React. Kinet. Catal. Lett., Vol. 16, No. 4, 345–348 (1981)

HYDROGENATION REACTIONS OVER ALKALI METAL DOPED MgO, II.

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Received August 11, 1980
Accepted December 5, 1980

The hydrogenation of benzene, styrene and isoprene over magnesia doped with sodium and potassium vapors has been studied. Neither system displays a catalytic activity towards benzene hydrogenation. The initial rate, turnover number and time of half-decay for styrene and isoprene hydrogenation have been determined.

Была проведена реакция гидрирования бензола, стирола и изопрена на окиси магния с присадками паров натрия и калия. Обе системы не проявляют каталитической активности по отношению к гидрированию бензола. Были определены величина начальной скорости реакции, атомная каталитическая активность и время полупревращения в гидрировании стирола и изопрена.

In previous papers /1, 2/ we have reported the results of investigations on the activity of MgO-alkali metal catalytic systems in the hydrogenation of simple alkene molecules. In the presence of sodium and potassium doped magnesium oxide, ethylene, propylene and cyclohexene hydrogenation occurs under normal pressure at 423 K. We have demonstrated that the very strong one-electron donor centers convert a nitrobenzene molecule (electron affinity 0.7 eV) to an anion radical. This form is responsible for the catalytic activity in these transformations. These centers were identified as surface color centers of the F_s^+ type, formed as a result of one electron transfer from a metal atom to an anionic vacancy on the oxide surface /2, 3/. Comparison of the catalytic activity of alkali metal doped MgO with the activity of SiO_2–Na and NaCl–Na systems led to the supposition that the catalytic activity is determined by the ionization energy of the surface color center dependent on the evaporated metal and the solid used as the second component of the system.

The aim of this work was to check the possibility of application of MgO-alkali metal systems as catalysts for the hydrogenation of unsaturated molecules with

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**Institute of Industrial Chemistry, Rydygiera 8, 01 793 Warszawa, Poland more complicated structure than simple alkenes: aromatic benzene and conjugated isoprene and styrene.

Similarly as in the case of our previous work reactions were carried out in a batch type reactor under normal pressure: hydrogenation of benzene and styrene at 453 and 523 K, hydrogenation of isoprene at 373 K. Each reaction was run with 240 cm^3 of an equimolar mixture of hydrocarbon and hydrogen and 300 mg of catalyst. The catalysts used were MgO-Na and MgO-K systems obtained by evaporation of the corresponding metals onto MgO calcined previously at 1023 K, according to the method described elsewhere /4, 5/. Reaction products were analyzed using a "Chrom 4" gas chromatograph with 30 m Carbowax 20M capillary column. The initial rates (measured as rates of substrate disappearance) were found by a graphical method. The values of turnover number were established on the basis of initial rates as the ratio of the number of substrate molecules reacting in unit time (s) to the number of one-electron donor sites capable to reduce nitrobenzene on the surface of the catalyst sample. The number of these centers was established via adsorption of nitrobenezene and recording its anion radical spectrum by ESR /4, 5/.

Both catalytic systems under study were found to be completely inactive in benzene hydrogenation under the conditions used, however, they displayed a high activity and relatively high selectivity in styrene and isoprene hydrogenation reactions (Table 1).

The main product of styrene hydrogenation was ethylbenzene. According to the results of benzene hydrogenation the aromatic ring in styrene did not undergo hydrogenation. Higher selectivity accompanied by lower activity (measured as initial rate or turnover number) was displayed by the MgO-Na system. Styrene hydrogenation over MgO-K catalyst was accompanied by hydrogenolysis, toluene being its main product. In the case of MgO with evaporated potassium at 523 K during the hydrogenation of styrene, the deposition of a surface polymer of aliphatic character has been observed already at the start of the reaction. This is probably the reason for tha slightly lower activity of the MgO-K system in the hydrogenation of styrene at 523 K relative to the activity of the MgO-Na catalyst at the same temperature.

Also in the case of isoprene hydrogenation the catalytic system MgO-K shows a higher activity than the MgO-Na system. The selectivity of transformation is considerable in both bases. There have appeared small quantities of isopentane – the product of total hydrogenation of isoprene. In the presence of MgO-Na and MgO-K catalysts the main reaction product is 2-methylbutene-2.

The general mechanism of hydrogenation is probably similar to that proposed by Tamaru et al. /6/ for the hydrogenation of charge-transfer complexes. In our case the first step is the formation of an EDA complex after alkene adsorption on the F_s^+ site, which was detected by ESR. After alkene adsorption the ESR spectra

Table 1
Catalytic activity of magnesium oxide-alkali metal systems in styrene and isoprene hydrogenation

Substrate	Catalyst	Initial rate (%/min)	Turnover number (mol spin/s)	Time of half-decay of substrate $\tau_{1/2}$ (min)	Composition of reaction products at $\tau_{1/2}$ (%)	
Styrene (T = 453 K)	MgO-Na[2]	0.72	14.3	115	ethylbenzene	50
	MgO-K[3]	2.2	55.0	62	ethylbenzene toluene benzene C_1, C_2	36.1 11.5 2.4 traces
Styrene (T = 523 K)	MgO-Na	4.2	83.4	12	ethylbenzene toluene benzene C_1, C_2	45.7 3.7 traces 0.6
	MgO-K	2.8	69.9	28	ethylbenzene toluene benzene C_1, C_2	25.8 17.3 5.1 1.8
Isoprene (T = 373 K)	MgO-Na	2.0	61.7	46	2-methylbutene-2 2-methylbutene-1 isopentane	43.0 7.0 traces
	MgO-K	4.6	183.3	12	2-methylbutene-2 2-methylbutene-1 isopentane 3-methylbutene-1	41.2 8.8 traces traces

[1] Concentration of one-electron donor sites capable of reducing NB: 8.2×10^{16} spin/g
[2] Concentration of one-electron donor sites capable of reducing NB: 6.5×10^{16} spin/g

of the catalysts reveal the signals of the corresponding anion radicals (e.g. a signal at g = 2.001 after cyclohexene adsorption, or a signal at g = 2.0012 after 1-pentene adsorption) /3, 5/. Demonstration of the simililarity of the phenomena observed by Tamaru et al. /6/ and by us has been given in Ref. /3/.

The higher turnover numbers calculated for the MgO-K catalyst indicate that the strongest one-electron donor centers (capable of reducing nitrobenzene) differ in reactivity towards the hydrocarbon molecules. Probably the lower ionization energy of F_s^+ centers in the MgO-K system (relative to their higher donor power) is responsible for their higher reactivity relative to that measured for F_s^+ centers in the MgO-Na system. This did not come as a surprise, as was shown formerly taking into consideration the lower ionization energy of potassium (4.37 eV) in relation to sodium (5.17 eV). One should expect that electron transfer to an anionic vacancy of MgO by a metal of a lower ionization energy would lead to an F_s^+ center also of a lower ionization energy, similarly to the case of color centers in alkali halides: the ionization energy of an F center in NaCl amounts to 2.7 eV, while in KCl to 2.4 eV.

Worth noticing is also the fact that the investigated systems are mild and selective hydrogenation catalysts.

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