THE ROLE OF APROTIC CENTRES ON MODIFIED ALUMINAS IN 1-BUTANOL DEHYDRATION

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Correlations of the initial rates of butene and dibutyl ether formation from 1-butanol at 300°C with strength and concentration of aprotic sites on aluminium oxides modified with various ions were examined. It was found that in the formation of dibutyl ether, weak aprotic acidic sites were active. Their specific activity increases with increasing strength of the sites, defined as the heat of adsorption of carbon monooxide, up to the value of 40 kJ/mol. The strongest aprotic sites do not take any important part in the reaction. In butene formation, both types of aprotic acidic sites, weak and strong, are active. It was found that the selectivity in 1-butanol dehydration depended on the concentration of stronger basic sites.

Dehydration of 1-butanol is very often used as a model reaction to characterize the acid-base properties of solid catalyts[1-7]. According to a proposed mechanism[8], the reaction proceeds both on acidic and basic centres. The role of protic sites in this reaction was examined earlier[9]. However, till now, quantitative relations between the strength of aprotic sites and the catalyst activity were determined neither for butene nor for dibutyl ether formation. The reason was the lack of quantitative information on strength and concentration of individual types of aprotic sites. In our recent paper[10], the acidic and basic properties of several modified aluminas were examined, which made it possible to differentiate aprotic sites according to their strength and concentration.

The objective of this work was to investigate the correlation between the properties of aprotic acidic and basic sites of aluminas modified by various ions and the catalytic activity of these samples in 1-butanol dehydration.

EXPERIMENTAL

The method of studying the acidic and basic centres of modified aluminas and of determining their strength and concentration by IR spectroscopy was described in the preceding paper[10]. The strength of aprotic acidic sites can be expressed as the heat Q_{CO} released in the formation of CO complex with these sites. The heat of adsorption Q_{CO} (kJ/mol) was determined[11] from the relation

$$Q_{CO} = 10.5 + 0.5\,\Delta\nu_{CO}, \qquad (1)$$

where $\Delta\nu_{CO}$ is the frequency shift (in cm^{-1}) of carbon monooxide adsorbed on the catalyst[10]. The centres with the Q_{CO} values up to 40 kJ/mol are denoted as type I (weak sites), and those with Q_{CO} values higher than 40 kJ/mol as type II (strong sites). The samples with Zn also possess sites of type III. The concentration of the respective centres was derived from the intensity of the band of CO complex with these centres and expressed in $\mu mol/m^2$. Basic properties of aluminas were determined from the spectra of deuterated chloroform. Dehydration of 1-butanol was performed[7] in a flow apparatus at 300°C and under partial pressure of the alcohol 20 kPa and of nitrogen 80 kPa. The surface and catalytic properties of the aluminas used (prepared in[7]) are given in Table I.

RESULTS AND DISCUSSION

In a preceding paper[7], a network of reactions involved in 1-butanol dehydration is shown; the scheme includes the reversible transformation of 1-butanol into dibutyl ether and the irreversible elimination of water from the alcohol with the formation of 1-butene. Dibutyl ether can be irreversibly transformed into 1-butene and 1-butanol or into two molecules of 1-butene and one molecule of water. It is supposed that 1-butene can be isomerized into cis- and trans-2-butene. In principle, these reactions can proceed on every type of acidic sites that is both on protic and aprotic sites. However, even on the most acidic aluminas containing F^- and SO_4^{2-} anions, there are no sufficiently strong protic acidic sites that could be responsible for these catalytic reactions[10,12]. Therefore, aprotic acidic sites are most important in aluminas, and the rates of individual reactions can significantly depend on their strength.

Since not only the strength of acidic sites, but also their concentrations were changed by aluminas modification, the initial reaction rates were related to the unit concentration of acidic sites (initial turnover number R_E^0 and R_B^0).

