

Infrared spectroscopy to study the mechanism of catalytic reaction on molecular scale from diffusion to limiting stage kinetics

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Abstract

Reported here are results recently obtained at the Institute of Catalysis with the IRS of adsorbed molecules used to study the mechanisms of catalytic reactions occurring on the surface of heterogeneous catalysts. It has been found that the structure and strength of OH groups complexes with diffusing molecules (M) are the key factors determining the rate of molecules transfer inside the zeolite crystals. Stoichiometry 2M:1OH appears to provide a higher diffusion rate. Original procedures allowing the identification of surface species nature were designed. One of these procedures is based on a quantitative measurement and dosing at a joint adsorption of reagents and probe molecules. Using a joint adsorption of CO and *tert*-butyl chloride on fluorinated alumina, we have proved that *tert*-butyl chloride forms complexes with the Lewis sites through the chlorine atoms. The alternating adsorption of aromatic molecules and ammonia proved the aromatic molecule protonation on V₂O₅/Al₂O₃ catalyst. A lot of examples of IR mechanistic studies of catalytic reaction on surface are presented. There are butyl alcohol dehydration, methane partial oxidation, *n*-butyl amine deamination, NO_x selective reduction. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Infrared spectroscopy; Catalytic reaction; Molecular scale; Diffusion; Stage kinetics

1. Introduction

At present, IR spectroscopy of adsorbed molecules becomes a routine. This means that its simplicity and availability combined with high efficiency stimulates IRS application for a wide range of problems in heterogeneous catalysis. Zamaraev considered IRS to be the simplest and most reliable method for studying

catalysts surface and chemistry of surface transformations.

In my presentation, I shall focus on the capabilities of the IRS of adsorbed molecules for studying the mechanisms of catalytic processes occurring on the surface of catalysis on molecular level. Any chemical reaction going on the catalyst surface may be represented by a simple sequence of stages such as:

- reagents adsorption,
- chemical transformation (or a chain of chemical transformations),
- desorption of reaction products.

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The IRS of adsorbed molecules may be efficiently applied for studying all the above stages.

2. Results and discussion

2.1. Adsorption

2.1.1. Diffusion

One may notice two aspects when studying adsorption. One aspect is related to adsorption rate and related diffusion processes. Another aspect considers the identification of surface complex structures. The identification aspect is quite traditional and reflects many years of research experience. Adsorption and diffusion studies with IRS are rather new and started only recently. Their fast development is because of the design of Fourier transform spectroscopy.

The IRS studies of diffusion in zeolites is based on the fact that molecule penetration inside the channels is easily followed by the changing concentration of OH groups that are uniformly distributed over the zeolite crystal bulk [1]. Fig. 1 schematically shows the structure of zeolite crystals. Each crystal with a linear dimension of about several microns consists of smaller single crystals, whose X-ray size is estimated by CSR ranging within 200–500 Å. Space between these single crystals forms a system of transporting pores. In these rather large pores, diffusion rate is high enough; but

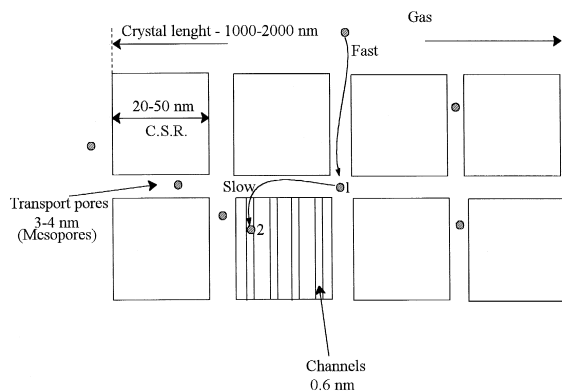


Fig. 1. Diffusion of molecules in zeolites crystals.

inside the single crystals, whose diameter of channels is less than the molecules', the diffusion becomes slow. Therefore, we may represent the process of filling of the single crystals with molecules adsorbed from the gas phase as follows. At first, molecules fill the outer parts of the zeolite crystal. Then, driven by the concentration potential, they progressively fill the whole crystal bulk. This filling process is easily monitored by the IRS method, since zeolite IR spectra show various OH groups.

