THE CONTROL OF SURFACE ACIDITY DISTRIBUTION OF MIXED OXIDE CATALYSTS

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The acid strength distribution of silica gel, magnesium, aluminium, and zirconium silicates, and magnesium alumosilicates was studied. Magnesium alumosilicates show additive properties of the distributions of the two-component catalysts $MgO-SiO_2$ and $Al_2O_3-SiO_2$, *i.e.* a continual distribution of the centers from $H_0 = 5\cdot0$ to $H_0 \leqq -3\cdot0$. By varying the components and their ratio in oxide catalysts, the distribution of surface acidity can be modelled over a broad region of the acid strength.

Acid surface properties of some catalysts are responsible for their catalytic activity in reactions such as dehydration of alcohols, isomerization and polymerization of olefins, cracking and alkylation of hydrocarbons. Individual types of catalysts may differ from each other by the total number of acid centers and by the acid strength distribution. The most common industrial acid catalysts are alumosilicates. Those with aluminium oxide content of around 25—30 per cent have majority of their centers in the very strong acid region of $H_0 \leqq -8\cdot2$ (ref.[1,2]). At a lower aluminium oxide content (around 11—13%) the catalyst has its centers more continuously distributed with respect to their acid strength[1,3]. Magnesium silicates (25—30% wt. MgO) have usually a higher total concentration of acid centers than have alumosilicates, their centers being mainly weakly or moderately acidic. As a rule, they do not possess more acidic centers than those with $H_0 = -3\cdot0$ (ref.[1,2]). Zirconium(IV) silicates, with a very broad range of zirconium oxide content (1—90%), all possess the most acidic centers of $H_0 \leqq -8\cdot2$ and their acid strength distribution is similar to that of alumosilicates[4].

The acid strength distribution may not be always the most suitable with respect to the purpose to which the catalyst is to be employed. Catalysts with maximum of centers in the most acidic region (commercial alumosilicates) are not for instance selective enough for dehydrating alcohols, since they induce isomerization of the olefins formed[5,6]. On the other hand, for some theoretical studies[7] it is necessary to use a catalyst having continuous distribution of centers over acid strength region as broad as possible.

The subject of the present communication is the study of surface acidity distribution of silica gel, magnesium, zirconium, and aluminium silicates and magnesium alumosilicates. The aim was to find the possibility of controlling the distribution of surface acidity by the choice and relative amounts of individual components of these mixed catalysts.

EXPERIMENTAL

Determination of the Acid Strength Distribution

Surface concentrations of centers of different acid strength were determined by the so-called indicator method[2], *i.e.* titration of the solid by a toluene solution of n-butylamine, the points of equivalence being indicated by the change of colour of an appropriate acid–base indicator. Differences in consumptions of the titrating agent in titrations on several indicators of different dissociation constants gave approximate acid strength distribution of the centers. The acid strength is expressed in units of the H_0 functions[8,9]. The technique used was a discontinual titration of the centers with n-butylamine. The original Benesi[2] procedure was somewhat modified[7]. The point of equivalence was sought by successive approximations, the time needed to achieve stable colouration of the catalyst by indicator was usually 20 h. The factor of the n-butylamine solution in toluene was determined by titration with standard $0.1\,\text{M-HClO}_4$ solution in glacial acetic acid using crystal violet[10] as indicator. The indicators employed were Methyl Red (pK 5·0), Dimethyl Yellow (pK 3·3), benzeneazodiphenylamine (pK 1·5), and dicinnamalacetone (pK − 3·0).

Preparation of Magnesium Silicates

These catalysts were prepared by following procedures.

A. Impregnation of the gel of silicic acid with magnesium acetate. A solution of sodium silicate was hydrolysed by a sulphuric acid solution. The alkalies were removed from silica gel by washing it with sulphuric acid. The washed gel was then impregnated with magnesium acetate solution and after c. 1 h this was hydrolysed with ammonia. The following day the gel was filtered off, washed with water and dried overnight in air at 110°C.

B. Mixing of the sol of silicic acid with magnesium acetate solution. The sol was prepared by decationization of a solution of alkali metal silicates on a Dowex cation exchanger. Mixing of the magnesium component with the sol led to immediate formation of the gel. The mixture was then stirred for about 1 h and hydrolysed with ammonia. After standing overnight, it was washed with water and dried overnight in air at 110°C.

C. Hydrolysis of magnesium acetate and tetraethoxysilane. A solution of magnesium acetate was hydrolysed with ammonia until visible formation of the hydroxide and to this mixture tetraethoxysilane was added as nonalkaline silicic component with simultaneous hydrolysis. The following day the precipitate was filtered off, washed with water and dried overnight in air at 110°C.

