Dehydrogenation of Ethylbenzene over Molten Binary Alloys

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Summary Several molten binary alloys containing Na or K have been found to catalyse effectively the dehydrogenation of ethylbenzene to form styrene and an approximately linear correlation has been found to exist between the catalytic activity and the work function estimated using simple assumptions

Molten metals such as In, Ga, Tl, Al and Zn and molten binary alloys containing any one of these active metals have been reported[1–4] to catalyse the dehydrogenation of alcohols and amines It has also been reported[5] that molten Te and molten Te–Se catalyse the dehydrogenation of polynuclear hydrocarbons and that molten Na–Pb catalyses the dehydrogenation of alkylbenzenes Of these reactions the last is the most important from the industrial point of view and we now report new molten alloy catalysts which are more active than molten Na–Pb

The molten alloy used in this work was prepared and purified by the methods used to make a pure molten In–Sn alloy[6] The purified molten alloy was transferred from the catalyst preparation tube through a vacuum line to a bubbling type reactor[2,3] and kept in an atmosphere of dry helium (reactor diameter 2·5 cm, vertical length 13 cm, inner diameter of the gas bubbling tube 0·6 cm) The reactant (ethylbenzene) was distilled *in vacuo* to remove dissolved air and water

The reaction was carried out by bubbling the reactant vapour (flow rate 0·04 mol/h) and purified helium (flow rate 0·15 mol/h) from the bottom of the reactor into the molten alloy catalyst The reaction products were analysed by gas chromatography

The results shown in Figure 1 clearly indicate that molten alloys of Na–Tl and Na–In (A), K–Pb (B), and K–In and K–Tl (C) are all more active than the molten Na–Pb alloy in the dehydrogenation of ethylbenzene The excellent selectivities of these catalysts for styrene formation can also

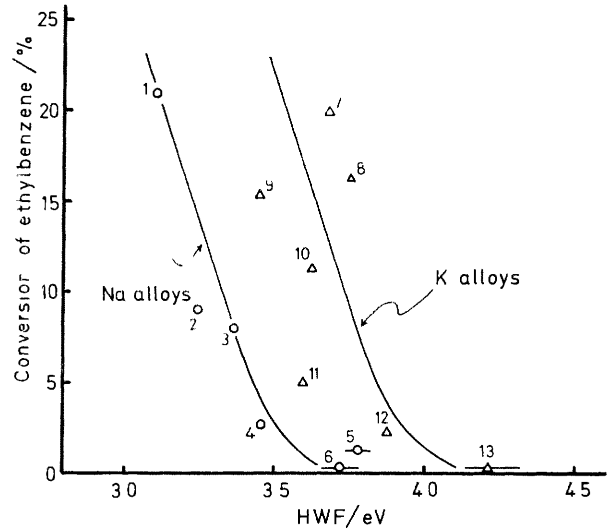

Figure 2 Correlation between catalytic activity at 550 °C and work function (HWF) 1 Pb(0·5)–Na(0·5) 2 Tl(0·7)–Na(0·3), 3 In(0·7)–Na(0·3) 4 Pb(0·7)–Na(0·3) 5 Sn(0·7)–Na(0·3), 6 Bi(0·7)–Na(0·3) 7 In(0·9)–K(0·1) 8 In(0·95)–K(0·05), 9 Pb(0·7)–K(0·3) 10 Pb(0·8)–K(0·2) 11 Tl(0·95)–K(0·05) 12 Pb(0·95)–K(0·05) 13 Bi(0·95)–K(0·05) 70 g of catalyst were used except for run 7 which used 35 g ○, Na alloys △ K alloys

