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Selective Synthesis of 1-butene through Positional Isomerisation of 2-butene over Mesoporous Silica MCM-41

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Abstract A highly selective and active catalyst for the positional isomerisation of 2-butene into 1-butene has been developed by using a mesoporous silica, MCM-41. The yields of 1-butene as well as total conversion decrease when aluminium or lanthanum was added to the MCM-41 even though the amounts of acid sites increase. FT-IR spectra proved that the H site due to the silanol group may act as an active site for the positional isomerisation of 2-butene to 1-butene.

Keywords Positional isomerisation · Butene · MCM-41

1 Introduction

1-butene has been used as a co-monomer for the production of linear low-density polyethylene and polybutene, and the need for it is continually increasing. Currently, 1-butene is produced through separation processes from C_4 fractions in the naphtha cracking center of a petrochemical plant. When these processes are completed, C_4 raffinate-III, which contains much 2-butene, is remained. Therefore, it is necessary to convert 2-butene into 1-butene with higher added values through positional isomerisation. Since there are possibilities of generating iso-butene through skeletal isomerisation, octene and dodenene through oligomerization, and other light hydrocarbons through cracking, selective positional isomerisation of 2-butene into 1-butene is needed.

The technology for the production of isobutene through skeletal isomerisation of normal butene has already been commercialised [1–3]. In skeletal isomerisation, the ferrierite catalyst is mainly used because it has a micropore, many acid sites, and high acid strength [4]. However, there is yet no commercial process producing 1-butene through positional isomerisation of 2-butene, and there are only a few research results about it [5–9]. The results presented so far with respect to positional isomerisation mainly used catalysts modified based on Al_2O_3 [5–7]. To generalise the research results on the positional isomerisation of 2-butene, the catalysts with fewer and weaker Brönsted acid sites and many Lewis acid sites are useful for the synthesis of 1-butene [6, 8].

Mesoporous materials, obtained by the favourable self-assembly between organic templates and inorganic precursors, have opened many new possibilities for applications in catalysis, separation, and nano-science due to their large, controllable pore sizes, high surface areas and

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easy functionalisation [10]. In general, the mesoporous silica materials are modified with inorganic elements such as aluminium and transition metals or organic functional groups in order to utilise the mesoporous materials as a catalyst, because the silica framework is of limited use in catalysis.

In the present work, a highly selective and active catalyst for the positional isomerisation of 2-butene into 1-butene has been developed by using a mesoporous silica, MCM-41. To the best of our knowledge, the mesoporous silica material without any acid sites is utilised for the first time to the positional isomerisation of 2-butene. The mesoporous silica material gives very low side-reaction products such as isobutene through skeletal isomerisation and the generation of octene and dodecene through oligomerisation, because its acid sites are almost nil or very weak. Additionally, we have also investigated the active site of pure silica MCM-41 for the positional isomerisation of 2-butene to 1-butene.

2 Experiment

The mesoporous silica, MCM-41 was synthesized following the procedures described elsewhere [11, 12]. After dissolving 12.15 g of cetyltrimethylammonium bromide (CTABr) in 140 g of distilled water, the 50 g of sodium silicate solution (20 wt.% SiO_2, Na/Si = 0.5) was added. The reaction mixture was heated to 100 °C in an oven for 24 h, and subsequently cooled to room temperature. After adjusting the pH to 10 with 50% acetic acid solution, the mixture was reacted again at 100 °C for 24 h. The cycle of cooling, pH adjusting and heating the mixture was carried out twice more. The white precipitate was filtered, washed in distilled water and dried at 100 °C overnight. The product was washed with HCl/EtOH mixture, dried at 100 °C and finally calcined at 550 °C for 4 h. An aluminium-containing MCM-41 (Al-MCM-41, SiO_2/Al_2O_3 = 20) was prepared by impregnating $AlCl_3$ into the pure silica MCM-41 and by calcination at 550 °C. Lanthanum-containing material (La-Al-MCM-41, La 7 wt.%) was also made by impregnating lanthanum nitrate into the Al-MCM-41 and subsequent calcination. We also prepared La_2O_3/silicated Al_2O_3 [6], Na_2O-modified Al_2O_3 [6], and $MnO/\eta\text{-}Al_2O_3$ [5], following the procedures described in previous papers and patents, in order to compare their catalytic activities for positional isomerisation of 2-butene with that of MCM-41.

