

A comparative study of supported TiO₂ catalysts and activity in ester exchange between dimethyl oxalate and phenol

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Abstract

Various supported TiO₂ catalysts, TiO₂/SiO₂, TiO₂/Al₂O₃ and TiO₂/MgO, were prepared by impregnation method and their activities in the transesterification of dimethyl oxalate (DMO) with phenol were tested. To further investigate the relationship between the catalyst performances and carrier properties, a series of characterization methods, such as BET specific surface area measurement, temperature-programmed desorption (NH₃-TPD, CO₂-TPD), and FT-IR analysis of adsorbed pyridine were utilized. The results indicated that the carrier had an important effect on the selectivities to products. The activities of supported TiO₂ catalysts were improved significantly when TiO₂ was supported on high surface area carriers. The weak acid sites were responsible for the formation of methyl phenyl oxalate (MPO) and diphenyl oxalate (DPO), while the intermediate acid sites and base sites were favorable for the formation of byproduct, anisole (AN).

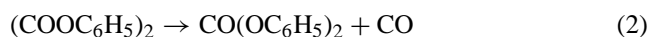
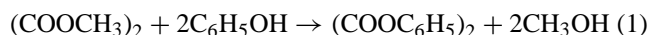
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Keywords: Diphenyl carbonate; Diphenyl oxalate; Methyl phenyl oxalate; Dimethyl oxalate; Supported TiO₂ catalysts

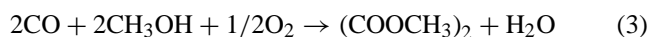
1. Introduction

Polycarbonates (PCs) are excellent engineering thermoplastics and substitutes for metals and glass because of their high impact strength and transparency [1]. In recent years, there has been an increasing demand for safer and more environmentally friendly processes for PCs syntheses, and non-phosgene processes have been proposed to replace the traditional phosgene process [2]. Such a process includes the synthesis of diphenyl carbonate (DPC) followed by the transesterification between DPC and bisphenol A. Several alternative non-phosgene methods for the synthesis of DPC have also been proposed [3–10], e.g. oxidative carbonylation of phenol and transesterification. Among them, the transesterification of dimethyl oxalate (DMO) with phenol to prepare diphenyl oxalate (DPO), followed by the decarbonylation of DPO to produce DPC, as shown in reactions (1) and (2), is

an available route [11,12].



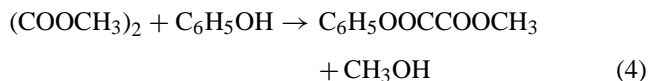
This method is more effective because no azeotrope is formed in the reaction system; thus, co-products of methanol and CO can be separated more easily compared with the synthesis of DPC by the transesterification of dimethyl carbonate (DMC) with phenol. The methanol and CO produced in the transesterification and decarbonylation reaction can be reused in the dimethyl oxalate synthesis via oxidative carbonylation of methanol, as shown in reaction (3) [13].



In fact, a pilot plant test in DMO production has been completed by Ube Industries and the technology for large-scale commercial production has been established. One of the possible applications of this process is to supply DMO for the preparation of DPC [14].

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The decarbonylation of DPO to produce DPC could be carried out easily over PPh_4Cl catalyst, and the yield of DPC was up to 99.5% [15]. Moreover, the synthesis of DPO from the transesterification of phenol with DMO follows a two-step reaction module consisting of the transesterification of DMO with phenol into methyl phenyl oxalate (MPO), and then the production of DPO via the disproportionation of MPO, as shown in the following reaction.



Ube Industries reported the transesterification of DMO with phenol carried out in the liquid phase using homogeneous catalysts such as Lewis acids or soluble organic Pb, Sn, or Ti compounds [12]. But the selectivities to MPO and DPO were low over these catalysts; e.g. the selectivities to MPO and DPO were only 30.8% and 2.1% over AlCl_3 , and 20.6% and 2.8% over $\text{Ti}(\text{O}i\text{Bu})_4$. Moreover, the separation of the homogeneous catalysts from products will be complicated when applied to the industrial process. Therefore, the development of solid catalysts with better activity and selectivity is highly desirable in view of regeneration and separation. However, there are few reports on the development of active heterogeneous catalysts for the reaction.

In this work, we prepared supported TiO_2 catalysts by the impregnation method, and carried out characterization of surface properties by BET measurement, FT-IR of adsorbed pyridine, NH_3 -TPD, and CO_2 -TPD in order to elucidate the effect of support on the transesterification of DMO with phenol.

