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Nature of active sites in catalytic ammoximation of cyclohexanone to the corresponding oxime on amorphous silica: E.P.R. investigations

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Superoxide radical ions were observed at the surface of an amorphous silica active in the catalytic ammoximation of cyclohexanone with molecular oxygen. They were generated by the contact of oxygen with a thermally activated sample. The presence of organic radicals on the spent catalyst, which probably played a role in the catalytic process, was also observed.

Keywords: Amorphous silica; superoxide radical; ammoximation

1. Introduction

Oxidation catalysts essentially consists of transition metals supported on inert solids or oxides of transition elements. However, some cases have been reported in the literature in which simple SiO_2 acts as an oxidation catalyst: (i) oxidation of methanol to methyl formate [1] and (ii) cyclohexanone ammoxidation [2–7]. The latter reaction transforms the cyclohexanone into the corresponding oxime by interaction with ammonia and an oxidizing agent (scheme in fig. 1). Ammoximation with molecular oxygen as the oxidizing agent was first studied by Armor et al. of Allied Chemical Corporation [2,3] and, more recently, by our group [4–7]. The reaction is carried out with molecular oxygen, ammonia and an amorphous silica as the catalyst. This reaction is very interesting since simple silica is not considered an oxidation catalyst [8]. In a previous work [6,7],

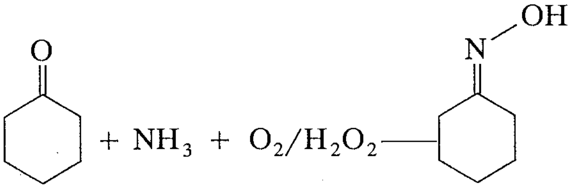

Fig. 1. Selective reaction pathway.

concerning the reaction network and the mechanism of the steps involved by flow-reactor experiments and FT-IR measurements, we have shown that the key step is the oxidation of the intermediate cyclohexanone imine into the oxime, even though the selectivity and the catalyst life are decreased by the deposition of tars on the catalyst. Nevertheless, the previous investigations did not clarify the nature of the active sites of the catalyst and did not give any explanation of the activation process that the catalyst undergoes. During the first 10–15 h of reaction, in fact, the conversion and the oxime yield increase. This activation, however, may be correlated to the tar deposition and to the total tar content.

In this paper, we report some preliminary E.P.R. data which provide information on the nature of the activated oxygen species that are considered to be responsible for the oxidizing processes, and on the presence of organic radical species in the tars deposited on the catalyst surface and their role in the catalyst activity.

2. Experimental

The catalyst used in the present work, as well as in previous work, is a commercial amorphous silica by AKZO CHEMIE (AKZO F-7), whose main characteristics are: surface area 472 m^2/g, pore volume 2.0 cm^3/g, apparent density 0.246 g/cm^3, Al_2O_3 and Na_2O impurities (0.07%wt, 0.01%wt respectively) and Ca (0.03%wt), Fe (0.002%wt), Ti (0.005%wt). The catalytic tests were carried out in a tubular glass fixed-bed plug flow micro-reactor. Details on the laboratory plant used in this work are contained elsewhere [6]. EPR spectra were recorded at room temperature (r.t.) and liquid nitrogen temperature (77 K) using an X-band Varian E109 spectrometer. A special cell containing EPR tubes and suitable connections with conventional gas manipulation and evacuation ramps was employed.

3. Results and discussion

In order to verify the presence of oxygen radical species on the silica surface during the catalytic test, a sample of AKZO silica was activated by annealing

