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Acid sites investigation of simple and mixed oxides by TPD and microcalorimetric techniques

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Abstract

The present work deals with the acid properties of silica, alumina and two mixed oxides obtained by grafting silica on alumina (SA sample) or alumina on silica (AS sample). The surface acidity of the samples, of both Lewis and Brønsted type, was determined by means of microcalorimetry and temperature programmed desorption (TPD), using pyridine and 2,6-dimethylpyridine as probe molecules. Both techniques point out that the grafted mixed oxides SA and AS have acidic properties different from those of the pure alumina and silica starting supports. Some differences exist, in terms of acid sites strength distribution, between TPD and calorimetric results, which can be reasonably attributed to the different activating conditions of the samples. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Grafting; Silica–alumina mixed oxides; TPD; Microcalorimetry

1. Introduction

Metal oxides are largely used as catalysts in chemical industry. Many organic reactions, such as cracking, isomerisation, alkylation and partial oxidation are performed over metal oxides catalysts [1–3]. The catalytic behaviour of metal oxides, in terms of both activity and selectivity, is related to their acid–base properties. As well-known, some reactions occur on acid or basic sites, while others, i.e. alcohol dehydration [4–6], require acid–base pair sites. Hence, a deep knowledge of the surface properties is of great importance to develop catalysts with suitable and tailored acid–base characteristics.

The acid–base properties of metal mixed oxides have been found to change with the nature of the constituents, with their relative concentration and with the preparation and pre-treatment procedures [7]. Accordingly, mixed oxides can be used to obtain catalysts with proper acid–base characteristics by appropriately choosing the above-mentioned variables.

With regard to the preparation procedures, grafting of metal alkoxides on surface hydroxy groups of different carriers, followed by steaming and calcination, is a convenient way to modify the acidity of a surface. The mixed oxides prepared by grafting markedly differ from those obtained by the usual coprecipitation procedure. A range of possibilities can be achieved by appropriately choosing the coverage extent. Submonolayer coverages can lead to systems where the corresponding oxide is highly dispersed on

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the other component or even result in materials where isolated sites of particular strength are present on the surface. Starting from a monolayer coverage completely alters the surface of the support oxide in terms of its hydroxyl density and acidity. Multilayer coverage, achieved by repeated grafting, steaming and calcining treatments, leads to solids with a surface chemically different from that of the support oxide.

The present work deals with the acid properties of silica, alumina, and multilayers of silica on alumina (SA) and alumina on silica (AS), obtained by grafting. The surface acidity of the samples, both of Brønsted and Lewis type, was determined by means of microcalorimetry and temperature programmed desorption (TPD), using pyridine and 2,6-dimethylpyridine as probe molecules, since, as reported by Benesi [8], 2,6-dimethylpyridine is almost selectively adsorbed on Brønsted sites, while pyridine reacts with both Brønsted and Lewis sites.

2. Experimental

2.1. Catalyst preparation

Silica (surface area, 280 m^2/g) was supplied by Fluka/Sigma/Aldrich at the highest available purity, while γ-alumina (surface area, 180 m^2/g) was obtained from Dutral Montedison. The SA sample was prepared by directly contacting silicon tetraethoxide with the γ-alumina support, followed by washing, drying, steaming and calcination; AS sample was prepared by contacting the silica support with an aluminium isopropoxide solution in toluene, followed by treatments as in the previous case; the preparing procedure was repeated three times in both cases to obtain a multilayer adsorption of silicon or aluminium oxides on the carrier surfaces. Details on the preparation procedures can be found elsewhere [9,10]. Textural analyses were carried out on a Sorptomatic 1990 System (Fisons Instruments), by determining the nitrogen adsorption/desorption isotherms at 77 K. Before analysis, the samples were heated overnight under vacuum up to 473 K (heating rate = 1 K/min). Compared with the carriers, no significant changes in the specific surface areas, assessed by the BET method, were found in the case of the mixed oxides.

2.2. Catalyst characterisation

Calorimetric runs were performed on a Tian–Calvet heat-flow equipment (Sétaram). Each sample was pretreated overnight at 673 K in vacuo (10^{-3} Pa) before the successive introduction of small doses of the probe gas. The equilibrium pressure relative to each adsorbed amount was measured by means of a capacitive pressure transducer (Leybold). The adsorption temperature was kept at 423 K.

