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Isomerization of 1-Butene to 2-Butene Catalyzed by Metal−Organic Frameworks

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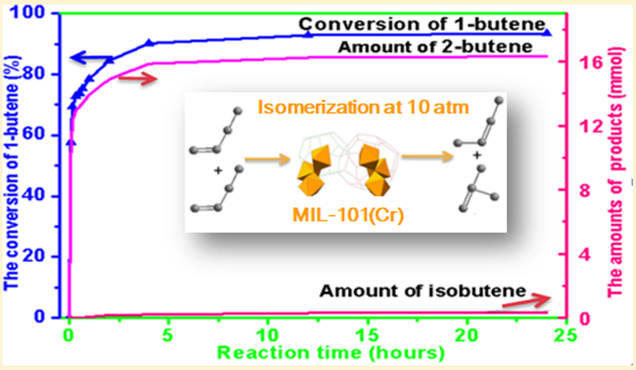
Supporting Information

ABSTRACT: MIL-100 and MIL-101 were synthesized and evacuated to generate a series of heterogeneous catalysts for isomerization of 1-butene. Their crystal structures and pore properties were characterized by PXRD and nitrogen adsorption−desorption techniques. These catalysts showed high catalytic activity for isomerization of 1-butene and high selectivities for 2-butene at room temperature. Moreover, the MIL-101 (Cr) catalyst evacuated at 200 °C exhibited the largest BET surface area of 2759 m^2 g^{-1}. At the same time, conversion of 1-butene and the highest selectivity to 2-butene were up to 93.38% and 98.08%, respectively. This work indicated that MOFs containing coordinatively unsaturated metal sites might be promising catalysts for olefin isomerization under mild conditions.



■ INTRODUCTION

As environmental requirements have become more stringent, methyl *tert*-butyl ether (MTBE) has been banned as a gasoline additive in some developed countries and regions due to contamination of groundwater as a carcinogen.[1] Isooctane is regarded as an ideal alternative component with a high octane number. At present, in industry isooctane is obtained through alkylation of butene with isobutane. Because the alkylation of 2-butene or isobutene with isobutane produces isooctane with a higher octane number, 1-butene is usually isomerized to 2-butene or isobutene, which is then alkylated with isobutane to obtain isooctane.

The isomerization of 1-butene has attracted wide interest from the perspectives of commercial demand and catalytic issues. A large amount of catalysts have been reported for the reaction, such as liquid and solid acids,[2] metal halide,[3] and zeolite molecular sieves.[4] They are all acidic catalysts with different acid centers, acid types, acid intensity, and distribution of acidic sites.[5] Generally, the butene isomerization reaction is carried out following a single molecule carbon cation mechanism,[6] and reaction conditions are harsh, requiring high temperature and high pressure.

Additionally, liquid and solid acid catalysts have obvious disadvantages such as serious corrosion of equipment, difficulty in recovery, and large environmental pollution. Metal halide catalysts are sensitive to water in the feedstream and the presence of water can lead to halogen elution, thereby decreasing the catalytic activity. For widely used zeolite molecular sieve catalysts, carbon deposition is a major concern resulting in the reduction of catalytic activity or even deactivation.[7] Highly active, recyclable, and environmentally friendly catalysts for butene isomerization under mild reaction conditions are extremely desirable but challenging.

Metal−organic frameworks (MOFs) are a new family of crystalline porous materials formed by self-assembly of organic ligands and metal ions. Due to their special periodic structures, large specific surface areas, high porosity, and unique adsorption properties, they have been widely applied in storage, adsorption, electrochemistry, and catalysis.[8] In particular, some MOFs possess coordinatively unsaturated metal sites (CUS), which are evenly and stably distributed due to the crystalline nature of MOFs. These CUS can interact with guest molecules in adsorption and catalysis and serve as catalytic active sites. As far as we know, it has not been reported that MOFs with CUS are used as catalysts in olefin isomerization.

