Editor's Choice

doi:10.1246/cl.2011.614

Fast and Quantitative Dehydration of Lower Alcohols to Corresponding Olefins on Mesoporous Silica Catalyst

Teruki Haishi, Kouji Kasai, and Masakazu Iwamoto*
Chemical Resources Laboratory, Tokyo Institute of Technology,
4259-R1-5 Nagatsuta, Midori-ku, Yokohama, Kanagawa 226-8503

(Received March 25, 2011; CL-110254; E-mail: iwamoto@res.titech.ac.jp)

Ethanol, 1-propanol, 2-propanol, and 1-butanol were quantitatively dehydrated to the corresponding olefins on mesoporous silica MCM-41 catalyst. The reaction rates were high and no deactivation was observed for 50 h. Two reaction routes were suggested: the intermolecular dehydration of alcohol and subsequent decomposition of ether and the direct dehydration of alcohol.

Utilization of bioethanol (bEtOH) as alternative to or as an additive of automobile fuel has rapidly expanded all over the world. This is of course a way to use renewable resources and suppress carbon dioxide emission, while another challenge is the conversion of bEtOH to various olefins and their use for production of chemicals and polymers.[1] The latter would be very significant to fix carbon dioxide for the long-term period. Many efforts have, therefore, been devoted to development of selective conversion systems of bEtOH to ethene ($C2^{=}$). It is widely known that the dehydration of alcohols is well catalyzed on various types of acids including modified aluminas,[2] supported heteropolyacids,[3] zeolites,[4–8] mesoporous materials,[9] and others,[10] but the activity and selectivity reported so far have been insufficient. For example, the reaction rates and the selectivity of $C2^{=}$ on proton- or metal-modified zeolites should be improved, the selectivity is often restricted to ca. 96% due to strong acidic sites which cause oligomerization, polymerization, and fission of the produced lower olefins.[5,6] The various reactions in the zeolite pores finally result in coke formation and short lifetime.[5–7] Niobium silicate[8] or silicotungstic acid supported on mesoporous silica[3] have been reported to show good selectivity for $C2^{=}$ formation, but the reaction rates are not high due to the low surface areas. In addition, the low stability of loaded active components under high partial pressure of water would be a disadvantage for practical use.

The novel acidic properties of mesoporous silica material, MCM-41 (M41), have been reported from the present[11,12] and other groups.[13] The acidity is not strong but unique to promote various selective catalyses. Our efforts have, therefore, been devoted to revealing the catalytic activity of M41 for the dehydration of EtOH, 1- and 2-propanol (PrOH), and 1-butanol (BuOH) to $C2^{=}$, propene ($C3^{=}$), and butenes ($C4^{=}$). We found the fast, quantitative, and stable catalyst can solve the above problems. The catalytic dehydration of alcohols is well known to be an easy heterogeneous catalytic reaction, but quantitative progress without deactivation is still necessary.

M41 was prepared in the reported manner by using $C_{12}H_{25}N(CH_3)_3Br$ as the template and colloidal silica as the silica source.[14] After calcination of M41 at 873 K for 6 h in air, the BET surface area and the BJH pore diameter determined by a N_2 adsorption measurement were $1010\,m^2\,g^{-1}$ and 2.12 nm, respectively. The hexagonal structure of resulting M41 was confirmed by appearance of $2\theta = 2.580$, 4.476, and 5.124 degree peaks in X-ray diffraction patterns (Cu Kα, Ni filter), which corresponded to (100), (110), and (200), respectively. The Si/Al atomic ratio was 237, in which the origin of Al was an impurity of the raw material, colloidal silica. The catalytic reaction was carried out by using a fixed bed flow reactor at atmospheric pressure. 0.05–0.5 g of catalyst was loaded in the reactor and heated under N_2 at 673 K, and then EtOH ($P_{EtOH} = 2.8$–12.6%, N_2 balance, total flow rate 10–300 mL min^{-1}) was allowed to flow into the reactor at the desired temperature. The product distribution was determined by an on-line gas chromatograph.

