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Surface complexes of cyclohexanone and aqueous solution of NH_3 on Ti-silicalite in liquid phase

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On the surface of the SiO_2 catalyst used in the ammoximation of cyclohexanone to cyclohexanone oxime in the gaseous phase the formation of the imine group (supposed precursor in the reaction) was found previously. The authors investigated the possibilities of the occurence of the imine group on Ti-silicalite used as catalyst in the same reaction when performed in liquid phase. The technique using Ti-silicalite (previously treated with H_2O_2) suspension in cyclohexanone, NH_4OH or their 1:1 mixture dried on an irtran disc gave the possibility of indicating the formation of surface adsorption complexes by IR spectroscopy. The appearance of a band at 1654 cm^{-1} corresponding to υ(C=N) after the adsorption of cyclohexanone together with NH_4OH indicates the formation of the imine group, whereas the simultaneous lowering of the intensity of the band 970 cm^{-1} (Ti-O vibration) indicates that the Ti centres take part in this process.

1. Introduction

The catalytic ammoximation of cyclohexanone to cyclohexanone oxime–both in liquid phase with H_2O_2 over Ti-silicalites [1] or in gaseous phase with O_2 over SiO_2-AKZO catalysts [2]–has been in the centre of interest in the last years, among others, also for ecological reasons. The mechanism of both types of ammoximation has not been fully elucidated up to now and a similarity between the mechanism of both types of reactions is questionable. This paper [3] is concerned with the investigation by IR spectroscopy of the sorption of cyclohexanone and NH_3 on the catalysts mentioned above and of the formation of the corresponding surface complexes under conditions nearing those of the catalytic ammoximation in gaseous phase. The investigations led to the finding that on the catalyst surface an imine group is formed which is then considered as the precursor of the oxidation step proper in the reaction in question.

The aim of this paper is to find whether under condition nearing those of the liquid phase reaction with Ti-silicalite as catalyst, the same group on the catalyst surface may be formed.

2. Experimental

The IR spectra were registered with the Nicolet spectrometer FTIR-MX1E at room temperature. The separation of the individual bands in the IR spectrum was performed with a computer system algorithm by A.E. Hughes and B.A. Sexton [4] using the Gauss-Lorentz product. The residua of the filtered spectrum were below 5%. The Ti-silicalite samples were adjusted by the so-called suspension technique: 0.2 g of the catalyst was ground with about 2 ml of cyclohexanone, an aqueous solution of NH_3 or their 1:1 mixture for about 5 minutes in an agate mortar. The resulting mixture was transferred with a pipette to an irtran disc. Before the measurement the disc with the suspension was dried at room temperature. Ti-silicalite was prepared according to [5,6] and the organic structuring agent (template) was eliminated by heating to 580°C for 4 hours in the air. Ti-silicalite synthesized in this way contained 1.10 wt% TiO_2 and exhibited good crystallinity; the ratio A_{545}/A_{450} of the absorbances of the bands 545 and 450 cm^{-1}, resp., in the region of skeletal vibrations, as determined with the KBr technique, was 0.55. The sample was subsequently treated with 30% aqueous H_2O_2 at room temperature for 24 hours. In the course of this procedure the colour of the sample changed from white to yellow.

3. Results and discussion

The suspension technique with irtran-2 as a support–which is chemically resistent towards the agents employed and exhibits transmission of IR radiation in the region of 4000 to 700 cm^{-1}–gives the possibility of investigating both the formation of adsorbed surface complexes (in this case in the ranges of 1800–1550 cm^{-1} and 4000–3000 cm^{-1} corresponding to the $>C=O$, $>C=N$ and N-H vibrations) and changes in the range of skeletal vibrations, especially those of the 970 cm^{-1} band ascribed to the Ti-O vibration in Ti-silicalite [7]. In the range of skeletal vibrations of the zeolite lattice also the band at 800–790 cm^{-1} may be formed, corresponding to the internal vibrations of the SiO_4 tetrahedra [8]. As it has been found already in our previous investigations [9] neither the intensity nor the frequency of this band undergo changes during the treatment of Ti-silicalite with H_2O_2 or after the adsorption of cyclohexanone, NH_3, H_2O etc. For this reason, this band may be used as an internal standard to which changes taking place with the 970 cm^{-1} band (Ti-O vibration) may be related. It is practially impossible to determine the quantity of the sample on the irtan disc by suspension technique. When using the absorbance of the 970 cm^{-1} band normalized to the absorbance of the 800–790 cm^{-1} band, the changes of the former which have taken place with the individual samples may be compared.