Isolated OH groups reacting with molecules produce ions or hydrogen-bonded complexes, whose concentration is proportional to that of reagent molecules in the zeolite. Therefore, following the intensity of OH group lines, we may estimate the filling of the zeolite crystal. The kinetics of crystal bulk filling is guided by the following law [2]:

$$\Theta = 6/r_0(D/\pi)^{1/2}\tau^{1/2}$$

where Θ is the equilibrium filling of sites, r_0 is the size of zeolite crystals, D is diffusion coefficient, and τ is time.

Included with the zeolite ZSM-5 studied was adsorption of water, ammonia, benzene, pyridine, butyl alcohol, and butylene. Diffusion coefficients did not correlate with the masses of molecules and their size, as could be expected from the Knudsen diffusion law. There is no contradiction, though, since the Knudsen diffusion theory assumes that diffusing molecules reflect from the walls of pores, where mass transfer occurs. Diffusion reflection (Fig. 2), i.e., molecule bounces in random directions after its contact with the pore wall, requires the necessary transfer of the forward motion energy onto the wall surface. For this transfer to occur, molecule must adsorb on the surface at least for a very short time. We may imagine two types of sites in the zeolite channels capable of providing this adsorption. The first type site is the Bronsted acid site, i.e., OH groups. The second type site is the oxygen atoms in fragment Si–O–Si. It is well known, however, that oxygen

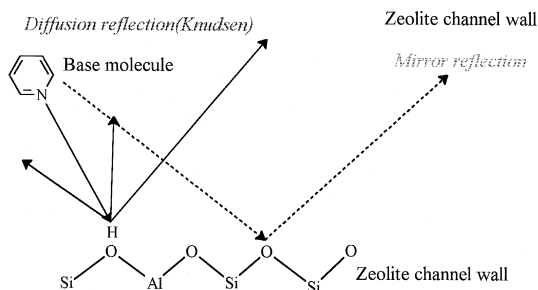


Fig. 2. Two types of base reflection on the walls in zeolite channels.

atoms are not able to adsorb any molecules. Thus, diffusing molecules cannot transfer their motion energy through oxygen atoms and reflect from the pore walls. On acid sites molecules readily adsorb, and then may quit sites in random direction. Therefore, diffusion rate in the zeolite channels is related to the concentration of the Brønsted sites. Moreover, it depends on the strength of molecule interaction with these sites. In literature, this fact is often mentioned with regard to a far slower diffusion of polar molecules than of non-polar ones [3].

As a result, molecules, which are weak bases, diffuse faster through the zeolite channels than are small in size and mass molecules, which are strong bases. Molecule size effect is not essential. In case, when such strong base as pyridine enters the channel, one might expect diffusion rate to be limited by desorption. However, measured diffusion activation energies comprise a small part of adsorption heats. The explanation is that molecules may form sophisticated stoichiometry complexes with the Brønsted sites. Fig. 3 shows the intensity of bands ascribed to pyridine ions versus time on zeolite HZSM-5. Apparently, intensity passes through a maximum provided by the formation of proton complexes with two pyridine molecules. These complexes most likely are intermediates in diffusion process. In whole, diffusion goes in the following manner. The pyridine molecule quickly reaches a Brønsted site in the zeolite channel and stays on this site until the next pyridine molecule approaches it. Then complex Py-H^+

Py forms, which quickly decays. Freed pyridine molecule transfers along the channel. The activation energy of the $\text{Py-H}^+\text{-Py}$ complex decay is thus the activation energy of diffusion.

