Temperature-programmed Desorption of Methanol, Ethanol, Propan-1-ol and Propan-2-ol on Silica-Magnesia Mixed Oxides

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The adsorption of methanol, ethanol, propan-1-ol and propan-2-ol on silica, silica-magnesia mixed oxides and magnesia has been studied by means of temperature-programmed desorption (t.p.d.). Besides the desorption of the alcohols themselves, CH_2O , CO and H_2 have been found to desorb upon adsorption of methanol, the corresonding olefins upon adsorption of the other alcohols and also propan-2-one upon adsorption of propan-2-ol. The desorption behaviour and alcohol conversion are discussed in terms of the EPA (electron-pair acceptor)–EPD (electron-pair donor) concept. The t.p.d. peaks of the alcohols have been assigned to two adsorption structures with different interaction strengths. The desorption maxima of the products have been found at higher temperatures than those of the alcohols, the difference being at least 50 °C. CO, H_2 or the olefins were found with all oxides, whereas formaldehyde was only observed with oxides of lower base strength and propan-2-one with oxides of higher base strength.

The interaction with and decomposition on oxide surfaces of lower alcohols has been extensively studied by means of i.r. spectroscopy and kinetic experiments. Four different adsorption structures (depicted in the Discussion section) were suggested by Tench *et al.*¹ on the basis of i.r. studies and found to be of different bond strengths. Besides i.r. spectroscopy, the t.p.d. technique is a powerful tool for studying bond strengths in adsorption structures. T.p.d. studies with methanol on magnesia were carried out by Foyt and White,² who compared it with the methanol/alumina system where bonding of methoxyl to the surface was found to be stronger. The interaction strength between the adsorptive and the surface in different adsorption structures is governed by the electron-donor and electron-acceptor capacities of both the adsorptive and the surface. The subject of the present work is to study the variation in the strength of the interaction of a series of alcohols with the same oxide (mixed oxide) and similarly of one alcohol with several mixed oxides of varying composition.

In order to note any regularities it was decided to vary the composition of the mixed oxide systematically. Mixtures of silica and magnesia were chosen for this purpose. T.p.d. was considered to be the most powerful tool for studying the interaction strength.

EXPERIMENTAL

MATERIALS

The silica-magnesia mixed oxides covered the range from 10 to 90 mol % magnesia. They are labelled with roman figures from I (10 mol % magnesia) to IX (90 mol % magnesia). The oxides were prepared by stirring Aerosil (Fluka) and magnesium hydroxide (Fluka purum p.a.) in water at 90 °C for 17 h, followed by centrifugation and drying to constant weight at 120 °C.

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Acidity values were determined according to Benesi^{3, 4} in the following way: three to five drops of a solution of 4-dimethylaminoazobenzene ($pK_a = 3.3$) in dry benzene were added to 1 g of calcined material (650 °C) in dry benzene. Subsequently, 0.5 mol dm⁻³ n-butylamine in benzene was added until the indicator changed colour. The consumption (mmol per g of sample or mmol per m² of sample) of butylamine indicated the number of acid centres ($pK_a = 3.3$). B.E.T. surface areas are listed in table 1.

sample	magnesia (mol %)	B.E.T. surface area /m ² g ⁻¹	acidity ($H_0 > 3.3$) /mmol m ⁻²
silica	0	330	
I	10	190	0.0085
II	20	240	0.0115
III	30	320	0.0131
IV	40	340	0.0153
v	50	190	0.0027
VI	60	150	0.0117
VII	70	130	0.0148
VIII	80	143	0.0075
IX	90	143	^a 0.0116
magnesia	100	81	

Table 1	Acidity (H_0)	< 3.3) and	B.E.T.	surface	areas of	silica-
	n	nagnesia mi	ixed oxi	ides		

^a Colour change only poorly pronounced.

Debye–Scherrer diagrams taken from oxides calcined at 650 °C (3 h) showed forsterite as well as magnesia in the range 60–90 mol % magnesia, whereas another solid phase, probably talc, was detected in addition to silica in the range 10–50 mol %.

Methanol (Merck, Uvasol), ethanol (Merck, dehydrated p.a.), propan-1-ol and propan-2-ol (Merck, Uvasol) were used without further purification.