D. Co-hydrolysis of magnesium methylate and tetraethoxysilane. Magnesium methylate was dissolved in tetraethoxysilane and the solution was hydrolysed with water. The precipitate was filtered off, washed with water and dried overnight in air at 110°C.

Preparation of Silica Gel with Traces of Aluminium or Zirconium

A solution of sodium silicate was hydrolysed by acidifying it with sulphuric acid. The alkalies were removed from the silica gel formed by washing it with sulphuric acid solution. One portion of the washed gel was impregnated with a solution of aluminium nitrate or zirconyl nitrate, the nitrates being used in an amount of c. 0·3 — 1 g per 100 g of the silicate (the other portion of the silica gel was left aside for comparison). This procedure was followed by washing with a small amount of water and by treatment with ammonia. The following day the gel was filtered off, washed with water and dried overnight in air at 110°C.

TABLE I

The Effect of Small Amounts of Aluminium or Zirconium (below 1% wt.) on the Acid Strength Distribution of Silica Gel

Component added	Surface acidity, mequiv./g			
	$5.0 \geqq H_0 \geqq 3.3$	$3.3 \geqq H_0 \geqq 1.5$	$1.5 \geqq H_0 \geqq -3.0$	$H_0 \leqq -3.0$
—	0.39	0.01	0.01	0
Al	0.18	0	0.02	0.03
Zr	0.14	0	0.02	0.01

TABLE II

Acid Strength Distribution of Magnesium Silicates Prepared

Procedure	MgO % wt.	Surface acidity, mequiv./g			
		$5.0 \geqq H_0 \geqq 3.3$	$3.3 \geqq H_0 \geqq 1.5$	$1.5 \geqq H_0 \geqq -3.0$	$H_0 \leqq -3.0$
A	7.6	0.03	0.02	0.21	0
A	18.8	0.10	0.10	0.35	0
A	22.2	0.17	0.05	0.55	0
B	5.4	0.20	0.05	0.16	0
C	17.9	0.10	0	0.15	0
D	15.9	0.14	0.10	0.45	0

Preparation of Three-Component Catalysts

The gel or sol of silicic acid (see preparation of magnesium silicates, method *A* or *B*) was divided into several portions and these were mixed with either aluminium nitrate solution, magnesium acetate solution or a solution of both salts. After c. 1 h, the mixtures were treated with ammonia. The following day the precipitates were filtered off, washed with small amount of water and dried overnight in air at 110°C.

Further Treatment of Catalysts

All dried samples of the catalysts of the above types were subjected to calcination at 550 ± 10°C for 4 h. The calcinates were crushed and the portion of 0.5—0.08 mm particles was further used. After calcination and crushing, the catalysts were re-hydrated and dried so that on their surface an equilibrium content of water was established corresponding to a temperature of 110°C, *i.e.* to the conditions used in the kinetic study[7] for which they were to be employed. The thus prepared samples were analysed on the content of magnesium[11] or aluminium[11] and their specific surface[12] (from 419 to 743 m^2/g) and acid strength distribution were determined (Tables I—III).

RESULTS AND DISCUSSION

As it is seen from the first line of Table I or Table III, the basic component of studied catalysts, silica gel, has majority of its surface centers only very weakly acidic $(5 \cdot 0 \geqq \geqq H_0 \geqq 3 \cdot 3)$, in agreement with literature data[13]. By contrast to silica gel, the $MgO-SiO_2$ system (Table II) has on its surface a sufficient number of weakly and medium acid centers, and that also in the $1 \cdot 5 \geqq H_0 \geqq -3 \cdot 0$ region. However, it is not obviously capable of forming strongly acidic centers of $H_0 \leqq -3 \cdot 0$. We have also qualitatively tested the acidity of samples directly after their calcination at 550°C and also the acidity of the samples containing up to 37% wt. MgO. Even in those cases the centers with the acid strength $H_0 \leqq -3 \cdot 0$ were not present. The results by Hirschler and Schneider[3], the only authors who observed the existence of these strongly acidic centers on surface of $MgO-SiO_2$ catalysts were not thus confirmed.