The acidic property of the samples was analysed using temperature-programmed desorption (TPD) of chemisorbed ammonia. A 0.02 g sample was placed in a quartz tubular reactor and pretreated in a helium flow, heated to 500 °C with 10 °C/min, and kept at 500 °C for 2 h. The samples were cooled to 100 °C, and an ammonia pulse was injected. After the physisorbed ammonia was purged with helium, TPD was carried out.

The natures of the acid sites were investigated using pyridine as the probe molecule. Self-supported wafers of the samples were prepared with 3 tons pressure applied. All the samples were subjected to a vacuum in the sample holder until a pressure of 10^{-3} Torr was attained, followed by their activation at 350 °C for 1 h. Pyridine vapor was admitted in doses until the catalyst surface was saturated. Pyridine was then desorbed until a pressure of 10^{-3} Torr was reached to ensure that there was no more physisorbed pyridine on the wafers. Infrared spectra were recorded using a Perkin–Elmer FT-IR PE2000 instrument. The wafers that contained chemisorbed pyridine were subjected to thermal treatment at 100, 150, 200, 250, and 300 °C, and the IR spectra were recorded in situ.

2-Butene isomerisation reaction was performed using a fixed bed reactor containing 0.13 g of the catalyst. The reaction temperature, pressure and the weight hourly space velocity (WHSV) of 2-butene were 450 °C, 1 atm and 70 h^{-1}, respectively. The products were analysed using a gas chromatography for 2 h from the beginning of the reaction.

3 Results and Discussion

Thermodynamic equilibrium of 2-butene isomerisation can be obtained by calculation. In order to obtain the heat of reaction generated from the conversion of cis-2-butene and trans-2-butene to 1-butene through isomerisation, we calculated the standard heat of formation for each component through PRO/II with PROVISION. After the standard enthalpy of formation and the standard Gibbs free energy of each component were obtained, they were used to calculate the equilibrium constant of chemical reaction. Equilibrium conversion was obtained from the equilibrium constant of chemical reaction and presented in Fig. 1. The equilibrium mole of 1-butene at this reaction condition is 26.3%.

In the case of the reaction without catalyst, 2-butene hardly reacts under the reaction condition, 450 °C, 1 atm, and WHSV 70.0 h^{-1}. Figure 2 shows the yields and product selectivity of 2-butene isomerisation using various catalysts. The ferrierite gives the highest conversion among the catalysts, but the selectivity for 1-butene is low because the ferrierite causes the formation of isobutene through skeletal isomerisation. Thus, the ferrierite seems to be inappropriate as a catalyst for positional isomerisation of 2-butene. Other modified Al_2O_3 catalysts, reported in various literatures, result in 1-butene as the major product under the same conditions. Surprisingly, the pure silica MCM-41 catalyst, which may not have any acid sites,

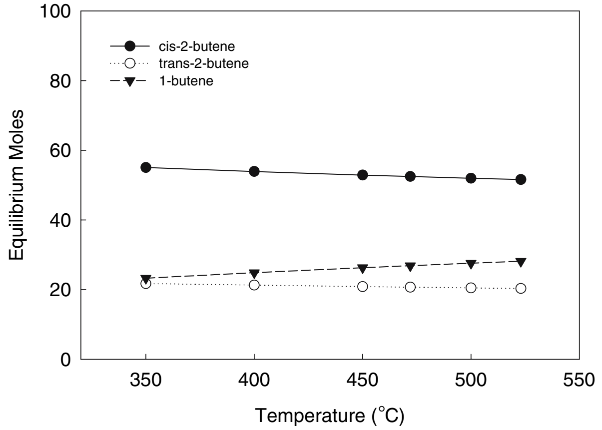

Fig. 1 Thermodynamic equilibrium of butane-2 positional isomerisation (1 atm)

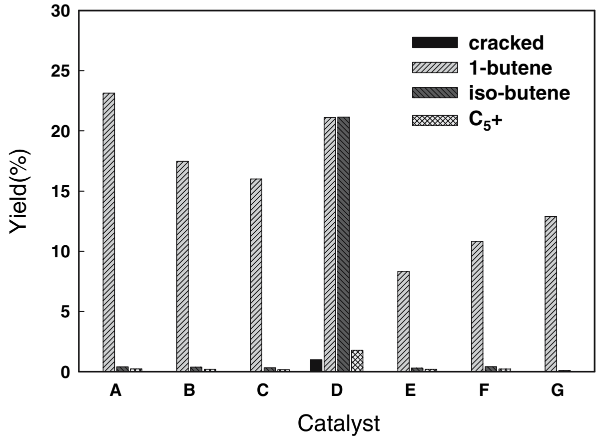

Fig. 2 Yield of 2-butene isomerisation over catalysts: (**A**) MCM-41, (**B**) Al-MCM-41, (**C**) La-Al-MCM-41, (**D**) ferrierite, (**E**) Na_2O/Al_2O_3, (**F**) La_2O_3/silicated Al_2O_3 and (**G**) $MnO/\eta\text{-}Al_2O_3$ (WHSV:70.0 h^{-1}, Reaction Temp.: 450 °C)