APPARATUS

T.p.d. was carried out *in vacuo* (*ca.* 1 Pa) with a heating rate of 10 °C min⁻¹ in the range between 30 and 750 °C. The reactor was a quartz glass tube (10 mm in diameter) which was connected to a vacuum pump and to a quadrupole mass spectrometer for detecting the desorbing species (m/e 1–100). The mass spectrometer and the t.p.d. furnace were coupled to a process computer IBM S/7. For further details, see ref. (5) and (6).

PROCEDURE

The oxide was calcined in the t.p.d. reactor *in vacuo* at 650 °C for 45 min and cooled to room temperature. An amount of alcohol, such that the initial pressure was 2000–2700 Pa, was injected through a septum. After 15 min the reactor was evacuated again for 45–60 min, this time at room temperature, before the t.p.d. was started. The amount of sample (24–100 mg) was adjusted in such a way as to obtain a total surface area of *ca.* 800 m² after calcination, except for magnesia, the total surface area of which was *ca.* 560 m².

RESULTS

In all cases, the desorption of products and of alcohol was observed. The desorbed alcohols and products were identified by comparison with mass fragmentation patterns obtained with the QMG 311 quadrupole mass spectrometer, which was also

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alcohol	SiO2	I	ΠI^a	VII ^a	IX	MgO
CH.OH	88	140	117	130	119	141
5	236	~ 250			230-280	250-300
CH,CH,OH	89	100	100	126	122	120
- 3 - 2	245	~ 220			250-270	~ 270
CH [°] CH [°] CH [°] OH	90	100	103	129	111	110
	239	~ 205			~ 260	~ 290
CH CHOH	87	80	105	128	96	92
	216	~ 200			~ 240	~ 200
CH,						

Fable 2. Desorption of the alcohols from silica-magnesia in the range $30-750$ °C (10 °C min ⁻¹)),
temperatures of t.p.d. maxima	

^a High-temperature tailing for each peak.

Table 3. Desorption from silica-magnesia of the products of alcohol conversion in the range 30-750 °C (10 °C min⁻¹), temperatures of t.p.d. maxima

products formed from (alcohol)	SiO ₂	I	III	VII	IX	MgO
$CO + H_2(M)$	> 700 ^a	650	648	517	510	512
ethene (E)	577	^b 300, 575	395, 560	360	359	357
propene (P-1)	577	336, 560	337, 531	381	393	394
propene (P-2)	490	269, 480	256, 464	316	317	303
CH ₂ O (M)	> 700	642	608			
$CH_{4}(E)$		-		476	476	480
CH ₃ COCH ₃ (P-2)				324	317	303

^a Beginning of desorption around 600 °C; ^b beginning of desorption.

E, ethanol; M, methanol; P-1, propan-1-ol; P-2, propan-2-ol.

used for detection in the t.p.d. experiments. Desorption maxima of the alcohols and products are listed in tables 2 and 3.

Representative t.p.d. spectra are shown in fig. 1(a)-(d).

DISCUSSION

COORDINATION CHEMICAL APPROACH TO CATALYSIS; EPA AND EPD STRENGTHS OF THE SURFACES AND THE ALCOHOLS

The coordination chemical approach to catalysis^{7,8} will be used in this discussion of the results. Its main feature is that all interactions are considered to take place between an electron-pair donor (EPD, synonymous with a Lewis base) and an electron-pair acceptor (EPA, synonymous with a Lewis acid).

The EPA sites on the surface of our oxides are all cationic sites, namely Mg and Si ions and the protons of hydroxyl groups. The EPD sites are all anionic sites, in our case oxygen. For the alcohols, the strongest EPA function is localized in the proton of the hydroxyl group, which interacts with surface EPD sites. (It seems convenient to use the term site when referring to the catalyst, the term function when referring





to the reactant.) Other groups or atoms of the alcohols also exhibit EPD or EPA functions, but to a much lesser extent so they will not be taken into account here.

The behaviour of the system (with respect to adsorption, desorption and catalysis) is governed, to a great extent, by the strength of these interactions, which in turn depend upon the strengths of the EPD and EPA species involved in each interaction. Therefore it is important to have an idea of these EPA and EPD strengths.