As it follows from figs. 1a, b, in the suspension of H_2O_2-treated Ti-silicalite with cyclohexanone a surface complex is formed, indicated by the formation of a

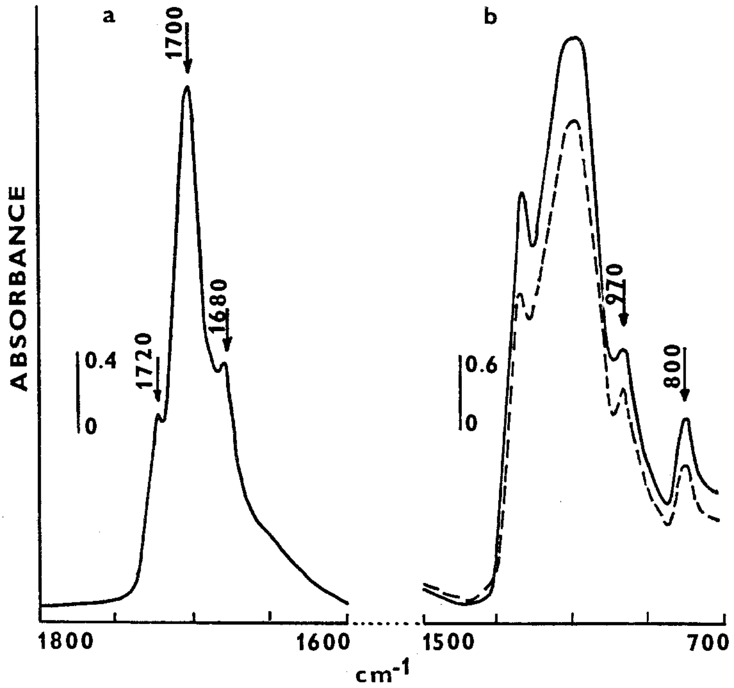

Fig. 1. a) IR spectra of Ti-silicalite suspended in cyclohexanone; b) IR spectra of Ti-silicalite in the range of skeletal vibrations: ——— suspended in cyclohexanone — — — suspended in H_2O.

1700 cm^{-1} band corresponding to υ(C=O) and by the simultaneous lowering of the intensity of the 970 cm^{-1} band (Ti-O vibration) in the range of zeolite skeletal vibrations. By repeated suspension experiments and by comparison with IR spectra of a Ti-silicalite suspension with only H_2O it was found that the band intensity decreases by 42%.

The similar results obtained with 25% aqueous solution of NH_3 are presented in figs. 2a, b. In this case, a surface complex is formed indicated by a band at 3400 cm^{-1} corresponding to υ(N-H), whereas the intensity of the 970 cm^{-1} is lowered again (by 9%).

Figs. 3a, b show the IR spectra of the suspension of H_2O_2-treated Ti-silicalite in the mixture of cyclohexanone with 25% aqueous solution of NH_3 in (1 : 1) the range of 1800–1500 cm^{-1} as well as in that of 1200–700 cm^{-1} (skeletal vibrations). Fig. 3a shows a broad band with several less distinguishable shoulders indicating the superposition of several bands. By the separation method mentioned above bands with maxima at 1723, 1648, 1676, 1654 and 1621 cm^{-1} were found. The bands at 1723, 1698 (vs) and 1676 cm^{-1} are ascribed to the υ(C=O) vibration of cyclohexanone adsorbed on the heterogeneous surface of Ti-silicalite; they were found also in the case of adsorption of cyclohexanone alone. The band at 1654 cm^{-1} is ascribed to the υ(C=N) vibration [10], it has been found also in the case of the imine group formation after the adsorption of

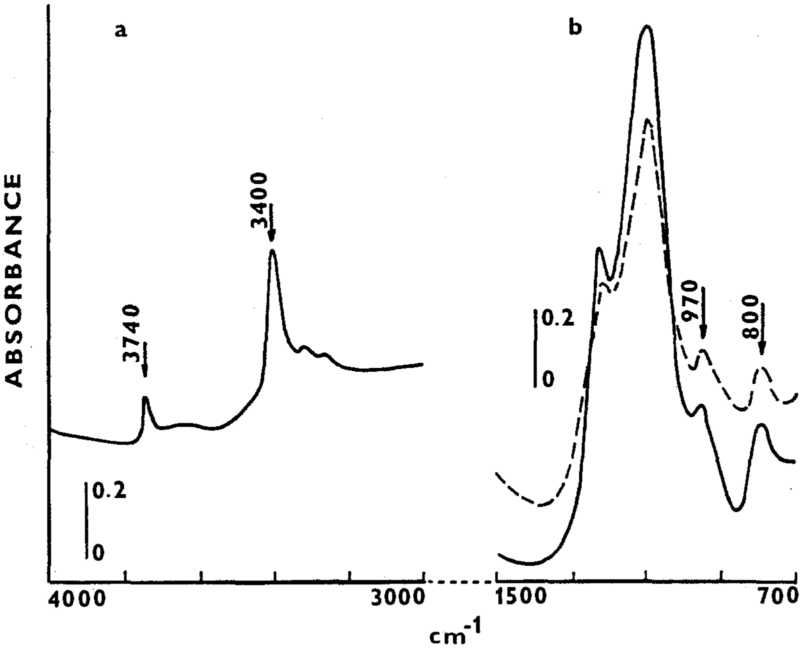

Fig. 2. a) IR spectra of Ti-silicalite suspended in aqueous solution of NH_3; b) IR spectra of Ti-silicalite in the range of skeletal vibrations: ——— suspended in aqueous solution of NH_3; suspended in H_2O.

