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Synthesis of Methyl Acetate by Dimethyl Ether Carbonylation over Cu/HMOR: Effect of Catalyst Preparation Method

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Dimethyl ether carbonylation to methyl acetate was comparatively investigated over mordenite supported copper (Cu/HMOR) catalysts prepared by different methods including evaporation, urea hydrolysis, incipient wetness impregnation and ion-exchange. The results showed that Cu/HMOR prepared via iron-exchange method exhibited the highest catalytic activity due to the synergistic effect of active-site metal and acidic molecular sieve support. Conversion of 95.3% and methyl acetate selectivity of 94.9% were achieved under conditions of 210 °C, 1.5 MPa, and GSHV of 4883 h^{-1}. The catalysts were characterized by nitrogen absorption, X-ray diffraction, NH$_3$ temperature program desorption, and CO temperature program desorption techniques. It was found that Cu/HMOR prepared by ion-exchange method possessed high surface area, moderate strong acid centers, and CO adsorption centers, which improved catalytic performance for the reaction of CO insertion to dimethyl ether.

Key words: Biomass energy, Methyl acetate, Dimethyl ether, Carbonylation, HMOR catalyst

I. INTRODUCTION

Methyl acetate (MA) is an important solvent and platform for other chemical compound synthesis as acetic anhydride [1, 2]. Typically MA synthesis involves complicate carbonylation, esterification, and hydrogenation processes from methanol and acetic acid, using corrosive halide and expensive rhodium catalysts in the homogeneous processes. Searching for cost-effective and eco-friendly catalysts for MA production still continues for its future applications. With the success of dimethyl ether (DME) synthesis from coal, natural gas or biomass-derived syngas, the following catalytic carbonylation of DME to MA is considered to have economic advantage [3−6]. And using heterogeneous catalysts like solid acid catalysts or heteropoly acids has also attracted great interest [7, 8].

Acidic zeolites as hmordenite (HMOR) and keggin polyoxometallate clusters were proven to have high selectivity to MA by DME carbonylation [9−11]. Positions inside the 8-member-ring (MR) channels of HMOR have the similar activated energy with those T4 sites inside 12MR channels by studying the mechanism of CO and methoxy carbonylation over HMOR [12, 13].

To avoid heavy hydrocarbon and carbon deposition in 12MR channels of mordenite during DME carbonylation, pyrimidine pre-adsorption method was used to neutralize acid sites, which improved the catalytic activity up to 48 h [14]. And Iglesia found that the methoxy and CO carbonylation was the rate-determining step for DME carbonylation and that occurred more easily inside the 8MR channel of HMOR due to the unusual orientation of methoxy groups, which is parallel to the cylinder axis of T3-O33 site [15].

The modification of HMOR to improve the activity of DME carbonylation was carried out, Cu loaded HMOR showed good catalytic performance, but the reaction mechanism of Cu/HMOR catalysts is not clear [16, 17]. In this work, Cu-loaded HMOR catalyst was prepared by ion-exchange method (IE), ammonia evaporation method (AE), urea hydrolysis method (UH) and incipient wetness impregnation method (IWI) and tested for DME carbonylation to MA in the fixed-bed reactor to obtain the proper catalyst preparing method for MA production. Particular attention was paid towards the influence of preparation method on surface area, acidity, CO adsorption properties and carbonylation performance of those Cu/HMOR catalysts.

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TABLE I Textural properties and copper loading of the Cu/HMOR catalysts prepared by different methods.

Samples	Cu loading amount/%	BET/(m^2/g)	Pore area/(m^2/g)	Pore volume/(cm^3/g)	Pore size/nm
HMOR		574	548	0.21	0.61
AE-Cu/HMOR	4.76	506	447	0.17	0.44
UH-Cu/HMOR	6.92	486	431	0.17	0.46
IE-Cu/HMOR	1.80	511	465	0.18	0.48
IWI-Cu/HMOR	5.00	509	446	0.17	0.42

