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Transesterification of ethyl butyrate with methanol over 1-butyl-3-methylimidazolium exchanged mordenite

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ABSTRACT

Transesterification of ethyl butyrate with methanol on the organic cation-exchanged mordenite ([bmim]M20) was studied in order to examine the reactivity of the methoxide ions that were generated on [bmim]M20 by the dissociation of methanol. Since transesterification occurred by addition of NaCl, the methoxide ions on [bmim]M20 were demonstrated to be utilizable in the reaction. The activity improved with a concentration of NaCl below 3 mmol L⁻¹, whereas it was constant at concentrations above 3 mmol L⁻¹. The adsorption of ethyl butyrate on the partially ion-exchanged [bmim]M20 samples was observed by FT-IR spectroscopy. It was found that it was difficult for ethyl butyrate to enter the micropores of [bmim]M20. From these results, a reaction mechanism was proposed in which the methoxide ions generated in the micropores of [bmim]M20 reacted with ethyl butyrate after they diffused outside of the micropores.

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1. Introduction

We previously reported that the H⁺ on H-type mordenite zeolite (HM20) is ion exchangeable with an organic cation, i.e., 1-butyl-3-methylimidazolium ([bmim]) [1]. The ion exchange process is shown in Scheme 1. Ion exchange of HM20 in 1-butyl-3methylimidazolium chloride ([bmim]Cl) aqueous solution gives [bmim]M20 by the ion exchange between H⁺ on the zeolite and [bmim]. On the [bmim]M20, dissociative adsorption of water and alcohols (R-OH) such as methanol, ethanol, 1-propanol and 2propanol has been revealed by FT-IR spectroscopy (Scheme 2) [1,2]. In these IR studies, bands attributed to the acidic OH groups hydrogen-bonded with water and alcohols were observed, although the acidic OH groups were absent on [bmim]M20. This indicates that the acidic OH groups were regenerated by the dissociation of water or alcohol and that another molecule of water or alcohol was adsorbed on the generated acidic OH groups as shown in Scheme 2. These results imply the generation of OH⁻ or alkoxide ions (RO⁻) as well. In addition, the interaction between generated OH⁻ or RO⁻ and [bmim] has been observed by IR spectroscopy [1,2]. Therefore, it was confirmed that dissociative water or alcohol adsorption leads to the generation of OH⁻ or RO⁻ on [bmim]M20.

It would be very interesting to demonstrate that alkoxide ions generated on [bmim]M20 by the dissociation of alcohols were uti-

lized in reactions. In this study, the reactivity of the methoxide ions generated on [bmim]M20 was evaluated by transesterification of ethyl butyrate with methanol as a test reaction.

2. Experimental

2.1.1. Sample preparation

Mordenite zeolite (HM20, Catalysis Society of Japan; SiO₂/Al₂O₃ = 20) was used as the catalyst. HM20 was calcined at 773 K for 5 h under ambient conditions. HM20 (5 g) was added to 100 mL of a 10 mmol L⁻¹ [bmim]Cl (Kanto Chemical) aqueous solution and stirred for 3 h. After this ion exchange procedure, the ion-exchanged zeolite was filtered off, washed five times with distilled water, and dried at room temperature. This prepared sample is referred to as [bmim]M20(10). The number in parentheses denotes the concentration in mmol L⁻¹ of [bmim]Cl solution used for the ion exchange. To prepare [bmim]M20 with a different ion exchange rate, 1 g of HM20 was ion-exchanged with 20 mL of 1 or 5 mmol L⁻¹ [bmim]Cl aqueous solution under the same conditions as described above. The prepared samples are referred to as [bmim]M20(1) and [bmim]M20(5).

2.1.2. IR measurements

Approximately 30 mg of HM20 and [bmim]M20 samples were pressed into a self-supporting disk (20 mm in diameter) and placed into an IR cell connected to a conventional closed gas-circulation

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Scheme 1. Ion exchange of H⁺ on the acidic OH groups of HM20 by [bmim]Cl.

system. The sample disk was pretreated by outgassing for 1 h at 483 K. After cooling to room temperature under evacuation, IR spectra of the pretreated catalysts were collected. After that, the OH groups on the catalysts were deuterated by repeated contact with about 0.4 kPa of deuterium and evacuation at 423 K. After deuteration, the sample disk was outgassed for 1 h at 483 K. After cooling the sample to room temperature under evacuation, IR spectra of the catalysts were collected.

