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COLOUR CENTRES AS CATALYTIC ACTIVE SITES

By

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Abstract

The catalytic activity of MgO, SiO_2 and NaCl doped with metallic sodium vapour and MgO doped with metallic potassium vapour was studied in alkylaromatic hydrocarbons dehydrogenation and in alkenes hydrogenation. Evidences were found of the colour centres appearence after alkali metal evaporation on investigated solids and their promoting action in reactions under study was established.

Introduction

The presence of defects such as colour centres in the crystal lattice of a solid has a large influence on the change of the activation energy of chemical reactions connected with electron transfer processes. Colour centres are the cause of greater electron accessibility in donor-acceptor processes; this may be reflected in the lower ionization energy corresponding to F centres in alkali metal halides as compared with the ionization energy of pure metals. For example, the ionization energy of the F centre equals 2.3 eV in NaBr and 2.7 eV in NaCl, whereas the ionization energy of metallic sodium equals 5.14 eV. The relation among the number of defects and colour of the catalysts and their catalytic activity was observed by Roginski.[1] The role of surface defects in the catalysts of the alfin and Ziegler-Natta type was also studied by Bychowskij and Minsker.[2]

In our previous papers we called attention to the possibility of the occurence of F-type centres in the case of catalysts obtained by evaporation of metallic sodium onto magnesium oxide surface.[3] We postulated that these centres are formed as result of the reaction of sodium atoms with anionic vacancies present on the oxide surface, as in the case of the reaction of hydrogen atoms with anionic vacancies on MgO observed by Svejda *et al.*[4] The presence of F-type centres served to explain the very strong one-electron

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donor properties of catalysts obtained through the action of sodium vapour on magnesium oxide. It seemed very probable that other catalytic system containing colour centres would also have such strong one-electron donor properties and similar catalytic activity.

Polycrystalline sodium chloride, silica gel and magnesium oxide doped with metallic sodium (vapour) and MgO with evaporated metallic potassium were the subject of the present investigations. Sodium chloride subjected to the action of sodium vapour is a classic model containing F-type centres. The mechanism of the formation of such centres was given by Schottky and de Boer. They found that it is caused by chemisorption of the metal on the surface of the crystal.

In our previous work we found that silica gel doped with metallic sodium (vapour) possesses very strong one-electron donor properties.[5] After evaporation of the metal SiO_2 changes its colour to violet-brown. One could therefore believe that also in this case colour centres occur on the surface of the system. Magnesium oxide doped with potassium (vapour) was the next in the series of catalytic systems investigated by us. This type of catalyst was obtained by evaporation of an alkali metal onto an alkaline earth metal oxide.

In this work the one-electron donor properties of the above mentioned system were investigated by the method of adsorption of organic electron acceptors (tetracyanoethylene —TCNE and nitrobenzene— NB). Their paramagnetic properties were investigated by ESR spectroscopy. Catalytic activity was studied in the conversion of cumene and ethylbenzene as well as in ethylene, propylene and cyclohexene hydrogenation.

Experimental

The sodium chloride employed was of commercial grade (Reachim). Magnesium oxide was obtained by the hydrolysis of $Mg(NO_3)_2 \cdot 6H_2O$ with aqueous ammonia. Silica gel was obtained through the hydrolysis of silicone ethoxide. Before evaporation of the alkali metals MgO and SiO_2 were calcined in a stream of dry and deoxygenated argon at a temperature of 750°C, where as the sodium chloride was dried at 500°C under vacuum of 10^{-2} Torr. Evaporation of alkali metals was carried out under vacuum of 10^{-2} Torr : sodium at temperature 450°C and potassium at 400°C. After evaporation of the metal the MgO–Na_m and SiO_2–Na_m system were evacuated under 10^{-2} Torr at 500°C for 2 hr, whereas the MgO–K_m system was evacuated under 10^{-2} Torr at 450°C for 2 hr. Sodium chloride with evaporated alkali metal was not subjected to the following vacuum treatment.

ESR measurements were carried out using Jeol JMX spectrometer. Spectra of the samples with adsorbed electron acceptors were obtained at room temperature, whereas the spectra of pure catalysts at room temperature and at *ca.* −100°C. Adsorption of TCNE and NB was performed by a method described earlier.[6] The reactions of cumene and ethylbenzene conversions were carried out in a conventional flow reactor with a fixed catalyst bed at a temperature of 550°C, the space velocity was 1 g hydrocarbon per 1 g of catalyst per hour. Ethylene, propylene and cyclohexene hydrogenation was carried out in static reactor at a temperature 150°C under normal pressure. Each reaction was run with 80 cm^3 of an equimolar mixture of alkene and hydrogen in the presence of 300 mg of the catalyst.