II. EXPERIMENTS

A. Catalyst preparation

HMOR (Si:Al=10, BET=574 m^2/g, Nankai University Catalyst Co. Ltd., China) was used as support. The copper loaded HMOR catalyst (Cu/HMOR) was prepared by IE, AE, UH and IWI methods as follows: for IE method, the mixture of copper nitrate solution and commercial HMOR was heated to 80 °C for 2 h by ion exchanging. For AE method, copper nitrate solution was added by ammonia aqueous solution until pH reached 11−12. The mixture was kept at 60 °C for 0.5 h, then a certain amount of HMOR was added and heated at 90 °C to evaporate ammonia to make pH decrease to 7−8. For UH method, commercial HMOR was added to solution of copper nitrate and urea, then heated to 90−95 °C until pH reached 7.5 and washed with distilled water. For IWI method, commercial HMOR support was impregnated by copper nitrate solution and kept stirring for 2 h at room-temperature with ethanol as solvent. All of obtained samples were dried at 110 °C for 12 h and calcined in air at 500 °C for 4 h, followed by granulation into the size of 20−40 mesh. The prepared catalysts were denoted as IE-Cu/HMOR, AE-Cu/HMOR, UH-Cu/HMOR, and IWI-Cu/HMOR, respectively.

B. Catalyst characterization

The textual properties of the catalysts were determined by N$_2$ physisorption at −196 °C with Quantachrome ASIQMO002-2. The temperature-programmed desorption of NH$_3$ (NH$_3$-TPD) was measured at 120−650 °C (0.15 g sample, 10 °C/min, 30 mL/min helium as carrier flow) after the sample was saturated with NH$_3$ for 20 min at 120 °C. The amount of desorbed NH$_3$ was then measured by a thermal conductivity detector (TCD). The CO-TPD was conducted under the similar process with NH$_3$-TPD, except that the adsorption temperature and the initial desorption temperature were 80 °C for CO. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/max-rC using Cu Kα radiation (λ=0.154056 nm).

C. Carbonylation reaction system and operation procedures

Gas phase carbonylation reaction of DME was carried out in a stainless-steel fixed-bed reactor at 1.5 MPa by the gas mixture with CO/DME ratio of 47 and 4%N$_2$ as internal standard. In each run, 0.50 g of catalyst was activated *in situ* at 270 °C for 7 h with 20%H$_2$/80%N$_2$ gas flow at atmosphere pressure. After activation, the reactor was cooled to 180 °C and purged with reactant gas. The flow rate of the reactant gas was adjusted by the Brooks 5850E mass flow controller. The typical operation conditions were T=210 °C, P=1.5 MPa and W/F=4.33 g$_{cat}$/(h mol). The tail gas flow rate was monitored by a mass flow meter.

D. Product analysis

Tail gas was heated at 110 °C and analyzed by two online gas chromatographs. CO, N$_2$, and CH$_4$ were analyzed by carbon-sieve column with TCD detector. DME, MA, CH$_4$, and MeOH were analyzed by HP-PLOT/Q column with FID detector.

III. RESULTS AND DISCUSSION

A. Textural properties of the catalysts

Textural properties of the catalysts are shown in Table I. Compared with HMOR, the BET surface area, pore volume and pore size of Cu/HMOR decreased when Cu was loaded by AE, UH, IE or IWI method. The BET decrease was relatively less than the micropore area did, which further proved that micropore of HMOR played important role in its structure and Cu adding affected the micropores significantly. UH-Cu/HMOR with the highest Cu amount of 6.92% shows the lowest BET of 486 m^2/g and micropore area of 431 m^2/g, respectively. And IE-Cu/HMOR shows the minimum decrease of textual property due to its low Cu loading amount of 1.8%. The high BET of 511 m^2/g and micropore area of 465 m^2/g with low Cu loading amount for IE-Cu/HMOR indicated the high Cu dispersion on the surface and in the micropores of HMOR, which may affect its carbonylation performance mentioned below.
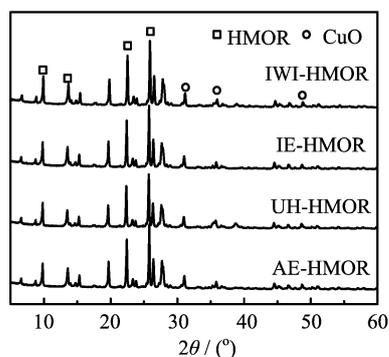
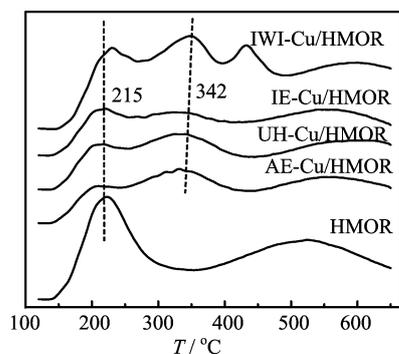FIG. 1 XRD patterns of the Cu/HMOR catalyst samples before reduction.

FIG. 2 NH$_3$-TPD profiles of the Cu/HMOR catalyst samples.

