FTIR STUDY OF THE INTERACTION
OF d₃-ACETONITRILE WITH SURFACE
OF V_2O_5-MoO_3 MIXED CATALYST

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The infrared spectra of adsorbed d₃-acetonitrile on V_2O_5-MoO_3 catalysts and for comparison on MoO_3 and V_2O_5 have been investigated at room temperature (RT). A general feature of all the V_2O_5- MoO_3 systems was the presence of Lewis acid sites capable of adsorbing d₃-acetonitrile on their surfaces by the formation of a coordination bond with metal cations. Two types of Lewis acid sites were reflected in bands at 2314 and 2306 cm^{-1}. In addition, d₃-acetonitrile adsorption on V_2O_5-MoO_3 mixed oxides yielded a band at 2296 cm^{-1} corresponding to the interaction with Brönsted acid sites.

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Introduction

MoO_3 and V_2O_5 oxides are frequently used in heterogeneous oxidation catalysis due to their high surface acidity [1]. The experimental data of Davydov [2,3] show that the Mo and V atoms in the highest state of oxidation (Mo^{6+}, V^{5+}) may produce the strongest Brönsted sites that are removed by reduction. The concentration of acid sites on the MoO_3 and V_2O_5 surface has been estimated from the IR spectra of adsorbed pyridine and ammonia molecules [1-4].

Because of its small size, the molecule of acetonitrile is often used as a probe to estimate the strenght of aprotic (Lewis) acid centers of zeolites and oxides. When the molecule of acetonitrile is free, the $\upsilon(C\equiv N)$ vibrations of CH_3CN are observed at 2251 cm^{-1} but are affected by a Fermi resonance with the $\upsilon(C-C)$ + $\delta(CH_3)$ combination, lying at 2287cm^{-1} [5]. Exchange of the CH_3 by the CD_3 fragment removes the effect of the Fermi resonance due to the strong decrease of the frequency of the combination vibration. This Fermi resonance complicates determination of the $\upsilon(C\equiv N)$ shift in complexes. Therefore, the use of CD_3CN is preferred for surface acidity measurements in this molecule [6]. In the present work we have performed an IR study of the adsorption forms of d_3-acetonitrile to investigate the role of acid sites of V_2O_5-MoO_3 catalysts in the oxidative dehydrogenation of crotonaldehyde (CRA) to maleic anhydride (MA).

Experimental

Pure oxides MoO_3, V_2O_5 (Sigma-Aldrich) and the V_2O_5-MoO_3 catalysts with Mo/(V+Mo) = 0.1, 0.4, 0.8 and 0.9 were used for the measurements. The preparation of the catalysts started with respective mixing of the hexaammonium heptamolybdate solution and ammonium vanadate solution. The mixture formed was evaporated to give a paste, which was then dried at 393 K. Consecutive calcination at 453 K and annealing in air at 573 K gave the optimum catalyst. The crystalline phases of the samples were studied by the X-ray analysis and the IR spectra of crystals were measured by using the KBr disc technique.

The pellets of samples (10-20 mg cm^{-2}) were heated at 573 K and evacuated before adsorption. D_3-Acetonitrile was then adsorbed at 1 kPa. IR transmission spectra were recorded on a Nicolet Protege 460 FTIR spectrometer with the resolution of 2 cm^{-1} by collecting 256 scans. The reported spectra of adsorbed species were obtained by subtraction of the spectra measured before adsorption (pure catalysts) from those taken after adsorption. IR bands of adsorbed d_3-acetonitrile were deconvoluted using a procedure consisting of identification of the band position in second derivative mode of the spectrum, and the least square minimalization routine approximating the bands by a Gaussian profile.

Results and Discussion

The adsorption of d_3-acetonitrile on V_2O_5, MoO_3 and the V_2O_5-MoO_3 samples leads in IR spectrum to the appearance of the group of overlapping bands in the 2290-2320 cm^{-1} region, corresponding to the complexes of acetonitrile molecules with electron-accepting sites on the surface (Fig. 1). Both single oxides exhibit a strong symmetrical band at 2314 and 2310 cm^{-1}, respectively, which reflects in the interaction of d_3-acetonitrile with (strong) Lewis sites. In addition, symmetrical band of $\upsilon(C\equiv N)$ mode at 2298 cm^{-1} of substantially lower intensity corresponds to the interaction of the $C\equiv N$ group with the OH groups of both oxides (Brönsted acid sites) [7,8].
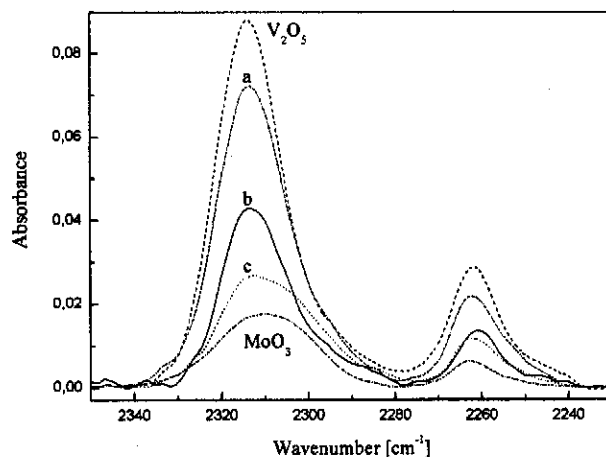