In this paper, two common types of MOFs with zeolite-type architecture, i.e., MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) have been used to catalyze the isomerization of 1-butene. The MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) are heated under vacuum to produce high content of CUS. The CUS-containing MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) can isomerize 1-butene to 2-butene and isobutene almost completely at room temperature and 10 atm, and the selectivity to 2-butene is as high as 98%. Furthermore, the

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MIL-101 (Cr) catalyst can be recycled at least four times maintaining most of its original catalytic activity. Finally, the catalytic mechanism for the isomerization of 1-butene to 2-butene is discussed.[9]

■ RESULTS AND DISCUSSION

Characterization of the Catalysts. For the as-synthesized MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr), inorganic metal ions and organic ligands are coordinatively bonded to each other to form network structures with abundant pores, and these pores are occupied by free water molecules, bound water molecules, and F^- or OH^- counteranions. After the removal of the guest molecules, MIL-100 (Fe and Cr) has two types of mesoporous cages with free internal diameters of 2.5 and 2.9 nm, respectively. The large cage has a window opening of 0.86 nm × 0.86 nm and the small cage has a window opening of 0.55 nm × 0.55 nm.[10] MIL-101 (Fe and Cr) possess two larger mesoporous cages with free internal diameters of 2.9 and 3.4 nm and window openings of 1.2 nm × 1.2 and 1.6 nm × 1.6 nm, respectively.[10]

The structural units of MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) are μ_3-oxo-centered trimers of Fe (III) or Cr (III) octahedra. At the end of the octahedron of per trimer, there are two bound H_2O molecules and one F^- or OH^- group. The free water molecules located in pores can be easily removed by heating under vacuum below 100 °C, while the terminal bound water molecules can be removed at more than 100 °C under vacuum, forming a lot of CUS in the structure.[11]

The powder X-ray diffraction (PXRD) patterns of the as-syntheszied MIL-100 (Fe), MIL-101 (Fe), MIL-100 (Cr), and MIL-101 (Cr) were consistent with the simulated data reported in the literature (Figure 1A and Figure S1), confirming the pure phase. Fourier transformation infrared spectra (FT-IR) characterization results showed the presence of the characteristic vibration bands of carboxylic groups in the MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) frameworks at 1630 and 1400 cm^{-1} in Figure S3, confirming that the carboxylic groups were coordinated to the metal ions in the frameworks. Large bands around 3500 cm^{-1} also confirmed the presence of an amount of water molecules in the four samples.

In order to give a reference for the choice of treatment temperature to remove water molecules in the pore channels and thus expose CUS, thermal gravimetric analysis (TGA) of MIL-101 (Fe and Cr) and MIL-101 (Fe and Cr) was performed in nitrogen atmosphere. TGA results revealed that there were weight losses from approximately 40−150 °C for the as-synthesized samples, which could be attributed to the release of the guest water molecules. Another weight loss from approximately 350−550 °C was due to decomposition of the whole framework and the departure of OH^-/F^- groups. The moisture contents of MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) were widely varied from 10% to 25% in Figure S4, depending on the coordinating water molecules and laboratory humidity. Based on the TGA, the appropriate evacuation temperature range for the samples was 150−350 °C.

According to the literature reports,[12] when MIL-100 (Fe) and MIL-100 (Cr) were evacuated from 150 to 250 °C, the diffraction peaks and specific surface areas gradually became strong. The higher evacuation temperature than 250 °C resulted in the decrease of PXRD peak intensity and specific surface areas. MIL-100 had the largest specific surface areas, the strongest diffraction peaks, and thus the highest crystallinity when the evacuation temperature was 250 °C. We treated MIL-101 (Fe) and MIL-101 (Cr) under vacuum from 160 to 220 °C (Figure S2a,b) and found that when the evacuation temperature was 200 °C, MIL-101 (Fe and Cr) had the strongest diffraction peaks. However, when the evacuation temperature was increased to 220 °C, the diffraction peak at $2\theta = 5.10°$ disappeared, indicating that the crystal structure was destroyed. Therefore, the optimal evacuation temperatures for MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) were 250 and 200 °C, respectively. The PXRD of MIL-100 and MIL-101 (Fe and Cr) evacuated under optimal temperatures were shown in Figure 1B. The evacuated MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) samples maintained all the diffraction peaks for the corresponding as-synthesized samples, showing that the crystal structures were intact.