TPD runs were performed by first treating the sample at 673 K for 1 h, under air flow, and then saturating it with the organic base at temperatures 20 K higher than the boiling point of the base itself. The temperature was then increased, under helium flow up to 443 K, with a rate of 10 K/min and kept isothermal for 2 h in order to purge the surface from the physisorbed molecules. Finally, desorption was carried out from 443 to 693 K (heating rate = 10 K/min) and the final temperature was kept isothermal until the TCD signal came back to zero. Higher temperatures were avoided to prevent the decomposition of the probe molecules.

3. Results and discussion

Calorimetric results are presented in Fig. 1a and b, where the differential heats of adsorption (Q_{diff}) of pyridine (bp 115°C) and lutidine (bp 143°C), respectively, are plotted versus coverage. From the calorimetric data, the number of sites and their distribution, according to the adsorption energies, can be determined. It has been reported in [11] that non-specific adsorption through hydrogen bonding of pyridine on silica is responsible for differential heat values of about 90 kJ/mol. Consequently, pyridine and 2,6-dimethylpyridine uptakes originating differential heats <90 kJ/mol were neglected in calculating the concentration of acid sites for all the samples. In previous papers [9,10], dealing with the acid properties of similar catalysts, the following acid strength distribution has been considered, according to the differential heat of adsorption: weak acid sites, w ($90 \leq Q_{\mathrm{diff}} < 120$ kJ/mol), medium acid sites, m ($120 \leq Q_{\mathrm{diff}} < 150$ kJ/mol) and strong acid sites, s ($Q_{\mathrm{diff}} \geq 150$ kJ/mol). For consistency reasons, the same sites strength distribution has been considered in the present case.

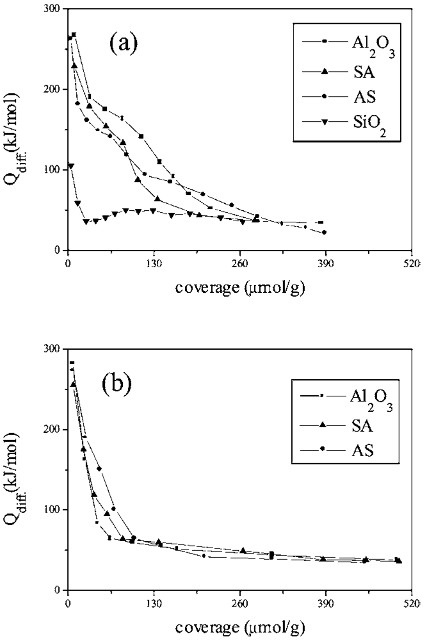


Fig. 1. Differential adsorption heats as function of the coverage degree: (a) pyridine adsorption; (b) 2,6-dimethylpyridine adsorption.

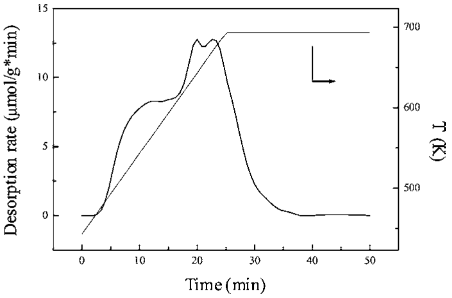


Fig. 2. TPD curve for γ-alumina, using pyridine as probe molecule.

Table 1 shows that when alumina is supported on silica (AS sample), a very high acidity (Brønsted + Lewis), compared with the carrier, is developed. However, the acidity of the mixed oxide is different from that of the pure Al_2O_3: on AS sample, the number of strong acid sites is remarkably lower compared with alumina, while that of the weak and medium acid sites is higher. For the SA sample, the number of total acid sites is decreased with respect to the carrier, but their strength distribution, in terms of percent amounts, seems to be very similar to the pure alumina, in spite of the presence of a high amount of silica, which should completely cover to the alumina surface. To XPS results [10] showed that a "patchy monolayer" forms upon grafting; it is the top of this "monolayer" phase which grows, upon further addition of silica (multilayers), instead of the occupation of the still available alumina surface. The occurrence of such a mechanism could explain why the surface of the mixed oxide retains in part the acid character typical of the carrier. Both AS and SA samples exhibit a higher percent of Brønsted acid sites with respect to alumina, while the extent of the Lewis acidity is markedly reduced mainly at the expense of the strong sites.