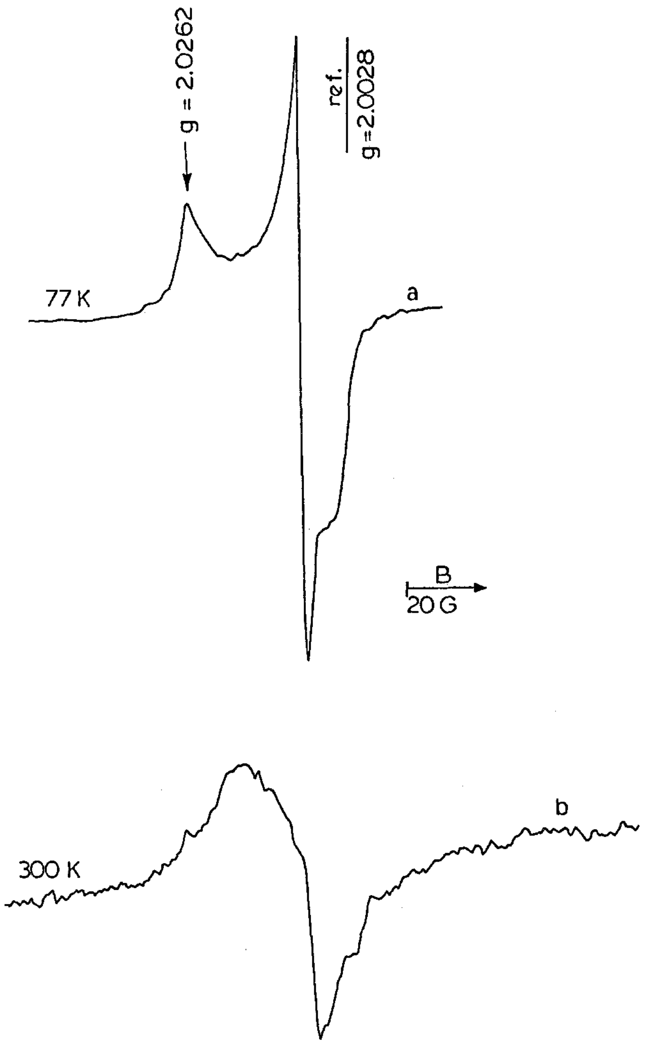

Fig. 2. EPR spectra obtained annealing the AKZO F-7 silica at 473 K and adding O_2 at room temperature. Spectra recorded at 77 K (a) and 300 K (b).

overnight at 473 K under dynamic vacuum. Then, molecular oxygen (200 Torr) was added at room temperature, kept in contact with the solid for one hour and, finally, pumped off. After this treatment the E.P.R. spectra shown in fig. 2 (respectively at (a) 77 and (b) 300 K) were observed. The spectrum, which was recorded in vacuum, is the typical anisotropic spectrum of the superoxide radical anion ($O_2^{\cdot -}$) adsorbed on a surface positive ion [9] and exhibits the following principal values of the g tensor: $g_{zz} = 2.0262$, $g_{yy} = 2.0096$, $g_{xx} = 2.0046$.

The experiment described above demonstrates that molecular oxygen is activated at the surface of the catalyst in the form of superoxide which is a well known electrophilic intermediate in oxidation reactions. The g_{zz} parameter (which is the most sensitive one to the electric field exerted by the adsorption site on the $O^{\cdot}_{2-}$ moiety) observed in the present case is typical of superoxide on a tetravalent cation [9,10]. The g_{zz} values reported in the literature for $O^{\cdot}_{2-}$ on SiO_2 amorphous systems range between 2.024 and 2.032 [11–14] while slightly higher values are given for quartz (2.044) [15]. However, the formation of $O^{\cdot}_{2-}$ on a SiO_2 system has never been observed, as in the present case, by simple thermal activation of the solid. A scrutiny of the literature, in fact, indicates that such a species can be formed by contacting oxygen with χ-irradiated silica [11], or by UV irradiation under oxygen [12,13] or by mechanical activation in air [14,15].

It should be noted that the parameters found for the superoxide ion in the present case are very close to those observed in the case of well dispersed Ti^{4+} ions grafted on a Vycor glass [16,17]. This solid is a high-area-porous silica glass which also contains boron. The spectra of $O^{\cdot}_{2-}$ ions adsorbed on Ti^{4+} were obtained either by photochemical activation [17] or by a procedure of thermal activation, very similar to that adopted in the present case [16]. The spectrum reported in fig. 2a more closely resembles those reported in refs. [16] and [17] than those observed on silica systems [11–15]. The agreement between g values is also very good. Moreover, in the case of ref. [16], the spectra recorded at room temperature exhibit a modified shape due to rotation of the adsorbed radical on the Ti^{4+} site. The same effect was observed in the present case (fig. 2b) and the similarity between the R.T. spectrum in fig. 2b and that reported in ref. [16] is again very strong. For these reasons, the possibility that the Ti impurity in the catalyst employed in the present work plays a role in the catalyst activity should be taken into account.

The role of Al^{3+} and Na^+ ions (also present as impurities in the sample) in the coordination of adsorbed superoxide is not taken into consideration since the value of the g_{zz} parameter would be, in that case, definitely higher than the present one [9].