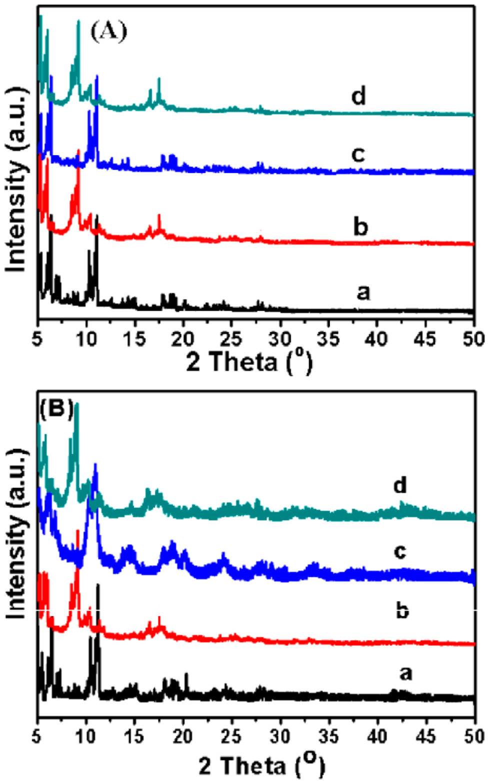

Figure 1. (A) PXRD patterns of the as-synthesized (a) MIL-100 (Fe), (b) MIL-101 (Fe), (c) MIL-100 (Cr), and (d) MIL-101 (Cr). (B) PXRD patterns of (a) MIL-100 (Fe) evacuated at 250 °C, (b) MIL-101 (Fe) evacuated at 200 °C, (c) MIL-100 (Cr) evacuated at 250 °C, and (d) MIL-101 (Cr) evacuated at 200 °C.

The nitrogen adsorption−desorption isotherms were measured for MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) evacuated under optimal temperatures at 77 K and shown in Figure S5. All evacuated samples showed a typical type-I isotherm with the presence of both micropores and mesopores. As shown in Table S1, the MIL-100 (Fe) and MIL-100 (Cr) displayed the BET areas of 1920 and 2340 $m^2 \cdot g^{-1}$ and the pore volumes of 0.92 and 1.32 $cm^3 \cdot g^{-1}$, respectively. For MIL-101 (Fe) and MIL-101 (Cr), the BET areas were 2010 and 2759 $m^2 \cdot g^{-1}$, and the pore volumes were 1.09 and 1.98 $cm^3 \cdot g^{-1}$, respectively.

Isomerization of 1-Butene. The catalytic performances of evacuated MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) for the isomerization of 1-butene were investigated. The conversion percentage of 1-butene and the amounts of isomerization products and selectivity of 2-butene were

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shown in Figure 2 and Figure S6 and Table S2. MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) catalysts could catalyze the conversion of 1-butene to 2-butene or isobutene, and had good conversion and high selectivity under 1 atm. As the reaction time was increased, the conversion percentage of 1-butene and the amounts of isomerization products were increased, and then the equilibrium was reached at 24 h. The equilibrium conversion percentages of 1-butene ranged from 12.96% to 38.78% under 1 atm, while the equilibrium conversion percentages under 10 atm and under nitrogen atmosphere ranged from 92.31% to 95.57%. The selectivities of 2-butene were in the range of 73.20−100%. Therefore, under 10 atm the MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) catalysts had faster reaction rates and higher conversion percentages of 1-butene, but the same selectivities for 2-butene. The faster reaction rate and higher conversion percentages were possibly because more 1-butene molecules entered the catalyst pores at high pressure, which greatly increased the concentration of 1-butene as well as the contact chances between 1-butene and CUS of catalysts. Additionally, the reaction pressure had little effect on the catalytic selectivity, suggesting the same catalytic mechanism was followed under 1 and 10 atm.

