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Selective Transformation of Dimethyl Ether into Small Molecular Hydrocarbons Over Large-pore Beta Zeolite

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Abstract In dimethyl ether (DME) conversion, large-pore beta zeolite is found possessing a novel performance of selectively synthesizing small molecular hydrocarbons, around 95% selectivity to $C_3 + C_4 + C_5$ with hardly any large molecular C_{6+} products, which does not follow the shape selectivity of zeolite with large pore system completely.

Keywords DME conversion · Beta zeolite · Large pore system · Small molecular hydrocarbons · Shape selectivity

1 Introduction

The conversion of methanol/dimethyl ether (DME) to gasoline (MTG) or to olefin (MTO) has been widely studied since discovered by Chang and Silvestri in 1977 [1]. It provided a new route for fuel synthesis from coal, natural gas and biomass via syngas, especially at present with high-priced crude oil [1–5]. According to the published literatures, zeolite-type materials are generally considered as favorable catalysts and research focus is on small- and medium-pore type zeolitic materials like SAPO-34 or ZSM-5, not on large-pore type zeolites considering the shape selectivity of zeolite. Only a few studies have been published so far with respect to large-pore type zeolites such as mordenite, Y, SAPO-5 and so on [6–9]. Among them, mordenite zeolite behaves some favorable performances with a high activity to the conversion of methanol to hydrocarbons and much narrower product distribution of light hydrocarbon. However, mordenite deactivates rapidly, though the selectivity to olefins and the resistance to deactivation can be promoted by dealumination and/or barium ion exchange of H-mordenite [10–14].

To the best of our knowledge, large-pore zeolites like mordenite, beta might allow the formation of big molecular hydrocarbons and do not contribute to the synthesis of small ones. However, besides mordenite, Hutchings et al. [15] also briefly reported some results over H-beta zeolites with around 30–50% isobutane and little C_{6+} in methanol conversion in 1994. But Mikkelsen et al. [16] obtained opposite results with C_{6+} aromatic compounds as main products under the comparable reaction conditions as they expected. From then on, no further study was reported on zeolite beta for methanol/DME conversion to hydrocarbons.

In this work, H- and Pd-beta zeolites are used as catalysts for DME conversion and a novel catalytic performance of zeolite beta is found. Pd-beta zeolite with a high SiO_2/Al_2O_3 ratio of 200 is very selective to the small molecular hydrocarbons, around 95% selectivity to $C_3 + C_4 + C_5$ in DME conversion, and hardly any large products C_{6+} as well as only small amount of $C_1 + C_2$ are formed, which do not follow the shape selectivity of large-pore zeolite completely. Furthermore, it possesses a favorable stability. The synthesis of small molecular hydrocarbons ($C_3 + C_4 + C_5$) over large-pore beta zeolite with so high selectivity in DME conversion is first to be reported.

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2 Experimental

Two types of H-beta zeolites with different SiO_2/Al_2O_3 ratio of 37 and 200 were used in this study and referred to as H-beta-37 and H-beta-200. Pd-beta zeolites were prepared by ion-exchanged method from the corresponding H-beta in palladium nitrate solution with same concentration, and noted as Pd-beta-37 and Pd-beta-200 respectively. A tubular reactor with 6 mm inner diameter was employed in study and feed was a mixture of DME and hydrogen. Since DME is liquid under 0.5 MPa at room temperature, it was brought into the reactor by hydrogen. The amount of DME is controlled by helium flow rate and DME temperature. When pressure is 2.0 MPa, DME temperature is 20 °C and hydrogen flow rate is 30 mL min^{-1}, the ratio of H_2/DME is around 3. There is another hydrogen route to adjust the ratio of H_2/DME during the tests. Before the introduction of feed into reactor, catalysts were activated by hydrogen. The products in gaseous state were analyzed by two on-line GC with FID and TCD detector respectively. Argon in the feed was used as an internal standard for calculation. All results shown here were repeated with a good reproducibility within a few percents.