Results

1. *ESR measurements*

Relatively narrow ($\Delta H_{max} \sim 1.5$ Gs) signals with a g factor value close to 2.003 (Fig. 1) were found to occur in the ESR spectra of all catalysts under study. The intensity and the shape of those signals did not depend upon the temperature of the measurement. It may be presumed that, as was postulated in the case of magnesium oxide doped with sodium (vapour)

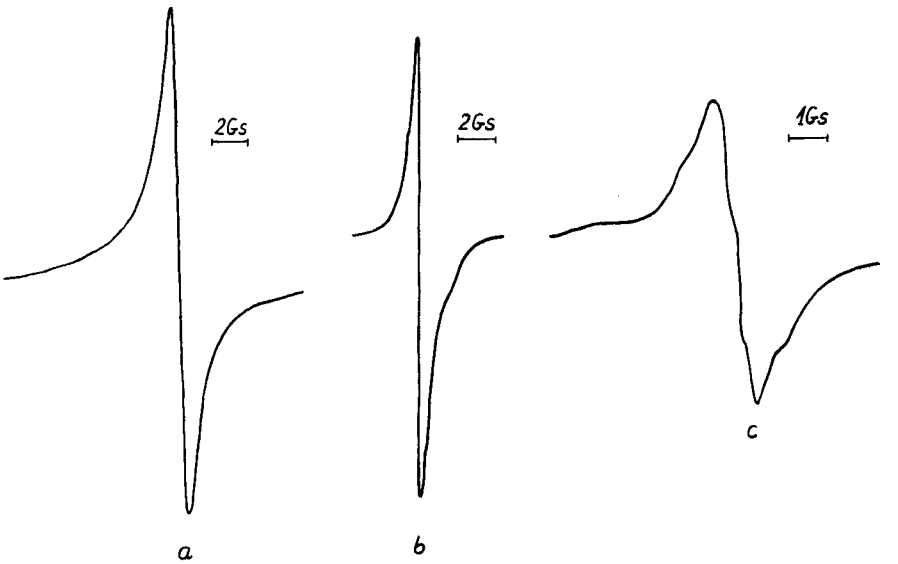

Fig. 1. ESR signals of paramagnetic species formed after alkali metal evaporation: a—potassium on MgO, b—sodium on NaCl, c—sodium on SiO_2.

these signals originate from the electrons given away by the alkali metal atom to the surface defect of the MgO (anionic vacancy), that is from F-type centres. This is confirmed by the colour of the catalysts obtained: MgO doped with sodium and potassium (vapour) are navy-blue, NaCl with evaporated sodium is violet and SiO_2 with evaporated sodium is violet-brown. The lack of differences in the shape of signals registered at $-100°C$ and at room temperature also suggests that the sources of paramagnetism observed are electrons localized in lattice defects. Kazanski *et al.* based his reasoning on similar premises when analysing spectra of catalysts obtained by the dispersion of alkali metals on the surface of alumina.[7]

After the adsorption of TCNE and NB on the surfaces of all the investigated catalysts ESR signals originated from the surface radical anions being formed were registered. The numbers of surface paramagnetic species form were very large and equaled approximately 10^{20} spin/g. The signals registered (Fig. 2) did not show any hyperfine structure; this fact may be explained in terms of the high radical ions concentration and, in this case,