Fig. 1   IR spectra of d_3-acetonitrile adsorbed on MoO_3, V_2O_5 and V_2O_5-MoO_3 with Mo/(V+Mo) = 0.1(a), 0.4(b), 0.9(c) at room temperature

The adsorption at room temperature (RT = 298 K) also resulted in the formation of absorption bands in the wavenumber region above 2260 cm^{-1}. The intensity of the absorption bands at 2262 and 2250 cm^{-1} decreased after evacuation at RT (Fig. 2, dotted spectra). Positions of these bands are very close to those of gaseous d_3-acetonitrile [4,6] and can be associated with the $\upsilon(C\equiv N)$ and the $\upsilon_a(CD_3)$ vibration in molecular d_3-acetonitrile. Increase in the desorption temperature up to 373 K resulted in a substantial decrease in the intensity of all the observed absorption bands.

The deconvolution procedure of the IR spectra of d_3-acetonitrile adsorbed on V_2O_5-MoO_3 samples with variable molar ratio Mo/(V+Mo) yielded bands at 2314, 2306, 2296, 2285, 2275, 2262 and 2248 cm^{-1} (Fig. 3). The bands at 2314 and 2306 cm^{-1} were attributed to the adsorption of acetonitrile on two types of Lewis sites, strong and weak, respectively. By comparison with IR spectra of
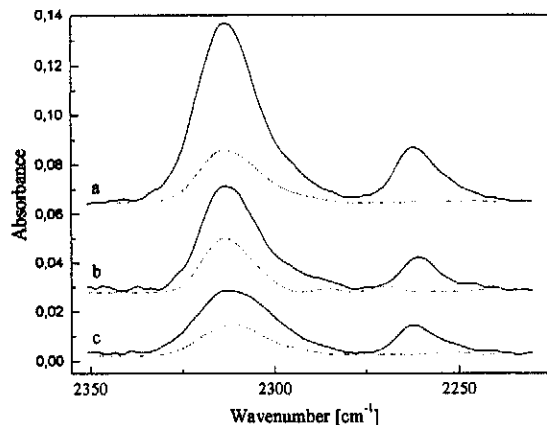
Fig. 2   IR spectra of d₃-acetonitrile adsorbed on V_2O_5-MoO_3 with Mo/(V+Mo) = 0.1(a), 0.4(b), 0.8(c) at RT(solid) and evacuated at RT (dotted)
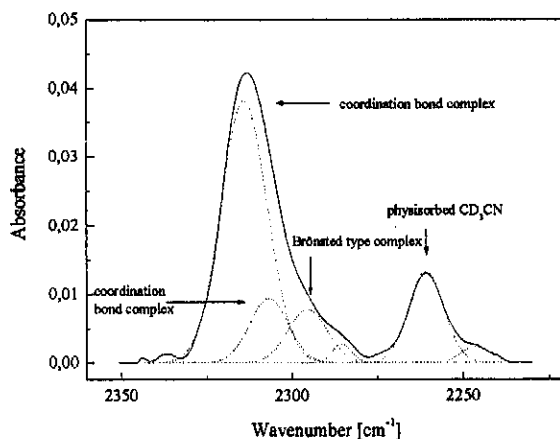

Fig. 3   Deconvolution of the IR spectrum of d₃-acetonitrile adsorbed on V_2O_5-MoO_3 with Mo/(V+Mo) = 0.4 at RT

V_2O_5, MoO_3, the peak at 2296 cm⁻¹ can be assigned to the C≡N stretching vibration of the CD_3CN bound to hydroxyl groups [7,8]. The bands at 2275, 2262 and 2248 cm⁻¹ are similar to those of gaseous d₃-acetonitrile and can be associated with the υ(C≡N) and the $υ_a(CD_3)$ vibration in physisorbed d₃-acetonitrile.

Conclusion

Our FTIR study of the d₃-acetonitrile adsorption on MoO_3, V_2O_5 and V_2O_5-MoO_3 oxides performed at 298 K indicates formation of several surface complexes: molecularly bonded one (physisorbed d₃-acetonitrile), the complex with

coordination bond with metal cations (Lewis acid sites) and the complex with Brönsted acid sites.

The physisorbed d_3-acetonitrile is very weakly bound to the surface and can be easily removed by short application of vacuum at room temperature.

Two types of Lewis acid sites on V_2O_5-MoO_3 surface were reflected in bands at 2314 and 2306 cm^{-1}. Surface coordinated species are formed by coordination of the nitrogen lone electron pair with Me^{n+} (Me = V or Mo). The bond strength of this surface coordination complex depends on the Lewis acidity of the particular site. One electron acceptor site prevailing in a whole concentration range of Lewis sites exhibits $\upsilon(C\equiv N)$-V^{5+} at 2314 cm^{-1}, while the other with $\upsilon(C\equiv N)$-Mo^{6+} at 2306 cm^{-1} represents a weaker and much less populated electron pair acceptor site.

In addition, d_3-acetonitrile adsorption on V_2O_5- MoO_3 mixed oxides yielded a band at 2296 cm^{-1} corresponding to the interaction with Brönsted acid sites. These data indicate that d_3-acetonitrile is adsorbed on the V_2O_5- MoO_3 surface by forming a hydrogen bond between the hydroxyl group and the nitrogen lone-pair electrons. The number of both acid sites depends on variable content vanadium and molybdenum in mixed oxides.

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