A simple correlation of the turnover numbers of butene formation with the strength of type I of aprotic sites was not successful. Obviously, stronger aprotic sites (type II) also take part in this reaction. Therefore, reaction rates r_B^0 for catalysts that contained both types of aprotic sites were divided into two contributions related to each type of centres. These contributions to reaction rates were determined from the relation

$$r_B^0 = z[c^I \exp(\alpha Q_{CO}^I) + c^{II} \exp(\alpha Q_{CO}^{II})], \tag{2}$$

where constant z includes partial pressure of 1-butanol and the preexponential part of the rate constant, and α the proportionality factor of the relation between the activation energy and the adsorption heat of carbon monooxide; c^I and c^{II} are relative concentrations of each type of centres (Table I). Relation (2) is justified if we suppose an identical mechanism of the formation of butene and practically the same entropy of activation on both types of centres. Then, the difference between the reactions on the two types of centres consists only in the difference in the activation energies which is proportional to the adsorption heat of carbon monooxide.

Moreover, the latter assumption is supported by the fact that the transition from the adsorbed state to the activated adsorbed state is usually combined with a negligible change of entropy.

By successive approximations, the value of coefficient $\alpha = 0.3$ in Eq. (2) was determined as an optimal value. Using this coefficient, the contributions to the reaction rate corresponding to each type of centres were calculated. The same procedure and the same α coefficient were applied to the catalysts with Zn that contained the types I and III (Zn sites) of centres. In Fig. 1, the dependence of the turnover number R_B^0 on the strength of aprotic sites Q_{CO} for various aluminas is represented. From Fig. 1 it is evident that the turnover number of butene formation correlates (in logarithmic coordinates approximately linearly) with the acid strength of all the three types of aprotic sites. Sample 2 containing Cl^- deviates from the correlation; another reaction mechanism is likely to be operating with the sample. The correlation coefficient without the Cl^- samples is 0.85.

Concerning dibutyl ether formation, it was found that the turnover number did not correlate with the strength of aprotic sites according to relation (2). However, it correlates fairly well with the first member of Eq. (2) using $\alpha = 0.57$. From Fig. 2, it is evident that the turnover number R_E^0 increases with the strength of type I of aprotic sites (correlation coefficient 0.88). The reaction of dibutyl ether formation probably proceeds only on the weaker aprotic sites (type I) of aluminas. Such a behaviour

TABLE I

Surface and catalytic characterization of aluminas used

Sample	Ion	Wt.% of ion	Initial reaction rates[7]		Strength Q_{CO} (kJ/mol), concentration c (μmol/m^2) of three types of aprotic acidic sites and relative concentration of stronger basic sites c^B (see[10])						
			r_E^0	r_B^0	Q_{CO}	c^I	Q_{CO}^{II}	c^{II}	Q_{CO}^{III}	c^{III}	c^B
1	F^-	2.6	2.95	2.15	36	1.5	43	1.62	0	0	0
2	Cl^-	0.99	2.3	1.3	34.5	1.8	40.5	0.7	0	0	0.5
3	SO_4^{2-}	4.85	1.7	0.7	37	0.7	44	0.8	0	0	0
4	PO_4^{3-}	3.0	2.35	0.35	35.5	2.2	43	0.4	0	0	1.2
5	—	0	2.3	0.1	34	2.7	0	0	0	0	4.8
6	Zn^{2+}	1.28	2.35	0.15	33.5	2.9	0	0	0	0	1.7
7	Zn^{2+}	2.12	1.25	0.25	33	2.9	0	0	40.5	0.4	1.3
8	Zn^{2+}	4.14	1.5	0.25	33	3.2	0	0	40.5	0.8	1.2
9	Mg^{2+}	0.89	1.18	0.07	33.5	3.1	0	0	0	0	3.1
10	Na^+	0.62	0.36	0.07	33	2.6	0	0	0	0	3.0

can be explained as follows: According to the data[13], the heat of the reaction of ethers with typical Lewis acids — $AlCl_3$ and $AlBr_3$ — achieves considerably high values of $168-180$ kJ/mol. A similar value of the heat of reaction was observed even in the reaction of these acids with pyridine. Experimentally it was found[14] that the heat of adsorption of pyridine on the strongest aprotic sites of aluminas was slightly lower (155 kJ/mol). Hence, the activation energy of dibutyl ether desorption cannot be lower than this value. In such a case it can be expected that the rate of dibutyl ether formation on sufficiently strong aprotic sites will be limited by ether desorption and will be so low that the contribution of these sites to the overall reaction rate would be negligibly low.