The dependence of conversion of EtOH on the reaction temperature was first measured. The degree of EtOH conversion reached approximately 100% at 623 K as shown in Figure 1. $C2^{=}$ was almost quantitatively produced at this temperature though diethyl ether (DEE) was produced as a by-product at 473–573 K. It is worth noting that no $C4^{=}$ was observed at 473–773 K, being completely different from the results on zeolites on which the productions of $C4^{=}$ and C6 olefins ($C6^{=}$) and some aromatics were reported.[4–8] It is widely recognized that strong acid sites induce oligomerization of $C2^{=}$ to $C4^{=}$ and $C6^{=}$; therefore, the quantitative progress in dehydration shown in Figure 1 could be clearly attributed to mild and uniform acidity of the M41 catalyst.

To reveal the effect of the mesoporous structure of M41 on the catalytic activity, SiO_2 was separately prepared under vigorous stirring by using the same raw materials as those

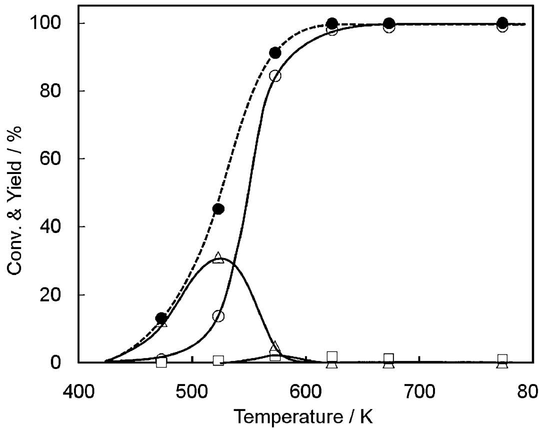

Figure 1. Reaction temperature dependence of conversion of EtOH on M41. Catalyst wt. 0.5 g, total flow rate 10 mL min^{-1} (GHSV 400 h^{-1}), P_{EtOH} 5.5% (N_2 balance). Symbols: closed circle, conversion of EtOH; open circle, yield of $C2^{=}$; open triangle, DEE; open square, acetaldehyde (AA).

employed in the preparation of M41. The components of SiO_2 obtained were, therefore, the same as those of M41 within experimental error, and the major difference between M41 and SiO_2 was the presence/absence of pore structures. This SiO_2 was inert for the present reaction; the conversion level of EtOH on 4.1 g of SiO_2 was only 1% at 673 K, total flow rate 10 mL min^{-1}, and P_{EtOH} 5.5%. It should be noted that the BET surface area of SiO_2 was 122 $m^2 g^{-1}$ and that the surface area of 4.1 g SiO_2 used in this experiment was identical with that of 0.5 g M41 in Figure 1. The results indicate that the presence of mesoporous structures was significant for the catalysis.

On the basis of the above results two experiments were performed. First, influence of Al contents was examined. Al-containing MCM-41 (Al-M41) catalysts were prepared by using template ion exchange.[14,15] The Al-M41 with Si/Al = 50–100 gave similar results to those in Figure 1, suggesting the small effect of Al content on the reaction. Second, the effect of pore size was investigated. When M41 samples with the BJH pore diameters of 2.2, 2.9, and 3.3 nm were employed as the catalyst at 673 K and 20000 h^{-1} of GHSV, the degrees of conversion of EtOH were 75, 60, and 50%, respectively. It is clear that the pore size was one of the factors determining the catalytic activity. The small effect of Al content and the significant effect of pore size, observed here, should be revealed in more detail in the future.

When the catalytic reaction was continued for 50 h and the reaction temperature was repeatedly raised or lowered in the range 473–773 K, the activity and selectivity of M41 were entirely stable, showing no deterioration of the catalyst in contrast to deactivation observed on H-zeolite catalysts.[5,6] After the reaction no change in the XRD patterns and the surface areas of the catalysts was observed. The dependence on the partial pressure of EtOH was examined in the range 2.8–12.6 kPa at 673 K. The degrees of EtOH conversion and $C2^{=}$ yield were always above 99%. The effect of water addition on the dehydration was also investigated. The mixtures of EtOH and water of 100/0–75/25 by weight were introduced at 673 K onto the M41 catalyst, and the conversion levels to $C2^{=}$ did not change. It follows that crude bEtOH will be able to be employed as the starting material for the production of $C2^{=}$, and rigorous distillation of bEtOH is unnecessary.

