

Study of Propylene- d_6 and Acrolein Interaction with Silica Gel by Infrared Spectroscopy*

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The interaction of propylene- d_6 and acrolein at room temperature with silica gel dehydrated at 420°C has been investigated taking into consideration the use of silica as a carrier of oxide catalysts for propylene oxidation. Propylene- d_6 was found to be physisorbed on the surface "free" OH groups of silica gel. No evidence about the presence of chemisorbed complexes was obtained even after heating the adsorbent in the propylene- d_6 atmosphere at 225°C. After interaction of acrolein with silica gel the existence of physisorbed acrolein on the "free" OH groups of the adsorbent and of firmly bound complexes (probably of acrolein polymers) were revealed. The surface polymer species are quite stable; they were not fully desorbed even after heating at 320°C under vacuum. The type of bonding to the silica gel surface of both types of acrolein complexes has been discussed. The experimental data imply that in the studies of the properties of oxide catalysts supported by silica in propylene oxidation to acrolein the possibility of carrier influence cannot be neglected.

INTRODUCTION

Taking into consideration the industrial importance of mixed catalysts based on molybdenum for the selective oxidation of hydrocarbons much attention has also been drawn to the study of the nature of active sites on the Bi-Mo-O catalyst (unsupported or supported by SiO₂) for propylene oxidation to acrolein.

For this purpose of obtaining a more profound view into the role of silica we used infrared spectroscopy for the investigation of complexes formed on the silica surface during the interaction with propylene- d_6 and acrolein. In such a way we wanted also to complete our previous work on the same field dealing with the properties of the Bi-Mo-O/SiO₂ catalyst (1). Propylene- d_6

was used in adsorption studies to distinguish between hydrogen atoms coming from silica gel and from the adsorbate.

EXPERIMENTAL

Materials. Silica gel-Cabosil M 5 (Cabot Corporation, Boston) of 200 m²/g specific area was pressed under 1000 kg/cm² pressure into self-supporting plates of "thickness" 12 mg/cm². The sample was mounted in a holder in a vacuum infrared cell with NaCl windows (2). Before the adsorption experiments the sample was heated for 2.5 hr at 420°C under vacuum and oxidized for 2 hr ($p_{O_2} = 40$ Torr) at the same temperature. Then followed an evacuation of oxygen at room temperature and the record of the original spectrum of silica gel. The conditions of pretreatment were chosen to be similar to those described for the Bi-Mo-O/SiO₂ catalyst (1).

The propylene- d_6 consisted of 73.5% C₃D₆, 20.5% C₃D₅H, 3% C₃D₄H₂, 1% C₃D₃H₃ and 2 C₃H₆. The description of the

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process of propylene purification has been given elsewhere (1) together with data concerning acrolein (supplied by Fluka) and oxygen (obtained by thermal decomposition of KMnO₄).

Vacuum apparatus and spectroscopic measurements. The vacuum apparatus was of a conventional type with two infrared cells and a vacuum between 10⁻⁵–10⁻⁶ Torr could be obtained. A McLeod gauge enabled us to measure the adsorbate pressures. Thermal treatment of the sample was performed in the upper part of the cell outside the ir beam.

The spectra were recorded on double beam Perkin-Elmer 21 and 221 spectrometers in the frequency range 4000–1300 cm⁻¹. By arranging for the second cell (without sample) to be in the reference beam of the spectrometer the bands of the gas phase could be eliminated from the spectra. The spectra of the gas phase were recorded after evacuation of the reference cell and after removing the sample from the infrared beam.

RESULTS AND DISCUSSION

Adsorption of propylene-d₆. As seen from the original spectrum (Fig. 1), silica gel after thermal pretreatment described above contains surface "free" hydroxyls, not mutually influenced by hydrogen bonding—sharp band at 3745 cm⁻¹ and bulk "intraglobular" OH groups—shoulder at about 3650 cm⁻¹. The shape of the shoulder does not allow us to exclude also a possibility of presence of a comparatively small amount of mutually hydrogen bonded "bound" hydroxyls (3, 4).