Then empirical values of α found for butene and dibutyl ether formation can be analyzed and compared with the parameters α_{BP} from Brønsted–Polanyi relation. Thus, when writing

$$k = k_0 \exp\left(-E_i/RT\right) \qquad (3)$$

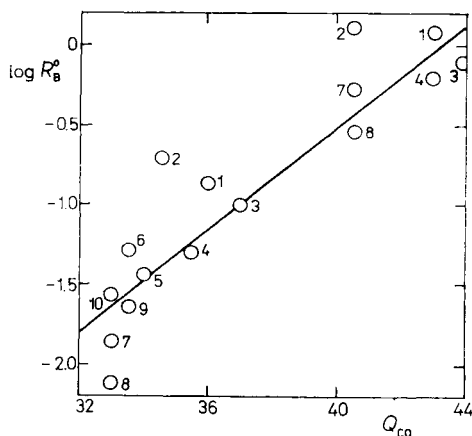

Fig. 1

Dependence of the turnover number of bute-ne formation R_B^0 (h^{-1}) corresponding to various types of centres on the strength of aprotic sites Q_{CO} (kJ/mol) of aluminas modified by various ions 1 F^-, 2 Cl^-, 3 SO_4^{2-}, 4 PO_4^{3-} 5 0, 6 $1\cdot28\%$ Zn^{2+}, 7 $2\cdot12\%$ Zn^{2+}, 8 $4\cdot14\%$ Zn^{2+}, 9 Mg^{2+}, 10 Na^+. Points for samples 1, 2, 3, 4, 7, 8 are doubled because two bands were observed in the spectra
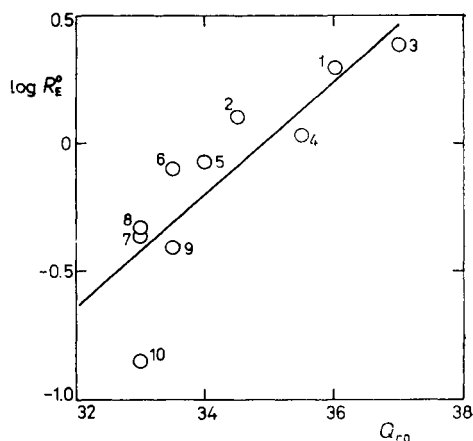
Fig. 2

Dependence of the turnover number of dibutyl ether formation R_E^0 (h^{-1}) on the strength Q_{CO} (kJ/mol) of the type I of centres of modified aluminas (notation of samples see Fig. 1)

and substituting for the activation energy E_i from the Brønsted–Polanyi relation

$$E_i = E_0 - \alpha_{BP}Q_i \tag{4}$$

we have

$$k = k'_0 \exp\left(\alpha_{BP}Q_i/RT\right). \tag{5}$$

From the above considerations concerning the heat of formation of the complex $(C_4H_9)_2 - O:Al{\Large\lessgtr}$, the Q_i value for the ether can be estimated to be approximately four times higher than the heat of adsorption of carbon monooxide Q_{CO}. In our case, however, the Q_i value for the alcohol should be substituted into Eq. (5). From the published data[13] it follows that this value is only slightly lower than the Q_i value for the ether (for the same aprotic acids and when hydrolysis does not take place). Then a comparison of the exponents in Eqs (2) and (5) leads to the expression