The space velocity dependence of the dehydration is summarized in Figure 2. The conversion levels of EtOH to $C2^{=}$ decreased above SV = 10000 h^{-1} and that to DEE increased. The results could be compared with a report that the most active zeolite catalyst, H-mordenite, gives 85% conversion of EtOH at SV = 3000 h^{-1}.[6] It follows that the M41 catalyst was very active for the dehydration even at high space velocity. In addition, DEE would be the intermediate for the $C2^{=}$ formation because DEE was formed at low temperatures or at high space velocities as shown in Figures 1 and 2. The reaction of DEE on M41 was separately investigated, and the results are depicted in Figure 3. DEE mainly reacted above 573 K and gave $C2^{=}$ and EtOH. It should be concluded that DEE was not dehydrated to give two $C2^{=}$ molecules but decomposed to give one $C2^{=}$ and one EtOH molecule on the M41 catalyst. Namely, in the reaction of EtOH, the intermolecular dehydration of two EtOH molecules to form DEE and the decomposition of resulting DEE to give $C2^{=}$ and EtOH consecutively proceeded on M41. The same type of reaction was reported to progress in supercritical carbon dioxide[16] which is well known to work as an acidic medium.

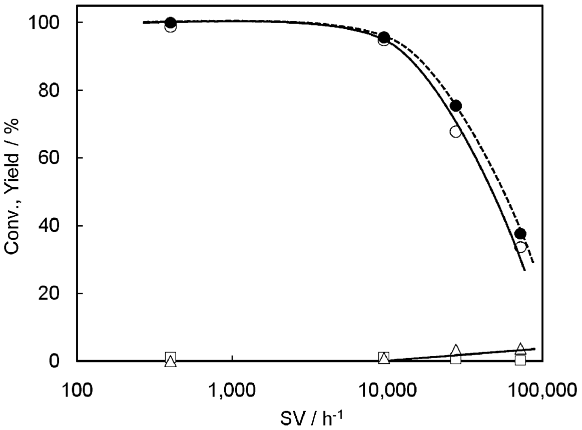

Figure 2. Change in the conversion of EtOH (closed circle), yields of $C2^{=}$ (open circle), DEE (open triangle), and AA (open square) at 673 K with the space velocity (SV). P_{EtOH} 5.5% (N_2 balance).

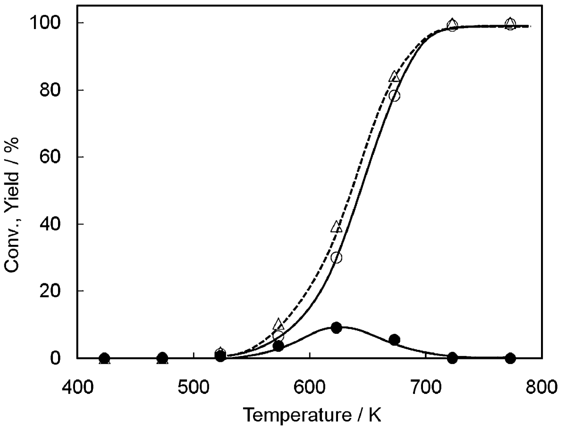

Figure 3. Reaction of DEE on M41. Catalyst wt. 0.2 g, total flow rate 100 mL min^{-1} (SV 9200 h^{-1}), P_{DEE} 5.0% (N_2 balance). Symbols: open triangle, conversion of DEE; open circle, yield of $C2^{=}$; closed circle, yield of EtOH.

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \quad (1)$$

$$C_2H_5OC_2H_5 \rightarrow C_2H_4 + C_2H_5OH \quad (2)$$

The reaction mechanism shown by eqs 1 and 2 was quite different from those suggested on various acidic solid catalysts. Usually EtOH first reacted with a proton on the catalyst, formed $CH_3CH_2OH_2^+$ and released a carbocation and H_2O, and finally the carbocation intermediate changed to $C2^{=}$ and proton (regeneration of an acid site) or eq 1 proceeded first and resultant DEE changed to two $C2^{=}$ and released H_2O.[4–8,17] It should be noted that the results in Figures 1 and 3 could not exclude these two possibilities at higher reaction temperatures though the progress in eqs 1 and 2 was sure at 473–573 K.