Isotope experiments with water were done with a $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}/\text{SiO}_2$ (see Fig. 4). The experiment was done in the following manner. Sample pellet was put into the IR cell, and air was removed from the cell for 30–60 s. Therefore, there was no time for water to be removed from the sample. Then deuterated water was supplied, and its vapors adsorbed on the tablet. Two processes occurred simultaneously. The first process was the isotope-exchange of some hydrogen atoms by deuterium atoms. The second process was the complete substitution of H_2O molecules by D_2O molecules. Apparently, for several seconds, practically all H_2O molecules turned to HDO molecules, while D_2O production was far slower. Most likely, all water in the sample was in the hydrogen-bonded state. This allowed hydrogen atoms to diffuse along the hydrogen-bonded fragments. It is well known that in liquids such transfer of hydrogen atoms goes with high rates. D_2O formation is limited by the full exchange of water by heavy water, and is thus related to the substitution of oxygen atoms in the surface water by the gas phase water.

Therefore, IR spectroscopy allows efficient studying of molecular aspects of water molecule diffusion in porous samples. Using IRS, one

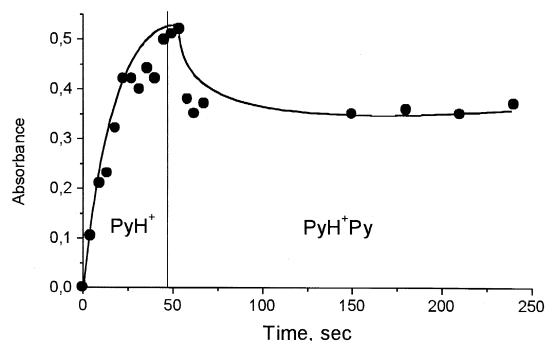


Fig. 3. Time dependence of IR band at 1540 cm^{-1} during pyridine diffusion in zeolite HZSM-5.

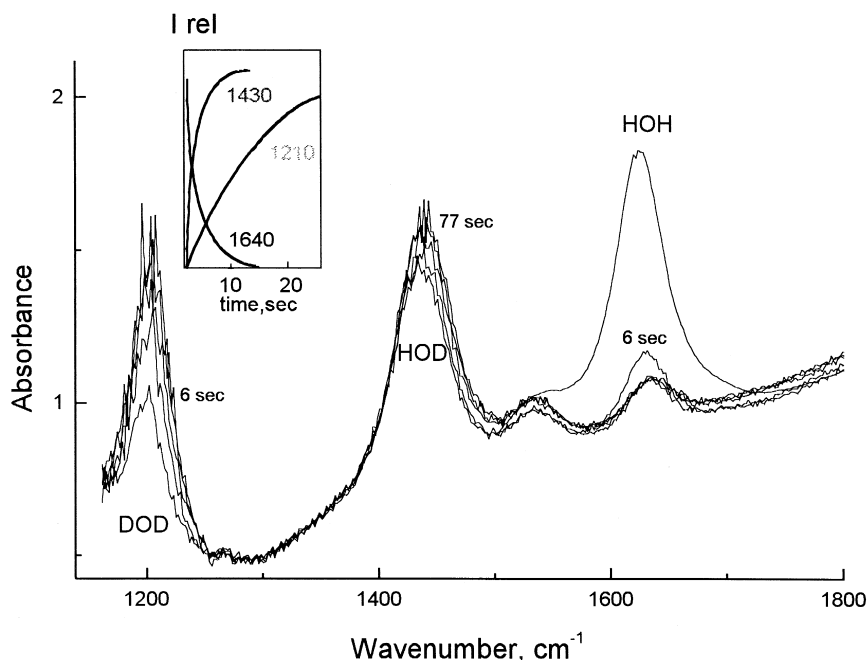


Fig. 4. IR spectra of molecular water in the course of H–D exchange of $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}/\text{SiO}_2$ with D_2O .

may not only measure diffusion rate, but also reveal the character of interaction between the diffusing molecules and sample surface. Most important are data related to diffusion in zeolites. They show that the size of zeolite channels and the mass of diffusing molecules are not the key factors determining diffusion coefficient values.

2.1.2. Surface complexes nature

It is of importance to reveal the nature of surface complexes between reagents and active surface sites, when studying adsorption. It is well known that IRS allowed a successful identification of various adsorption sites long time ago. In this presentation we shall consider the Electron State of adsorbed molecules and their geometry.