Another modification of the acid strength distribution of silica gel arises upon addition of aluminium or zirconium. The small amount added $(<1\%$ wt.) (Table I) causes formation of a small number of strongly acidic centers with $H_0 \leqq -3 \cdot 0$. This is accompanied by a substantial decrease in the number of weakly acidic centers in the $5 \cdot 0 \geqq H_0 \geqq 3 \cdot 3$ region and by the preservation of the original small amount of centers in the medium acidic region $3 \cdot 3 \geqq H_0 \geqq -3 \cdot 0$. By the action of aluminium or zirconium the total number of centers is reduced to approximately a half of the original value. The amount of aluminium affects also distribution of the surface acidity of alumosilicates, as follows from comparison of the distribution of the catalyst with the low aluminium content (Table I) with commercial alumosilicates that contain a higher amount of aluminium[1-3]. The latter have majority of their centers in the $H_0 \leqq -8 \cdot 2$ region.

By the above-mentioned modifications of silica gel we prepared two basic types of catalysts which markedly differed in acid strength distributions. The catalyst with added aluminium (or zirconium) contained strongly acidic centers with $H_0 \leqq -3 \cdot 0$ but it did not practically possess the centers in relatively broad $+3 \cdot 3 \geqq H_0 \geqq -3 \cdot 0$ region. On the other hand, the $MgO-SiO_2$ catalyst exhibited a considerable amount of medium acidic centers, especially in the $1 \cdot 5 \geqq H_0 \geqq -3 \cdot 0$ region. It did not contain, however, strongly acidic centers with $H_0 \leqq -3 \cdot 0$. We assumed therefore that by addition of both components $(MgO$ and Al_2O_3 or $ZrO_2)$ to silica gel it could be possible to prepare a catalyst which would contain both strongly acidic centers with $H_0 \leqq -3 \cdot 0$ (the effect of aluminium or zirconium) and a sufficient number of medium acidic centers $(3 \cdot 3 \geqq H_0 \geqq -3 \cdot 0)$ (the effect of magnesium), *i.e.* it would have centers in a broad region from $H_0 = +5$ to $H_0 \leqq -3 \cdot 0$. The Al_2O_3-MgO- $-SiO_2$ system was studied experimentally (Table III). The results showed that the above assumption is justified. Small amounts of aluminium in magnesium silicates shift the acid strength properly to more negative H_0 values so that these catalysts

TABLE III

Influencing of Acid Strength Distribution by Adding Aluminium and Magnesium Components to Silica

Batch	Catalyst	Form of SiO_2	MgO % wt.	Al_2O_3 % wt.
1	SiO_2	gel	—	—
1	Al_2O_3–SiO_2	gel	—	—[a]
1	MgO–SiO_2	gel	22·4	—
1	Al_2O_3–MgO–SiO_2	gel	21·9	0·2
2	Al_2O_3–SiO_2	sol	—	0·2
2	MgO–SiO_2	sol	5·4	—
2	Al_2O_3–MgO–SiO_2	sol	—[a]	—[a]
3	Al_2O_3–MgO–SiO_2	sol	4·9	0·2
4	Al_2O_3–MgO–SiO_2	gel	—[a]	—[a]

contain centers with $H_0 \leqq -3\cdot0$. At the same time, the number of weakly and medium acidic centers, and thus also the total surface concentration of centers, remains essentially unaffected. The acid strength distribution of these catalysts has thus additive properties of the distributions of the two-component catalysts Al_2O_3–SiO_2 and MgO–SiO_2. At the ratio of components employed, the three-component catalysts prepared had a continuous distribution of centers in the whole H_0 region mentioned above, the most acidic centers $\left(H_0 \leqq -3\cdot0\right)$ being less frequent than medium acidic ones $\left(1\cdot5 \geqq H_0 \geqq -3\cdot0\right)$. This was desirable with regard to the kinetic study of dehydration of tert-butanol[7,14] for which these catalysts were being developed. It seems likely that by proper variation of the ratio of components one could model the distribution of surface acidity of oxide catalysts in a broad acid strength region and prepare thus the optimum catalysts also for other purposes.

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Tᴀʙʟᴇ III

(continued)

Surface acidity, mequiv./g			
$5.0 \geqq H_0 \geqq 3.3$	$3.3 \geqq H_0 \geqq 1.5$	$1.5 \geqq H_0 \geqq -3.0$	$H_0 \leqq -3.0$
0·39	0·01	0·01	0·00
0·18	0·00	0·02	0·03
0·17	0·05	0·55	0·00
0·13	0·09	0·34	0·15
0·11	0·02	0·11	0·06
0·20	0·05	0·16	0·00
0·15	0·07	0·24	0·03
0·10	0·00	0·23	0·10
0·02	0·10	0·30	0·01

[a] Not determined.

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