At last the reaction of EtOH was expanded to 1-PrOH, 2-PrOH, and 1-BuOH. The corresponding olefins were quantitatively obtained in all experiments; therefore, only the conversion levels to olefins are summarized in Figure 4 with the results of EtOH. In the reaction of 1-BuOH the production ratio of 1-, *trans*-2-, and *cis*-2-$C4^{=}$ was 0.5:1.0:0.3 at 623 K. The

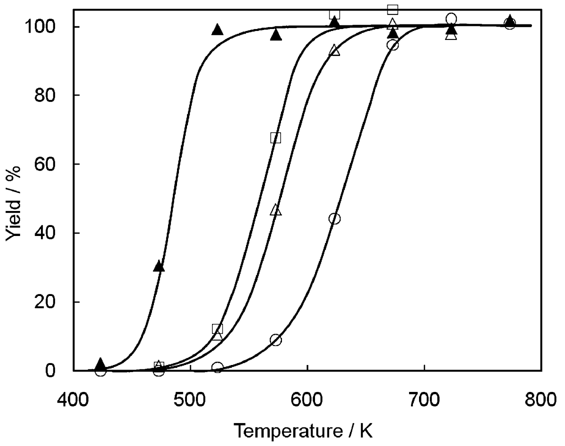

Figure 4. Comparison of reactivity of various lower alcohols on M41. The vertical axis indicates the yield of C2$^=$, C3$^=$, or C4$^=$. The GHSV and P_{EtOH} in EtOH (open circle) experiments were 9500 h^{-1} and 5.6%, 1-PrOH (open triangle) 16400 h^{-1} and 5.0%, 2-PrOH (closed triangle) 16400 h^{-1} and 5.0%, 1-BuOH (open square) 16500 h^{-1} and 5.1%.

reactive temperature ranges were dependent on the kinds of alcohols, and the order of reactivity was 2-PrOH > 1-BuOH > 1-PrOH > EtOH. This order is the same as the stabilities of carbocations, that is, secondary > primary, and C4 > C3 > C2. The reaction mechanism of EtOH on M41 was different from that on the other type of acidic catalysts as discussed in the previous section, but the reactivity of alcohols was well explained by the conventional rules of the organic chemistry. Though methanol (MeOH) does not have any corresponding olefin, the results of MeOH would be worth adding. In the reaction of methanol as the substrate we found the selective formation of dimethyl ether (DME) at around 623 K with ca. 75% conversions and the decrement of DME yield above 673 K due to the formation of various by-products.

In conclusions, the mesoporous silica MCM-41 with Al was found to show an excellent catalytic activity for the dehydration of lower alcohols to the corresponding olefins; namely, the reaction rates were very high and the selectivity is so great that the olefins could be obtained quantitatively. The catalytic activity was very stable. M41 would be usable as an ideal catalyst for the dehydration of bEtOH in the near future.

This work was supported by Grants-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