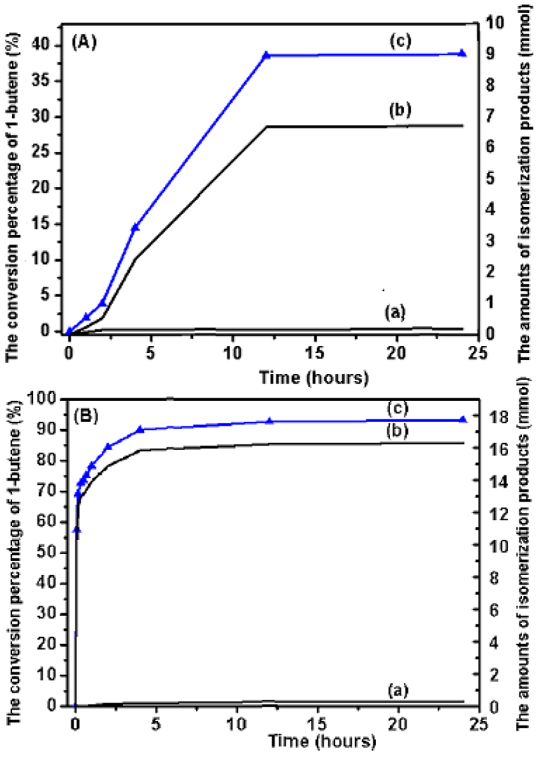

Figure 2. Conversion percentage of 1-butene and the amounts of isomerization products (A) at 1 atm and (B) at 10 atm based on the catalyst MIL-101 (Cr). (a) Plot of amount of isobutylene vs reaction time. (b) Plot of amount of 2-butene vs reaction time. (c) Conversion percentage of 1-butene vs reaction time. Reaction conditions: 1-butene (wt % = 10%, 17.82 mmol) in *n*-hexane 15 mL (10 g), catalyst 3 μmol, N_2 atmospere, reaction time 24 h, temperature 25 °C, [Al]/[Cr] = 500, GC measurement.

The equilibrium catalytic performances of the four MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) catalysts at 24 h under 10 atm as well as other reported catalysts for isomerization of 1-butene were listed in Table 1. For montmorillonite K10 and H_2SO_4 (3 M) catalysts, the conversion percentages of 1-butene and the selectivity of 2-butene were 74.44% and 94.68% at 400 °C,[13] respectively. For the MeCl/BeO catalyst, the conversion percentages of 1-butene and the selectivity of isobutylene were 29.20% and 76.20% at 430 °C,[14] respectively. H-HPM-1 zeolites were used as catalysts and the conversion percentages of 1-butene and the selectivity of isobutylene were 61.19% and 97.00% at 400 °C,[15] respectively. Notably, the MOF catalysts in this paper showed the conversion percentages of 1-butene and selectivity of 2-butene over 92.00% and 91.00%, respectively. Moreover, the MOFs catalysts were relatively environmentally friendly and the reaction conditions were mild.

Comparing the isomerization performances of the four MOFs catalysts (Table S2), we found that the Fe-containing MOFs had higher conversion of 1-butene, while the Cr-containing MOFs had better selectivity of 2-butene. For the two MOFs containing the same metal, MIL-101 (Fe or Cr) had slightly higher conversion percentage of 1-butene and slightly better selectivity of 2-butene than MIL-100 (Fe or Cr). However, the influence of the pore structure was relatively small compared with the metal nature, indicating that the pores of MIL-100 (Fe and Cr) were already sufficiently large to expose sufficient metal sites to isomerize 1-butene.

In order to further comfirm the effect of metal active site exposure on catalytic performance, MIL-101 (Cr) was evacuated at 100, 200, and 220 °C. The conversion percentage of 1-butene, the amounts of isomerization products, and the selectivity of 2-butene are shown in Table 2. When the vacuum temperature was as low as 100 °C, the active sites were not sufficiently exposed and the conversion percentage of 1-butene was only 53.19%. However, when the high vacuum temperature was 220 °C, the structure was destroyed resulting in the low conversion percentage of 24.29%. The optimal evacuation temperature for MIL-100 (Cr) was 250 °C, at which MIL-101