Methanol adsorption was performed on undeuterated [bmim]M20(10). After pretreatment, IR spectra of [bmim]M20(10) only were collected as background spectra at each temperature while cooling the pretreated [bmim]M20(10) to room temperature. 0.13 kPa of methanol (Kanto Chemical; 99.8%) was introduced into the IR cell, followed by evacuation, and IR spectra were measured. IR spectra were then observed while gradually increasing the temperature up to 393 K under evacuation.

Ethyl butyrate adsorption was performed on deuterated HM20, [bmim]M20(1) and [bmim]M20(5). Ethyl butyrate (Kanto Chemical; 98.0%) was introduced to each pretreated substrate at 353 K, and the time courses of IR spectra were observed in the presence of about 0.1 kPa of gaseous ethyl butyrate.

IR spectra were measured with a JASCO FT-IR 460 spectrophotometer equipped with a mercury cadmium telluride (MCT) detector. All spectra were collected at a resolution of 4 cm^{-1} .

2.1.3. Transesterification

The transesterification reaction was performed in a glass batch reactor equipped with a water-cooled condenser and a magnetic stirrer. The flask was immersed in an oil bath to keep the reaction temperature constant throughout the reaction. The mixture of 4 mL of ethyl butyrate and 5 mL of methanol (ethyl butyrate:methanol molar ratio = 1:4) was reacted with 0.1 g of [bmim]M20(10) in the temperature range between 323 K and 363 K. The analysis of methyl butyrate and ethyl butyrate was performed using a Hitachi 663-50 gas chromatograph equipped with a flame ionization detector (FID) and a 2 m Unisole 400 5% Uniport S column (GL Sciences; 3 mm inner diameter). The methyl butyrate yield Y_m (%) was defined as

given below:

$$Y_{\rm m}$$
 (%) = $\frac{\rm Mol \ of \ methyl \ butyrate}{\rm Mol \ of \ ethyl \ butyrate \ loaded} \times 100.$

3. Results and discussion

3.1. FT-IR measurements

3.1.1. Ion exchange of HM20 with [bmim]

IR spectra of HM20 and a series of [bmim]M20 are shown in Fig. 1. Since the amount of catalyst used for each sample disk was changed for each experiment, the thickness of the sample disks was different. In such cases, the direct comparison of absorbance between different samples is not allowed, thus the absorbance is normalized using the bands attributed to the skeletal vibration modes on HM20 (1800–2000 cm⁻¹). Fig. 1 shows normalized IR spectra. As the concentration of [bmim]Cl for ion exchange increases, the intensity of the bands attributed to ν CH and δ CH of [bmim][3,4] also increases. Simultaneously, the band at 3603 cm⁻¹ attributed to ν OH of the acidic OH groups on the zeolite [5–7] decreases as the concentration of [bmim]Cl increases. Therefore, it is indicated that the ratio of ion exchange with [bmim] is higher at higher concentrations of [bmim]Cl solutions.

Fig. 2A shows expansions of the vOH region in Fig. 1. The bands at 3665 and $3744 \,\mathrm{cm^{-1}}$ are attributed to the vOH of the extra-framework Al species on the zeolite [6,8] and to the silanol groups [6,8,9], respectively. The band from the acidic OH groups (3603 cm⁻¹) seems to be absent on [bmim]M20(10) [spectrum (d) in Fig. 2A] due to complete ion exchange. However, spectral noise makes it difficult to distinguish and quantify the peaks. Therefore, the OH groups were deuterated to minimize the noise, and the results are shown in Fig. 2B. In spectrum (d) in Fig. 2B, the band at 2659 cm⁻¹ attributable to the acidic OD groups on the zeolite appeared for [bmim]M20(10), indicating that the ion exchange of H⁺ with [bmim] was not complete. Mordenite zeolite has two channel sizes of 12- and 8-membered rings (MR), and it is known that the band of the acidic OH (OD) groups on 8-MR appear at



Scheme 2. Dissociative water or alcohol (ROH) adsorption on [bmim]M20.