The acid properties of catalyst were investigated by temperature programmed desorption (TPD) of ammonia on TPDRO-1100 catalytic Surface Analyzer. 100 mg sample with 30–40 mesh was pretreated at 550 °C for 1 h in helium atmosphere, and then adsorbed ammonia at 100 °C for 45 min. After flushed by He flow at 100 °C for 60 min, the sample was measured with a heating rate of 10 °C min^{-1} to 550 °C and kept at this temperature for 30 min.

The properties of palladium particle over beta zeolite were characterized on Quantachrome Instruments Autosorb automated Gas Sorption system. Hydrogen was used as the adsorbed gas and the analysis temperature is 323.2 °C.

3 Results and Discussion

The conversion of DME to hydrocarbons was first investigated over H-beta-37 and H-beta-200 at P = 2.0 MPa (P: reaction pressure) and W/F = 1.0 (residence time, g h mol^{-1}). Results are shown in Table 1. It can be seen that, in comparison with the results over H-beta-37, the carbon distribution over H-beta-200 demonstrates higher selectivity to C_3, and lower selectivity to C_1, C_2, and $\geq C_7$ hydrocarbons. H-beta with high SiO_2/Al_2O_3 ratio contributes to the formation of light hydrocarbons C_3. In addition, H-beta-200 exhibits much more resistance to deactivation than H-beta-37 though DME converts completely over both H-beta catalysts in a significant length of time. Zeolite beta is an active catalyst in the conversion of DME to hydrocarbons. However, when deactivation occurs over two catalysts, a rapid increase of aromatic products is observed and large molecular polymethylbenzenes like tri-, tetra-, penta- and hexamethylbenzene are formed. It should be pointed out that, only after the occurrences of deactivation over two catalysts, an increasing number of polymethylbenzenes can be detected in the products, and from then on product distribution of hydrocarbons accords to the shape selectivity of zeolite with large pore system in DME conversion, as reported by Mikkelsen [16]. But before the deactivation, main products are small molecular hydrocarbons like C3, C4 and C5, and only small amount of aromatic products like toluene, ethylbenzene are formed over H-beta zeolite.

In order to further study the catalytic performance of zeolite beta in DME conversion, H-beta-37 and H-beta-200 were ion-exchanged into Pd-beta-37 and Pd-beta-200 respectively. The tests over both Pd-beta catalysts were performed under the same reaction conditions as over H-beta: P = 2.0 MPa, W/F = 1.0 g h mol^{-1}. Results are shown in Figs. 1 and 2 respectively. Since there is palladium over zeolite beta as hydrogenation catalyst, no olefin is observed in product streams. It is surprising that results over both catalysts are very distinct. In the case of Pd-beta-37, the dominant product is methane, around 97.5% at low temperature of 385 °C. Since only a small amount of CO and CO_2 in the products, the observation is due to the hydrogenolysis of DME to water and methane over acid sites in the presence of palladium metal. The interesting observation is that, with the increase of reaction

Table 1 DME conversion to hydrocarbons over two types of H-beta zeolites with different ratio of SiO_2/Al_2O_3

Catalyst	DME Conv.%	Carbon distribution (%)						
		C1	C2	C3	C4	C5	C6	$\geq C_7$
H-beta-37	100	2.09	8.62	14.58	14.15	14.15	10.12	16.96
H-beta-200	100	0.72	3.33	24.92	15.09	15.09	10.71	7.91

[a] Reaction conditions: T = 450 °C, P = 2.0 MPa and W/F = 1.0 g h mol^{-1}

[b] Both product streams were analyzed 2 h after the beginning of the reactions. The selectivity to certain hydrocarbon includes olefin and paraffin with same carbon number

[c] No CO_x (CO + CO_2) were detected in the product stream

temperature from 385 °C to 475 °C, CH_4 selectivity sharply drops from 97.5% to 4.5%, and meanwhile $\geq C_2$ hydrocarbons increase rapidly. At 475 °C, some aromatic products are detected, but dominant product is still $C_3 + C_4 + C_5$.