B. Crystalline phase and morphology

Figure 1 illustrates the XRD patterns of the Cu/HMOR catalysts before reduction. It exhibited obvious presence of highly crystalline of HMOR at 9.2°, 20.5°, and 23.6° for different Cu/HMOR catalysts [14]. The CuO diffraction peaks were detected at 2θ=35.5°, 38.7°, and 48.7°. And the corresponding intensity increased with enhanced Cu loading amounts. While the relative crystallinity of HMOR in Cu/HMOR catalysts decreased with increasing copper loading amount, which was attributed to the covering and blocking of Cu on the surface and in the pores of HMOR with decreased micropore area and pore volume in Table I.

C. Acid property

It was reported that Bronsted acid centers and active sites for CO insertion were essential for DME carbonylation catalyst [11, 15]. The desorption curves derived from NH$_3$-TPD desorption over different Cu/HMOR catalysts are presented in Fig.2. It exhibited three desorption peaks with different intensity and strength. The desorption peak at about 215 °C could be attributed to weak adsorption of NH$_3$ on the Bronsted acid site as reported by Iglesia and Corma [10−12] and NH$_3$ asso-
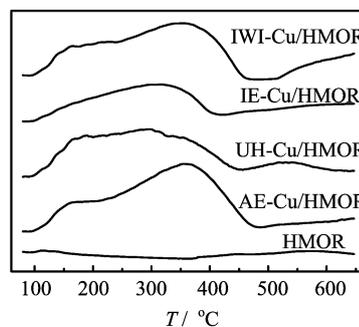

FIG. 3 CO-TPD profiles of the Cu/HMOR catalysts.

ciation with Si-OH group. The peak at about 342 °C was ascribed to the acid centers with medium strength. While the peak at about 554 °C was assigned to strong desorption of NH$_3$ adsorbed on the acidic Si−OH−Al group. An additional relatively stronger desorption peak at 416 °C was detected for IWI-Cu/HMOR, which may be attributed to the solvent of ethanol and it is in agreement with the result reported by Vinu [18]. The weak and medium acid sites at 215 and 342 °C were reported to be the active centers on the Cu/HMOR catalyst for carbonylation [9, 15] and DME was dissociatively chemisorbed to the formation of surface methoxy on the catalyst surface through the synergetic effect. However, the moderate acid center at 416 °C might accelerate the carbon deposition and decrease the stability of DME carbonylation activity. IE-Cu/HMOR possessed large amount of Bronsted acid centers and certain amount of moderated acid sites, which would have synergetic effect to keep its high catalytic performance.

D. CO adsorption property

CO-TPD profiles of Cu/HMOR are shown in Fig.3. Commercial HMOR zeolites show faint CO adsorption peak below 300 °C. The relatively strong absorbed-CO desorption peaks occur at 354, 271, 329, and 383 °C for AE-Cu/HMOR, UH-Cu/HMOR, IE-Cu/HMOR, IWI-Cu/HMOR catalyst respectively. According to the mechanism research work by Corma [12], the rate-determining step for DME carbonynation is the insertion of CO (from gas phase or via weakly adsorbed CO species) to the surface adsorbed methoxy, which may form acetyls consequently. The CH$_3$ groups derived from DME dissociation were also adsorbed on the catalysts surface, which formed non-competitive adsorption with CO species for further conversion. The intensity of CO adsorption played an important role during carbonylation. Normally, high CO partial pressure in the reactant gas increases its competitive adsorption capacity [10, 11]. The temperate CO-desorpbtion intensity of IE-Cu/HMOR at 329 °C (in Fig.3) may favor the syn-

TABLE II The amount and strength distribution of acidic surface sites and CO desorpbtion sites over various catalysts.

Catalyst	Cu adding amount/%	CO adsorption site[a]/%	Acid amount[b]/(mmol/g)		
			Weak	Medium	Strong
IE-1-Cu/HMOR	1.05	71	0.52	–	0.30
IE-2-Cu/HMOR	1.41	85	0.48	0.03	0.26
IE-3-Cu/HMOR	1.80	96	0.35	0.10	0.30
IE-6-Cu/HMOR	2.18	100	0.43	0.07	0.39