A second E.P.R. experiment was carried out to investigate the presence of organic radical species on the catalyst surface dirtied by the tars, and the changes occurring at the silica surface due to the tar deposition. For this purpose, six samples of spent catalysts, containing different amounts of tars deposited on the catalyst surfaces, were prepared by running the reaction in the standard conditions and then stopping the reaction at different time-on-stream values (0.5, 2.0, 4.0, 8.0, 16.0, 32.0 h). All samples gave rise to the same EPR spectrum consisting of a single broad line, with a peak to peak width of 0.56 mT, characterized by a g value of 2.0035. The lack of hyperfine structure did not allow the identification of the paramagnetic species responsible for the observed spectrum. The intensity of the signal increases with the time-on-stream, but, unlike the total tar content (g of tars per g of catalyst), the increase is not linear with time-on-stream (fig. 3). The intensity increases linearly during the first 4 hours of the reaction and then jumps up in correspondence to the large increase

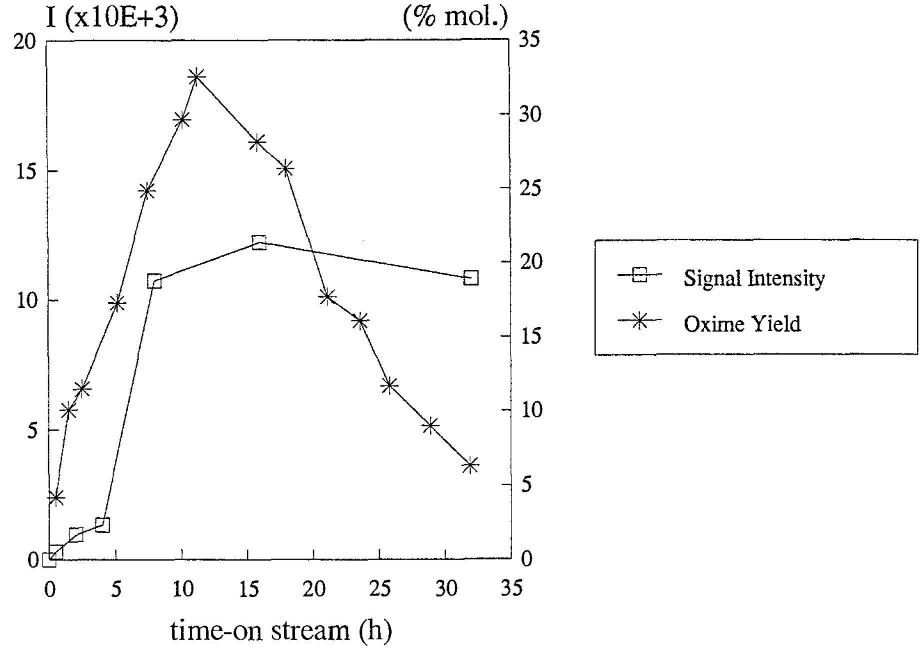

Fig. 3. Time evolution of the oxime yield and of the intensity of EPR signal corresponding to organic radicals observed on the discharged catalysts.

in activity and selectivity that occurs during the catalytic test [6]. After the first 10 h of the reaction, when the maximum in oxime selectivity has been reached, the signal intensity remains fairly constant up to complete catalyst deactivation, whereas the yield in oxime decreases rapidly. On the contrary, the rate of deposition of tars on the catalyst remains constant during the catalytic test up to 32 h of time-on-stream.

4. Conclusions

The EPR evidence presented in this work shows that the amorphous silica sample used as a catalyst for the gas-phase ammoximation of the cyclohexanone to the oxime with molecular oxygen is a real oxidation catalyst since it activates O_2 in the form of a superoxide radical ion ($O_2^{\cdot -}$) which is known as a very reactive electrophilic species. It is remarkable that this activation is achieved in experimental conditions very similar, indeed, to the real reaction conditions. On the other hand, the principal values of the *g* tensor seem to indicate a possible role of Ti incorporated into the lattice or segregated on the silica surface. In catalytic tests carried out with catalysts in which Ti traces were absent a lower activity and lower selectivity were observed [5] indicating that, even though the Ti ions may play a role in the chemical process, they can not be considered as the only sites involved in oxygen activation. EPR experiments analogous to those presented in this paper are in progress on samples with very little Ti content. Preliminary results indicated that no superoxide radical signals are observed.

The EPR results also show that the silica surface covered by tars is rich in organic radicals. The signal intensity can not simply be correlated to the tar content (g tars/g SiO_2) but seems to be more easily related to the activation process of the catalyst which takes place during the first 10–15 h of reaction, suggesting that these radicals may play a role in the catalytic process. Therefore, in the samples investigated, two types of active species are present at the surface of the catalyst and involved in the oxidation process: (i) a $O_{2-}^{\cdot}$ species formed on silica and trapped on tetrahedral cations, probably Ti^{4+}, and (ii) organic radicals contained in large amounts in the catalyst tars whose possible role in H-abstraction from the imine or in O-insertion can not be ignored. Further investigation is required in order to verify this hypothesis and give a satisfactory explanation of the oxidizing power exhibited by silica.

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