The results over Pd-beta-200 with high ratio of SiO_2/Al_2O_3 of 200 are shown in Fig. 2. In contrast to the corresponding H-beta-200 zeolite, Pd-beta-200 displays a narrower product distribution in the range of C_1–C_6: higher selectivity to $C_3 + C_4 + C_5$ and lower selectivity to C_1, C_2 and $\geq C_6$ hydrocarbons. Furthermore, in comparison with the results over Pd-beta-37 as shown in Fig. 1, carbon number distribution over Pd-beta-200 in Fig. 2 changes greatly: (1) the selectivity to methane is much lower, only 4.1% even at low temperature of 385 °C and continuously drops with the increase of reaction temperatures; (2) the dominant products is $C_3 + C_4 + C_5$, high to 95% at 475 °C; (3) only a small fractions of reaction products over C_6 are observed at low reaction temperature, but disappear at the elevated temperatures over 430 °C. Since both catalysts were prepared exactly through the same process and employed for DME conversion under the same reaction conditions, it is reasonable to propose that the ratio of SiO_2/Al_2O_3 exerts a significant impact on the catalytic performance of beta zeolite in DME conversion.

In order to display the differences in acid properties between two Pd-beta zeolites with different ratio of SiO_2/Al_2O_3, temperature programmed desorption (TPD) of ammonia was carried out and the results are shown in Fig. 3 and Table 2. The amount of desorbed ammonia is defined as the acid amount and the temperature of peak maximum is defined as the acid strength. It can be seen that two kinds of desorbed ammonia peaks are observed at low and high temperatures in both NH_3-TPD profiles, but the TPD profile of Pd-beta-200 is greatly different from that of Pd-beta-37 though high temperature peaks are both at 410 °C. It is apparent that Pd-beta-200 possesses less acid than that of Pd-beta-37 in two kinds of acid. Maybe, the less acid over Pd-beta-200 zeolite play an important role in the selective formation of light molecular hydrocarbons in DME conversion. Furthermore, the results of hydrogen chemical adsorption are shown in Table 3. It is obvious that the Pd-beta-200 possesses bigger palladium particle size and lower monolayer uptake of hydrogen. Therefore, it is reasonable to propose that less acid and lower uptake of hydrogen over Pd-beta-200 minimizes the occurrence of hydrogenolysis of DME at low temperature. While over Pd-beta-37 catalyst, the hydrogenolysis rate of DME to

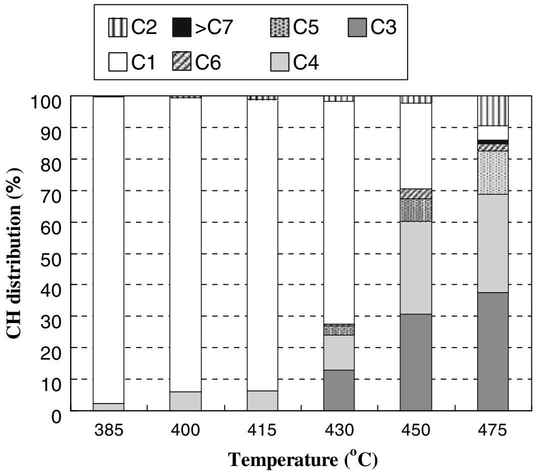

Fig. 1 The effect of temperature on hydrocarbon distribution in DME conversion over Pd-beta-37. (1) Reaction conditions: P = 2.0 MPa and W/F = 1.0. (2) DME converts completely. Around 4.7–0.6% CO_X is produced with the increase of reaction temperatures from 385 °C to 475 °C