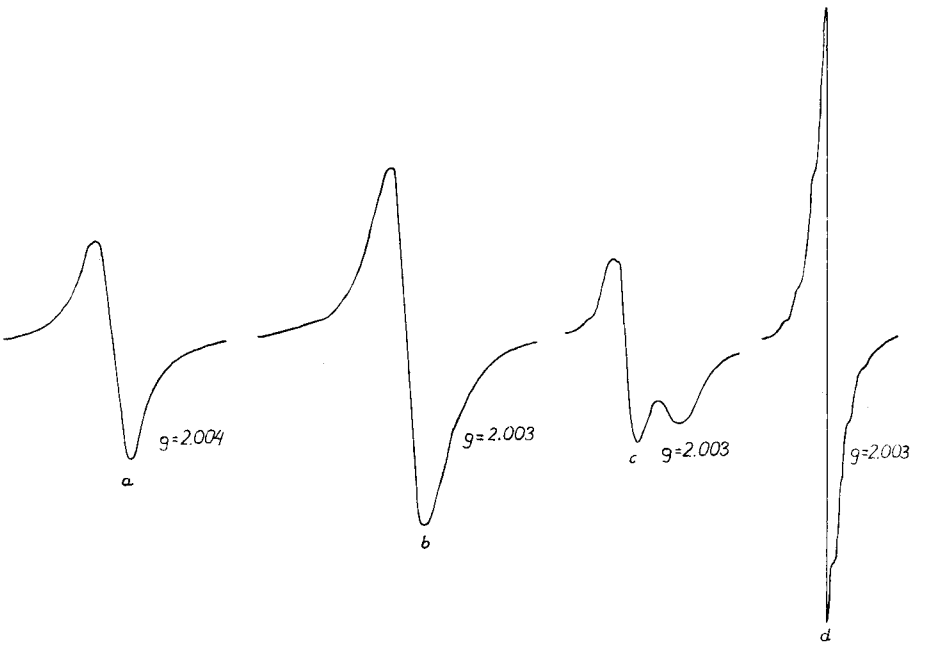

Fig. 2. ESR signals of anion radicals formed after adsorption of: a—NB on the surface of SiO_2–Na_m system, b—TCNE on the surface of NaCl–Na_m system, c—NB on the surface of pure MgO treated under vacuum of 10^{-4} Torr at 750°C, d—TCNE on the surface of pure MgO calcined in argon at 750°C.

strong exchange interactions; their total width ΔG_{tot} equaled about 40 Gs and $\Delta H_{max} = 4-5$ Gs.

On the surfaces of MgO–Na_m and MgO–K_m systems adsorption of reaction substrates, cumene, ethylbenzene and cyclohexene was performed and such treated catalyst samples were investigated using ESR spectroscopy. Adsorption of cumene on the surface of magnesium oxide doped with metallic sodium was performed at 250°C, adsorption of ethylbenzene on the surface of MgO–K_m system at 300°C and the adsorption of cyclohexene on the surface of this same catalyst at 150°C. In all cases as a result of adsorption the disappearence of navy-blue coloration of samples was observed. The ESR spectroscopic method revealed the signals of the organic radicals resulting from cumene, ethylbenzene and cyclohexene adsorbed on the catalysts surfaces. The g values of these signals were estimated to be 2.006 for cumene and ethylbenzene and 2.001 for cyclohexene. The formation of paramagnetic intermediate compounds as a result of hydrocarbons adsorption indicates that their further transformations may be initiate (with the action of one-electron donor centres.)

2. *Catalytic activity*

a) *Alkylaromatic hydrocarbons conversion*

The main product of cumene reaction carried out at 550°C was dehydrogenation product — α-methylstyrene. Apart from it small quantities of

TABLE 1. Yields of products of cumene and ethylbenzene conversion

Catalyst	Substrate of reaction	Yields of products [moles per 100 moles of substrate]				
		benzene	toluene	ethyl-benzene	styrene	α-methyl-styrene
MgO–Na_m	cumene	0.8	1.4	1.0	0.4	27.0
	cumene+TCNE*	trace	0.4	0.1	0	3.1
	ethylbenzene	0.8	5.2	—	25	0
MgO–K_m	cumene	2.0	trace	2.4	trace	14.4
	ethylbenzene	2.9	13.5	—	27.1	0
SiO_2–Na_m	cumene	4.0	1.0	6.0	5.1	10.2
	ethylbenzene	2.5	3.0	—	15.0	0
NaCl–Na_m	cumene	1.1	6.0	2.1	3.0	9.2
	ethylbenzene	0.7	4.2	—	9.3	0

* catalyst poisoned with stoichiometric amount of TCNE

decomposition products, benzene, toluene and ethylbenzene, were found (Table 1). In gaseous products hydrogen and C_2 and C_3 alkanes and alkenes were identified. Catalysts obtained through evaporation of alkali metals on MgO proved to be more active than the SiO_2–Na_m and NaCl–Na_m catalytic systems.

