Selective Formation of Alkenes in the Conversion of Methanol into Hydrocarbons on Barium Ion-exchanged Mordenite

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Summary C_2—C_4 alkenes were formed with more than 80% selectivity in the conversion of methanol into hydrocarbons over Ba ion-exchanged mordenite.

RECENTLY, Mobil announced that in the conversion of methanol the yield of low molecular weight alkenes may be increased to >70% by modifying the ZSM-5 zeolite catalyst used with phosphorus compounds.[1] We have reported previously that the product distribution for the same reaction is affected by the ion exchange of H-mordenite with alkali ions.[2] The effect of barium ion exchange on the selective formation of lower alkenes is described here.

H-mordenite (HM) was commercially available from Norton Co. (Zeolon 100H) and was used as the starting material for the ion exchange. Cation-exchanged mordenites were prepared by a conventional ion-exchange procedure with an aqueous solution of the appropriate acetate salt. The catalysts were washed and dried at 378 K, and calcined at 673 K in an O_2 flow to remove further acetate ions. Experiments were carried out using the pulse reaction technique under the following conditions: temperature, 698 K; helium flow rate, 40 cm^3 min^{-1}; methanol pulse size, 2 μl. The catalyst was pretreated at 773 K for 3 h with helium flowing at a rate of 40 cm^3 min^{-1} and was brought to the reaction temperature *in situ*.

The Table shows the product distributions obtained in the conversion of methanol into hydrocarbons. Potassium ion exchange (KHM) resulted in an increase in the aromatic portion and a decrease in the alkane portion to a significant degree. The selectivity for C_2—C_4 alkene formation showed only a slight increase, although the selectivity for ethene formation decreased and selectivities for propene and butenes increased. On the barium-exchanged (BaM) catalyst, the selectivity for alkane formation decreased in accordance with the results on KHM. However, in contrast with the results on KHM, the production of aromatic compounds was reduced drastically to trace level and C_2—C_4 alkene compounds were formed with a 90% selectivity in the hydrocarbons obtained. The distribution of ethene, propene, and butenes in the alkene products from BaM changed in a similar manner as on KHM. It is worth noting

TABLE. Conversion of methanol into hydrocarbons on cation-exchanged mordenites.

		HM	KHM[a]	BaM[a]	BaM[a]
Catalyst weight/mg		20·1	20·4	20·2	201·2
Recovery of hydrocarbon/μmol[b]		40·3	43·5	2·0	33·5
Distribution of hydrocarbons/C %[c]					
Alkane	C_1	1·5	0·5	5·7	1·0
	C_2	1·4	0·2	0·4	0·1
	C_3	25·6	7·4	1·4	2·5
	C_4	17·5	17·0	trace	7·5
Total C_1—C_4 alkanes		46·0	25·1	7·5	11·1
Alkene	C_2	19·2	9·2	5·9	5·5
	C_3	11·6	19·6	59·9	56·0
	C_4	7·1	14·4	24·2	20·3
Total C_2—C_4 alkenes		37·9	43·2	90·0	81·8
$C_{>4}$[d]		1·6	6·1	2·5	6·8
Aromatics		14·5	25·7	trace	0·2
C_2—C_4 alkene/C_1—C_4 alkane		0·82	1·72	12·0	7·37

[a] The degrees of ion-incorporation into KHM and BaM are 41 and 64%, respectively. [b] μmol (calculated on a carbon atom basis) of hydrocarbons obtained. [c] Percentage (calculated on a carbon atom basis) in total amount of hydrocarbons obtained. [d] Aliphatic compounds with more than 4 carbon atoms.

that the selectivity for propene formation was more than 55%. The recovery of hydrocarbons on BaM (20·2 mg) was 2 μmol (calculated on a carbon atom basis), indicating the fairly low activity of BaM. When the catalyst weight of BaM was increased from 20·2 to 201·2 mg, the product distribution was in good agreement with that obtained with 20·2 mg. The selectivity for formation of aromatic compounds was still only 0·2% and that for C_2—C_4 alkenes was as high as 81·8%. This result shows that the selective production of the low molecular weight alkenes may be attributed to the intrinsic property of the BaM catalyst. Thus, it is found that a hydrocarbon product distribution with more than 80% selectivity for formation of C_2—C_4 alkenes can be obtained by the ion-exchange of HM with barium cations.

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