cyclohexanone and NH_3 on AKZO silica gel [3] in gaseous phase. The 1621 cm^{-1} band corresponds to the deformation vibration of OH groups in adsorbed H_2O. In spite of the more hydrophobic character of Ti-silicalite in comparison with other zeolites, the existence of adsorbed H_2O on Ti-silicalite may be supposed for two reasons: (i) water is introduced into the suspension in the aqueous solution of NH_3, (ii) in the reaction between cyclohexanone and aqueous solution of NH_3 water is formed. This analysis of the bands in the IR spectrum indicates the formation of the imine group. In the region of skeletal vibrations the normalized absorbance of the 970 cm^{-1} band decreased after the treatment with H_2O_2 from 1.09 to 0.70. After the subsequent treatment with the mixture cyclohexanone + aqueous solution of NH_3 the absorbance decreases from 0.70 to 0.39 which indicates that the Ti-centres in the Ti-silicalite take part in the formation of surface complexes.

We may therefore conclude that in the sorption of cyclohexanone, an aqueous solution of NH_3 and their mixture the Ti-O centres in Ti-silicalite take part. We may also conclude that during the adsorption of cyclohexanone-aqueous solution of NH_3 mixture the imine group is formed also under conditions nearing those of the catalytic ammoximation of cyclohexanone to cyclohexanone oxime with H_2O_2 in liquid phase at 25°C (where this catalyst already exhibits a certain,

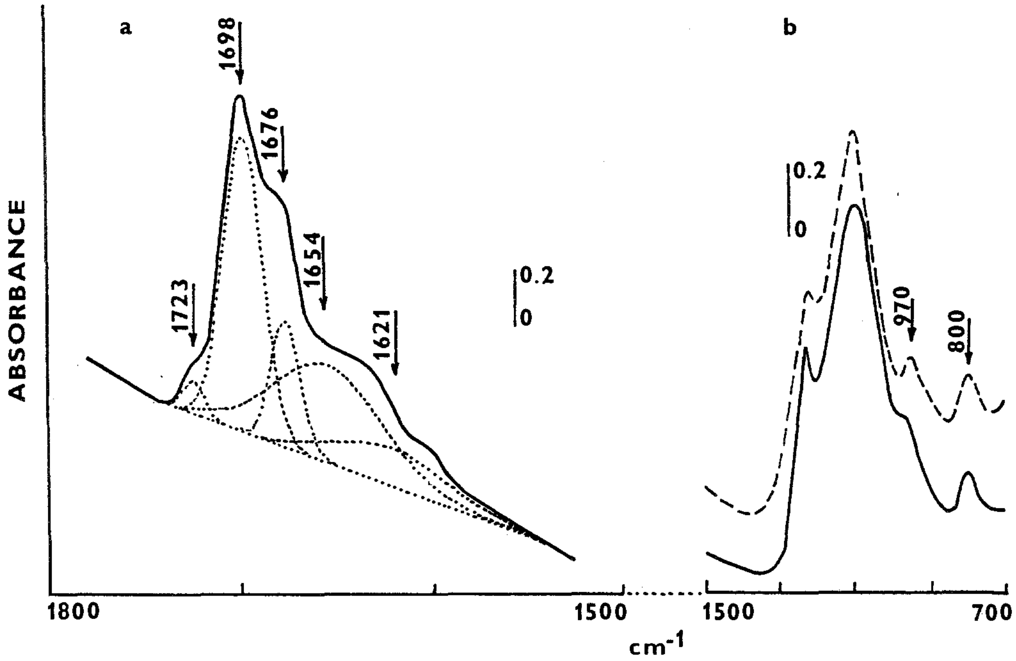

Fig. 3. a) IR spectra of Ti-silicalite suspended in the mixture of aqueous solution of NH_3 + cyclohexanone; b) IR spectra of Ti-silicalite in the range of skeletal vibrations: ——— suspended in the mixture of aqueous solution of NH_3 + cyclohexanone; — — — — suspended in the H_2O.

although low catalytic activity). The formation of this group is of importance as it seems that it may represent the precursor for the next oxidation step.

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