Table 1. Conversion Percentage of 1-Butene, Amounts of Isomerization Products, and Selectivity to 2-Butene or Isobutylene[a]

entry	catalysts	pressure (atm)	temperature (°C)	2-butene (mmol)	isobutene (mmol)	conversion percentage (%)	selectivity (%)
1	MIL-100 (Fe)	10 atm	25	15.47	1.39	94.61	91.76 (2-butene)
2	MIL-101 (Fe)	10 atm	25	15.84	1.19	95.57	93.01 (2-butene)
3	MIL-100 (Cr)	10 atm	25	16.00	0.45	92.31	97.26 (2-butene)
4	MIL-101 (Cr)	10 atm	25	16.32	0.32	93.38	98.08 (2-butene)
5	K10/H_2SO_4 (3 M)	1 atm	400	–	–	74.44	94.68 (2-butene)
6	MeCl/BeO	1 atm	430	–	–	29.20	76.20 (isobutylene)
7	H-HPM-1 zeolites	1 atm	400	–	–	61.19	97.00 (isobutylene)

[a] Reaction conditions: MIL-100 (Fe and Cr) activated at 250 °C, MIL-101 (Fe and Cr) activated at 200 °C, 1-butene (w% = 10%, 17.82 mmol) in *n*-hexane 15 mL (10 g), catalyst 3 μmol, N_2 atmospere, reaction time 24 h, pressure 10 atm, and temperature 25 °C, [Al]/[Fe] = 500 or [Al]/[Cr] = 500, GC measurement.

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Table 2. Effects of the Cocatalyst and Activated Temperature on 1-Butene Isomerization for MIL-101 (Cr) Catalyst[a]

entry	activated temperature (°C)	catalyst	Et_2AlCl	2-butene (mmol)	isobutene (mmol)	conversion percentage (%)	$S_{2\text{-butene}}$ (%)
1	200	+	+	16.32	0.32	93.38	98.08
2	200	+	-	1.13	0.00	6.34	100.00
3	200	-	+	0.00	0.00	0.00	0.00
4	100	+	+	9.38	0.10	53.19	98.95
5	220	+	+	4.26	0.07	24.29	98.38

[a] Reaction conditions: MIL-101 (Cr) activated at 200 °C, 1-butene (w% = 10%, 17.82 mmol) in *n*-hexane 15 mL (10 g), Catalyst 3 μmol, N_2 atmospere, reaction time 24 h, pressure 10 atm, and temperature 25 °C, [Al]/[Cr] = 500, GC measurement, + : represent addition, -: represent not addition.

(Cr) presented the largest specific surface area, the highest crystallinity, and the highest catalytic activity.

When cocatalyst diethylaluminum chloride (Et_2AlCl) or MIL-101 (Cr) catalyst was added separately (Table 2), there was almost no catalytic activity. This suggested the cocatalyst Et_2AlCl participated the isomerization reaction and assisted the MIL-101 (Cr) catalyst for catalysis. The amount of cocatalyst Et_2AlCl on the isomerization was further investigated. The decrease of the ratio of [Al]/[Cr] to 100:1 and 10:1 resulted in the greatly reduced conversion of 87.37% and 22.95%, respectively. When the[Al]/[Cr] ratio was increased to 600:1, the conversion was 93.94% (Table S3), which was only slightly higher than the corresponding conversion 93.38% at the [Al]/[Cr] ratio of 500:1. So, the [Al]/[Cr] ratio of 500:1 was chosen considering the cost of catalyst and cocatalyst under the premise of high conversion.

We speculated that the ethyl anion of the Et_2AlCl was first inserted into the CUS. Then, the ethylene was produced and left, forming complex metal hydride, which was regarded as the catalytically active center of the isomerization reaction (see the following discussion on catalytic mechanism for detail). In addition, cocatalyst might clean up impurities in the pores, allowing more CUS to be exposed and improve catalytic activity. Therefore, MOFs with CUS might be promising catalysts for isomerization of olefins.

The recycling performance of MIL-101 (Cr) catalyst was measured and shown in Table 3. The MIL-101 (Cr) catalyst could be recycled at least four times maintaining >60.00% of the initial conversion and >98.00% of the 2-butene selectivity. However, the conversion percentage of 1-butene decreased with an increasing number of cycles. This was possibly because after the metal active center was alkylated by cocatalyst Et_2AlCl, the $AlCl_3$ produced was decomposed to form $Al(OH)_3$ precipitate in contact with the water vapor in the air, which covered the active sites and decreased the catalytic activity.

