2672 © *1986 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *59*, *2672—2674 (1986)* [Vol. 59, No. 8

Dehydrogenation of Ethylbenzene on Potassium-Promoted Iron Oxide Catalyst Containing Magnesium Oxide

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(Received March 26, 1986)

Synopsis. Among potassium-promoted iron oxide catalysts containing a minor chromia and a series of alkaline earth oxides, i.e., MgO, CaO, SrO, and BaO, the MgO-containing catalyst showed the best performance with respect to the dehydrogenation activity and the stability even at a steam-to-ethylbenzene molar ratio (H_2O/EB ratio) as low as 6.

The styrene monomer has commercially been produced by the dehydrogenation of ethylbenzene over potassium-promoted iron oxide catalysts in the presence of steam; the usual industrial catalysts consist of iron oxide, potassium carbonate and chromia:[1] known as Shell 105 or G-64A. Nowadays, styrene producers are making efforts to reduce steam consumption from a standpoint of saving energy, that is, lowering the H_2O/EB ratio has the advantage of reducing cost of styrene. Therefore, a more active and stable catalyst is desired in order to obtain an appreciable styrene yield at a low steam condition.[2] In order to modify the catalytic properties of the potassium-promoted iron oxide containing a minor chromia, various alkaline earth oxides were added to the system and the effects of these additives, especially of magnesium oxide, upon the catalytic properties were investigated. Although some patents on dehydrogenation catalysts containing alkaline earth oxides have been published,[3] few basic studies on the catalysts have been carried out.

Experimental

All the catalysts examined were prepared as follows: iron oxide (α-Fe_2O_3, 23 m^2g^{-1}), chromia (Cr_2O_3) and suitable amounts of potassium carbonate (K_2CO_3) and alkaline earth carbonate were mixed and extruded to pellets of 3.2 mm dia. and 4—6 mm length. These were crushed into 16/20 mesh granulates for activity tests at a high H_2O/EB ratio of 11.8, and were used without crushing for long-run tests at a low H_2O/EB ratio of 6. The pellets were dried at 120 °C overnight followed by calcination at 600 °C for 4 h in a muffle furnace. The reactor made of stainless steel (20 mm i.d.) was used for the activity tests at atmospheric pressure. The products were analyzed by gas-chromatography. The surface areas were measured by the BET method. The amounts of carbonaceous deposits, including polymers, were determined by trapping the CO_2 released during oxidation at 450 °C in a closed system (138 cm^3) after vacuum treatments at 250 °C for 30 min. XRD measurements were carried out on a Rigaku X-ray diffractometer with Co $K\alpha$ radiation. The pore volumes and their distributions were measured on an Amco Hg-porosimeter.

Results and Discussion

In order to evaluate the intrinsic activities of catalysts whose compositions are listed in Table 1, dehydrogenation tests on granulated (16/20 mesh) catalysts were carried out at a low conversion region, a high H_2O/EB ratio of 11.8 and in the temperature range 550—620 °C. Since the catalysts were granulated and the H_2O/EB ratio was high, the influences of the pore structure and the deposited carbon on the activity could be eliminated; all the activities reached a steady state within about 20 h after starting a run. The rates and selectivities for styrene formation at 580 °C, and the activation energies for styrene, benzene and toluene formations over various catalysts are listed in Table 1. Among the alkaline earth oxides added, only MgO enhanced the dehydrogenation activity of the potassium-promoted iron oxide without decreasing the selectivity, and CaO enhanced the selectivity although the activity was decreased. The order of promoting effect on the activity was as follows: MgO > SrO > CaO > BaO.