A mixing rule was proposed by Noller *et al.*⁹ which stated that the acid and base strengths of mixed oxides are always between the acid and base strengths of the constituent oxides. Acid (base) strength rises monotonically with increasing fraction of the acidic (basic) component. The same tendency is expected on the basis of Sanderson electronegativity.¹⁰ Hence a monotonic variation of site strength is expected from silica to magnesia, decreasing strength for EPA sites, including hydroxyl groups, and increasing strength for EPD sites. This was indeed found in i.r. studies of the adsorption of acetonitrile¹¹ and of acetone¹² on silica, magnesia and mixed oxides. Silica always turned out to have the most acidic hydroxyl groups. An important detail was that the EPA strength of the hydroxyl groups was in all cases lower than that of cationic sites (here Mg and Si sites).

Acidity measurements by the method of Benesi shown in table 1 do not appear to favour the idea of a monotonic variation of EPA strength. Acidity was found to be highest for sample VII, followed by samples III, I and IX, whereas silica and magnesia do not show acidity ($H_0 < 3.3$). Note, however, that acidity as determined in this way is the number of acid sites within the range of strength determined by an indicator. Noller and Parera¹³ and Vinek¹⁴ suggested that silica does not exhibit cations, which they ascribed to the perfect shielding of Si sites by oxygen. The hydroxyl groups of silica on the other hand are not acidic enough to be detected with an indicator of pK_a 3.3, as their pK_a is as high as 7 according to Hair and Hertl.¹⁵ Magnesia on the other hand is a solid base rather than a solid acid, with $pK_a > 3.3$.

The EPA strength of the alcohols (in terms of acceptor numbers given by Gutmann¹⁶ and Mayer and Gutmann¹⁷ and listed in table 4) decreases from methanol to propan-2-ol while their EPD strength (in terms of Gutmann's donor numbers) slightly rises in this order.

	DN	AN		
water	18.0	54.8		
methanol	19.0	41.7		
ethanol	20.0	37.9		
propan-1-ol		37.3		
propan-2-ol		33.3		

 Table 4. Donor numbers (DN) and acceptor numbers (AN) of water and alcohols according to Gutmann

DESORPTION OF ALCOHOLS

As the t.p.d. spectra of alcohols [fig. 1(a)-(d)] are rather complicated, we turn first to simpler systems. In the t.p.d. spectra of acetonitrile, diethyl ether and pyridine on silica,^{11, 18} only one relatively narrow peak was found with its maximum below 100 °C and desorption was complete between 150 and 200 °C. This behaviour was assigned to adsorption on hydroxyl groups exclusively, which led to weak interaction. On mixtures with alumina or magnesia, and on magnesia alone, the same peak, but with pronounced high-temperature tailing, or several peaks appeared. Addition of lowervalent oxides to silica had obviously created strong adsorption sites, which in our opinion should be identified with cations exposed in the surface as some of the oxygen is now missing.¹³

With this relatively simple view in mind, it was surprising when studying alcohols to find that not only with the mixtures and magnesia but also with silica, several peaks appeared (one at *ca.* 90 °C, a second between 216 and 245 °C and a third one, which is not given in table 2 and may be classified as high-temperature tailing). There must be alcoholic species on silica comparable to those on mixtures, but with so high an interaction strength as to be retained up to at least 500 °C (see the results of the desorption of the products of alcohol conversion, table 3). With samples I and IX and with magnesia one peak with a shoulder at higher temperature tailing was found. Obviously, we are dealing with more than one type of interaction in each case (several interaction structures).

The interaction of alcohols with oxides has already been investigated by means of i.r. spectroscopy.^{1, 19, 20} Investigating the system methanol/magnesia Tench *et al.*¹ proposed four adsorption structures (fig. 2), which appear suitable for discussing our results. S1 is for alcohol molecules adsorbed in a second layer and interacting so weakly with the surface as to desorb on evacuation even at room temperature. S2 describes interaction of the alcoholic oxygen with a Lewis acid or EPA site of the surface, accompanied by the interaction of the hydrogen of the alcoholic hydroxyl group with a surface Lewis base or EPD site. S3 is the result of dissociative adsorption where the alkoxy group is bound to a surface EPA site and the proton to a surface EPD site (surface oxygen), thus giving a surface hydroxyl group.



Fig. 2. Adsorption structures S2, S3 and S4 of alcohols on oxides. \oplus , EPA site; \ominus , EPD site, RCH₃, CH₃CH₂, CH₃CH₂CH₂ or CH₃CHCH₃.