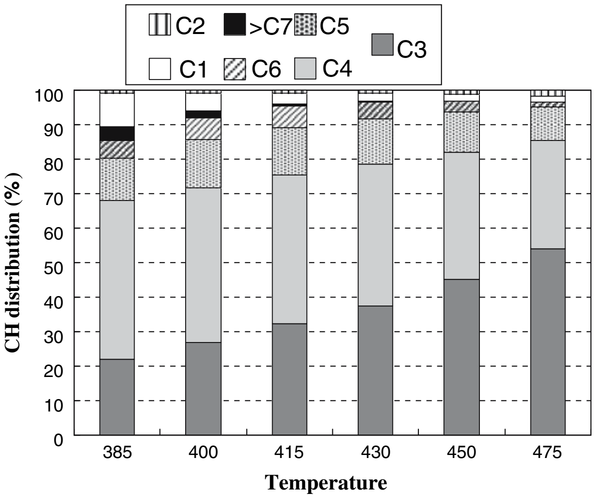

Fig. 2 The effect of temperature on hydrocarbon distribution in DME conversion over Pd-beta-200. (1) Reaction conditions: P = 2.0 MPa and W/F = 1.0 g h mol^{-1}. (2) DME converts completely. Around 0.6–0.3% CO_X is produced with the increase of reaction temperatures from 385 °C to 475 °C

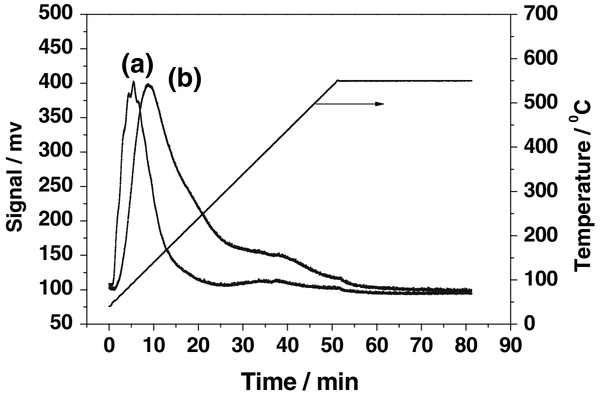

Fig. 3 NH_3–TPD profiles of Pd-beta zeolites with different ratio of SiO_2/Al_2O_3. (a) Pd-beta-200 (b) Pd-beta-37

Table 2 NH_3-TPD data of Pd-beta-37 and Pd-beta-200

Catalyst	T_{peak}/°C		Acid amount, n (NH_3)/mmol g^{-1}			W/S[c]
	LT-peak[a]	HT-peak[b]	Weak acid	Strong acid	Total acid	
Pd-β-37	115	410	0.57	0.12	0.69	4.9
Pd-β-200	100	410	0.32	0.02	0.34	8.3

[a] LT-peak: low-temperature peak

[b] HT-peak: high-temperature peak

[c] W/S: the ratio of weak acid amount to strong acid amount

Table 3 The properties of palladium particle over beta zeolite

Catalyst	Crystallite size (Å)	H_2 Monolayer uptake (μmol/g)
Pd-β-37	22.79	11.55
Pd-β-200	44.49	5.914

methane is much faster than that of the initial formation of C–C bond from C1 reactants at low temperatures and thus forms a great amount of methane. With the increase of reaction temperature, the hydrogenolysis race drops greatly and main reactions of DME conversion transfer to C–C formation and hence synthesize $\geq C_2$ hydrocarbons.

As we know, beta zeolite has a 12-ring pore system and would be expected to produce larger molecular hydrocarbons than small- or middle-pore type zeolites like ZSM-5 or SAPO-34 under the comparable reaction conditions. However, the difference in the selectivity is not just a manifestation of shape selectivity of zeolite, as the results shown in this study. In MTO over mordenite zeolite with dealumination and/or barium ion exchange, the narrow distribution of light hydrocarbons was due to the considerable low strong acid over zeolites [10–14]. Barthomeuf [17] reported that, when the aluminum concentration in zeolite framework is smaller than 1.41 mmol g^{-1} (SiO/Al_2O_3 = 18.8), no aluminum atoms have aluminum atoms as second neighbors. Since the bulk aluminum concentration of both beta zeolites in this study was smaller than 1.41 mmol g^{-1} ($SiO_2/Al_2O_3 > 18.8$), the dispersed acid sites do not contributes to the polymerization reactions, but are in favor of the formation of light hydrocarbons.