2.1.2.1. Structure of ammonia ions in zeolites.

This is one of the ancient questions of the acid–base catalysis, quite well answered by complex IRS and quantum chemical studies

[4,5]. In the gas phase, ideal ammonia ion should be a perfect tetrahedron. When this ion adsorbs on the negatively charged surface oxygen, this structure is distorted, since hydrogen bonds form. There may be several versions of surface ammonia ions. Mono-, bi-, and tri-dentate structures are presented on Fig. 5. The first and the last structures are similar by symmetry, but differ by the number of hydrogen-bonded fragments. As a result, theoretical spectra of all complexes are different. IR spectra, registered at the temperatures far below the ambient one (160–170 K) show three bands at 1380–1480 cm^{-1} ascribed to bending, and two bands at 3300–3400 cm^{-1} . These bands are enough to state that ammonia ions bind with the zeolite surface through two hydrogen bonds. IRS spectra combined with ab initio calculations provided relationship between the proton affinity of adsorbing molecules and the heats of their protonation on the surface of zeolites: $Q = \text{PA}^{\text{base}} - \text{PA}^{\text{acid}} + Q_{\text{el.st.inter.}} + NxQ_{\text{H bonds}}$, where N is the number of hydrogen bonds of ion with the surface.

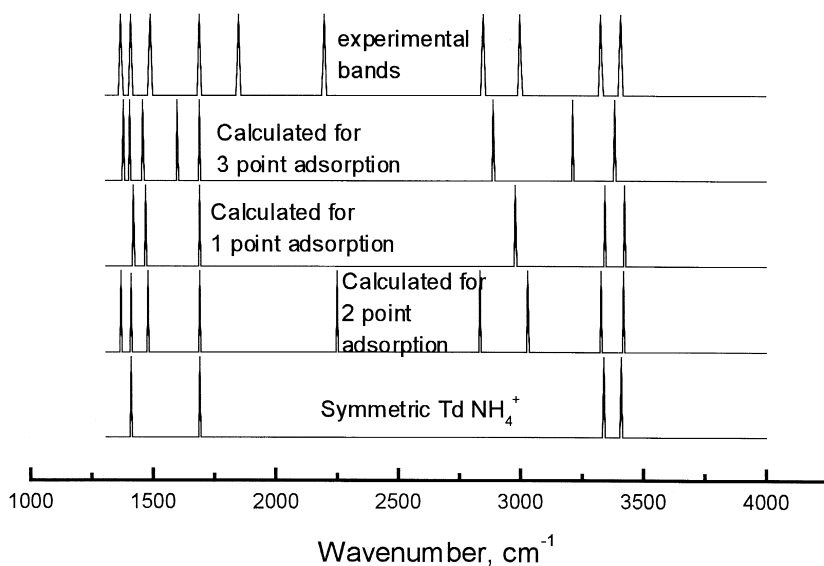


Fig. 5. Experimental and calculated IR spectra of ammonium ions on the surface.

2.1.2.2. *tert*-Butyl chloride adsorption. Surface complexes of reagents are sometimes identified using their adsorption together with special probe molecules. Thus, for example, it is necessary to reveal adsorption sites and adsorption complexes on alumina surface to understand the mechanism of dehydrochlorination of chlorobutanes. IR spectra show the observed structures to relate to neither carbenium ions, which in case of *tert*-butyl chloride are expected to provide band at 1260 cm^{-1} , nor physically adsorbed reagent, since band C–Cl is shifted to towards the lower frequencies (Fig. 6). However, *tert*-butyl chloride adsorption performed together with CO proves that chloride selectively adsorbs on the Lewis sites [6,7]. With this regard, dehydrochlorination is assumed to involve strong Lewis sites. These sites redistribute the electron density in the chloride, thus allowing the cleavage of the C–H bond with hydrogen chloride elimination.