Table 3. Catalytic Cycle Performance for MIL-101 (Cr) Catalyst[a]

number of cycles	2-butene (mmol)	iso-butene (mmol)	conversion percentage (%)	$S_{2\text{-butene}}$ (%)
0	16.32	0.32	93.38	98.08
1	15.33	0.33	87.91	97.89
2	13.41	0.35	77.21	97.46
3	11.15	0.35	64.53	96.96
4	10.29	0.36	59.76	96.62

[a] Reaction conditions: MIL-101 (Cr) activated at 200 °C, 1-butene (w % = 10%, 17.82 mmol) in *n*-hexane 15 mL (10 g), catalyst 3 μmol, N_2 atmospere, reaction time 24 h, pressure 10 atm, and temperature 25 °C, [Al]/[Cr] = 500, GC measurement.

Discussionon Catalytic Mechanism for 1-Butene to 2-butene. At present, it is generally believed that transition metal complexes catalyze the isomerization of olefins with two mechanisms, namely, metal hydride addition−elimination mechanism and π-allylic mechanism.[16] For the metal hydride addition−elimination mechanism, olefin is adsorbed to active sites, hydrogen and metal are added to the hydrocarbon double bond, and then the metal and the α-H are removed to change the position of the double bond. For π-allylic mechanism, olefin is adsorbed on active sites to produce a thermodynamically unstable cyclopropyl transition state complex. Then α-H of olefin transfers, and ring opens to form an olefin with the position of double bond changed.

Based on the results reported in the literature as well as our catalytic results,[17] we proposed a metal hydride addition−elimination mechanism for isomerization of 1-butene in Figure 3. First of all, guest molecules or ions in the pore channels of MOFs were removed to produce CUS by heating under vacuum, and the ethyl anions of the Et_2AlCl were inserted into the CUS. Then, the removal of ethylenes from ethyl anions resulted in the formation of complex metal hydrides, which were the catalytically active centers of the isomerization reaction. The complex metal hydrides were added to the double bond of 1-butene, and then along with the elimination of α-H anion of 1-butene and its addition to the metal center to form new active sites, 2-butene was released.

In order to confirm the isomerization mechanism of 1-butene, we tried to separate the intermediates from the reaction mixture and found that they were particularly sensitive to air. For this reason, the reaction mixture was measured through GC/MS and we found that the product contained ethylene as shown in Figure S7. For the π-allylic mechanism, 1-butene is adsorbed on CUS to produce a thermodynamically unstable cyclopropyl transition state complex, and then α-H of olefin transferred, ring-opened to form an olefin with the position of double bond changed, and ethylene cannot be produced during the reaction. Additionally, the MIL-101 (Cr) catalyst was pretreated using $LiAlH_4$ in *n*-hexane under stirring for 30 min to catalyze the isomerization of 1-butene, showing an equilibrium conversion of 23.96%. This result suggested that metal hydride as active species did catalyze the isomerization of 1-butene. Such metal hydride addition−elimination mechanism for olefin isomerization has been reported by Lehmkuhl and Tsienin.[17c] In the paper, the removal of propylenes from allyl anions resulted in the formation of complex metal hydrides, which were the catalytically active center for the isomerization reaction of 1,5-hexadiene at room temperature.