exhibits very high yield and excellent selectivity for the production of 1-butene from 2-butene, as shown in Fig. 2. Furthermore, the yields of 1-butene as well as total conversion decrease when aluminium or lanthanum was added to the MCM-41 even though the amounts of acid sites increase [12], while there are few differences between these catalysts in terms of their selectivity with respect to 1-butene. Generally, it is expected that the catalytic activity of the isomerisation should be improved as the acid site increases, but the results in Fig. 2 shows the opposite tendency.

Ammonia-temperature-programmed desorption (NH_3-TPD) [13] and pyridine infra-red spectroscopy (Py-IR) [14] are obtained in order to characterise the amount, strength, and types of acid sites which are useful for the interpretation of the differences between the catalytic activities in Fig. 2. Figure 3 shows a comparison of the results of the NH_3-TPD with ferrierite, alumina and pure silica MCM-41.

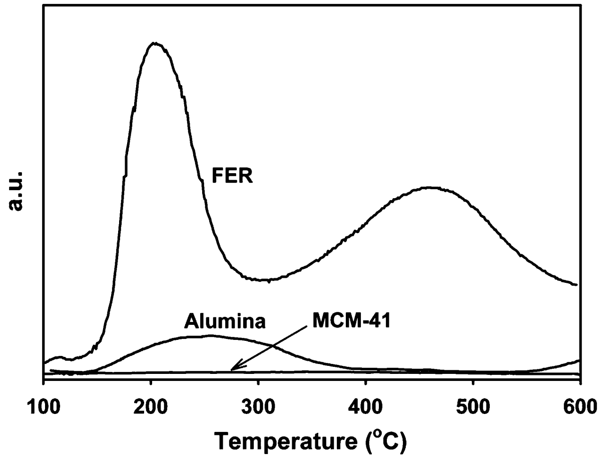

Fig. 3 NH_3-TPD results of ferrierite, Al_2O_3 and pure silica MCM-41

The ferrierite shows two peaks around 220 °C and 470 °C, which can be indexed to the weak acid site and strong acid site, respectively. In case of Al_2O_3, a weak acid site only around 260 °C is appeared and the amount of this acid site is much less than that of the ferrierite. As expected, the MCM-41 does not show any peak in NH_3-TPD. The strong acid site of ferrierite plays a significant role in the production of isobutene, a skeletal isomerisation product. On the other hand, the Al_2O_3 has more advantages in the production of 1-butene through positional isomerisation rather than the isobutene through skeletal isomerisation, because it does not have a strong acid site [6, 8]. However, it is very strange that the pure silica MCM-41 exhibits excellent activity and selectivity for 1-butene formation from 2-butene via the positional isomerisation due to its lack of acidity.

Figure 4 shows the FT-IR spectra of the –OH group of MCM-41, Al-MCM-41, and La-Al-MCM-41 yielded in 350 °C and vacuum (10^{-3} Torr). There is a peak of 3,740 cm^{-1}, which falls into the isolated Si–OH of the

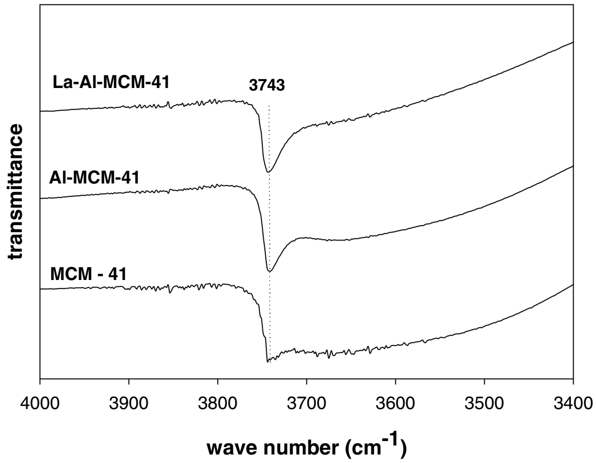

Fig. 4 FT-IR spectra of the hydroxy regions (350 °C, 10^{-3} Torr)