It is well known that there are primary and secondary reactions in conversion of methanol to hydrocarbon over H-ZSM-5 [18–20], and Furthermore, over the large pore dealuminated mordenite, a high selectivity to light alkenes can also be obtained, and C_3–C_7 alkenes were considered as primary products from the direct transformation of DME, but ethylene mainly results from secondary cracking of C_5–C_7 alkenes [21]. The product distribution in DME conversion over Pd-beat zeolite may also be controlled by primary or secondary reactions or both of them. The lower carbon number products over large pore beta zeolite may indicate a lower reactivity of the active sites for the secondary conversion reaction. As mentioned above, the reason may be the active centers being more remote from each other in zeolite beta due to the wider pore structure, or by the fact that methanol may not be able to cluster around these active center owning to the pore geometry [15]. Furthermore, there is hydrogenation catalyst, palladium, over beta zeolite converting olefin to paraffin in time and preventing the occurrence of secondary reactions. Therefore, to some extent, product distribution over Pd-beta catalyst can really reflect the composition of primary products of DME conversion. In addition, in this case, Pd-beta-200 catalyst displays very stable catalytic performance in 200 h. 100% DME conversions and around 95% selectivity to $C_3 + C_4 + C_5$ are achieved with 0.3–0.6% CO_x ($CO + CO_2$), as shown in Fig. 4.

On the other hand, it is well known that zeolite beta, which possesses 3-dimensional 12-membered-ring pore openings, is an intergrowth hybrid of two distinct but closely related structures with diameters of 5.5 × 5.5 Å channels along [001] and 6.4 × 7.6 Å channels perpendicular to [001] [22, 23], which, to some extent, is similar to the pore structure of mordenite, where two kinds of

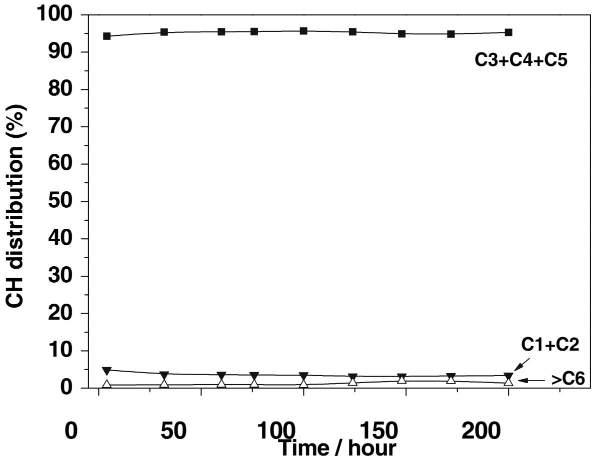

Fig. 4 Product composition as a function of time on stream over Pd-beta-200 catalyst. (1) Reaction conditions: $T = 450$ °C, P = 2.0 MPa and W/F = 7.0 g h mol^{-1}. (2) DME converts completely and around 0.1–0.5% CO_X is produced

channels are found and considered favorable for the formation of light hydrocarbons [21, 24]. Hence, the structure of zeolite beta may produce some impacts on the catalytic performance of zeolite beta. Therefore, it is suggested that, before deactivation, the conversion of DME to hydrocarbons may take place mainly in the 5.5 × 5.5 Å channels, which contributes to the synthesis of small molecular hydrocarbons and diffuse readily through 12-membered ring channels, as Lee suggested [25]. While, alone with time on stream, an increasing number of small channels are blocked by coke and then more and more DME conversion will take place in the bigger 12-ring channels, where large molecular hydrocarbons are synthesized. The transfer of reaction place possibly leads to the great change of product distribution. But there is a need for further studies to explore these interesting phenomenons.

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