On all the catalysts under study the main product of ethylbenzene reaction at 550°C was styrene. Small quantities of cracking products, toluene and benzene were formed during reaction (Table 1). Similarly as in cumene dehydrogenation, the catalysts obtained by evaporation of alkali metals onto MgO were found to be more active than catalytic systems SiO_2–Na_m and NaCl–Na_m.

b) *Hydrogenation reactions*

Both catalysts obtained by evaporation of alkali metals onto magnesium oxide were active in hydrogenation of ethylene, propylene and cyclohexene at 150°C (Table 2). The catalytic system MgO–K_m exhibits considerably greater activity, especially in the case of cyclohexene hydrogenation. Catalysts obtained by evaporation of metallic sodium onto NaCl and SiO_2 surfaces and pure MgO proved to be completely inactive in the hydrogenation of investigated alkenes under adopted conditions. The alkanes formed in transformations over investigated catalysts are undoubtedly products of reactions taking place with hydrogen participation. The possibility of a self-hydrogenation process (C=C→C−C+surface coke) may be excluded, as we have not observed any traces of hydrogenation products in absence of hydrogen (similarly as any traces of products of other transformations *e. g.* polymerization).

TABLE 2. Initial rates of alkenes hydrogenation

Catalyst	Initial rate of hydrogenation reaction [min^{-1}]		
	ethylene	porpylene	cyclohexene
MgO–Na_m	7.4	4.4	0.4
MgO–K_m	10.2	6.5	4.9
SiO_2–Na_m	0	0	0
NaCl–Na_m	0	0	0

3. *Catalysts poisoning*

In order to block one-electron donor centres TCNE was adsorbed on the surface of MgO–Na_m system. The amount of TCNE was stoichiometric with respect to the amount of the radical centres found on catalyst surface.

On thus prepared catalyst the reaction of cumene was carried out. The poisoning of one-electron donor centres resulted in a great decrease of cumene conversion (Table 1). The amount of α-methylstyrene decreased almost ten times and the yields of the other products also largely diminished.

The hydrogenation of ethylene and propylene was carried out in the presence of the MgO–Na_m catalyst and propylene hydrogenation in the presence of the MgO–K_m system, both of which having blocked one-electron donor centres with stoichiometric amount of TCNE. Thus prepared catalysts exhibited a complete lack of activity for the investigated reactions.

Conclusion

Evaporation of alkali metals onto the surface of magnesium oxide, silicon dioxide and sodium chloride leads to the appearance of coloration, which disappears immediately after contact with oxygen or traces of water. At the same time one can observe using ESR spectroscopy the formation of new paramagnetic centres, which give signals with a g factor value close to 2.003. These effects are most probably results of the formation of surface F-type colour centres. Systems with evaporated alkali metals gain very strong one-electron donor properties. The concentration of such centres and their strength are many times higher than in the case of the pure MgO (pure NaCl and SiO_2 completely lack one-electron donor sites). The one-electron donor centres formed are, without doubt, electrons originated from the evaporated alkali metal atoms, localized on surface anionic vacancies (in other words, colour centres).

The catalytic systems obtained by evaporation of alkali metals onto oxides and sodium chloride are active in the reaction of alkylaromatic hydrocarbons dehydrogenation while the MgO–Na_m and MgO–K_m systems are also active in the hydrogenation of ethylene, propylene and cyclohexene. The catalytic activity is most probably connected with the presence of very strong one-electron donor centres (F centres) and the course of the reaction is in agreement with the mechanism proposed by Krause[8] and by us in the case of MgO–Na_m system.[6] The additional evidences of such reaction pathway are the results of poisoning experiments. The formation of paramagnetic surface species after adsorption of cumene, ethylbenzene and cyclohexene vapours on MgO–Na_m and MgO–K_m catalysts may also testifiy to the radical character of the activation of dehydrogenated alkylaromatic hydrocarbons and hydrogenated alkenes. The more so, that in the case of NaCl–Na_m and SiO_2–Na_m systems which do not give any activity for the reaction of hydrogenation of olefins, the cyclohexene adsorption does not

lead to a formation of any surface forms detected by the ESR method.

Only catalytic systems obtained from magnesium oxide are active for alkenes hydrogenation, the more active catalyst being that doped with potassium (vapour). It seems probable that the differences in ionization energies of the colour centres are responsible for the differing activity in the hydrogenation reaction. It is beyond doubt that the colour centre obtained as a result of interaction between a potassium atom and a MgO surface anionic vacancy possesses a lower ionization energy than the colour centre obtained through the interaction between a sodium and a vacancy, because of lower ionization energy of metallic potassium in comparison with metallic sodium. It is plausible that the ionization energy of electrons in colour centres on the surfaces of SiO_2-Na_m and NaCl-Na_m is too high, and therefore as in the case of pure metals, they are not able to activate hydrogenation reaction.

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