

IR STUDY OF DYNAMIC BEHAVIOUR OF 2-PROPANOL ON ALUMINA

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Received August 12th, 1987

Dynamic behavior of surface complexes of 2-propanol on alumina during adsorption and dehydration was studied using IR spectroscopy. Good agreement was found between the first-order rate constants of alkene formation in pulse-flow experiments and that of disappearance of a reactive surface complex. It was shown that the simple surface alkoxide 2-Pr—O—Al remains on the surface at constant temperature, but it can be completely removed by hydrolysis, or by heating up to 200°C. The surface carboxylates are formed very slowly and are stable even in the presence of water vapour at 300°C.

The dehydration of alcohols on alumina has been studied in many laboratories and the results are summarized in several reviews¹⁻⁵. One of the still open problems is the nature of active sites and the structure of surface intermediates. Knözinger and coworkers^{4,6-8} have found a relatively stable surface alkoxide using IR spectroscopy, and then the alcohol bonded by hydrogen bond was assumed to be the reactive intermediate^{4,6}. On alumina, free Lewis centres exist but they are almost completely blocked by bases like water or alcohols (e.g.^{9,10}). It was shown that the surface alkoxide can decompose to an alkene (e.g.¹¹), and that the precursor of alkene has longer life-time than the molecularly bonded forms of alcohol under conditions of dehydration reaction of primary alcohols¹¹⁻¹⁸.

The adsorption of methanol, ethanol, and 2-propanol is accompanied by a displacement of water from the surface¹⁵⁻¹⁸, which has been proved by isotopic exchange of oxygen and by measurement of the concentration of OH groups before and after adsorption at reaction temperature^{16,17}.

The bridged alkoxides, which have been proved on a large number of oxides¹⁸⁻²³, are supposed to exist on alumina^{24,25}. Moreover, the interaction of an alcohol with two electron acceptors²⁶ and the geometric condition²⁷ are favourable for transformation into an alkene.

The purpose of the present work is a comparison of kinetic parameters of decomposition of the long-lived surface species the concentration of which was deter-

mined by IR spectroscopy, with rate data on alkene formation under dynamic conditions.

EXPERIMENTAL

Alumina Pural SB (Condea, F.R.G.) was calcinated at 550°C and dried before using at 300°C for 1 h. Its specific surface area was 206 m²/g. The sample of catalyst was pressed into pellets of area density 10–14 mg/cm²; for kinetic pulse-flow measurements, fraction 0.16–0.35 mm was applied. 2-Propanol (Lachema Brno, purum) was dried over sodium and rectified. The IR cell and experimental conditions were described elsewhere⁹. The concentration of the aprotic acid sites was determined by the low-temperature CO adsorption (e.g.²⁸).

Rate of decomposition of surface species was measured by reading the intensity of the band at 2975 cm⁻¹ which has been attributed to the ν(C—H) vibration in the methyl group (cf. ref.⁶). This band can be used for kinetic study as has been shown in our more detailed investigation of the behaviour of time dependence of isolated bands¹⁸.

Rate of propene formation was taken as its output rate, the experimental details are described in our previous communications^{16,29}.

RESULTS AND DISCUSSION

The comparison of the spectra of adsorbed and liquid 2-propanol (Fig. 1) shows formation and shift of the bands in the region 1000–1300 cm⁻¹, caused by interaction of alcohol OH groups with alumina surface. The band at 1580 cm⁻¹ corresponds to the —COO group of the surface carboxylates^{4,6,30}.

The measurement of time dependences of the intensity of alkoxide and carboxylate bands from the first contact of 2-propanol vapour showed that the rate of alkoxide formation is comparable to the rate of adsorption and that the development of the carboxylate band is very slow (cf.^{30,31}). Both alkoxide and carboxylate bands remain

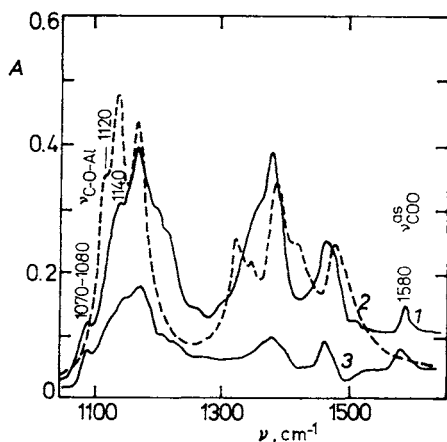


FIG. 1

Comparison of IR spectra of 2-propanol: 1 in adsorbed state on alumina at 110°C; 2 in liquid phase at 25°C; 3 spectrum of the catalyst with non-reactive alcohol formed after pumping out the reaction mixture at 110°C

unchanged after pumping out the vapours of reaction mixture. However, the alkoxides band disappears in the presence of water vapour at reaction temperature, or by heating to about 200°C. On the other hand, the carboxylates withstand heating to 300°C even in the presence of large excess of water in the gas phase.