[a] Calculated with Gaussian function fit and using IE-6-Cu/HMOR as standard.
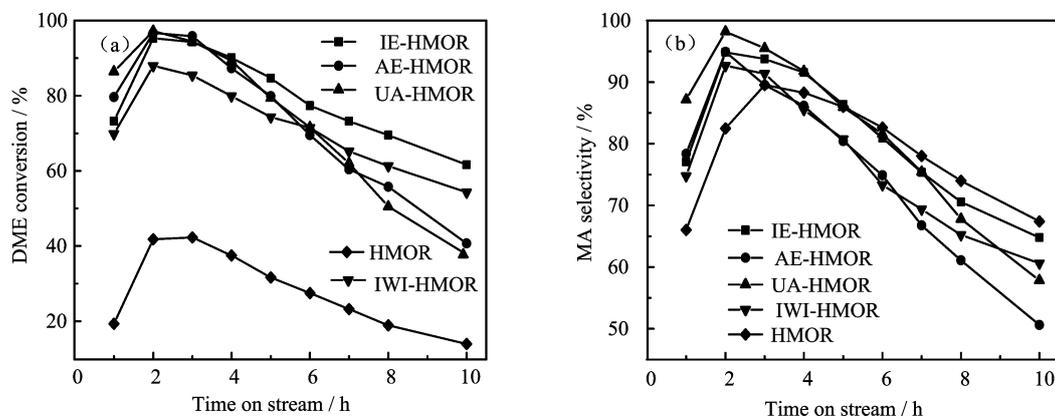[b] Calculated with Gaussian function fit.

FIG. 4 (a) Conversion of DME and (b) selectivity to MA over Cu/HMOR catalyst samples on time on stream.

ergetic effect of CO adsorption and its insertion to the surface methoxy, which may be the reason for the excellent DME carbonylation performance mentioned below.

E. Gas-phase carbonylation of DME

Figure 4 shows dependence of DME conversion and MA selectivity over various Cu/HMOR catalyst samples on time-on-stream (TOS). DME conversion was low (below 42%) over HMOR catalysts during the 10-h's reaction. DME conversion achieved to its maximum of more than 90% after about 2 h steady period over all Cu/HMOR catalysts. After that, DME conversion and MA selectivity decreased with TOS, resulting from the increasing of by-products for methanol as well as carbon deposition. For UH-Cu/HMOR catalyst, the highest DME conversion of 96.7% and MA selectivity of 94.9% were obtained at 2 h TOS. However, its catalytic performance decreased quickly with TOS, which was DME conversion of 37.8% and MA selectivity of 57.9% at 10 h TOS. It could be attributed to its relatively small micropore area and weak CO adsorption intensity. This quick conversion decrease may be also caused by carbon deposition on the acid sites in 12 MR channel of the HMOR zeolite due to its strong acid sites and large pore channels [14].

The DME conversion of 95.3% and MA selectivity of 94.9% over IE-Cu/HMOR at 2 h TOS was similar to that of UH-Cu/HMOR. But its

DME conversion decreased much slower than the other three Cu/HMOR catalysts. As shown in Fig.4(a), the effect of CO adsorption and acid property of the catalysts after about 8 h reaction followed the order: IE-Cu/HMOR>IWI-Cu/HMOR>AE-Cu/HMOR>UH-Cu/HMOR>HMOR. DME conversion of 61.6% and MA selectivity of 64.8% were achieved at 10 h TOS. It is easy to ascertain that the activity and stability of IE-Cu/HMOR are best, which may owe to its larger BET, the favorable CO adsorption ability and the synergistic effect of moderated intensity acid sites.

F. Optimizaion of Cu exchanging times for IW-Cu/HMOR catalyst

We discussed the effect of catalyst preparation method and the Cu loading mount on DME carbonylation and compared to the work reported by Tsubaki *et al.* [16, 17]. To obtain the optimum Cu content of IE-Cu/HMOR catalysts, the HMOR was treated with Cu ion solution for ion-exchange process by 1, 2, 3, and 6 times respectively and the catalysts were denoted as IE-1-Cu/HMOR, IE-2-Cu/HMOR, IE-3-Cu/HMOR, and IE-6-Cu/HMOR, as shown in Table II. It was shown that 1.05%Cu was exchanged on the surface of HMOR for the first ion-exchange process. Another 0.36%Cu and 0.39%Cu was exchanged for the second and third ion-exchange process respectively. With the increase
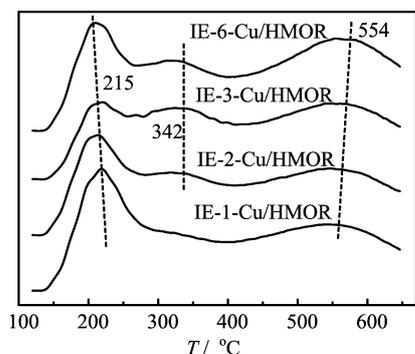
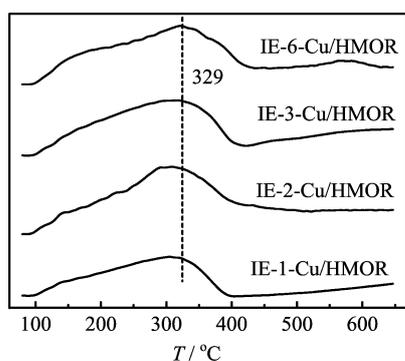FIG. 5 NH$_3$-TPD profiles of the IE-Cu/HMOR catalyst samples.