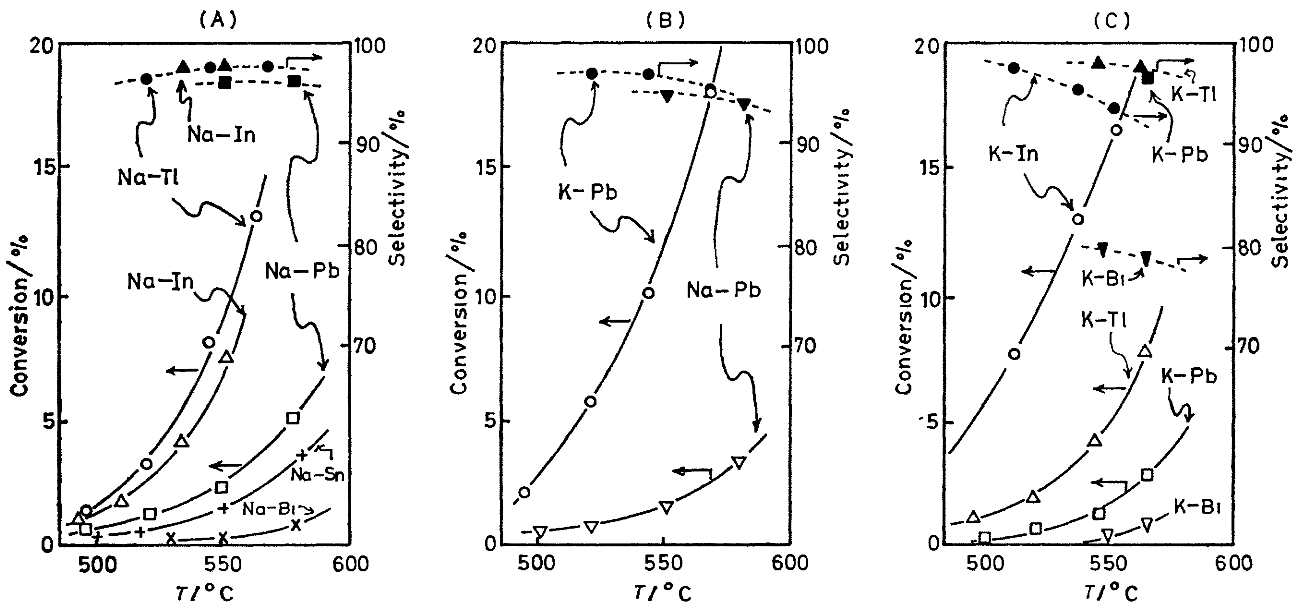

Figure 1 Catalytic activities of various binary liquid alloys containing Na or K (A) catalysts containing 30% (atom) of Na, (B) catalysts containing 20% (atom) of Na or K (C) catalysts containing 5% (atom) of K *Ca* 70 g of catalyst were used in each case Full lines, open symbols, conversion, broken lines, filled symbols, selectivity

be seen in Figure 1. A long catalyst life (>20 h) was obtained provided precautions were taken against the mixing of air or moisture with the reaction system.

The data shown in Figure 2 which are concerned with the electronic aspect of the catalysis over the molten alloy are interesting. The ordinate of this Figure represents the catalytic activity of the molten alloy and the abscissa indicates the hypothetical work function (HWF) tentatively estimated using the following assumptions; (i) the work function of a molten metal may be approximated by the work function of the solid metal and (ii) the work function of a molten alloy may be approximated by a linear combination[7] of the work functions of the elements constituting the alloy. The Figure qualitatively shows that the lower the HWF the higher the catalytic activity. Although further experiments to measure the true work function of the molten alloy are necessary to make a decisive conclusion, this relationship suggests that the electron donating ability of the molten alloy determines the catalytic activity. A similar suggestion has been made by Krause,[8] who emphasized the importance of electron transfer from the catalyst surface (a promoted Fe_2O_3 catalyst) to the adsorbed reactant (*e.g.* ethylbenzene).

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[1] Y. Saito, A. Miyamoto, and Y. Ogino, *Kogyo Kagaku Zasshi*, 1971, **74**, 1521.
[2] K. Kashiwadate, Y. Saito, A. Miyamoto, and Y. Ogino, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3004.
[3] K. Okano, Y. Saito, and Y. Ogino, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 69.
[4] Y. Saito, N. Hiramatsu, N. Kawanami, and Y. Ogino, *Bull. Jpn. Pet. Inst.*, 1972, **14**, 169.
[5] K. Takahashi and Y. Ogino, *Chem. Lett.*, 1978, **423**, 549; K. Honda, K. Takahashi, and Y. Ogino, *ibid.*, p. 693.
[6] Y. Saito, H. Yoshida, A. Miyamoto, T. Yokoyama, and Y. Ogino, *J. Catal.*, 1978, **55**, 36.
[7] Ju. I. Malov, M. D. Shebzukhov, and V. B. Lazarev, *Surf. Sci.*, 1974, **44**, 21.
[8] A. Krause, *Sci. Pharm.*, 1970, **38**, 266.