Changing the magnesium content in the Fe_2O_3-K_2CO_3-Cr_2O_3-MgO system, the rate and selectivity for the styrene formation were investigated as functions of the magnesium contents. The results are shown in Fig. 1, where the rate and the selectivity are plotted against the content. A plot of the rate shows a folded straight line, in which the rate increases with an increase in the content at low levels (0—4 wt%). It is almost independent of the content at high levels (4—12 wt%), although the selectivity does not show any significant change with the content. X-ray diffraction analyses of the Mg catalyst indicated that a part of the magnesium oxide was contained as a form of magnesium ferrite ($MgFe_2O_4$), the XRD patterns being shown in Fig. 2. When the MgO content was changed, as depicted in Fig. 3, the XRD peak intensity of the magnesium ferrite (d: 2.97 Å) increased with an

Table 1. The Dehydrogenation Activities,[a] Selectivities and Activation Energies on Various Granulated[b] Catalysts at High H_2O/EB Ratio

Catalys designation	Composition/wt%				r_{ST}[c]	Selec. to ST/%	*Ea*/kcal mol^{-1}		
	Fe_2O_3	K_2CO_3	Cr_2O_3	Others			ST	BZ	TOL
K	65	32	3	—	26.8	95.1	26.6	31.6	51.3
Mg	52	33	3	12 MgO	33.8	95.4	27.8	32.0	50.6
Ca	52	33	3	12 CaO	14.6	96.4	34.2	28.8	56.4
Sr	50	32	3	15 SrO	21.0	95.6	32.4	28.4	53.3
Ba	50	32	3	15 BaO	8.0	92.9	36.2	30.8	58.8

a) Test conditions: H_2O/EB ratio =11.8, SV=39100 ml $g^{-1}h^{-1}$, 3 g cat. b) 16/20 mesh. c) Rate of styrene formation (mol $g^{-1}min^{-1}$, $\times 10^5$) at 580 °C.

increase in the content below 4 wt%. It then changed little in the content range 4—12 wt%; this behavior of the peak intensity of the magnesium ferrite with the magnesium content is similar to that of the activity with the content. On the other hand, the XRD peak intensity of magnesium oxide (MgO, d: 2. 11 Å) increased linearly with the content (Fig. 3). From these results, it is guessed that the formation of magnesium ferrite on iron oxide can participate in the effect of the magunesium addition on the activity of the potassium-promoted iron oxide catalyst.

For the ethylbenzene dehydrogenation catalyst, a stable activity is required under reaction conditions as well as the activity since the catalyst is used for one or two years at any styrene plant. In order to examine the stability of the Mg catalyst, the change in activity (% EB conversion) with time was investigated at a H_2O/EB ratio as low as 6 and 620 °C. It was then compared with the changes of the K and Ca catalysts; all the catalysts (3.2 mm dia. and 4—6 mm length) were used to investigate the pore structure in addition to the activity. As shown in Fig. 4, the Mg catalyst exhibited an appreciable activity and stability under such severe conditions, while other catalysts, i.e., K and Ca, showed a significant deterioration of the activity with time.

The physical properties of the catalysts in fresh and used states are listed in Table 2; increases in both surface area and pore volume were found on the Mg catalyst after a reaction, whereas those properties of other catalysts were decreased. The mean pore diameter of the Mg catalyst was not greatly altered after a reaction, compared to those of the K and Ca catalysts. These showed remarkable enlargements of the mean pore diameter; the mean pore diameters (***mPD***) were defined by the value at the midpoint of the cumulative pore distribution curve, because all the catalysts showed nallow distributions. Since the mean pore diameter can be determined from the size of the skeletons forming the pore structure of a pellet, the extent of pore destruction under reaction conditions can be expressed by the change in the mean pore diameter. The mean pore diameters of the K and Ca

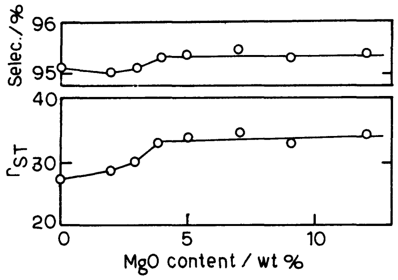

Fig. 1. Plots of the styrene formation rate (r_{ST}/mol g^{-1} min^{-1}, $\times 10^5$) and the selectivity to styrene at 580 °C vs. MgO content in the potassium-promoted iron oxide catalyst.