FIG. 6 CO-TPD profiles of the IE-x-Cu/HMOR catalyst samples.

FIG. 7 (a) Conversion of DME and (b) selectivity to MA over IE-x-Cu/HMOR catalyst samples on time on stream.

of Cu exchanging time, relatively less Cu was loaded on HMOR zeolite for each time and about 0.38%Cu was exchanged by the last three times of ion-exchange process. Figure 5 shows NH$_3$-TPD profiles of various IE-Cu/HMOR catalysts. Based on these curves, the amount and strength distribution of acidic sites were investigated and the results are listed in Table II.

Three desorption peaks at 215, 342, and 554 °C can be observed over the IE-Cu/HMOR zeolite, which are attributed to the weak, medium and strong intensity acid of HMOR [9, 10, 15]. The amount of weak acid sites gradually decreased from 0.52 mmol/g to 0.31 mmol/g when ion-exchange process was performed three times with the increasing of Cu loading amount from 1.05% to 1.80% and medium acid amount to 0.023 mmol. The IE-6-Cu/HMOR catalyst exhibited a slight increase of weak acid amount with the amount of medium acid dropping to 0.07 mmol.

CO desorbed on IE-Cu/HMOR catalysts at 329 °C is shown in Fig.6. The relative amount of CO adsorption over the IE-Cu/HMOR catalysts was measured based on the peak area using IE-6-Cu/HMOR as standard, which was 71%, 85% and 96% for IE-1-Cu/HMOR, IE-2-Cu/HMOR, and IE-3-Cu/HMOR respectively. It was proven that absorbed-CO over HMOR was combined with metal-alkyl bonds, which was activated by
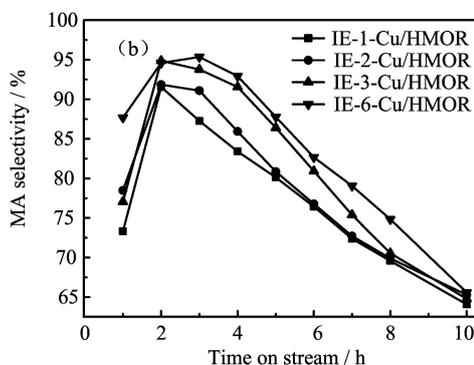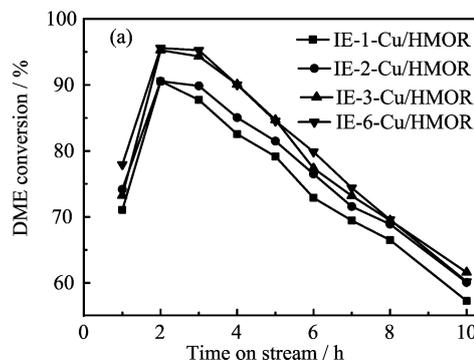
adsorbed-DME on the acid sites of Cu/HMOR catalyst, in a certain proportion and then generated MA [11]. The CO insertion into methoxy adsorbed on the catalyst surface is the rate-controlling step of the carbonylation reaction [12], so more CO adsorption sites prompt the activity. That may lead to the excellent carbonylation performance of IE-3-Cu/HMOR and IE-6-Cu/HMOR.

Figure 7 compared the DME conversion and MA selectivity over IE-Cu/HMOR on TOS during DME carbonylation. After 2 h reaction, DME conversion was the highest, which was similar to the results of Cu/HMOR by different preparation method in Fig.4. Compared with IE-3-Cu/HMOR, DME conversion and MA selectivity over IE-1-Cu/HMOR and IE-2-Cu/HMOR are relatively lower. The copper loading amount of IE-6-Cu/HMOR is 0.38% higher than that of IE-3-Cu/HMOR, but the maximum value of DME conversion is 95.6% and MA selectivity remains 95.4% over IE-6-Cu/HMOR, which is similar to the reactivity over IE-3-Cu/HMOR. It can be concluded that the catalytic performance is not significantly improved by increasing ion-exchange times. This may be due to the similar amount of CO adsorption over IE-3-Cu/HMOR and IE-6-Cu/HMOR catalyst as shown in Table II [11−14]. It is easy to ascertain that the IE-3-Cu/HMOR preparation process is a promising and cost-competitive one.