2.1.2.3. Protonation of toluene and other methyl-substituted benzenes on vanadium catalyst. Another example relates to adsorption of aromatic compounds on vanadium–alumina catalyst. Toluene adsorption on this catalyst IRS

bands is similar to those observed for benzolonium ions [8]. However, one should prove that the spectra changes are not caused by the partial oxidation processes (Fig. 7). For this purpose, displacing ammonia adsorption is performed. Indeed, toluene thermal desorption is not possible owing to the high oxidative activity of vanadium oxide catalysts. Temperature increase of 100°C only causes toluene oxidation by methyl group. In the case when toluene adsorbs with

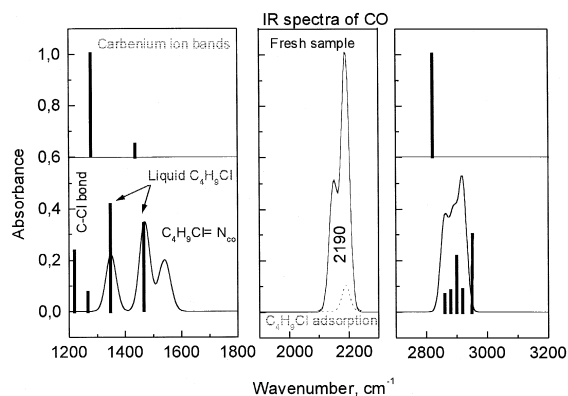


Fig. 6. IR spectra of *tert*-C₄H₉Cl on Al₂O₃ + 3% F. CO adsorbed at 77 K and pressure 5 Torr. Concentration of adsorbed *tert*-C₄H₉Cl is equal to Lewis sites number.

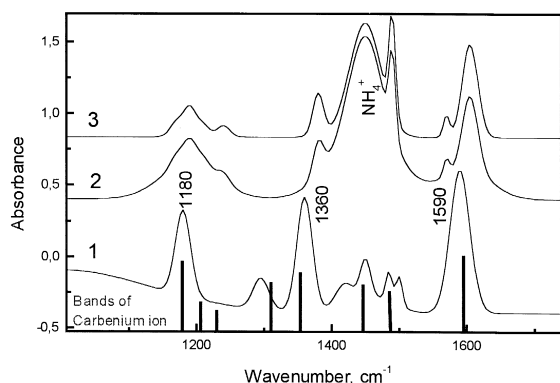


Fig. 7. IR spectra of toluene adsorbed on V_2O_5/Al_2O_3 . (1) Adsorbed at room temperature, (2) after ammonia adsorption, and (3) liquid toluene.

protonation on the surface proton sites, one might expect ammonia, being a far stronger base, to compete for the acid site and to displace toluene from this site at room temperature. As a result, ammonia ions form on the surface, and regeneration of “molecular” toluene should occur. IR spectra obtained on vanadium oxide catalyst show this particular reaction to occur. This means that bands from protonated toluene disappear, and bands appear from molecular toluene and ammonia ions.

In general, it is necessary to use a wide range of methods to identify adsorption complexes on the surface of catalysts starting from theoretical quantum chemical calculations and ending with on-purpose chemical experiments.

2.2. Identification of limiting stages

2.2.1. Dehydration of butyl alcohols

Dehydration of butyl alcohols was studied with a complex of methods including IRS. For the purpose, chosen was a series of well characterized zeolites and silica–alumina catalyst of known textures [9]. Primary experiments have shown that butyl alcohols quickly fill the porous space of zeolites in approximately 2 min, and then slow processes of chemical conversion go. Catalytic experiments combined with the IRS ones, measuring the rates in the gas phase and on the surface, show that on zeolites (unlike

amorphous silica–alumina) dehydration occurs in two stage. At temperature below 80°C , alcohols convert to dibutyl ethers evolving water. Ethers practically do not desorb into the gas phase, and their formation rate, measured with IRS (Fig. 8) by molecular water evolution (band 1640 cm^{-1}), is essentially higher than that measured in the catalytic experiment. At higher temperatures alcohols convert to water and olefin, as on amorphous alumina silicas. Experiments demonstrate that alcohol reacts with the Broensted sites yielding hydrogen-bonded complexes. On heating these complexes convert to water and olefin, and on zeolite ZSM-5 dibutyl ether is the first to form, since hydrogen-bonded complexes exist as both monomers and dimers. On zeolite ZSM-5 channel structure favors dimers formation.