Fig. 1. IR spectra of HM20 and [bmim]M20 samples. (a) HM20, (b) [bmim]M20(1), (c) [bmim]M20(5), and (d) [bmim]M20(10).

lower frequency than those on 12-MR [7,10–12]. Since pyridine is inaccessible to the acidic OH groups on 8-MR [11,13], the acidic OH groups in 8-MR on [bmim]M20(10) may also not be ion-exchanged with [bmim]. However, the $2659 \, \mathrm{cm}^{-1}$ band assigned to the acidic OD groups on [bmim]M20(10) is observed at the same frequency as that of HM20 [spectra (d) and (a) in Fig. 2B], but a peak at a lower frequency assigned to the acidic OD groups in 8-MR does not appear alone, indicating that the acidic OH groups in 8-MR are also ion-exchanged with [bmim]. The ion exchange rates of each [bmim]M20 are estimated as [bmim]M20(1)=57%, [bmim]M20(5)=70% and [bmim]M20(10)=93% from the integrated intensities of the bands of acidic OD groups ($2659 \, \mathrm{cm}^{-1}$).

3.1.2. Methanol adsorption on [bmim]M20(10)

Fig. 3(a) shows the IR spectra of methanol adsorbed on [bmim]M20(10) at 303 K under evacuation. The spectra in Fig. 3 represent subtracted spectra of the before and after methanol adsorption spectra. The IR spectrum in Fig. 3(a) is similar to the previously reported results [2]. Therefore, dissociative methanol adsorption as shown in Scheme 2 is confirmed on [bmim]M20(10). In Fig. 3(a), the band at 2440 cm⁻¹ is attributed to the acidic OH groups hydrogen-bonded with methanol. Since the acidic OH groups are almost absent on [bmim]M20(10), the presence of a band at 2440 cm⁻¹ indicates the regeneration of the acidic OH groups by dissociative methanol adsorption. Moreover, negative bands attributed to ν CH of [bmim] [marked with an asterisk in Fig. 3(a)] are observed as well. It is reported that methoxide

ions generated by dissociative methanol adsorption interact with [bmim] on [bmim]M20 and this interaction causes a decrease in the original vCH bands of [bmim] [2]. Therefore, the decrease of vCH bands of [bmim] also supports the occurrence of dissociative methanol adsorption on [bmim]M20(10).

In order to investigate the stability of the methoxide ions and the acidic OH groups generated by methanol dissociation, the [bmim]M20(10) substrate with methanol adsorbed was gradually warmed under evacuation [Fig. 3(a)-(d)]. When methoxide ions stably interact with [bmim], isolated acidic OH groups and methoxide ions are expected to remain on [bmim]M20(10) after desorption of methanol from the acidic OH groups that are generated by dissociative methanol adsorption. In this case, it is expected that the vOH band of acidic OH groups hydrogen-bonded with methanol (2440 cm^{-1}) will disappear, the vOH band of isolated acidic OH groups (3603 cm⁻¹) will appear, and the negative vCH peaks of [bmim] will remain. In Fig. 3, the band at 2440 cm⁻¹ decreases during the warming procedure, indicating the decrease of methanol hydrogen-bonded with the acidic OH groups. However, the negative vCH peaks of [bmim] simultaneously decrease. In addition, the band of the isolated acidic OH groups does not appear. These results indicate that although the acidic OH groups and methoxide ions can exist when methanol adsorbs on the acidic OH groups, methoxide ions return to methanol by recombination with H⁺ on the acidic OH groups that are isolated from methanol. This result is consistent with the report on dissociative water adsorption on [bmim]M20[1]. In that report, it was shown that although acidic OH groups existed when water was adsorbed on the acidic OH groups



Fig. 2. IR spectra of expanded ν OH region of Fig. 1 (panel A) and IR spectra of deuterated HM20 and [bmim]M20 samples (panel B). (a) HM20, (b) [bmim]M20(1), (c) [bmim]M20(5), and (d) [bmim]M20(10).



Fig. 3. IR spectra of methanol adsorbed on [bmim]M20(10) under evacuation at 303 K, followed by gradual warming under evacuation. (a) 303 K, (b) 333 K, (c) 363 K, and (d) 393 K.