2. Experimental

2.1. Catalyst preparation

The supported Ti catalysts were prepared by impregnation of 20 g of supports with tetrabutyl titanate (Tianjin No.1 Chemical Corporations) using the conventional impregnation technique.

Commercial SiO_2 (Jiangyan Chemical Corporations), Al_2O_3 , and MgO (Tianjin No.1 Chemical Corporations) were used as the supported material. Prior to impregnation, they were dried in an oven at 393 K for 24 h and then calcined in a muffle furnace at 823 K for 4 h in the air atmosphere.

To prepare TiO_2 -supported catalysts, the supports, SiO_2 , Al_2O_3 and MgO , were respectively impregnated with a toluene solution of tetrabutyl titanate for 24 h. The resultant samples were dried in an oven at 393 K for 12 h and calcined in a muffle furnace at 823 K for 4 h.

2.2. Transesterification of dimethyl oxalate with phenol

The reaction was conducted in a 250 ml glass flask equipped with a thermometer, a distillation apparatus, and

a stirrer under refluxing condition at atmosphere pressure. Especially, the top of distillation column was kept at 353 K by flowing through recycled hot water in order to remove methanol from the reaction system. After raw materials and catalyst were delivered into the batch reactor, the nitrogen gas was flowed at 30 SCCM to purge the air from the reaction system. After 10 min, the nitrogen flow was stopped and the flask was heated at a rate of 10 K min^{-1} . Qualitative and quantitative analyses of reaction products were carried out on a spectrometer of HP 5890-HP 5971MSD and a gas chromatograph equipped with a flame ion detector. An OV-101 packed column was used to separate products for GC analysis. The conversions were reported on the basis of the limiting reagent, DMO, and defined as the ratio of the moles of converted DMO to the moles of DMO fed initially to the reactor. The selectivities to MPO and DPO were defined as the moles of MPO and DPO produced per 100 mol of consumed DMO, and the yields of MPO and DPO were obtained from multiplication of DMO conversion by the selectivity to MPO and DPO.

2.3. Catalyst characterization

The specific surface areas of the catalysts were determined on a constant volume adsorption apparatus (CHEMBET-3000) by the N_2 BET method at the liquid nitrogen temperature.

The IR spectroscopic measurements of adsorbed pyridine were carried out on a Bruker VECTOR22 FT-IR spectrometer. The scanning range was from 500 to 4000 cm^{-1} and the resolution was 4 cm^{-1} . The sample powder was pressed into a self-supporting wafer. Prior to each experiment, the catalysts were evacuated (1 Pa) at 693 K for 1.5 h. Then they were heated to 303 K for 2 h. Following this, the material was exposed to 30 Torr of pyridine for 30 min, and finally evacuated for additional 1 h at 473 K. After adsorption, the samples were out-gassed and the spectra were recorded at room temperature.

NH_3 -TPD and CO_2 -TPD spectra were recorded using a Micromeritics 2910 chemical adsorption spectrometer. The catalysts was heated to 393 K in flowing Ar for 1 h, and then cooled to room temperature. The gases adsorption (NH_3 or CO_2) was carried out at 323 K to saturation. NH_3 or CO_2 was replaced with argon and the sample was heated to 873 K at a rate of 10 K min^{-1} .

3. Results and discussion

3.1. Performances of catalysts

For the transesterification of DMO with phenol, as shown in Table 1, SiO_2 , Al_2O_3 , MgO , TiO_2 and supported TiO_2 catalysts exhibited the different activities. The conversion of DMO was up to 67.6% over Al_2O_3 , which was the highest among these catalytic materials. However, the selectivities

Table 1
The activities of the different catalysts

Sample	Conversion (%)	Selectivity (%)				Yield (%)	
		DMO	AN	MPO	DPO	MPO	DPO
SiO ₂	1.7	0.8	99.2	0	1.7	0	
Al ₂ O ₃	67.6	55.5	31.5	7.4	21.3	5.0	
MgO	25.0	20.9	62.3	16.7	15.6	4.2	
TiO ₂	32.1	0.6	79.9	19.5	25.7	6.3	
TiO ₂ /SiO ₂ ^a	57.1	1.0	82.5	16.5	46.5	10.0	
TiO ₂ /Al ₂ O ₃ ^a	62.0	22.9	58.1	16.9	36.0	10.5	
TiO ₂ /MgO ^a	48.7	9.7	74.3	15.5	36.2	7.6	

Reaction conditions: 0.1 mol DMO, 0.5 mol phenol, 1.8 g catalyst, conducted at 180 °C for 2 h.