2.2.2. Deamination of butyl amines

This reaction appears to be mostly favorable for demonstrating the IRS capabilities in static condition and flow experiments [10]. In flow regime (Fig. 9), when butyl amine flow passes through the catalyst containing cell, the concentrations of various surface species were studied regarding the catalyst temperature. It is easy to distinguish butyl ammonium and ammonia ions in the IR spectra. The steady state concentration of ammonia ions appears to exceed the equilibrium at the same temperatures. Therefore, ammonia ions are assumed to be reaction products,

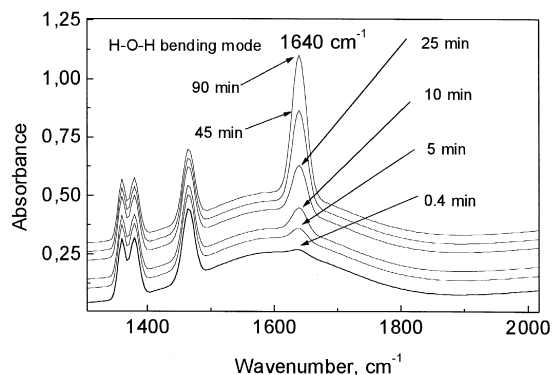


Fig. 8. FTIR difference spectra showing the course of *n*-butanol dehydration on HZSM-5 catalyst at 100°C as a function on time.

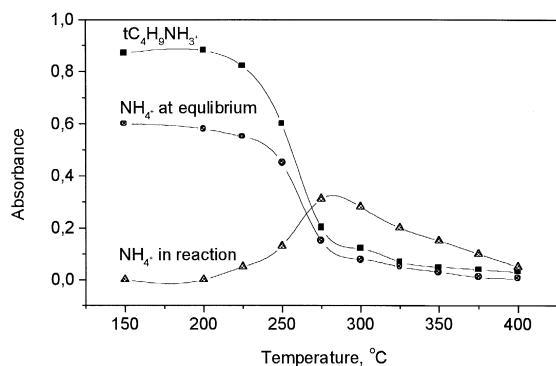
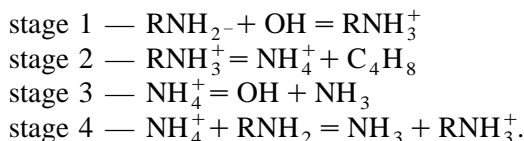


Fig. 9. Temperature dependence of IR bands intensities for HNaY zeolite during *tert*-butylamine deamination in IR flow cell.

but do not reflect the processes of ammonia re-adsorption. Butyl amines rapidly displace ammonia ions from the surface at room temperature (most likely via the mechanism involving sophisticated complexes with surface protons like $\text{NH}_3\text{-H-NH}_2\text{R}$). In the stirred tank measured were the rate constants of decomposition of butyl ammonium ions at different temperature. Found activation energies coincide with those obtained in the catalytic tests. All these data deliver the following reaction mechanism assumptions [10]:

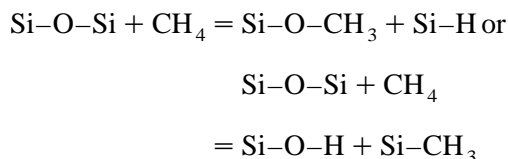


It is very important that these results agreed with the earlier studies of the surface ammonia ion structure that allowed the estimation of activation energy for the deamination of butyl amines, which appeared to equal $Q_{\text{reaction}} + (\text{PA}^{\text{BA}} - \text{PA}^{\text{HN}_3}) + Q_{\text{NHO}}$ (H bond). Therefore, in order to convert butyl ammonium ion to ammonia, it is necessary to break one hydrogen bond of ion with the surface oxygen for the C–H–O to form.

