Dehydrogenation of Ethylbenzene on Potassium-Promoted Iron Oxide Catalysts Containing Various Transition Metal Oxides

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Synopsis. Various transition metal oxides, i.e., CeO_2, Cr_2O_3, ZrO_2, V_2O_5, WO_3, and MoO_3, were added to a potassium-promoted iron oxide catalyst to study their effects on the dehydrogenation activity of the catalyst. CeO_2 was found to promote styrene formation most strongly among the oxides examined, by lowering the activation energy.

The catalytic dehydrogenation of ethylbenzene is of importance in the manufacture of styrene, which is used for various processes such as the production of synthetic rubber and resins by polymerization. Potassium-promoted iron oxide with a minor amount of chromium oxide incorporated as a structural stabilizer, known as Shell 105, has widely been used in most dehydrogenation plants.[1] As the flow rate of ethylbenzene is high, even small improvements in the activity and selectivity of a catalyst bring about substantial advantages; it has recently been discovered that a potassium-promoted iron oxide catalyst containing minor but effective amounts of cerium oxide and molybdenum oxide but no chromium oxide exhibits a high selectivity at a high overall conversion level.[2] Dehydrogenation has extensively been studied on potassium-promoted iron oxide containing chromium oxide;[3] and reported in numerous patent papers, however, few basic studies on the catalysts containing other transition metal oxides, such as cerium oxide and molybdenum oxide, have been reported. In this work various transition metal oxides were added to the potassium-promoted iron oxide and the resulting effects upon the catalytic activity and selectivity were studied in the present work.

Experimental

All the catalysts examined were prepared by wet mixing of iron(III) oxide, potassium carbonate and a suitable amount of transition metal oxide; cerium(IV) oxide was initially added as carbonate, which decomposed to oxide in a calcination process. The resulting pastes were transformed into 3.2 mm dia. and 4—6 mm length extrudates; the extrudates were dried at 120 °C overnight and calcined at 600 °C for 4 h in the presence of air, then crushed into granules of 16/20 mesh before being used for the activity test. Each catalyst contained 28% potassium carbonate and 5 or 2.5% of a transition metal oxide, i.e., 5% of cerium(IV) oxide, chromium(III) oxide and zirconium(IV) oxide or 2.5% of vanadium(V) oxide, niobium(V) oxide, tungsten(VI) oxide, and molybdenum(VI) oxide, the rest was iron oxide. The activity test was carried out in a temperature range from 550 to 620 °C in the presence of steam; a steam to ethylbenzene molar ratio of 11.8 was maintained under atmospheric pressure. A differential-type reactor consisted of stainless steel (20 mm dia.) containing 3 g catalyst was used with a total *SV* of 39100 ml g^{-1} h^{-1}.** The products were condensed in an annular condenser; in addition to ethylbenzene (EB) and water, the condensate contained styrene (ST) and small amounts of benzene (Bz) and toluene (Tol). The surface area was measured by the BET method. The acidity and basicity of the catalysts were determined by the irreversibly adsorbed amounts of butylamine (nBA) at 80 °C and acetic acid (AA) at 130 °C, respectively, using the gas chromatographic pulse technique;[4] nBA pulses and AA pulses were fed into a U-tube containing 2 g of catalyst.

Results and Discussion

The activities measured for the various catalysts are given in Fig. 1: The natural logarithms of the rates of styrene, benzene and toluene formations at 580 °C are plotted against the electro-negativities (*EN*) of the transition metal oxides added; the *EN* values are the geometric means of Pauling's values[5] for the elements included in the oxides, calculated on the basis of the electronegativity equalization postulated by Sanderson.[6] It is found that all rates were

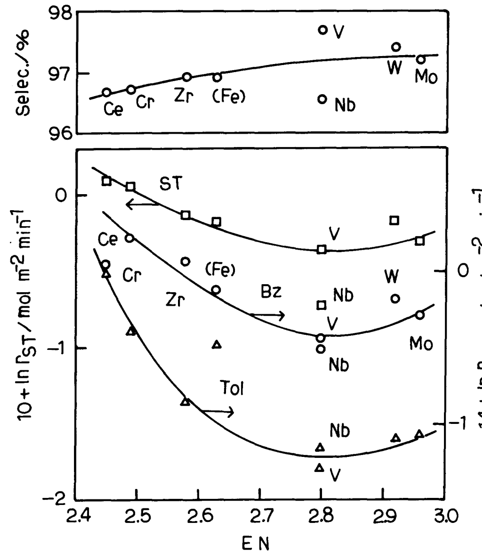

Fig. 1. Relations of the rates of ST, Bz, and Tol formation and the selectivity to ST with the *EN* of various transition metal oxides added to potassium-promoted iron oxide; 580 °C.

** The reaction rates were determined from the relation of $r=(F/S)\cdot X$, where F, S, and X represent the feed rate of ethylbenzene, the surface area of the catalyst, and the fraction of ethylbenzene converted into each product, respectively.