^a Ti was supported on SiO₂, Al₂O₃, MgO in 8 wt.%. MPO: methyl phenyl oxalate, DPO: diphenyl oxalate, AN: anisole.

to MPO and DPO were only 31.5% and 7.4%, respectively. SiO₂ demonstrated an excellent selectivity to MPO, 99.2%. Unfortunately, the conversion of DMO was only 1.7%. Although MgO showed better total selectivity to MPO and DPO compared with Al₂O₃, the conversion of DMO was still not high (25.0%). Especially, TiO₂ catalyst exhibited the excellent total selectivity to MPO and DPO with the DMO conversion being 32.1%. When TiO₂ was supported on Al₂O₃, SiO₂ and MgO, higher DMO conversions were obtained compared with non-supported TiO₂. The selectivities to MPO and DPO in the transesterification over TiO₂/SiO₂ were much higher than over TiO₂/Al₂O₃ and TiO₂/MgO. In the previous study, we reported that the total selectivity to MPO and DPO were up to 99.2% over TS-1 catalyst, while the conversion of DMO was only 26.5% [16,17]. Compared with TS-1, TiO₂/SiO₂ exhibited the excellent total selectivity to MPO and DPO (99.0%) as well as the fairly high conversion of DMO (57.1%). The yield of MPO and DPO reached 46.5% and 10.0%, respectively, which were much better than the results over other supported catalysts and single oxides.

From Table 1, we can also find that TiO₂/SiO₂, TiO₂/Al₂O₃, and TiO₂/MgO presented similar conversions. However, the selectivities to MPO and anisole of these supported catalysts were dependent on carriers. It was worth noticing that the selectivity to DPO was nearly the same over different supported catalysts, suggesting that the properties of the carrier were more correlative to the production of MPO and anisole.

3.2. Specific surface area measurement

The specific surface areas of different oxides are presented in Table 2. When TiO₂ was supported on a different car-

Table 2
Surface area of the catalyst samples

Sample	SiO ₂	Al ₂ O ₃	MgO	TiO ₂	TiO ₂ /SiO ₂ ^a	TiO ₂ /Al ₂ O ₃ ^a	TiO ₂ /MgO ^a
A (m ² /g)	231.1	202.4	41.3	11.1	252.4	237.5	43.8

^a Ti was supported on SiO₂, Al₂O₃, and MgO in 8 wt.%.

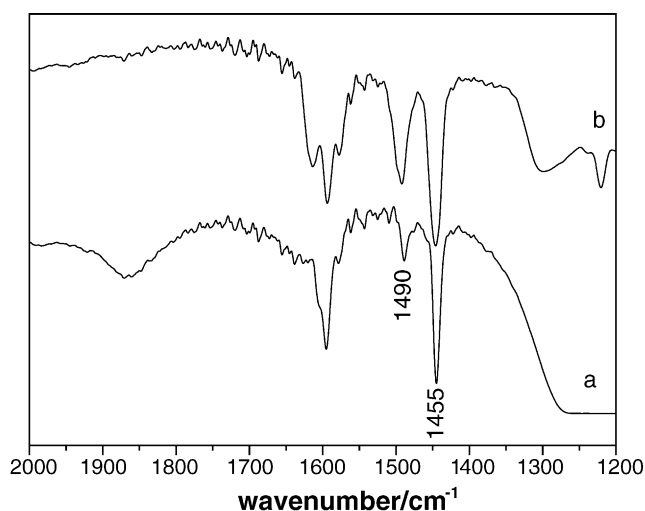


Fig. 1. Adsorbed pyridine IR spectra of TiO₂-supported catalysts: (a) 8%TiO₂/SiO₂; (b) 8%TiO₂/Al₂O₃.

rier, the specific surface areas of TiO₂/SiO₂, TiO₂/Al₂O₃ and TiO₂/MgO were 252.4, 237.5 and 43.8 m² g⁻¹, respectively, which were close to specific surface areas of SiO₂, Al₂O₃, and MgO. Therefore, the specific surface area of each supported TiO₂ catalyst was dependent on the carrier. Table 1 demonstrated that TiO₂/SiO₂, TiO₂/Al₂O₃ and TiO₂/MgO catalysts all showed higher activities for the transesterification of DMO with phenol than TiO₂, which may be due to the increase of specific surface area. So, we can deduce that Ti active centers dispersed on the carriers with high surface area would promote the catalytic efficiency for the transesterification of DMO and phenol.