$$\alpha_{BP} = \alpha\left(Q_{CO}RT/Q_{alc}\right). \tag{6}$$

For our experimental conditions $\alpha_{BP} = 1 \cdot 187\alpha$. Accordingly, for $\alpha = 0 \cdot 3$ (for butene formation) α_{BP} equals approximately $0 \cdot 36$, and for $\alpha = 0 \cdot 57$ (for ether formation) α_{BP} is about $0 \cdot 68$. Thus, both α_{BP} values ($0 \cdot 36$ and $0 \cdot 68$) lie in the interval of $0 \cdot 25 - 0 \cdot 75$ following from the Brønsted–Polanyi assumptions. Consequently, the coefficients α for butene and ether formations obtained from our experimental data by successive approximations can be considered as having a physical meaning.

It was also found that the concentration of basic sites of aluminas played a role and substantially affected the selectivity of 1-butanol dehydration, *i.e.* the ratio of the initial rates of ether and butene formations. From Fig. 3 it follows that this
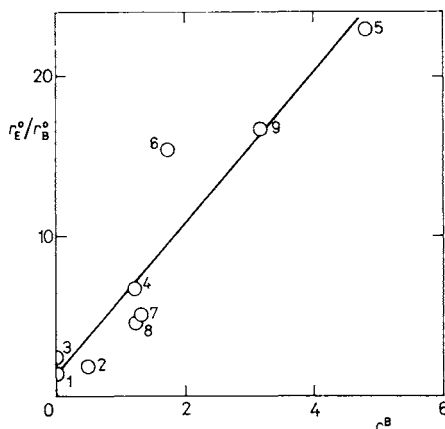

FIG. 3

Dependence of the ratio of initial reaction rates of ether and olefin formation on the relative concentration of stronger basic sites c^B (oxygen combined with two Al atoms[10]) — notation of samples see Fig. 1

ratio is proportional to the concentration of stronger basic sites (oxygen combined with two aluminium atom which is characterized[10] by frequency shift of deuterated chloroform of 40 cm^{-1}). Samples 10 with 0.62% Na which has a more complicated system of basic sites and on which the kinetics of 1-butanol dehydration is quite different[15] was not included into correlation. Then, the correlation coefficient is 0.94. In the preceding paper[10], a very close relation between the strength of aprotic acidic sites and the concentration of basic sites was demonstrated for this series of aluminas: the stronger aprotic sites the modified alumina has, the lower the concentration of basic sites is. Therefore, the correlation in Fig. 3, *i.e.* the dependence of the selectivity r_E^0/r_B^0 on the concentration of basic sites, can also be interpreted as a dependence on the acid strength. Both interpretations are reasonable since it is known[7] that the olefin formation is more sensitive to the catalyst acidity than the ether formation and that the increase of alumina basicity suppresses olefin formation more strongly than ether formation[15].

LIST OF SYMBOLS

c	concentrations of centres $[\mu\text{mol m}^{-2}]$
E_i	activation energy of intermediate complex
E_0	constant term of Brønsted–Polanyi relation
k	rate constant
k_0, k_0'	preexponential factors
Q_i	heat of formation of intermediate complex
Q_{CO}	adsorption heat of carbon monoxide $[\text{kJ mol}^{-1}]$
r_B^0, r_E^0	initial reaction rate of butene and dibutyl ether formation, resp. $[\mu\text{mol m}^{-2}]$
R_B^0, R_E^0	initial turnover number of butene and dibutyl ether formation, resp. $[\text{h}^{-1}]$
z	constant in Eq. (2)
α	experimental proportionality factor between the activation energy and adsorption heat of carbon monooxide
α_{BP}	parameter of Brønsted–Polanyi relation
$\Delta\nu_{CO}$	frequency shift of adsorbed carbon monooxide $[\text{cm}^{-1}]$

Indices (upper)

I, II, III	acidic centres of various types
B	basic centres

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