

Pronounced Catalytic Activity and Selectivity of MgO–SiO₂–Na₂O for Synthesis of Buta-1,3-diene from Ethanol

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MgO–SiO₂ (molar ratio = 1 : 1) prepared from ethyl orthosilicate and magnesium nitrate and promoted with 0.1 wt% Na₂O exhibited a high catalytic activity (100%) and selectivity (87%) for formation of buta-1,3-diene at 350 °C.

A large amount of ethanol produced from sugar cane is being utilized not only as an energy source in place of gasoline, but also as a raw material for synthesis of various chemicals. Among the chemicals, buta-1,3-diene is an important one. Several studies have been made of the synthesis of buta-1,3-diene from ethanol over heterogeneous catalysts such as MgO–SiO₂–Cr₂O₃,¹ MgO–SiO₂–Ta₂O₅,¹ Al₂O₃–ZnO,² MgO–SiO₂,³ and Sepiolite (fibrous silica–magnesia clay mineral)–MnO₂ (79 mol%).⁴ However, the selectivity for the formation of buta-1,3-diene is not sufficient (73% at most). In the present work we have found an efficient catalyst, MgO–SiO₂(1 : 1)–Na₂O(0.1 wt%), which works at relatively low reaction temperature. It will be emphasized that the particular preparation method and the optimum composition of MgO–SiO₂ and the addition of a small amount of a basic oxide are essential for the high catalytic activity and selectivity.

Magnesia–silica of different compositions were prepared by three kinds of preparation methods. MgO–SiO₂(A) was prepared by kneading a mixture of magnesium hydroxide(A) and silica gel(A) for 4 h followed by drying and calcining at 500 °C in a stream of nitrogen for 3 h. Magnesium hydroxide(A) was obtained by hydrolysis of an aqueous solution of magnesium nitrate with aqueous ammonia and filtering the precipitate. Silica gel(A) was obtained by hydrolysis of an aqueous solution of tetraethyl orthosilicate, nitric acid, and

ethanol with aqueous ammonia and filtering the precipitate. MgO–SiO₂(B) was prepared from magnesium hydroxide(B) and silica gel(B), as for MgO–SiO₂(A). Magnesium hydroxide(B) and silica gel(B) were obtained from magnesium chloride and from tetraethyl orthosilicate, hydrochloric acid and ethanol, as for magnesium hydroxide(A) and silica gel(A), respectively. MgO–SiO₂(C) was prepared by hydrolysis of a mixed solution of magnesium chloride, hydrochloric acid, and tetraethyl orthosilicate with aqueous ammonia followed by drying and calcining at 500 °C as above. MgO–SiO₂–Na₂O and MgO–SiO₂–K₂O were prepared by impregnating MgO–SiO₂(A) with aqueous NaOH and KOH followed by drying and calcining at 500 °C in a nitrogen stream for 3 h. The reaction was carried out at 350 °C by use of a conventional flow reactor under atmospheric pressure with 0.2 g of catalyst, the flow rate of nitrogen and ethanol being 4×10^{-2} and 6.5×10^{-4} mol/h, respectively. Reaction time was set at 10 min. The products were analysed by gas chromatography. Besides buta-1,3-diene, small amounts of ethane, ethene, propane, propene, acetaldehyde, and ethyl ether were found in the products.

The results obtained are shown in Table 1 together with those reported in the literature. MgO–SiO₂(A) prepared from nitrates showed much higher selectivity than MgO–SiO₂(B) and MgO–SiO₂(C) which were prepared from chlorides. The activity of MgO–SiO₂(B) was very high (98%), but it formed

Table 1. Comparison of activity of MgO–SiO₂–Na₂O and its selectivity for buta-1,3-diene formation with those of the other catalysts.^a

Catalyst ^b	Reaction temp./°C	Conversion /%	Selectivity /%	Yield /%	Ref.
MgO–SiO ₂ –Cr ₂ O ₃ [*] (59 : 39 : 2)	425	—	—	39	1
MgO–SiO ₂ –Ta ₂ O ₅ [*] (60 : 38 : 2)	425	—	—	39	1
Al ₂ O ₃ –ZnO ^{*c} (6 : 4)	425	100	73	73	2
Al ₂ O ₃ –ZnO [*] (6 : 4)	425	94	58	55	2
MgO–SiO ₂ (3 : 1)	380	54	62	33	3
Sepiolite–MnO ₂ ^d (21 : 79)	300	70	63	44	4
MgO–SiO ₂ (A) (1 : 1)	350	50	84	42	
MgO–SiO ₂ (B) (1 : 1)	350	98	2	2	
MgO–SiO ₂ (C) (1 : 1)	350	71	7	5	
MgO–SiO ₂ –Na ₂ O (1 : 1)(0.1 wt%)	350	100	87	87	
MgO–SiO ₂ –K ₂ O (1 : 1)(0.1 wt%)	350	80	87	70	

^a All reactions were carried out by using a fixed bed flow reactor except for ^c (a fluidized bed flow reactor) and ^d (a circulation reactor). ^b Components were mixed in molar or weight(*) scale.

49% of C₂-hydrocarbons and 49% of ethyl chloride in the products, thus lowering the selectivity. The selectivity of MgO-SiO₂(C) was also low. According to E.S.C.A. analysis, the atomic ratios of Mg/(Mg + Si) on the surfaces of MgO-SiO₂(1:1)(A), (B), and (C) were 0.42, 0.45, and 0.40, respectively, *i.e.* very similar. The temperature programmed desorption (T.P.D.) measurements indicated that MgO-SiO₂(B) and (C) calcined at 500 °C contained a considerable amount of chloride ion. Thus, chloride ion appears to decrease the selectivity.

As for the effect of the composition of MgO-SiO₂(A), both acidity and selectivity showed maximum values when the molar ratio of MgO to SiO₂ was 1:1. The selectivity was much higher than that of MgO-SiO₂(A) with molar ratio = 3:1 prepared in the present work and that of MgO-SiO₂(3:1) prepared from Mg(OH)₂ and colloidal silica by Niiyama *et al.*³

The MgO-SiO₂(A) of molar ratio = 1:1 exhibited very high activity and selectivity when 0.1 wt% of Na₂O or K₂O was added. In particular, the effect of Na₂O addition was surprising, 100% activity and 87% selectivity being observed as shown in Table 1. The yield ($100/100 \times 87 = 87\%$) over

this catalyst was the highest at relatively low reaction temperature (350 °C). The yield over Al₂O₃-ZnO catalyst was fairly high (73%), but this value was obtained at higher temperature (425 °C) and by using a fluidized bed reactor. The Sepiolite-MnO₂ was an active catalyst (44% yield) at lower temperature (300 °C), but this value is an accumulated one obtained during long contact times by using a circulation reactor.

Received, 31st July 1985; Com. 1128

References

- 1 B. B. Corson, H. E. Jones, C. E. Welling, J. A. Hinckley, and E. E. Stahly, *Ind. Eng.*, 1950, **42**, 359.
- 2 S. K. Bhattacharyya and N. O. Ganguly, *J. Appl. Chem.*, 1962, **12**, 105.
- 3 H. Niiyama, S. Morii, and E. Echigoya, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 655.
- 4 Y. Kitayama and A. Michishita, *J. Chem. Soc., Chem. Commun.*, 1981, 401.