3.3. IR characterization of adsorbed pyridine

FT-IR analysis of adsorbed pyridine allows a clear distinction between Brønsted and Lewis acid sites. The IR absorption bands at 1545 and 1455 cm⁻¹ are assigned to adsorbed pyridine coordinated with Brønsted acid sites and Lewis acid sites, respectively. The peak at 1490 cm⁻¹ can be ascribed to the overlapping of Brønsted acid and Lewis acid sites [18–20]. Fig. 1 shows the adsorbed pyridine IR spectra of TiO₂/SiO₂ and TiO₂/Al₂O₃, both of which had peaks at 1455 and 1490 cm⁻¹ and no peak at 1545 cm⁻¹. This indicated that there were only Lewis acid sites, but no Brønsted acid sites on TiO₂/SiO₂ and TiO₂/Al₂O₃. It was deduced that Lewis acid sites played important roles in the transesterification of DMO with phenol to produce MPO and DPO over TiO₂/SiO₂ and TiO₂/Al₂O₃.

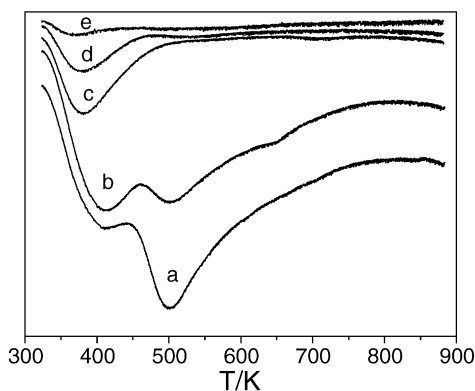


Fig. 2. NH_3 -TPD profile of oxides and TiO_2 -supported catalysts: (a) Al_2O_3 ; (b) $\text{TiO}_2/\text{Al}_2\text{O}_3$; (c) $\text{TiO}_2/\text{SiO}_2$; (d) SiO_2 ; (e) TiO_2 .

3.4. Temperature-programmed desorption of NH_3

NH_3 -TPD characterization was conducted to survey the acid strength of each catalyst. Fig. 2 represents the strength of acid sites on the single oxides and supported TiO_2 catalysts. The peaks in the high and low temperature regions can be attributed to the desorption of NH_3 from the strong and weak acid sites, respectively. The peaks in the high temperature region above about 673 K can be attributed to the desorption of NH_3 from strong Brönsted and Lewis type acid sites, the peaks in the temperature between 450 and 673 K can be attributed to the desorption of NH_3 from intermediate acid sites, and the peaks in the temperature below 450 K can be attributed to the desorption of NH_3 from weak acid sites, respectively [21]. For SiO_2 and TiO_2 , the peaks appeared only in the low temperature region, indicating that there existed only weak acid sites on SiO_2 and TiO_2 . For Al_2O_3 , the significant peaks appeared in the 420 and 510 K temperature regions simultaneously. Therefore, there must exist both weak and intermediate acid sites on Al_2O_3 , while amount of intermediate acid sites were more than that of weak acid sites. It can also be observed that the characteristics of acid sites varied greatly when TiO_2 oxide was supported on different oxide carriers. For $\text{TiO}_2/\text{Al}_2\text{O}_3$, the relative positions of the peaks were consistent with that of Al_2O_3 . However, the amount of the intermediate acid sites decreased. The amount of acid sites on $\text{TiO}_2/\text{SiO}_2$ were more than those on TiO_2 while strength of the acid sites on $\text{TiO}_2/\text{SiO}_2$ was the same as that of TiO_2 . The selectivities to MPO and DPO over Al_2O_3 and $\text{TiO}_2/\text{Al}_2\text{O}_3$ are relatively lower those over $\text{TiO}_2/\text{SiO}_2$. In the case of Al_2O_3 and $\text{TiO}_2/\text{Al}_2\text{O}_3$, the selectivity to anisole was also closely related with the amount of acidity. More intermediate acidity, more anisole. So, we can infer that the weak acid sites are responsible for the formation of MPO and DPO, while the intermediate acid sites were in favor of the formation of anisole.