In structures S2 and S3 we have EPA_S/EPD_A , as well as EPA_A/EPD_S , interactions (A, adsorbate, S, surface), *i.e.* EPA and EPD functions of both the adsorbate and the surface are assumed to be involved. S2 and S3 are considered to be responsible for the desorption of the alcohols themselves. The desorption of alcohol from S3 must be preceded by the recombination of the alkoxy species with the proton, while no such recombination will be required for the desorption of alcohol from S2. Therefore we suggest that alcohol desorption observed at lower temperatures may be associated with desorption from S2. Alcohol desorption in the higher-temperature range (> ca. 200 °C: second peak, shoulder, high-temperature tailing) may be assigned to desorption from S3, after recombination.

S4 corresponds to a second type of alkoxy group on the surface where the alkoxy group is within the surface layer rather than on it. S4 is expected to be the most tightly bound surface species, the desorption of which may result in the appearance of products rather than alcohol.

There are also indications of alkoxy species formed upon the adsorption of ethanol and propan-2-ol on magnesia.^{19, 20} We believe that this system can also be used for silica and silica-magnesia mixed oxides.

The next question is whether the EPA sites for S2 are hydroxyl groups or other cationic sites, namely Mg or even Si sites. This question is easiest to answer for silica. The first peak, assigned to S2, appears at approximately the same temperature as the peaks for the systems silica/acetonitrile,¹¹ silica/diethylether and silica/pyridine.¹⁸ As these latter peaks can only be assigned to adsorption on hydroxyl groups, we assign the peak that with alcohols appears at the lowest temperature to adsorption on hydroxyl groups as well, possibly accompanied by adsorption on oxygen sites (interacting with the proton of the alcoholic hydroxyl group).

The second peak or the shoulder or the high-temperature tailing is assigned to S3, for which an Mg or Si site is assumed to be the EPA site. As this interaction is considerably stronger than that with surface hydroxyl groups, the alcoholic hydroxyl groups dissociate. An Mg or Si site is easily accessible on all samples except silica, because of the above-mentioned shielding of Si by oxygen. We assign the second peak observed with silica to a surface species (fig. 3) which is formed by reaction of alcohol with strained Si—O—Si bridges, as discussed by Borello *et al.*²¹ for silica/methanol. Note that such a structure is impossible for acetonitrile, diethylether and pyridine for stoichiometric reasons, which is why only one peak, appearing below 100 °C, is observed with these molecules on silica.

$$si \xrightarrow{O} si + CH_3OH \longrightarrow 1$$

 $Si \xrightarrow{Si} si$

Fig. 3. Adsorption of methanol on silica leading to surface methylation reaction.

We now discuss the variation of desorption temperature as a function of the oxides and alcohols. Taking into account that there are at least two interactions between the alcohols and the surface in structures S2 and S3 enables us to interpret several details. Usually more emphasis is given to acidic rather than basic surface sites. However, much evidence on the role of basic sites can be obtained from our results.

We will first compare silica and magnesia. Except for the second peak of propan-2-ol, desorption temperatures are higher with magnesia. As magnesia is more basic than silica, this must be attributed to the EPA_A - EPD_S interaction being the decisive factor.

A further interesting phenomenon is the difference of the desorption temperatures of the four alcohols on the same oxide. When both EPA_S and EPD_S are very weak sites, interaction will be weak, even though the strengths of EPA_A and EPD_A are notable. This is so with silica, whose hydroxyl groups and oxygen sites are relatively weak EPA and EPD sites, respectively. Thus, the first peak of the four alcohols appears at nearly the same temperature. However, with magnesia, which has strong EPD and moderately strong EPA sites, a difference of *ca*. 50 °C is observed. Again the EPA_A-EPD_S interaction appears to be decisive. An increase in the EPA strength of the alcohols leads to stronger retention on the surface. Propan-2-ol, which is the weakest EPA, is desorbed at lower temperature than the other alcohols, not only from silica and magnesia but also from samples I and IX.

With samples III and VII, only one peak with high-temperature tailing was observed, appearing at roughly the same temperature for all four alcohols. Possibly on these oxides acid and base strengths are more balanced than on the other oxides.

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As the increasing EPA strength of the alcohol is accompanied by decreasing EPD strength, a compensation effect may be operative which reduces the differences between the desorption temperatures.