2.2.3. Methane oxidation to formaldehyde by oxygen on silica

At 500 °C on silica, methane was shown to convert to formaldehyde with a slow rate, but

selectively. The oxidation rate was demonstrated to be proportional to the concentration of strained siloxane bridges on the silica surface, which formed on dehydroxylation [11]. These bridges disappeared when silica was treated with methane, but authors failed to reveal any intermediates. At 500 °C, spectra showed weak band, which could be ascribed to the Si–CH₃ fragments (Fig. 10), but bands intensity did not allow kinetic studies. To avoid the problem, various intermediates were modeled on the catalyst surface such as SiOCH₃ or Si–CH₃, since siloxane bridges were assumed to decompose on methane adsorption via one of two suggested mechanisms:



Modeling was done using chemical methods. Methoxide groups were produced in silica interaction with methanol, and methyl silane fragments were obtained with octamethyl-cyclo-tetrasiloxane adsorption on silica gel. Further studies done using a static high temperature IRS cell show that methoxide groups are oxidized with a high rate only above 700 °C, while methyl silane groups at 350 °C start decomposing into reaction products containing formaldehyde.

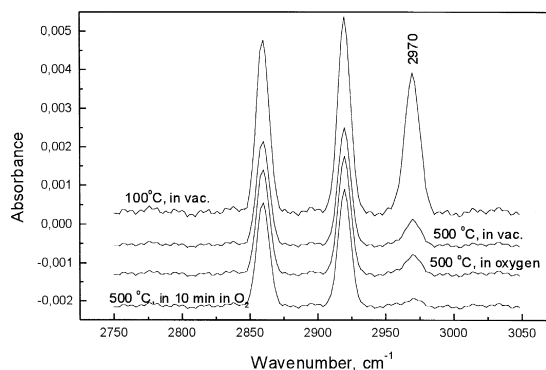


Fig. 10. IR spectra of CH₄ on silica at different temperature.

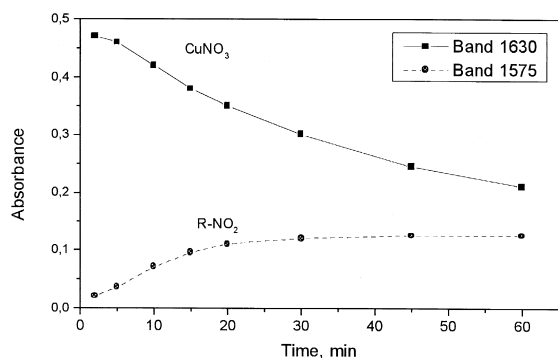


Fig. 11. Time dependence of the IR bands intensities for CuZSM-5 during nitrates titration of propane + oxygen.

2.2.4. Nitrogen oxide selective reduction by paraffin on metal containing zeolites

Experience accumulated in above described experiments, is at present successfully used to study the mechanism of nitrogen oxide reduction by methane and propane. For this purpose, at high temperatures, nitrite–nitrate structures are prepared on copper- and cobalt-substituted zeolites. This method is used to the presence of nitrates. Then after propane and methane supply, rates of nitrates conversion are measured (Fig. 11). It was found that the rate of nitrate consumption is similar to that of selective NO_x reduction to molecular nitrogen. Product spectra are studied to identify organic compounds containing nitrate groups.

3. Conclusions

In conclusion, let us list the stages important in studying catalytic reaction mechanisms with IR spectroscopy.

- It is necessary to characterize not only qualitatively also quantitatively the properties of fresh catalyst surface.

- It is advisable to use updated quantum chemical calculations, when interpreting the structure of surface complexes.
- It is reasonable to study surface kinetics in a wider temperature regime, including the temperatures of catalytic experiments, starting at low temperatures.
- A combination of static and flow methods is a necessary condition for revealing surface catalytic reaction mechanism on molecular scale.
- Chemical modeling of possible intermediates is a strong instrument for reaction mechanism studies, but one must carefully choose the approach.

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