Table 1
Results of calorimetric analyses: acid sites number (μmol/g) and strength distribution ($n_i^0/n_{total}^0 \times 100$; i = w, m, s)

Catalyst		Total			Brønsted			Lewis		
		w	m	s	w	m	s	w	m	s
γ-Alumina	n^0	30	31	100	8	15	20	22	16	80
	%	19	19	62	19	35	46	19	13	68
AS	n^0	46	44	42	19	16	47	23	22	5
	%	35	33	32	23	19	58	46	44	10
SA	n^0	25	27	62	23	18	35	2	17	27
	%	22	24	54	30	24	46	4	37	59
Silica	n^0	8	–	–	8	–	–	–	–	–
	%	100			100					

Fig. 2 shows the TPD curve of alumina as an example. A semi-quantitative estimation of the number of acid sites can be derived from TPD plots such as the one reported in the figure. As in the case of the microcalorimetric analyses, according to previous works [9,10], three classes of acid sites have been considered, depending on the desorption temperature: weak, w ($T_D < 523$ K), medium, m ($523 < T_D < 673$ K) and strong, s ($T_D > 673$ K) acid sites. In agreement with microcalorimetry, TPD results, summarised in Table 2, also point out that grafting alkoxides strongly change the acid–base properties of the pure oxides used as supports. Mixed oxides possess a very high acidity compared with silica and show a Lewis acidity significantly lower, both in terms of sites number and strength, than alumina.

Some differences exist between calorimetric and TPD results with regard to the sites strength distribution: in the case of TPD, the percent of medium acid sites is always remarkably higher than for

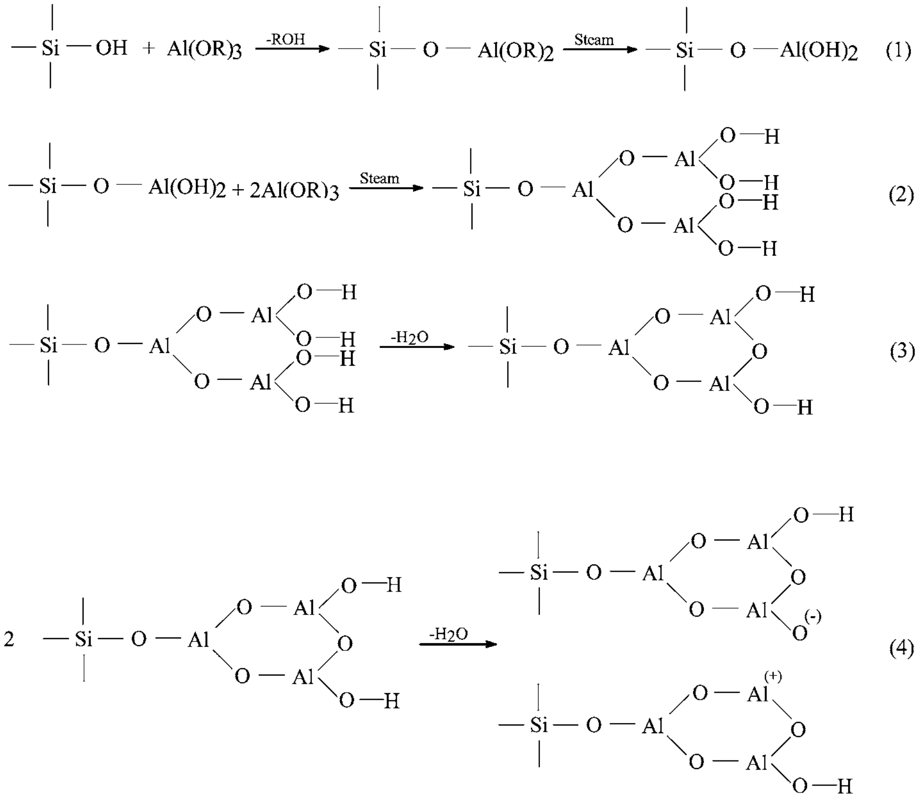
Table 2
Results of TPD analyses: acid sites number (μmol/g) and strength distribution ($n_i^0/n_{\mathrm{total}}^0 \times 100$; i = w, m, s).