The propylene-d₆ interaction with silica gel at room temperature ($p_{C_3D_6} = 80$ Torr) causes a decrease of the 3745 cm⁻¹ band height and an absorption increase on the low frequency side of this band. At the same time new weak bands appear in the spectral region 2300–2200 cm⁻¹ very near to the positions of the stretching vibration bands of CD_{*n*} (*n* = 1–3) groups of gaseous propylene-d₆ (Fig. 1). The original spectrum of silica gel may be easily restored by

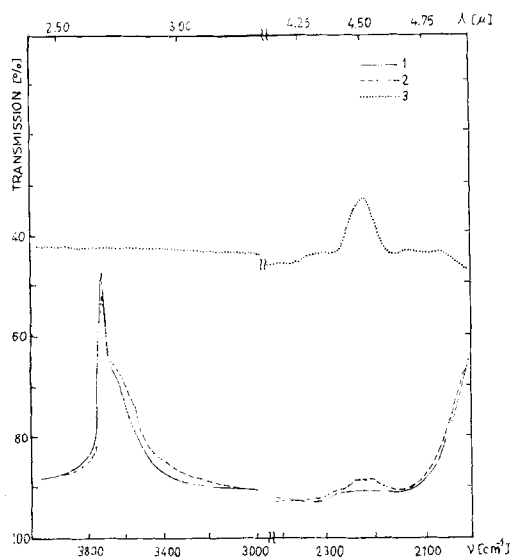


FIG. 1. Spectrum of silica gel: (1) after evacuation and calcination in O₂ at 420°C; (2) after 20 hr interaction with propylene-d₆ at room temperature ($p_{C_3D_6} = 80$ Torr); (3) Spectrum of gaseous propylene-d₆.

a 0.5 hr evacuation of the sample cell at room temperature.

Physisorbed propylene-d₆ is most likely responsible for the position of bands in the spectral region 2300–2200 cm⁻¹ as well as for the subsequent behavior of the silica gel sample under desorption conditions. From the spectral changes in the region 3800–3300 cm⁻¹ it follows that the centers on silica gel active for propylene adsorption are probably "free" surface hydroxyls absorbing under the influence of adsorbed species infrared radiation of lower wave numbers than the "free" OH groups not occupied by propylene. Our spectral data, however, cannot support the previously given suggestion (5) about participation of the C=C bond of propylene in the interaction with surface hydroxyls due to the weakness of the bands of adsorbed complexes.

Thermal treatment of silica gel in the presence of propylene-d₆ ($p_{C_3D_6} = 80$ Torr) at 225°C for 0.5 hr did not lead to additional spectral changes, so there was no evidence about formation of chemisorbed surface complexes. The exchange of hydrogen from hydroxyls of silica gel for

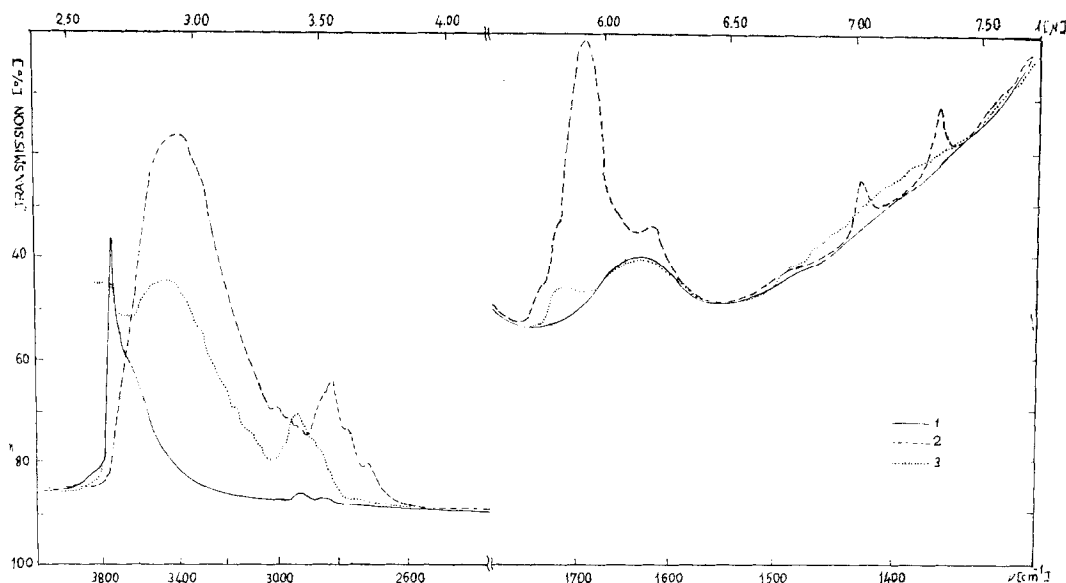


Fig. 2. Spectrum of silica gel: (1) after evacuation and calcination in O_2 at $420^\circ C$; (2) after 1 hr interaction with acrolein at room temperature ($p_{C_3H_4O} = 75$ Torr); (3) after subsequent 40 hr interaction with acrolein at room temperature ($p_{C_3H_4O} = 75$ Torr) followed by 1 hr desorption at the same temperature.

deuterium from propylene- d_6 was not observed either.