3.5. Temperature-programmed desorption of CO_2

CO_2 -TPD characterization was conducted to survey the base strength of catalyst. As was true for the NH_3 -TPD, the

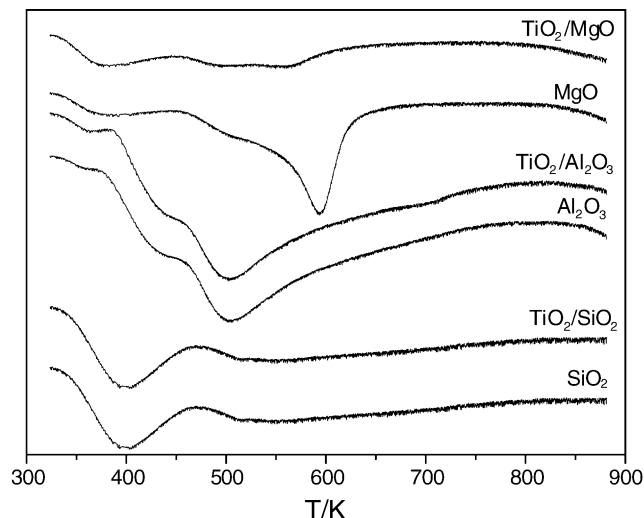


Fig. 3. CO_2 -TPD profile of TiO_2 -supported catalysts.

peaks in the high temperature region above about 673 K can be attributed to the desorption of CO_2 from strong Brönsted- and Lewis-type base sites, the peaks in the temperature range between 450 and 673 K can be attributed to the desorption of CO_2 from intermediate base sites, and the peaks in the temperature region below 450 K can be assigned to the desorption of CO_2 from weak base sites, respectively. As shown in Fig. 3, for MgO , a large peak appeared in the high temperature region around 600 K, indicating that there were mostly base intermediate sites on MgO . However, when TiO_2 was supported on MgO , the peak in the high temperature region decreased sharply, indicating that the basic strength of TiO_2/MgO became weak compared with MgO . For $\text{TiO}_2/\text{Al}_2\text{O}_3$, the peak positions were consistent with those of Al_2O_3 , while the amount of basic sites on $\text{TiO}_2/\text{Al}_2\text{O}_3$ was a little more than that on Al_2O_3 . Comparatively, the CO_2 -TPD profiles of $\text{TiO}_2/\text{SiO}_2$ and SiO_2 exhibited the desorption peaks appearing in the low temperature region (about 400 K), which suggested that there was only weak basic sites. When TiO_2 was supported on MgO and Al_2O_3 , the strength of the basic sites was weakened (the desorbed peaks shifted to low temperature), resulting in the decrease of anisole selectivity (Table 1). So, it can be deduced that intermediate basic sites (oxide), such as MgO and Al_2O_3 , took advantages of producing anisole, which was similar to the cases of acid sites.

From above observations, we can conclude that the supported TiO_2 catalysts are effective for the MPO and DPO synthesis. This may be attributed to the large amount of acid sites on the catalysts. According to our previous research work [17], the acid sites are the active centers for the reaction of DMO with phenol. TiO_2 catalysts supported on the various carriers showed the different conversion and selectivity because of the respective properties of carriers. Intermediate acid sites and base sites are suitable for anisole synthesis. Furthermore, the activities of TiO_2 catalysts was better than that of other solid catalysts such as TS-1 [17]. For $\text{TiO}_2/\text{SiO}_2$ as a catalyst, the total selectivity to MPO and DPO was up to

99%, which was much higher than that over the conventional ester exchange catalysts such as $\text{Ti}(\text{O}i\text{Bu})_4$ and AlCl_3 [17].

Therefore, acid strength was related to the selectivities to products. The weak acid sites were responsible for the formation of MPO and DPO, while the intermediate acid sites and base sites were favorable of the formation of anisole. When Al_2O_3 was used as catalyst, the selectivity of anisole was 55.5% due to the intermediate acids on Al_2O_3 . On contrast, there was a little amount of anisole produced over SiO_2 and TiO_2 catalysts because there were only weak acid sites on them. However, when TiO_2 was supported on Al_2O_3 , the total selectivity to MPO and DPO increased from 45.5% to 77.1% because of the weakening of the acid strength of catalyst compared with Al_2O_3 . The total selectivity to MPO and DPO remained about 99.0% due to the invariable weak acid strength of $\text{TiO}_2/\text{SiO}_2$ compared with SiO_2 . Therefore, TPD characterization of catalysts accounted for the different total selectivity to MPO and DPO over various single oxides and supported TiO_2 catalysts.

