Catalytic Activity of Fibrous Clay Mineral Sepiolite for Butadiene Formation from Ethanol

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Summary Manganese supported on sepiolite is an effective catalyst for the catalytic conversion of ethanol into buta-1,3-diene.

RECENTLY, the catalytic conversion of alcohols into higher hydrocarbons using the shape-selective catalyst, ZSM-5, has been studied by many workers.[1,2] Rajadhyaksha *et al.*[3] have reported the catalytic conversion of ethanol into aromatics also on ZSM-5. The catalytic conversion of ethanol into butadiene has been observed on silica–magnesia[4] and on other binary metal oxide catalysts (Al_2O_3–ZnO, Al_2O_3–MgO, *etc.*).[5]

Sepiolite is a fibrous magnesia–silicate clay mineral which contains zeolitic water in the intracrystalline channel. The idealised formula for the structure of this mineral is $(H_2O)_4$-$(OH)_4Mg_8Si_{12}O_{30}\cdot6$–$8H_2O$,[6] and the crystal contains uniform-size parallelepiped cavities ($11 \times 5{\cdot}6$ Å) along the fibre. The magnesium ion in sepiolite crystal is exchangeable with various transition metal ions.[7] Sepiolite is an effective catalyst for the dehydrometallation of heavy oils.[8] These characteristics of sepiolite have some resemblance to those of zeolite, though zeolites are aluminosilicates.

This paper reports that sepiolite is an effective catalyst for the conversion of ethanol into ethylene and that manganese supported on sepiolite is especially effective for the catalytic conversion of ethanol into buta-1,3-diene.

Samples of needle-shaped clay mineral sepiolite of Spanish origin were used.† Two preparative methods were used to support manganese on the sepiolite.‡ The reaction was carried out in a circulating system of volume *ca.* 240 cm^3.

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‡ Mn-sepiolite(I); Sepiolite was impregnated with an aqueous solution of $MnCl_2\cdot4H_2O$. This material was then treated with aqueous ammonia, washed with water, dried, and calcined in air at 500 °C for 1 h. Mn-sepiolite(II); Sepiolite was impregnated with an aqueous solution of $Mn(MeCO_2)_2\cdot4H_2O$. This material was then dried and calcined in air at 500 °C for 1 h.

TABLE.

				Composition of reaction mixture (mol %)						
Catalyst	Temp. /°C	Time	P_I[a] /mmHg	EtOH	C_2H_4	Butadiene	Et_2O	MeCHO	C_3[b]	C_4[b]
Sepiolite	280	30 min	22	72·0	19·4	—	7·4	0·9	0·3	—
0·1 g		5 h		5·5	86·9	0·7	4·5	0·8	0·9	0·7
260 m²/g										
Sepiolite	320	10 min	23	40·3	52·4	2·4	3·2	1·5	0·3	—
0·1 g		1 h		4·7	91·2	1·2	—	1·5	0·7	0·8
260 m²/g		6 h		—	96·8	1·1	—	0·6	0·9	0·7
Mn–sepiolite(I)	300	30 min	23	31·4	54·7	5·1	4·2	2·2	1·2	1·1
0·1 g										
Mn: 77 mol%		17 h		—	84·9	7·3	—	—	2·4	5·4
136 m²/g										
Mn–sepiolite(II)	300	30 min	20	39·9	24·6	20·6	5·5	2·9	2·9	3·7
0·3 g										
Mn: 56 mol%		4 h		9·4	43·7	25·8	4·2	5·7	4·8	6·4
113 m²/g										
Mn–sepiolite(II)	300	30 min	20	38·9	21·2	27·9	2·4	3·0	2·8	3·7
0·3 g										
Mn: 79 mol%		7 h		—	41·4	33·4	2·0	7·5	7·3	8·3
85 m²/g										

[a] P_I = initial pressure of ethanol vapour. [b] C_3; propene and propane. C_4; butene and butane.

The catalyst, which was packed in a reaction vessel (about 60 cm³) connected with a circulating system, was heated *in vacuo* at 350 °C for 2 h. The ethanol vapour was circulated by a magnetic pump through the reaction vessel at the reaction temperature. The reaction products were analysed by gas chromatography and i.r. and mass spectrometry, and the results are summarized in the Table.

Using sepiolite alone as catalyst, ethylene was the main product (C_2H_4 produced 96·8%, when unchanged ethanol was no longer detected at 320 °C) and a small amount of buta-1,3-diene was also found. The diethyl ether, produced in the initial stages of the reaction, decreased as the reaction proceeded.

The catalytic selectivity of Mn supported on sepiolite for the conversion of ethanol was different from that of sepiolite alone; the catalytic conversion of ethanol into buta-1,3-diene occurred more markedly than on sepiolite alone. The selectivity for butadiene formation on Mn–sepiolite(II) was higher than that on Mn–sepiolite(I) as is shown in the Table. Also, it was found from further experiments that the yield of butadiene increased from 8·4 to 33·4% while that of ethylene decreased from 76·4 to 41·4% when the manganese contents of Mn–sepiolite(II) increased in the range 39 to 79 mol% for the reaction at 300 °C for 7 h.

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