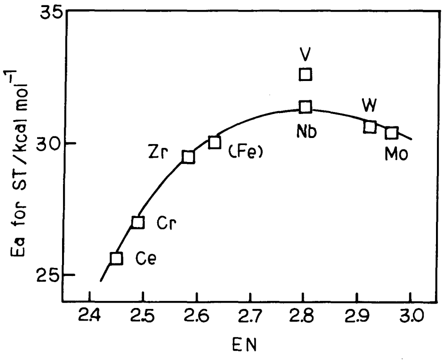

Fig. 2. Relation between the activation energies for ST formation and the *EN* of various transition metal oxides.

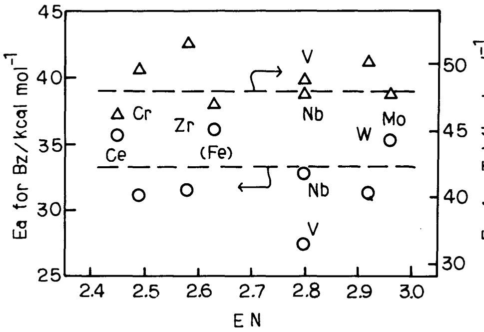

Fig. 3. Plots of the activation energies for Bz and Tol formations vs. *EN* of various transition metal oxides.

Table 1. Surface Area (*SA*), Acidity and Basicity of Various Catalysts

Catalyst	*EN*[a)]	*SA* m^2 g^{-1}	Acidity[b)] μmol m^{-2}	Basicity[c)] μmol m^{-2}
Fe-Ce-K	2.45	7.0	0.32	2.60
Fe-Cr-K	2.49	6.2	0.31	2.50
Fe-Zr-K	2.58	5.4	0.36	1.85
Fe-K	2.63	5.9	0.36	2.38
Fe-V-K	2.80	3.5	0.46	2.38
Fe-Nb-K	2.80	6.1	0.33	0.49
Fe-W-K	2.92	5.4	0.55	0.68
Fe-Mo-K	2.96	6.1	0.69	0.34
Fe	—	15.0	2.15	0.34

a) Electronegativity of the transition metal oxide (M_aO_b) added to the potassium-promoted iron oxide catalyst, determined from the relation of $EN=(X_M{}^a\cdot X_O{}^b)^{1/(a+b)}$, where X_M and X_O mean Pauling's electronegativity of each element.[5,6)] b) Adsorbed amount of butylamine at 80 °C. c) Adsorbed amount of acetic acid at 130 °C.

markedly influenced by the *EN* of the added oxides. All rates decreased with increasing the *EN*, then slightly increased after reaching the minimum at *EN* of 2.8, which corresponds to the promoters of vanadium oxide and niobium oxide. Since the extent of the initial reduction of the rate of toluene formation with the increase in *EN* was larger than those of styrene and benzene formations, the selectivity to styrene apparently increased with the increase in *EN*. Among the promoters examined, CeO_2 brought about the highest activity and V_2O_5 brought about the lowest activity, though the last promoter best improved the selectivity.

The activation energies (E_a) for the styrene, benzene and toluene formations over the various catalysts were obtained in a temperature range 550—620 °C, they are plotted in Figs. 2 and 3 against the *EN* values of the promoter oxides added. Indicated in Fig. 2 is a relation between the E_a for styrene formation and the *EN* of the promoters added. The change in E_a with *EN* seems to correspond to the behavior of the styrene formation rate with *EN*, given in Fig. 1: the E_a initially increased with the increase in *EN*, then slightly decreased after reaching a maximum. The CeO_2-containing catalyst had the lowest E_a of 25.6 kcal mol^{-1} (1 cal=4.184 J) and the highest rate of styrene formation. On the other hand, there seems to be no relation between the E_a for benzene or toluene formation and the *EN* of various promoters, as shown in Fig. 3. It is therefore suspected that the changes in the benzene and toluene formation rates with *EN*, shown in Fig. 1, are caused by the changes in the numbers of active sites for these formations by the additions of various promoter oxides.

The acid-base properties of the catalysts containing various promoter oxides were determined by the adsorption of butylamine at 80 °C and acetic acid at 130 °C, and are given in Table 1. It can be seen from the table that the *EN* of the promoter oxides added apparently influenced the acid-base property of the potassium-promoted iron oxide, although the correlation between the *EN* of promoters and the measured acid-base properties of the catalysts was not complete however there is a tendency that a promoter oxide of lower *EN* would give higher adsorbed amount of acetic acid, basicity, and lower adsorbed amount of butylamine, acidity, on the catalyst.

Consequently, it was found that the styrene formation rate increased and its E_a decreased as the *EN* of the transition metal oxide added decreased. Decreasing the *EN*, i.e., increasing the basicity of the promoter may give rise to the dehydrogenation activity of the catalyst, because each basic site is considered to abstract hydrogen from hydrocarbons,[7)] especially β-hydrogen from ethylbenzene.[8)] Cerium oxide was found to be the best promoter for accelerating the styrene formation, and a hydrogen-transfer reaction on this oxide was reported,[9)] though the dehydrogenation itself has never occurred on a pure cerium oxide. Interestingly, increasing the *EN*, i.e., acidity, decreased the formations of benzene and toluene; this result is opposite to what has been considered: the decomposition of ethylbenzene has been considered to take place on the acidic sites of the potassium-promoted iron oxide catalyst.[10)]

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