4. Conclusions

Supported TiO_2 catalysts, $\text{TiO}_2/\text{SiO}_2$, $\text{TiO}_2/\text{Al}_2\text{O}_3$ and TiO_2/MgO , showed higher activities and selectivities for the transesterification of DMO with phenol. The carrier had an important effect on the selectivities to products. The activities of supported TiO_2 catalysts were improved significantly with the increase of specific surface area compared with non-supported TiO_2 . SiO_2 was found to be the best support regarding the excellent total selectivity to MPO and DPO. The TPD characterization indicated that the selectivities to the products were closely related to the acid sites and basic sites on the catalyst. The weak acid sites were responsible for the formation of MPO and DPO, while the intermediate acid sites and base sites were favorable for the formation of anisole. The Ti species on the support and the weak Lewis acidic species coporately catalyzed the transesterification of DMO and phenol to produce MPO and DPO. The $\text{TiO}_2/\text{SiO}_2$ catalysts exhibited the best performance with the total selectivity to MPO and DPO up to 99.0% and the yields of MPO and DPO 46.5% and 10.0%, respectively. Further study regarding improving DMO conversion and DPO selectivity is underway.

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References

- [1] D. Freitag, U. Grigo, P.R. Müller, in: H.F. Mark, N.M. Bikales, C.G. Overberger (Eds.), *Encyclopedia of Polymer Science and Engineering*, New York, 1988, p. 648.
- [2] Y. Ono, *Pure Appl. Chem.* 68 (1996) 367.
- [3] F.M. Mei, G.X. Li, J. Nie, H.B. Xu, *J. Mol. Catal. A: Chem.* 184 (2002) 465.
- [4] W.B. Kim, Y.G. Kim, et al., *Appl. Catal. A: Gen.* 194/195 (2000) 403.
- [5] S. Kobayashi, I. Hachiya, T. takahori, M. Arika, H. Ishitani, *Tetrahedr. Lett.* 33 (1992) 6815.
- [6] J.L. Gong, X.B. Ma, S.P. Wang, *J. Mol. Catal. A: Chem.* 207 (2004) 215.
- [7] J.L. Gong, X.B. Ma, X. Yang, *Catal. Commun.* 5 (2004) 179.
- [8] X.B. Ma, J.L. Gong, S.P. Wang, *Catal. Commun.* 5 (2004) 101.
- [9] H. Ishii, M. Ueda, K. Takeuchi, *Catal. Commun.* 2 (1) (2001) 17.
- [10] B. Corrado, C. Martino, M. Elisabetta, *Synth. Commun.* 29 (6) (1999) 917.
- [11] K. Nishihira, S. Tanaka, K. Harada, R. Sugise, *US Patent* 5,834,615 (1997).
- [12] K. Nishihira, S. Tanaka, Y. Nishida, I. Hirofumi, S. Fujitsu, K. Harada, R. Sugise, *US Patent* 5,811,573 (1998).
- [13] T. Matsuzaki, A. Nakamura, *Catal. Survey Jpn.* 1 (1997) 77.
- [14] S. Vchumi, K. Ataka, T. Matsuzaki, *J. Organomet. Chem.* 576 (1999) 279.
- [15] K. Nishihira, S. Tanaka, K. Harada, R. Sugise, A. Shiotani, K. Washio, *US Patent* 5,922,827 (1999).
- [16] X.B. Ma, S.P. Wang, H.L. Guo, G.H. Xu, *Fuel Preprints, ACS Div. Fuel Chem.* 47 (2002) 146.
- [17] X.B. Ma, H.L. Guo, S.P. Wang, Sun Yongli, *Fuel Process. Technol.* 83 (2003) 275.
- [18] T. Barzetti, E. Selli, D. Moscotti, L. Forni, *J. Chem. Soc. Faraday Trans.* 92 (1996) 1401.
- [19] T.R. Hughes, H.M. White, *J. Phys. Chem.* 71 (1967) 2192.
- [20] C.A. Emeis, *J. Catal.* 141 (1993) 347.
- [21] F. Lónyi, J. Valyon, *Micropor. Mesopor. Mater.* 47 (2001) 293.