao, W. Gan, X. Fan, Z. Cai, P.J. Dyson, Y. Kou, *J. Catal.* 254 (2008) 244–250.
- [8] T. Wang, C.X. Xiao, L. Yan, L. Xu, J. Luo, H. Shou, Y. Kou, H. Liu, *Chem. Commun.* 12 (2007) 4375–4377.
- [9] N. Yan, C. Zhao, P.J. Dyson, C. Wang, L.T. Liu, Y. Kou, *ChemSusChem* 1 (2008) 626–629.
- [10] C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, *Chem. Commun.* 15 (2010) 412–414.
- [11] C. Zhao, J.A. Lercher, *Angew. Chem. Int. Ed.* 51 (2012) 5935–5940.
- [12] C. Zhao, J.A. Lercher, *ChemCatChem* 4 (2012) 64–68.
- [13] C.R. Lee, J.S. Yoon, Y.W. Suh, J.W. Choi, J.M. Ha, D.J. Suh, Y.K. Park, *Catal. Commun.* 17 (2012) 54–58.
- [14] H. Konno, T. Okamura, T. Kawahara, Y. Nakasaka, T. Tago, T. Masuda, *Chem. Eng. J.* 207 (2012) 490–496.
- [15] F. Xu, M. Dong, W. Gou, J. Li, Z. Qin, J. Wang, W. Fan, *Microporous Mesoporous Mater.* 163 (2012) 192–200.
- [16] H. Xin, A. Koekkoek, Q. Yang, R. van Santen, C. Li, E.J.M. Hensen, *Chem. Commun.* 14 (2009) 7590–7592.
- [17] H.C. Xin, X.P. Li, Y. Fang, X.F. Yi, W.H. Ju, Y.Y. Chu, F. Zhang, A.M. Zheng, H.P. Zhang, X. B. Li, *J. Catal.* 312 (2014) 204–215.

- [18] B.T.L. Bleken, D.S. Wragg, B. Arstad, A.E. Gunnaes, J. Mouzon, S. Helveg, L.F. Lundegaard, P. Beato, S. Bordiga, U. Olsbye, S. Svelle, K.P. Lillerud, *Top. Catal.* 56 (2013) 558–566.
- [19] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, *Catal. Today* 41 (1998) 207–209.
- [20] M. Choi, H.S. Cho, R. Srivastava, C. Venkatesan, D.-H. Choi, R. Ryoo, *Nat. Mater.* 5 (2006) 718–723.
- [21] F. Tian, Y. Wu, Q. Shen, X. Li, Y. Chen, C. Meng, *Microporous Mesoporous Mater.* 173 (2013) 129–138.
- [22] W. Xia, A. Takahashi, I. Nakamura, H. Shimada, T. Fujitani, *J. Mol. Catal. Chem.* 328 (2010) 114–118.
- [23] Y. Han, C. Lu, D. Xu, Y. Zhang, Y. Hu, H. Huang, *Appl. Catal. A Gen.* 396 (2011) 8–13.
- [24] C. Zhao, J. He, A.A. Lemonidou, X. Li, J.A. Lercher, *J. Catal.* 280 (2011) 8–16.
- [25] C. Zhang, J. Xing, L. Song, H. Xin, S. Lin, L. Xing, X. Li, *Catal. Today* 234 (2014) 145–152.
- [26] T. Meng, D. Mao, Q. Guo, G. Lu, *Catal. Commun.* 21 (2012) 52–57.