non-acidic silanol (Si–OH) group [13]. Thus, we can find out that even if they undergo calcination at a high temperature, MCM-41, Al-MCM-41, and Al-La-MCM-41 maintain the silanol group. On the other hand, MCM-41 shows a wide band of 3,600–3,700 cm^{-1} differently from Al-MCM-41, La-Al-MCM-41. The peak in this domain can be seen to be due to hydrogen bond to the silanol group of the geminal type or of the associated type [14]. That is to say, it can be interpreted as weak hydrogen bond generated by silanol. If aluminum or lanthanum is added, this silanol group seems to be decreased.

Figure 5 shows the FT-IR spectra of the pyridine adsorbed on the MCM-41 in the region 1,400–1,800 cm^{-1} subjected to different thermal treatments in the range of 25–300 °C. The samples exhibited bands at 1,445 and 1,596 cm^{-1} at 25 °C. These bands decreased with thermal treatment and disappeared at 300 °C. It was reported that these bands are the only bands found in pure siliceous material and could be produced by hydrogen-bonded pyridine with silanol groups [14–17].

Py-IR results (Fig. 6) also indicate that the MCM-41 does not have Brönsted (B) acid site and the Lewis (L) acid site, whereas there are both the B and L acid sites on the ferrierite. In the cases of Al-MCM-41 and La-Al-MCM-41, the acid sites increase slightly compared to those of pure silica MCM-41. However, the catalytic results in Fig. 1 do not correspond to such the amount of acid sites. Thus, it is difficult to explain the roles of L and B acid sites for the positional isomerisation, and why the MCM-41 gives the excellent activity, based only on the acid sites. As shown in the Py-IR results (Fig. 6), the mesoporous materials give peaks at 1,445 and 1,596 cm^{-1}, which can be indexed as bands generated by hydrogen-bonded pyridine (H) [14–17], whereas there is no H band in ferrierite. The amount of H band is greatest in the MCM-41, indicating that the H band seems to be come from the pyridine hydrogen bonded to the silanol group (Si–OH) [18]. Thus, it is reasonable that the H site may act as an active site for the positional isomerisation of 2-butene to 1-butene.

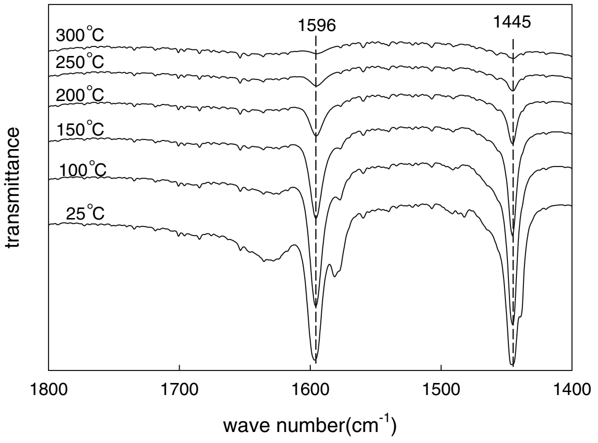

Fig. 5 FT-IR spectra of adsorbed pyridine on MCM-41 following thermal treatment (10^{-3} Torr)

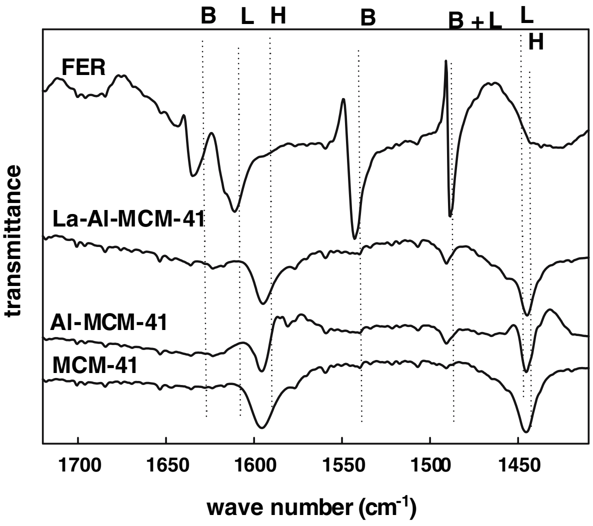

Fig. 6 FT-IR spectra of adsorbed pyridine (150 °C, 10^{-3} Torr)