FORMATION OF PRODUCTS

Product formation cannot be unambiguously assigned to one of the two surface alkoxy groups S3 or S4, but it seems likely that S4 will play a significant role.

Products are also formed over silica, whose catalytic activity is known to be very low. Indeed, the products do not appear until a temperature of ca. 500 °C is reached, even with propan-2-ol which is the most reactive alcohol in this series. This shows that the interaction with silica must be extremely strong, and we must now ask how is it possible that in spite of so strong an interaction the catalytic activity of silica is so poor? It has been pointed out for many years that for catalysis an interaction of medium strength is most favourable. Too weak an interaction cannot have a notable effect, but also too strong an interaction is of no use as the retention of reactants and products is too strong. This concept is known as the denomination volcano curves.²²

A further idea about the low catalytic activity of silica will now be put forward. There is no doubt that the EPA strength of silica is extremely high. Its EPD strength, on the other hand, is extremely low. Provided both EPA and EPD sites are indispensable for bringing about catalysis, as has been pointed out by several authors,^{6, 23} the EPD strength of silica could be too low.

METHANOL

CO and H_2 were the main products from methanol. Furthermore, CH_2O was found to desorb from silica and samples I and III. In agreement with ref. (24) we suggest a two-step base-catalysed reaction. The temperature of the maxima of desorption from the samples of higher base strength (samples VII and IX and magnesia) was at least 130 °C below that observed on silica and samples I and III:

$$CH_{3}OH \rightleftharpoons CH_{2}O + H_{2}$$
$$CH_{2}O \rightleftharpoons CO + H_{2}.$$

CH₂O was only found to desorb from oxides with lower basicity at temperatures (silica > 700 °C; I, 642 °C; III, 608 °C) below those of the desorption maxima of CO and H₂ (table 3). We would suppose that, on oxides with sufficient base strength, CH₂O is immediately transformed into CO and H₂. On silica and samples I and III, the formation of CH₂O occurs at higher temperatures and CH₂O may be partly desorbed before it is completely transformed to CO and H₂.

ETHANOL, PROPAN-1-OL AND PROPAN-2-OL

The main product was the corresponding olefin from these alcohols. Water formed by dehydration did not desorb simultaneously with the olefin. In some cases, on samples VII and IX and magnesia, broad water peaks were found at temperatures higher than those of the maxima of the olefin desorption peaks. Often only a rise of the base line of water occurred in the high-temperature range. This is a further clear indication of active sites being blocked by dehydration products, as has often been discussed in the literature. On samples I and III, two olefin desorption peaks were found. The first one (at lower temperatures) was associated with alkoxy species adsorbed on the mixed phase while the second one could be due to alkoxy species on excess silica.

With respect to the temperature of the desorption maxima (table 3), the oxides may

be divided into three groups: group A, silica; group B, samples I and III; group C, samples VII and IX and magnesia.

Dehydration is well known to be best catalysed by acid sites. The question is whether the olefin is desorbed once it is formed, *i.e.* if the temperature of its desorption is the temperature of its formation, or if it is formed below the temperature of its desorption. If the olefin were desorbed on formation, the olefin peaks in group B should be found at lower temperatures than those in group C. On the other hand, if the olefin, after its formation, were retained on the oxide (surface EPA interacting with CC double bond) the temperature of the desorption maxima would be determined by the strength of the interaction between the olefin and the surface EPA. In this case the olefin peaks in group B should be found at higher temperatures than those in group C. The temperature of the desorption maximum of propene in group B is at least 40 °C lower than in group C, showing that the temperature of desorption is determined by reaction and not retention of olefin. A second finding agrees with this: propene formed from propan-2-ol is desorbed at temperatures at least 65 °C lower than those for propene formed from propan-1-ol.

Nevertheless, ethene produced from ethanol was found at higher temperatures in group B. We suggest that ethene, in contrast to propene, does not desorb immediately after formation, at least on oxides which exhibit enough sites of sufficient acid strength. Possibly retention of ethene on the surface is favoured because of the smaller size of ethene.

On oxides of group B, products occur from ethanol and propan-2-ol which are typical results of base-catalysed reactions: CH_4 and propan-2-one. Propene and propan-2-one show desorption maxima at practically the same temperature (sample VII: propan-2-one 324 °C and propene 316 °C; sample IX: 317 °C; magnesia: 303 °C). We assume that propan-2-one and propene are evolved from the same adsorption sites.

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