The surface concentration of stable alkoxide 2-Pr—O—Al depends on temperature (Fig. 2). It is not decomposed to alkene (cf.^{4,6}) but it can be removed by hydrolysis. When the reaction temperature increases, a part of it is transformed to the alkene (cf.¹¹) and the rest remains stable. This behaviour resembles that of OH groups of alumina (cf. e.g.³²⁻³⁵).

The reversible transformation of simple alkoxide to the bridged one has been shown in the case of thoria¹⁸. It can be described by Eq. (A). The interaction of alcohol molecule with two electron acceptors activates it for elimination reaction^{26,27}. The bridged alkoxides on thoria can react to give the alkene¹⁸ according Eq. (B).

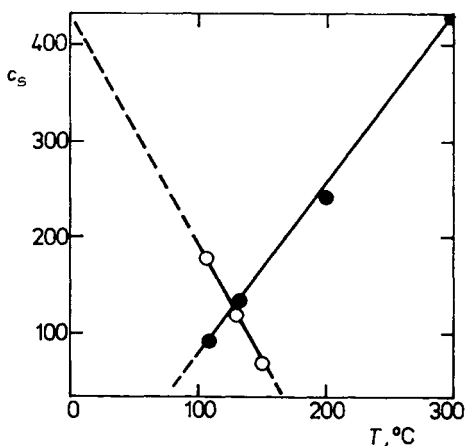
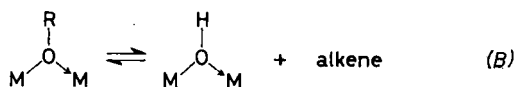
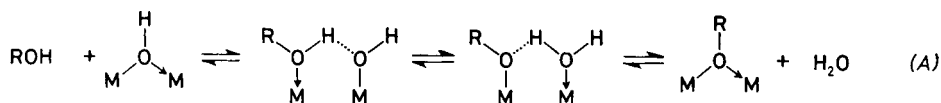


FIG. 2
Dependence of the surface concentration c_s ($\mu\text{mol/g}$) non-reactive form of the alkoxide (\circ , integral of the band $1\,070\text{--}1\,075\text{ cm}^{-1}$) and of Lewis centres (\bullet , measured by low-temperature adsorption of CO) on the reaction or activation temperature ($^{\circ}\text{C}$), respectively

In our experiments, we were not able to record the bridged alkoxides (cf. e.g.²⁴), but for the above reaction scheme of dehydration some indirect evidence is available: a) the simple alkoxide Al—O—R is not sufficiently activated for dehydration³⁶, b) for transformation of the adsorbed alcohol into the reactive intermediate at least one reaction step is necessary, as follows from pulse-flow kinetic experiments¹⁵⁻¹⁷, c) for activation of C—O and $\text{C}_\beta\text{—H}$ bonds two-electron acceptors are needed to interact with free electron pairs of oxygen of alcohol OH group^{26,27}. Further more direct evidence for the existence and reactivity of bridged alkoxides on alumina have been drawn from FT-IR spectroscopy by Lorenzelli, Lavalley and their co-workers^{19,37}.

Some authors³⁸ suggested that an alcohol molecularly bonded to Lewis sites is a reactive surface intermediate. However, the results of pulse-flow experiments¹⁵⁻¹⁷ seem to contradict this mechanism. Water is desorbed from the surface earlier than alkene and the rate of alkene formation is almost zero when the surface concentration of the molecularly bonded alcohol reaches maximum. Water is not displaced from the surface by ethers more basic than alcohols, and hence the displacement requires the dissociation of alcohol molecule and transfer of its proton to the OH group of the surface.

Nevertheless, we cannot exclude that different mechanisms operate at different reaction conditions (cf.^{1,4,6,16}). The activity of protons on alumina can be provoked

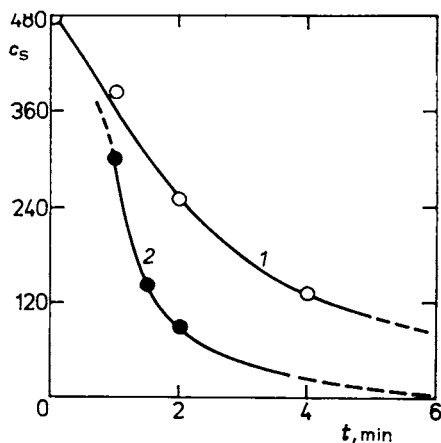


FIG. 3

Time-dependence of the surface concentration c_s ($\mu\text{mol/g}$) of the reactive intermediate (based on the band $2970\text{--}2975\text{ cm}^{-1}$) at 1) 130°C and 2) 150°C