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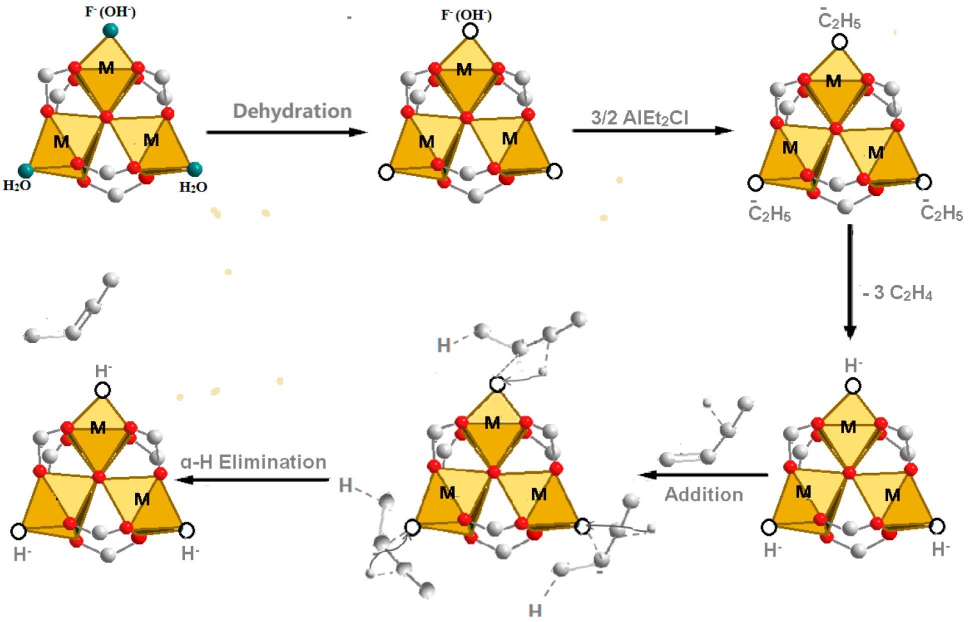

Figure 3. Proposed catalytic mechanism for 1-butene to 2-butene. Only one α-H atom of 1-butene is shown in the 1-butene molecule and all other hydrogen atoms are omitted; M represents Cr^{III} or Fe^{III}.

CONCLUSION

In summary, we have prepared a series of MOF catalysts for 1-butene isomerization by evacuating MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) under optimal temperatures. MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) catalysts can isomerize 1-butene to 2-butene and isobutene almost completely at room temperature and 10 atm with the conversion percentage of 1-butene and selectivity of 2-butene above 92.00% and 91.00%, respectively. In addition, the MOF catalysts are relatively environmentally friendly and the reaction conditions are mild. Furthermore, the MIL-101 (Cr) catalyst can be recycled at least four times maintaining above 60.00% of the initial conversion and above 98.00% of the 2-butene selectivity. This work indicates that MOFs with CUS may be promising isomerization catalysts for olefin.

EXPERIMENTAL SECTION

Preparation of the MIL-100 (Fe and Cr) and MIL-101 (Fe and Cr) Catalysts. MIL-100 (Fe) was prepared according to the literature,[18] MIL-100 (Fe) was hydrothermally prepared from a mixture of Fe (5.0 mmol, 0.28 g), trimesic acid (3.35 mmol, 0.70 g), HF (10.0 mmol, 0.20 g), and HNO_3 (3 mmol, 0.19 g) in deionized H_2O (25 mL). The reaction mixture was stirred for 10 min, then transferred to a Teflon autoclave, and heated at 150 °C for 12 h. The light orange solid product was filtered, washed with deionized water, and further purified using boiling water and hot ethanol for 5 h. The solid was finally dried 36 h at 100 °C in vacuum. MIL-101 (Fe) was synthesized according to the literature,[19] a mixture containing $FeCl_3{\cdot}6H_2O$ (2.45 mmol, 662.2 mg) and terephthalic acid (1.24 mmol, 206.0 mg) in DMF(15 mL). The reaction mixture was transferred to an autoclave and heated at 110 °C for 20 h, then slowly cooled to room temperature, and further purified using boiling water and hot ethanol for 5 h. The solid was dried 36 h at 100 °C in vacuum. MIL-100 (Cr) was obtained according to the literature,[10] CrO_3 (5 mmol, 0.5 g), trimesic acid (5 mmol, 1.05 g), and HF solution (5 mmol, 5 M, 1.0 mL) in deionized water (24 mL) was stirred for 10 min at room temperature. The reaction mixture was transferred to a Teflon Autoclave and heated for 4 days at 220 °C. The resulting green solid was washed with deionized water and hot ethanol, and dried in vacuum at 100 °C. MIL-101 (Cr) was hydrothermally synthesized according to the literature,[20] $Cr(NO_3)_3{\cdot}9H_2O$ (1 mmol, 400 mg), terephthalic acid (1 mmol, 166 mg), and HF (1 mmol, 0.02 mL) in deionized H_2O (4.8 mL, 265 mmol) was stirred for 8 h at 220 °C. The resulting green powder was washed with deionized water, and dried at 100 °C in vacuum.