1 A. Morschbacker, *Polym. Rev.* **2009**, *49*, 79.
2 S. Golay, R. Doepper, A. Renken, *Chem. Eng. Sci.* **1999**, *54*, 4469; D. N. Bakoyannakis, D. Zamboulis, G. A. Stalidis, E. A. Deliyanni, *J. Chem. Technol. Biotechnol.* **2001**, *76*, 1159; M. M. Doheim, H. G. El-Shobaky, *Colloids Surf., A* **2002**, *204*, 169; T. Zaki, *J. Colloid Interface Sci.* **2005**, *284*, 606.
3 D. Varisli, T. Dogu, G. Dogu, *Chem. Eng. Sci.* **2007**, *62*, 5349; D. Varisli, T. Dogu, G. Dogu, *Ind. Eng. Chem. Res.* **2008**, *47*, 4071; D. Varisli, T. Dogu, G. Dogu, *Ind. Eng. Chem. Res.* **2009**, *48*, 9394.
4 C. B. Phillips, R. Datta, *Ind. Eng. Chem. Res.* **1997**, *36*, 4466.
5 A. T. Aguayo, A. G. Gayubo, A. Atutxa, M. Olazar, J. Bilbao, *Ind. Eng. Chem. Res.* **2002**, *41*, 4216; A. T. Aguayo, A. G. Gayubo, A. M. Tarrío, A. Atutxa, J. Bilbao, *J. Chem. Technol. Biotechnol.* **2002**, *77*, 211.
6 I. Takahara, M. Saito, M. Inaba, K. Murata, *Catal. Lett.* **2005**, *105*, 249; I. Takahara, M. Saito, H. Matsuhashi, M. Inaba, K. Murata, *Catal. Lett.* **2007**, *113*, 82; M. Inaba, K. Murata, M. Saito, I. Takahara, *Green Chem.* **2007**, *9*, 638; I. Takahara, M. Saito, H. Matsuhashi, H. Aritani, M. Inaba, K. Murata, *J. Jpn. Pet. Inst.* **2007**, *50*, 227.
7 D. Arias, A. Colmenares, M. L. Cubeiro, J. Goldwasser, C. M. López, F. J. Machado, V. Sazo, M. M. R. de Agudelo, *Catal. Lett.* **1997**, *45*, 51; H. Oikawa, Y. Shibata, K. Inazu, Y. Iwase, K. Murai, S. Hyodo, G. Kobayashi, T. Baba, *Appl. Catal., A* **2006**, *312*, 181.
8 P. Brandão, A. Philippou, J. Rocha, M. W. Anderson, *Catal. Lett.* **2002**, *80*, 99.
9 Y. Guan, Y. Li, R. A. van Santen, E. J. M. Hensen, C. Li, *Catal. Lett.* **2007**, *117*, 18.
10 F. Carrasco-Marín, A. Mueden, C. Moreno-Castilla, *J. Phys. Chem. B* **1998**, *102*, 9239; S. Kamiguchi, T. Chihara, *Catal. Lett.* **2003**, *85*, 97; S. Kamiguchi, S. Nagashima, K. Komori, M. Kodomari, T. Chihara, *J. Cluster Sci.* **2007**, *18*, 414.
11 Y. Tanaka, N. Sawamura, M. Iwamoto, *Tetrahedron Lett.* **1998**, *39*, 9457.
12 M. Iwamoto, Y. Tanaka, N. Sawamura, S. Namba, *J. Am. Chem. Soc.* **2003**, *125*, 13032; H. Ishitani, M. Iwamoto, *Tetrahedron Lett.* **2003**, *44*, 299; M. Iwamoto, Y. Kosugi, *J. Phys. Chem. C* **2007**, *111*, 13.
13 D. T. On, P. N. Joshi, G. Lemay, S. Kaliaguine, *Stud. Surf. Sci. Catal.* **1995**, *97*, 543; M. Hartmann, A. Pöppl, L. Kevan, *J. Phys. Chem.* **1996**, *100*, 9906; T. Yamamoto, T. Tanaka, T. Funabiki, S. Yoshida, *J. Phys. Chem. B* **1998**, *102*, 5830; A. Itoh, T. Kodama, S. Maeda, Y. Masaki, *Tetrahedron Lett.* **1998**, *39*, 9461.
14 T. Abe, Y. Tachibana, T. Uematsu, M. Iwamoto, *J. Chem. Soc., Chem. Commun.* **1995**, 1617; M. Iwamoto, Y. Tanaka, *Catal. Surv. Jpn.* **2001**, *5*, 25; F. Hayashi, K. Ishizu, M. Iwamoto, *Eur. J. Inorg. Chem.* **2010**, 2235.
15 H. Murata, H. Ishitani, M. Iwamoto, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14452.
16 X. Xu, C. P. De Almeida, M. J. Antal, Jr., *Ind. Eng. Chem. Res.* **1991**, *30*, 1478.
17 J. N. Kondo, K. Ito, E. Yoda, F. Wakabayashi, K. Domen, *J. Phys. Chem. B* **2005**, *109*, 10969.