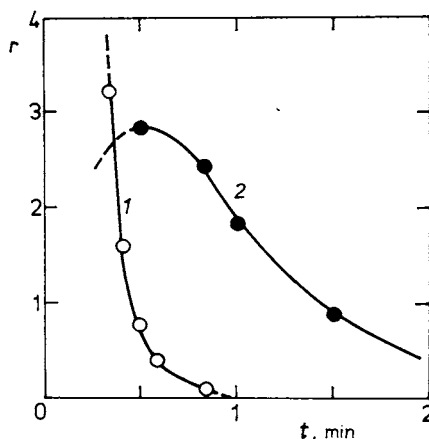


FIG. 4

Dependence of the output rate of alkene r ($\mu\text{mol g}^{-1}\text{ s}^{-1}$) from flow reactor following a pulse of 2-propanol (20.5 mg of catalyst, 25 ml/min at 1) 150°C and 2) 175°C

by introduction of some anions, such as fluorides, chlorides, sulphates, or by increasing reaction temperature¹⁶; the result will be mechanism including protonation of the hydroxyl group of the alcohol.

If prevailing species on the surface is the precursor of alkene, the rate of its transformation should correspond to that of the formation of alkene measured in the gas phase. The identity of the observed surface species with the reactive pre-

TABLE I

Comparison of concentration of Lewis sites and active sites for dehydration of alcohols

Method	Temperature °C	Concentration 10^{-17} m^{-2}	Ref.
Kinetic	170	9	15
Kinetic	175	11.4	14
Kinetic	250	11.2	29
Pyridine adsorption			
by IR spectroscopy	150	9	4
by pulse-flow method	180	6	39
TPD of amines	—	10–16	40
TPD of pyridines	—	3–4	41
CO adsorption	200	7.5	Fig. 2
Kinetic	130	11.9	Fig. 3
Calculated from geometric model	100	9.5	34

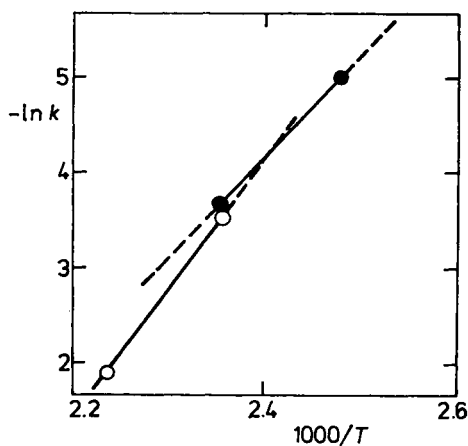


FIG. 5

Arrhenius plot of first-order rate constant obtained from the data in Fig. 3 in time span of 0.5 to 4 min (●) and from data in Fig. 4 in time span of 1–2 min for 150°C and 0.5–1 min for 175°C (○)

cursor of alkene can be confirmed or excluded by a comparison of the kinetic parameters of both reactions.

The band at $2970-2975\text{ cm}^{-1}$ has been attributed to the $\nu(\text{C}-\text{H})$ vibration in the methyl group (cf. e.g.⁴). It has been shown¹⁸ that this band can be used for kinetic measurements in the first period after starting the kinetic run, as it is almost parallel with that of $\nu(\text{C}-\text{O})$ at this time interval. The kinetic curves of the intensity of the band at $2970-2975\text{ cm}^{-1}$ for two temperature levels are seen in Fig. 3. Fig. 4 depicts the response curves of propene following a pulse of 2-propanol into a flow reactor for different temperature levels. Both sets of experimental data were treated with first-order rate equation which validity for description of the decomposition of the surface complex has been demonstrated by several authors^{15,18,29}. The obtained rate constants are plotted in the coordinates of the Arrhenius equation in Fig. 5. The agreement of activation energies of the decomposition of the surface complex and of the formation of alkene is satisfactory in the range of experimental errors (96 and 112 kJ/mol, respectively). The published data are also close to these values: Knözinger and coworkers⁶ have found 108 kJ/mol and Sadovnikov and Gefter¹⁵ 112 kJ/mol. It is remarkable that the activation energy for the other alcohols differs only little (see e.g.^{4,6}).

The bridged surface hydroxyl³⁴ is a complex adsorption site which can exhibit the properties both of Brønsted acid and Lewis acid-base pair. The dissociation of alcohol or water and their mutual displacement proceed on it according to Eq. (A). On thoria, the hydrolysis of bridged alkoxide to simple one has been demonstrated and also was the reverse reaction, the formation of the bridged alkoxide from the simple one by heating¹⁸. This reaction seems to be more general for the oxides capable to form the bridged surface species.

Table I shows a good agreement between the concentration of active sites determined by kinetic stop-flow and pulse-flow methods on one side and the concentration of Lewis sites measured by various physical and chemical methods on the other side. This can be taken as a further evidence of the identity of adsorption and active sites for dehydration of alcohols on alumina.

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Translated by the author (M.K.).