Adsorption of acrolein. The spectrum obtained after 1 hr interaction at room temperature of acrolein with silica gel ($p_{C_3H_4O} = 72$ Torr) is given in Fig. 2. Acrolein adsorption results in the disappearance of the silica gel "free" hydroxyl band at 3745 cm^{-1} and in the formation of the very broad strong band at 3420 cm^{-1} which may be assigned to the stretching vibration of OH groups influenced by hydrogen bonding. At the same time, the bands of adsorbed complexes were observed in the spectral region $3100\text{--}1300\text{ cm}^{-1}$. A 1 hr evacuation of the cells at room temperature following the 40 hr interaction of acrolein with silica gel at the same temperature ($p_{C_3H_4O} = 72$ Torr) substantially changes the spectral picture (Fig. 2). The band at 3745 cm^{-1} appears again, and the disappearance of the band at 3420 cm^{-1} is accompanied by the formation of the 3460 cm^{-1} band of lower intensity; in the frequency region $3100\text{--}1300\text{ cm}^{-1}$ only three bands of adsorbed species are found, viz., 2925 , 2850 , and 1725 cm^{-1} . This implies that together with the weakly adsorbed complexes which are desorbable at room temperature, the

TABLE 1
ASSIGNMENT OF THE BANDS OF WEAKLY
ADSORBED ACROLEIN ON THE SURFACE
OF SILICA GEL^a

Gaseous acrolein (cm^{-1})	Physisorbed acrolein silica gel (cm^{-1})	Assignment (θ)
3595 vw	?	Overtone or comb. tone?
3420 vw	?	$2 \times 1724 = 3448$
3095 vw	3020 vw	ν_{CH_2}
2985 vw	2975 vw	ν_{CH}
2810 m	2830 m	ν_{CH} (in CHO group)
2780 m ov	2775 sh	$1420 + 1360 = 2780$
		$1625 + 1158 = 2783$
2675-90 w	2710 w	$1420 + 1275 = 2695$
1915 vw, b	?	$2 \times 959 = 1918$
1815 vw, b	?	$2 \times 916 = 1832$
1728		
1712	1689 vs	C=C
1610 vw, b	1616 w	C=C
1426		
1408 w	1425 w	CH_2 scissoring
1360 vw		
1340	1368 w	CH bending

^a ν —Stretching vibration, w—weak, vw—very weak, m—medium, vs—very strong, sh—shoulder, b—broad, ov—overlapping.

firmly bound species of another composition are present on the surface of silica gel.

The comparison of the band positions of weakly adsorbed complexes in the spectral region 3100–1300 cm⁻¹ with the corresponding ones of gaseous acrolein (6) (Table 1) and changes of the hydroxyl stretching vibration bands in the course of the experiment have led to the conclusion that the acrolein molecules are probably physisorbed on the "free" OH groups of silica gel. The aldehydic groups probably take part in this interaction giving rise to hydrogen bonds with surface hydroxyls (cf. compared to gaseous acrolein, a shift of the C=O stretching vibration band of physisorbed acrolein 30 cm⁻¹ toward higher frequencies). A similar type of bonding was also observed by Young and Sheppard (7) in the case of adsorption of saturated aldehydes on silica gel. It seems that physisorption has no substantial influence on the C=C bond of acrolein.

The firmly bound complexes on the silica gel are quite stable. Under vacuum

conditions at elevated temperatures their amount diminishes. However, complexes are not fully removed from the surface even at 320°C. The desorption process is accompanied in the spectrum not only by an intensity decrease of the bands 2925, 2850 and 1725 cm⁻¹ but also by height changes of the stretching vibration bands of hydroxyls (rise at 3745 cm⁻¹, fall at 3460 cm⁻¹ (Fig. 3)).

The substance released from the silica surface at 200 and 320°C was collected in a trap cooled by liquid nitrogen and after evaporation was again adsorbed at room temperature. The bands in the spectrum recorded after this operation were found to be in the same positions as the bands in the spectrum of silica gel after acrolein adsorption.