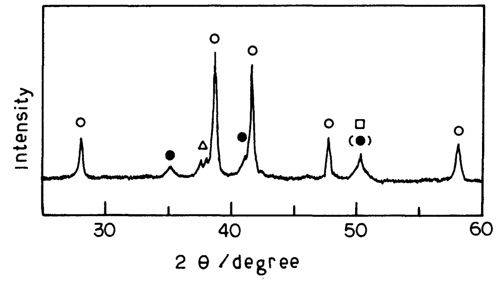

Fig. 2. X-Ray diffraction pattern of the Mg catalyst; ○: α-Fe_2O_3, △: K_2CO_3, ●: $MgFe_2O_4$, □: MgO.

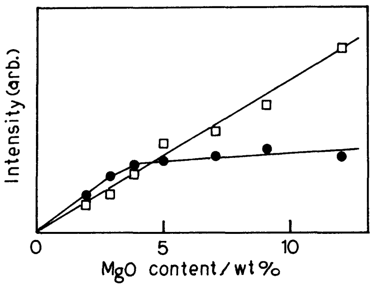

Fig. 3. Plots of the XRD peak intensities of $MgFe_2O_4$ (●; d: 2.97 Å) and MgO (□; d: 2.11 Å) vs. MgO content in the potassium-promoted iron oxide catalyst.

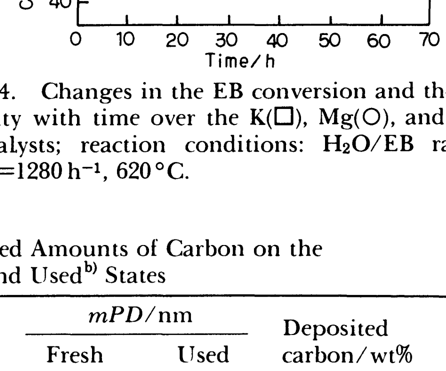

Fig. 4. Changes in the EB conversion and the selectivity with time over the K(□), Mg(○), and Ca(△) catalysts; reaction conditions: H_2O/EB ratio=6, *SV*=1280 h^{-1}, 620 °C.

Table 2. The Physical Properties and the Deposited Amounts of Carbon on the K, Mg, and Ca Catalysts[a] in Fresh and Used[b] States

Catalyst designation	*SA*/$m^2 g^{-1}$		*PV*/$cm^3 g^{-1}$		*mPD*/nm		Deposited carbon/wt%
	Fresh	Used	Fresh	Used	Fresh	Used	
K	4.8	3.8	0.27	0.24	266	412	0.117
Mg	3.4	4.4	0.39	0.47	457	430	0.127
Ca	4.0	2.7	0.28	0.27	282	397	0.039

a) Pellets of 3.2 mm dia. and 4—6 mm length. b) Reaction conditions; H_2O/EB ratio=6, *SV*=1280 h^{-1}, 50 cm^3 cat.

catalysts were enlarged and their surface areas were reduced; therefore, the pore skeletons, which may be constituted by iron oxide particles, of both catalysts might grow under the reaction conditions. On the other hand, the MgO catalyst exhibited little change in the mean pore diameter; hence, it is considered that the magnesium addition might prevent the pore destruction of the potassium-promoted iron oxide catalyst. From these results, it is suspected that the stability of the pore structure of the Mg catalyst might be associated with the observed stability of the activity at a low H_2O/EB condition.

The carbonaceous deposit on the catalyst was sometimes considered to deactivate the catalysts;[4] however, such a deactivating effect was not observed in this study because the deposited amounts on the K and Ca catalysts, which showed a deterioration in the long-run test, were not so large as that on the Mg catalyst, which showed little deterioration. Then, it can be presumed that the carbonaceous deposit does not exist on the active sites to inhibit the activities.

In earlier commercial dehydrogenation catalysts, MgO and CaO were used as a support.[5] Lee[6] investigated a binaly system of the iron oxide-alkaline earth oxide to find a relationship between the intrinsic activity and the first ionization energy for an alkaline earth atom. The order of the promoting effects of various alkaline earth oxides on iron oxide was as follows: BaO>SrO>CaO>MgO. This is different from the order obtained in this study. Accordingly, the promoting effect of MgO in the potassium-promoted iron oxide might be different from that in a binaly catalyst. From the results obtained in this study, the formation of magnesium ferrite in potassium-promoted iron oxide is considered to take part in the effects of a magnesium addition upon the activity and the stability of the catalyst.

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