Procedure for Isomerization of 1-Butene. The reaction was performed using a 300 mL stainless steel autoclave equipped with a stirring bar (Figure S8) and 100 mL Schlenk bottle, which were preheated at 150 °C in vacumm for 60 min and then cooled to room temperature under nitrogen atmosphere. The autoclave and the Schlenk bottle were evacuated using a vacuum pump and backfilled with nitrogen for three times, and then the nitrogen was released. A certain amount of MOF catalyst (3 μmol, based on the number of moles of SBU of MOF) was added to Schlenk bottle under nitrogen, and then the required amount of Et_2AlCl (0.9 M in toluene) cocatalyst was injected into the Schlenk bottle through a dry syringe, and the mixture was stirred for 10 min under nitrogen atmosphere. Subsequently, a suspension of MOF and Et_2AlCl was transferred into a stainless steel autoclave through a dry syringe under nitrogen atmosphere. Then, an ultradry solution of 1-butene in *n*-hexane (15 mL) was injected into the autoclave through the feeding valve. The nitrogen pressure was increased to 1 or 10 atm and kept constant during the reaction at room temperature. After finishing, the reaction steel autoclave was cooled down to −25 °C by the condensing circulation pump, and then depressurized. A small amount of reaction solution was taken out through the feeding valve with a syringe and qualitatively analyzed by GC/MS. All of above air- or moisture-sensitive substances were protected and transferred via Schlenk technique. The peak positions of the desired isomerization products of butene were shown at different retention times in gas chromatography (Figure S7).

The amounts of products, the conversion percentage of 1-butene, and the selectivity of 2-butene or isobutene were calculated according to the following equation:

$$n_i = \frac{A_i}{A_{\text{total}}} \times 17.82\ \text{mmol} \tag{1}$$

$$C\% = \frac{A_{\text{2-butene}} + A_{\text{isobutene}}}{A_{\text{total}}} \times 100\% \tag{2}$$

$$S_i = \frac{A_i}{A_{\text{2-butene}} + A_{\text{isobutene}}} \times 100\% \tag{3}$$

where A_i was the peak areas of 2-butene or isobutene; A_{total} was the total peak areas of C4 olefins. n_i was the molar amount of 2-butene or isobutene; $C\%$ was conversion percentage; S_i was selectivity of 2-butene or isobutene. Calculation based on the each fraction proportional areas to their the total peak areas of C4 olefins in the gas chromatography.

Characterization of the Catalysts and Isomerization Products. All reagents were purchased from commercial sources and used as received. The powder X-ray diffraction (PXRD) patterns were performed using a Rigaku D/MAX-2500 X-ray diffractometer at 40 kV and 40 mA (Cu Kα radiation, λ = 1.5406 Å) in the range of 2θ = 5−50° using a step scan mode with a step rate of 5° min^{-1}. Thermogravimetric analyses (TGA) were carried out on a Mettler Toledo TGA/SDTA851 analyzer under nitrogen flow with a heating rate of 5 K min^{-1} in the range of 40−850 °C. Nitrogen adsorption−desorption isotherms were measured on a Micromeretics model ASAP 2020 gas adsorption analyzer at 77 K. Fourier transform infrared spectra (FT-IR) were measured using KBr pellets with a DIGILAB FTS-3000 spectrometer in the range of 4000−400 cm^{-1}. GC/MS were taken with a Bruker Scion TQ Gas chromatography tandem mass spectrometer, hydrogen flame ionization detector (HFID), and 30 m × 0.2 mm × 0.25 μm OV101 capillary column.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00599.

> PXRD patterns, FTIR, TGA curves, nitrogen adsorption−desorption isotherms, conversion percentages of 1-butene and amounts of isomerization products, catalyst ratios, GC/MS analysis, and schematic diagram of 1-butene isomerization reactor (PDF)

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Notes

The authors declare no competing financial interest.

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