IV. CONCLUSION

Cu/HOMR catalysts prepared by evaporation, urea hydrolysis, incipient wetness impregnation and ion-exchange methods exhibited distinguished performances for DME carbonylation to MA. Cu/HMOR prepared via iron-exchange method exhibited the highest catalytic activity. The Cu loading of 1.05%−2.18% supported on mordenite catalysts played one key role in the catalytic activity and selectivity. The 1.80%Cu loading was found to be the best loading density based on ion exchange process, optimal DME conversion and MA selectivity. The N_2 physical absorption revealed that the 1.80% Cu/HMOR catalysts possessed larger surface area and micropore area and improved structural property compared with the other catalyst preparing methods. Combined with NH_3-TPD results, Cu/HMOR possessed large amount of Bronsted acid centers and certain amount of moderated acid sites, which synergistically affect reactivity. And the CO-TPD indicated that the moderate intensity of CO adsorption centers over 1.80% Cu/HMOR improved catalytic activity for the CO insertion to DME.

V. ACKNOWLEDGMENTS

[1] X. Y. Yu, W. Liang, Y. J. Du, and J. J. Cheng, Mater. Rev. **14**, 38 (2000).
[2] K. Fujimoto, T. Shikada, K. Omata, and H. Tominnaga, Chem. Lett. **12**, 2047 (1984).
[3] P. S. Sai Prasad, J. W. Bae, S. H. Kang, Y. J. Lee, and K. W. Jun, Fuel. Process. Technol. **89**, 1281 (2008).
[4] M. H. Qiu, Y. P. Li, T. J. Wang, Q. Zhang, C. G. Wang, X. H. Zhang, C. Z. Wu, L. L. Ma, and K. Li, Appl. Energy **90**, 3 (2012).
[5] K. Takeishi and A. Arase, *5th IASME/WSEAS International Conference on Energy and Environment*, 23 (2010).
[6] Z. F. Yan, J. Z. Xu, S. K. Shen, and H. L. Wang, Chin. J. Chem. Phys. **9**, 464 (1996).
[7] F. E. Paulik and J. F. Roth, Chem. Commun. 1578 (1968).
[8] G. J. Sunley and D. J. Watson, Catal. Today. **58**, 293 (2000).
[9] P. Cheung, A. Bhan, G. J. Sunley, and E. Igleisa, Angew. Chem. Int. Ed. **45**, 1617 (2006).
[10] P. Cheung, A. Bhan, G. J. Sunley, D. J. Law, and E. Igleisa, J. Catal. **245**, 110 (2007).
[11] G. G. Volkova, L. M. Plysova, A. N. Salanov, G. N. Kustova, T. M. Yurieva, and V. A. Likholobov, Catal. Lett. **80**, 175 (2002).
[12] M. Boronat, C. Martınez, and A. Corma, Phys. Chem. Chem. Phys. **13**, 2603 (2011).
[13] H. X. Li and Y. H. Wu, Chin. J. Chem. Phys. **9**, 543 (1996).
[14] P. Cheung, A. Bhan, H. C. Liu, G. J. Sunley, E. Iglesia, Abstracts of Papers of theE American Chemical Society. **231**, 430 (2006).
[15] J. L. Liu, H. F. Xue, X. M. Huang, P. H. Wu, S. J. Huang, S. B. Liu, and W. J. Shen, Chin. J. Catal. **31**, 729 (2010).
[16] X. G. San, G. H. Yang, Y. Zhang, X. G. Li, and N. Tsubak, J. Jpn. Petrol. Inst. **52**, 357 (2009).
[17] Y. Zhang, X. G. San, N. Tsubaki, Y. S. Tan, and J. F. Chen, Ind. Eng. Chem. Res. **49**, 5485 (2010).
[18] C. Anand, I. Toyama, H. Tamada, S. Tawada, S. Noda, K. Komura, Y. Kubota, S. W. Lee, S. J. Cho, J. H. Kim, G. Seo, A. Vinu, and Y. Sugi, Ind. Eng. Chem. Res. **51**, 12214 (2012).