Fig. 4. Time course of the integrated intensities of the isolated acidic OD groups for (a) ethyl butyrate adsorption on DM20, (b) deuterated [bmim]M20(1), and (c) deuterated [bmim]M20(5) at 353 K.

generated by water dissociation, they became absent after water desorbed from the acidic OH groups.

3.1.3. Ethyl butyrate adsorption on [bmim]M20

Because it has been reported that it is difficult for 2-propanol to enter the micropores of [bmim]M20 where bulky [bmim] exists, ethyl butyrate may also be inaccessible to the inside of the micropores [2]. Therefore, the adsorption of ethyl butyrate on [bmim]M20 was investigated. When ethyl butyrate forms hydrogen bonds with the acidic OH groups on zeolite, a decrease in the band of the isolated acidic OH groups and a lower frequency band of hydrogenbonded OH groups should be observed. Since it is believed that most of the acidic OH groups on zeolite are in the micropores [14], a decrease of the isolated acidic OH groups is expected to be observed when ethyl butyrate enters the micropores. To study this, [bmim]M20 samples with both [bmim] and a quantitative amount of acidic OH groups in the micropores are required. Thus, two partially ion-exchanged samples, [bmim]M20(1) and [bmim]M20(5), were prepared. The IR spectra of these samples are shown in Figs. 1 and 2.

Fig. 4 shows the time course of the ratio of the isolated acidic OD groups when ethyl butyrate was adsorbed on deuterated mordenite (DM20) and deuterated [bmim]M20(1) and [bmim]M20(5) at 353 K. The amount of the acidic OD groups on [bmim]M20(1) and [bmim]M20(5) is less than on DM20 because some of them are ion-exchanged with [bmim]. Therefore, the ratio of the isolated acidic OD groups is calculated by defining the amount of the isolated acidic OD groups on the ion-exchanged samples as 100%. The ratio of the isolated OD groups sharply decreases immediately after ethyl butyrate introduction (within 3 min) for each catalyst. It has been reported that even though the molecules cannot entirely enter the micropores, if the molecules have functional groups that can enter the micropores such as straight alkyl chains, these can form hydrogen bonds with acidic OH groups near the entrance of the micropores [15]. Therefore, the sharp decrease of the isolated acidic OD groups within 3 min is attributable to the interaction of the alkyl chains of ethyl butyrate with the acidic OD groups, but most of the molecules have not entirely entered the micropores. This indicates that isolated acidic OD groups near the entrance of the micropores on partially ion-exchanged [bmim]M20 still remain. It is supposed that ion exchange of the acidic OD groups in the micropores is comparatively homogeneous, and priority to ion exchange is not given to the acidic OD groups near the entrance. After 3 min, grad-



Fig. 5. Time on stream of the yield of methyl butyrate for the transesterification of ethyl butyrate with methanol over [bmim]M20(10) at 343 K. The concentrations of NaCl in the reaction solution are (a) 0.0 and (b) 10 mmol L^{-1} . The molar ratio of ethyl butyrate to methanol is 1:4, and 0.1 g of the catalyst is used.

ual penetration of ethyl butyrate into the micropores by diffusion is observed on DM20 [Fig. 4(a)] but 47% of the isolated acidic OD groups still remain even after 30 min. Therefore, it is shown that it is difficult for ethyl butyrate to enter the micropores of DM20. Similarly, on [bmim]M20 samples, penetration of ethyl butyrate into the micropores by diffusion is observed, but about 70% of the acidic OD groups did not interact after 30 min for [bmim]M20(5). Thus, it is also difficult for ethyl butyrate to enter into the micropores of [bmim]M20(5).