Catalyst		Total			Brønsted			Lewis		
		w	m	s	w	m	s	w	m	s
γ-Alumina	n^0	12	84	35	2	18	9	10	66	26
	%	9	64	27	7	62	31	10	65	25
AS	n^0	20	110	60	10	90	60	10	20	–
	%	10	58	32	6	56	38	33	67	–
SA	n^0	14	75	11	9	48	6	5	27	5
	%	14	75	11	14	76	10	14	72	14
Silica	n^0	10	40	10	10	40	10	–	–	–
	%	17	66	17	17	66	17			

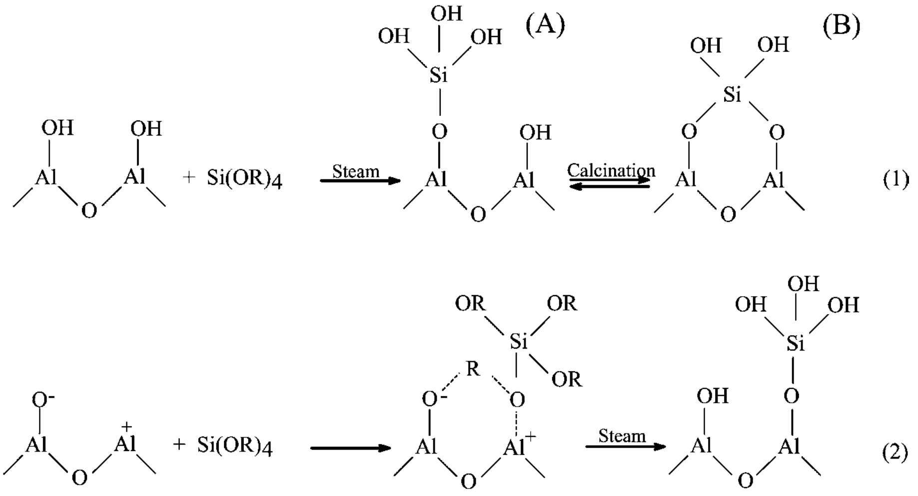
microcalorimetry. This can be due to fact that, as suggested in [12], strong acid sites having $Q_{\mathrm{diff}} >$ 180 kJ/mol may be not completely released from the organic base at 693 K and therefore not revealed by the TPD technique.

In order to understand the modifications in the number and nature of acid sites which occur on the mixed oxides, it is useful to take into account the possible grafting mechanisms (details on the changes in stoichiometry related to the differences in the alkoxide concentration can be found in [9,10]). Schemes 1 and 2 represent in a simplified way the most probable grafting reactions for high alkoxide concentrations in the case of AS and SA, respectively.

It can be noted from Scheme 1, that reactions (1–3) are in agreement with the TPD results, which pointed out a higher number of total acid sites compared with the support (the number of surface hydroxy groups is increased because of grafting) and the presence of mostly Brønsted acidity (about 85%). The discrepancy between TPD and calorimetric analyses, by which a 60% of Brønsted acidity was determined, can be explained taking into account that, as well-known, the degree of dehydroxylation of a surface is related to the activation conditions; thus it is reasonable to



Scheme 1.



Scheme 2.

suppose that the last reaction become more and more important as the operative conditions become more strict, as in the case of the microcalorimetric runs, for which activation is performed at 673 K under vacuum.

With regards to the silica on alumina sample SA, from the reaction Scheme 2 it can be noted that the effect of grafting is to convert the surface hydroxyls and the Lewis sites of alumina into silanols of two different types (A and B). The Brønsted acidity is then increased, but the presence of strong Brønsted acid sites, as well as that of the residual Lewis acidity can be reasonably ascribed to the retained acidity of the carrier, since, as already mentioned, the alumina surface is only partially covered by silica.

4. Conclusions

In the present work, we have shown that grafting is a promising preparation method to modify the surface properties of the pure oxides: AS and SA mixed oxides possess a very high acidity compared with silica and show a Lewis acidity significantly lower, in terms of sites number and strength, than alumina. The discrepancies between TPD and microcalorimetry, most in terms of acid strength distribution, can be easily explained by the different operative conditions adopted during the runs.

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