The observation given above concerning the firmly bound species on the surface of silica gel may be explained on the basis of the suggestion of acrolein polymerization. During this reaction a saturation of the C=C bond probably proceeds. This sup-

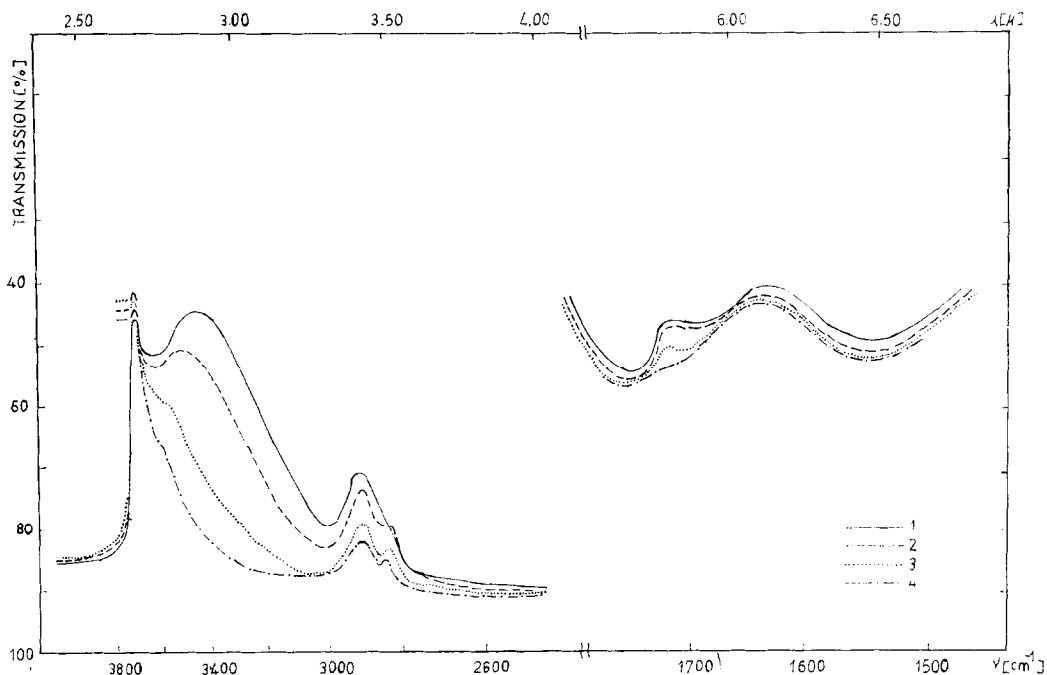


FIG. 3. Spectrum of silica gel evacuated and calcined in O₂ at 420°C after 40 hr interaction with acrolein at room temperature ($p_{\text{C}_3\text{H}_4\text{O}} = 75$ Torr) followed by 1 hr desorption at subsequent temperatures: (1) room temperature; (2) 125; (3) 200; (4) 320°C.

position is supported by the comparison of the positions of the 2925 and 2850 cm^{-1} bands assigned to stretching vibrations of CH_2 groups in saturated compounds and the position of the 1725 cm^{-1} band assigned to the $\text{C}=\text{O}$ stretching vibration with those of corresponding bands of acrolein polymers (8).

In the interaction with firmly bound species the "free" OH groups of silica gel are involved, as implied by the intensity changes of the 3745 cm^{-1} band in the course of desorption operations. The existence of the band at 3460 cm^{-1} may be explained by hydrogen bonding, probably of $\text{C}=\text{O}$ groups of polymer complexes with "free" hydroxyls of silica gel. However, the possibility of reaction of "free" OH groups with polymer species giving rise to hemiacetal or aldehyde hydrate structures (8) cannot be excluded.

The formation of polymer species is a time dependent process after 2.5 hr interaction of silica gel with acrolein at room temperature ($p_{\text{C}_3\text{H}_4\text{O}} = 72$ Torr) followed by the desorption of weakly adsorbed species the intensity of the bands of firmly bound complexes was found to be lower than after 40 hr interaction of acrolein with silica gel under the same experimental conditions.

Therefore, in the studies of the properties of mixed oxide systems supported by silica

in the oxidation of propylene to acrolein it is necessary to take into account the possibility of carrier influence not only on the physisorption of acrolein and propylene, but also on determining side reactions. These can lead to the formation of compounds which, by oxidation, may contribute in a certain way, to the formation of by-products.

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