3.2. Transesterification of ethyl butyrate with methanol

Fig. 5(a) shows time on stream of the yield of methyl butyrate for the transesterification of ethyl butyrate with methanol over [bmim]M20(10) at 343 K. Although the yield at 6 h is very low, transesterification is found to occur over [bmim]M20(10). As described above, since it is difficult for ethyl butyrate to enter the micropores of [bmim]M20, only the methoxide ions near the entrance of the micropores may react. In order to improve the yield, methoxide ions in the micropores have to diffuse outside of the micropores. From the results shown in Fig. 3, it is found that the methoxide ions interacting with [bmim] are stable when methanol adsorbs on the acidic OH groups generated by dissociative methanol adsorption. Simultaneously, it is indicated that desorption of methanol from the acidic OH groups makes methoxide ions return to methanol by recombination with H⁺. The very low yield for the transesterification over [bmim]M20(10) can be explained in two ways. The first possibility is that the methoxide ions are not released from [bmim]. The second possibility is recombination of the methoxide ions with acidic OH groups during diffusion in the micropores. These two possibilities are considered to interrupt the exit of methoxide ions from the micropores. In the former case, when Cl⁻ ions which could become counter ions of [bmim] are added to the reaction solution, the methoxide ions are expected to diffuse outside the micropores due to methoxide ion exchange with Cl⁻. In the latter case, when Na⁺ ions which could become counter ions of methoxide are added, the methoxide ions may diffuse outside the micropores due to suppression of the recombination between methoxide ions and acidic OH groups. Therefore, transesterification of ethyl butyrate with methanol over [bmim]M20(10) was carried out by adding NaCl to the reaction solution.

Fig. 5(b) shows time on stream of the yield of methyl butyrate for the transesterification in 10 mmol L^{-1} of NaCl-containing reac-



Scheme 3. Proposed reaction mechanism for the transesterification of ethyl butyrate with methanol on [bmim]M20 when NaCl is added.

tion solution. As expected, the yield at 6 h improves to 10.9%. This is about 15 times better than the case without NaCl addition. Because NaCl addition improved the yield, the participation of NaCl in the reaction is obvious. Scheme 3 shows a proposed reaction mechanism for the transesterification of ethyl butyrate with methanol over [bmim]M20 in NaCl solution as follows:

- (1) Dissociative methanol adsorption in the micropores of [bmim]M20 forms acidic OH groups and methoxide ions.
- (2) The methoxide ions interacting with [bmim] are exchanged with Cl⁻ ions in the micropores.
- (3) The methoxide ions released from the interaction with [bmim] diffuse outside of the micropores with Na⁺ as a counter ion, and react with ethyl butyrate, which gives methyl butyrate and C_2H_5ONa .
- (4) The Cl⁻ ions interacting with [bmim] react with H⁺ on the acidic OH groups, and form HCl.
- (5) The HCl diffuses outside the micropores and is neutralized with C₂H₅ONa, which gives NaCl and ethanol.

If the reaction proceeds by the reaction mechanism shown in Scheme 3, the activity is expected to improve with increasing concentrations of NaCl. Fig. 6 shows the NaCl concentration dependency for the transesterification. The horizontal axis and the vertical axis represent the NaCl concentration on a logarithm scale and the yield at 6 h, respectively. Although the yields improve with increasing NaCl concentration up to 3 mmol L⁻¹, they are constant above 3 mmol L^{-1} . At NaCl concentrations below 3 mmol L^{-1} , insufficient amounts of Cl- and Na⁺ restrict the exchange between methoxide ions on [bmim]M20 and Cl- and also restrict formation of C₂H₅ONa. Consequently, the methoxide ions are not able to diffuse outside the micropores. Thus, step (2) in Scheme 3 is the rate determining step. On the other hand, with NaCl concentrations above 3 mmol L⁻¹, sufficient amounts of Cl⁻ and of Na⁺ make it easy to exchange methoxide ions with Cl⁻ and form C₂H₅ONa. However, because it takes time to diffuse outside the micropores, the yield does not improve with increasing NaCl concentration. Thus, step (3) in Scheme 3 is the rate determining step.

The 10.9% of yield at 6 h (cf. Fig. 5) corresponds to the 3.3 mmol of methyl butyrate. The amount of the acidic OH groups on mordenite with $SiO_2/Al_2O_3 = 15$ has been reported to be 1.19 mmol/g [12]. Since the mordenite used in this study ($SiO_2/Al_2O_3 = 20$) is



Fig. 6. NaCl concentration dependency for the transesterification at 343 K. The yields at 6 h are plotted against NaCl concentration. The molar ratio of ethyl butyrate to methanol is 1:4, and 0.1 g of the catalyst is used.

considered to have less amount of the acidic OH groups than that in the reference, the amount of the active sites ([bmim] exchanged Brønsted acid sites) on 0.1 g of [bmim]M20 is expected to be less than 0.12 mmol. Therefore, this transesterification is considered to proceed in catalytic. Although to check the reutilization of the catalyst is a further study, this means that [bmim]M20 may have reusability.