Figure 7 shows the FT-IR spectra obtained from the MCM-41 depending on evacuation temperature. Two different peaks, a sharp peak at 3,740 cm^{-1} due to the isolated Si–OH, and a wide band in the range of 3,400–3,700 cm^{-1}

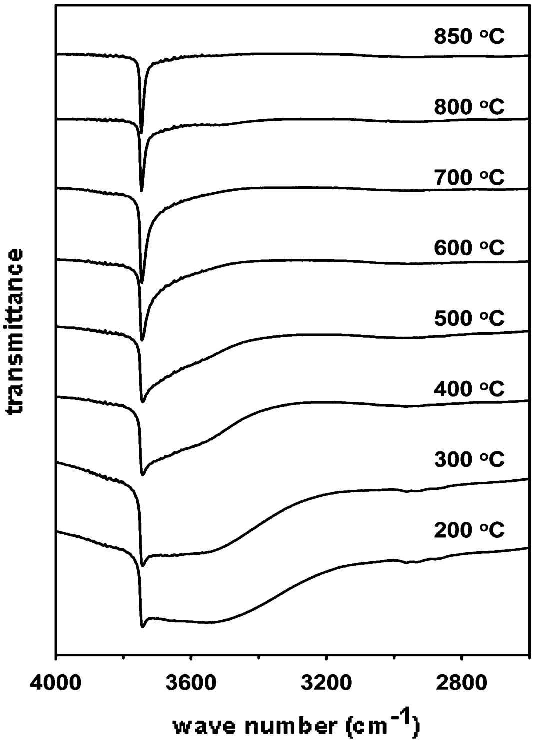

Fig. 7 FT-IR spectra of the pure silica MCM-41 depending on the evacuation temperature

due to the geminal-type or associated-type silanol group [18], are observed from the MCM-41 samples at low temperature (<500 °C). When the evacuation temperature is higher than 800 °C, the wide IR band disappears, and only the peak at 3,740 cm^{-1} exists.

Therefore, we have carried out the positional isomerisation reaction of 2-butene using the MCM-41 samples which are calcined at different temperatures, in order to investigate the active sites. Figure 8 shows the result of 2-butene isomerisation with the calcination condition on MCM-41 changed. When the MCM-41 samples are calcined at 550, 600, and 650 °C under ambient air conditions, all the catalysts give the yield of 1-butene around 23.5%, showing insignificant changes. However, the yield of 1-butene drops to 18.0%, when the MCM-41 is evacuated at 600 °C where a part of geminal-type or associated-type silanol group is remained. Furthermore, the yield of 1-butene drops to 5.4%, when the MCM-41 is evacuated at 800 °C where the geminal-type or associated-type silanol group is disappeared. Therefore, it is reasonable that not only the isolated silanol group but also the geminal-type or associated-type silanol groups play a very important role in the positional isomerisation of 2-butene.

In an attempt to figure out the roles of a weak acid site, MCM-41 was treated with 0.1 N NaOH. As shown in Fig. 10, the weak acid site was reduced by neutralization according to the pyridine FT-IR. Figure 11 shows that the yield of 1-butene dropped to 8.4% over the alkali-treated MCM-41. Thus it's confirmed that the weak acid site worked as an active site during the positional isomerisation of 2-butene.

The characteristics and reaction activity of pure silica were compared with those of MCM-41 to verify the roles of a silanol group. Silica was calcined at 600 °C under nitrogen flow in a fluidized bed quartz reactor for 10 h. The surface area of the silica was 475 m^2/g, which was about half that of MCM-41 (933 m^2/g). As shown in Fig. 9, it was found that the silica had relatively smaller amounts of the geminal-type or associated-type silanol groups than MCM-41. Figure 10 indicates that the silica contains much smaller amounts of weak acid sites than MCM-41. The results of reaction experiments with pure silica revealed that the yield of 1-butene (9.2%) was much less than that of MCM-41 but it had the activity of positional isomerisation of 2-butene (Fig. 11). Thus it's demonstrated that a weak acid site by the Si–OH group worked as an active site in the positional isomerisation of 2-butene and that both the isolated silanol group and the geminal-type or associated-type silanol group acted as an active site in the positional isomerisation of 2-butene.