Transesterification is applied to the synthesis of biodiesel fuels from renewable biological resources such as vegetable oils. On [bmim]M20, it was found that methoxide is generated in heterogeneous process whereas transesterification homogeneously occurs in the solution. Transesterification would be occur for the bulky molecules such as vegetable oils which are too large to enter the micropores of zeolites, by employing [bmim]M20.

4. Conclusions

In order to investigate the reactivity of methoxide ions on [bmim]M20 generated by dissociative methanol adsorption, transesterification of ethyl butyrate was examined over [bmim]M20. Since transesterification improved when NaCl was added to the reaction solution, it was concluded that methoxide ions generated on [bmim]M20 have the ability to be used in subsequent reactions. This means that [bmim]M20 is a promising heterogeneous catalyst for transesterification.

Ethyl butyrate adsorption on [bmim]M20 was studied by FT-IR spectroscopy to investigate the reaction mechanism for the transesterification over [bmim]M20. The FT-IR results showed that it is difficult for ethyl butyrate to enter the micropores of [bmim] exchanged mordenite. The NaCl concentration dependency on the activity of the transesterification revealed an improvement of the activity below 3 mmol L^{-1} of NaCl concentration, whereas the activity did not improve above 3 mmol L^{-1} . The temperature dependency was examined as well. Although the activity was improved at temperatures below 343 K, it was almost constant in temperatures above 343 K. From the results of NaCl concentration dependency and IR measurements, a reaction mechanism in which methoxide ions generated on [bmim]M20 by dissociative methanol adsorption react with ethyl butyrate after they diffuse outside of the micropores was proposed.

References

- [1] E. Yoda, J. Phys. Chem. C 113 (2009) 9851-9856.
- [2] E. Yoda, Apple. Catal. A 375 (2010) 230-235.
- [3] K.M. Dieter, C.J. Dymek, N.E. Heimer, J.W. Rovang, J.S. Wilkes, J. Am. Chem. Soc. 110 (1988) 2722–2726.
- [4] G. Ranga Rao, T. Rajkumar, B. Varghese, Solid State Sci. 11 (2009) 36-42.
- [5] P.A. Jacobs, R. von Ballmoos, J. Phys. Chem. 86 (1982) 3050-3052.
- [6] A. Zecchina, S. Bordiga, G. Spoto, D. Scarano, G. Petrini, G. Leofanti, M. Padovan, C. Otero Arean, J. Chem. Soc., Faraday Trans. 88 (1992) 2959–2969.
- [7] V.L. Zholobenko, M.A. Makarova, J. Dwyer, J. Phys. Chem. 97 (1993) 5962–5964.
 [8] L.M.K. Kustov, V.B. Kazansky, S. Beran, L. Kubelkova, P. Jiru, J. Phys. Chem. 91 (1987) 5247–5251.
- [9] A. Zecchina, F. Geobaldo, G. Spoto, S. Bordiga, G. Ricchiardi, R. Buzzoni, G. Petrini, J. Phys. Chem. 100 (1996) 16584–16599.
- [10] F. Wakabayashi, J.N. Kondo, K. Domen, C. Hirose, J. Phys. Chem. 100 (1996) 4154-4159.
- [11] O. Marie, P. Massiani, F. Thibault-Starzyk, J. Phys. Chem. B 108 (2004) 5073-5081.
- [12] M. Niwa, K. Suzuki, N. Katada, T. Kanougi, T. Atoguchi, J. Phys. Chem. B 109 (2005) 18749–18757.
- [13] M. Maache, A. Janin, J.C. Lavalley, E. Benazzi, Zeolites 15 (1995) 507–516.
- [14] J.N. Kondo, E. Yoda, H. Ishikawa, F. Wakabayashi, K. Domen, J. Catal. 191 (2000) 275-281.
- [15] E. Yoda, J.N. Kondo, F. Wakabayashi, K. Domen, Phys. Chem. Chem. Phys. 5 (2003) 3306–3310.