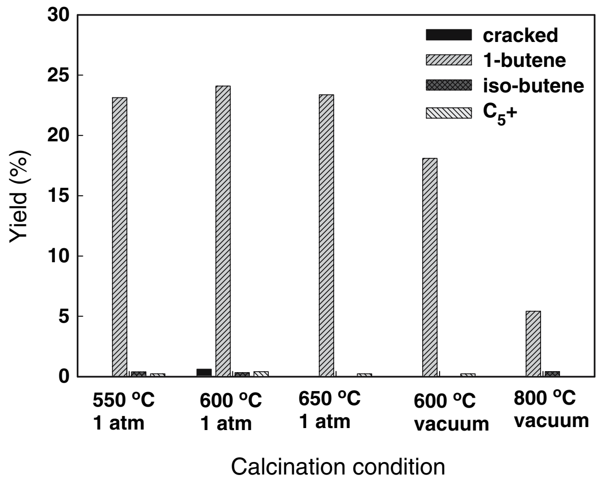

Fig. 8 Effect of calcination of MCM-41 on 2-butene isomerisation (WHSV: 70 h^{-1}, Temp.: 450 °C)

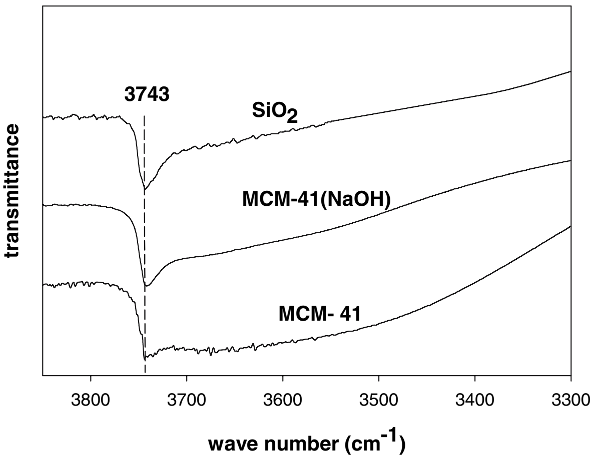

Fig. 9 FT-IR spectra of the hydroxy regions (350 °C, 10^{-3} Torr)

4 Conclusions

The pure silica MCM-41 exhibits the excellent activity and selectivity for the positional isomerisation of 2-butene to

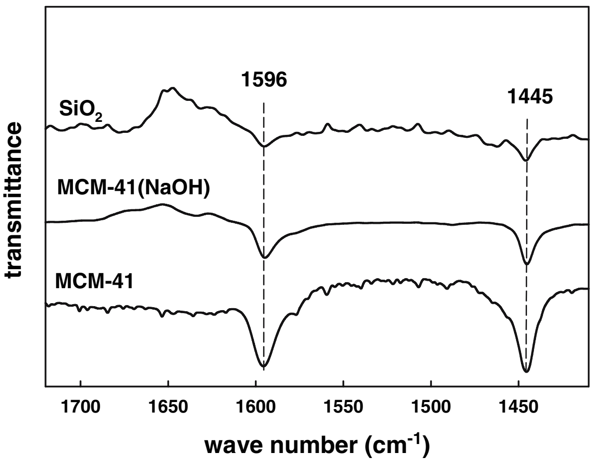

Fig. 10 FT-IR spectra of adsorbed pyridine (150 °C, 10^{-3} Torr)

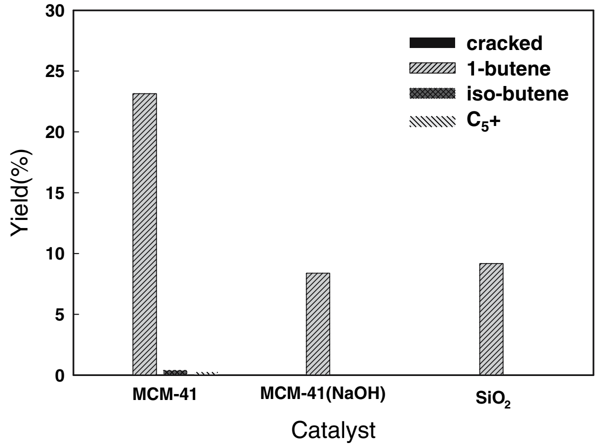

Fig. 11 Yield of 2-butene isomerisation over MCM-41, alkali-treated MCM-41 and silica (WHSV: 70.0 h^{-1}, Reaction Temp.: 450 °C)

1-butene, compared with those of the well-known Al_2O_3 -based catalysts and ferrierite zeolite. This unusual catalytic activity of MCM-41 in positional isomerisation is probably due to the silanol (Si–OH) group. The MCM-41 catalyst, composed of pure silica, is industrially useful because it shows better catalytic activity to produce 1-butene from 2-butene through positional isomerisation.

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