

EFFECT OF ACTIVATION TEMPERATURE ON ACIDITY OF ALUMINA, SILICA-ALUMINA AND COBALT-MOLYBDENUM-ALUMINA CATALYSTS

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The effect of surface dehydration on the acidity of silica-alumina and cobalt-molybdenum-alumina catalysts has been studied and compared with alumina. The catalysts were characterized by surface hydroxyl groups concentrations, acid sites concentrations and by catalytic activities in paraldehyde depolymerisation and cumene cracking. It was found that the acidity of alumina and cobalt-molybdenum-alumina catalysts increases significantly with surface dehydration and attains maximum after activation at 500–550°C. Silica-alumina is strongly acidic even in the hydrated state, the acidity being formed already at relatively low temperature around 100°C.

Mixed metal oxide catalysts with acidic properties such as silica-alumina or aluminas promoted by admixtures of other oxides are often used in industry. These catalysts exhibit the higher acidity than their single components^{1,2}. In addition to their composition, the acidity of the catalysts is also affected by the amount of the sorbed water that depends on the conditions of thermal treatment. As to alumina itself, it was observed that on increasing activation temperature to 500–600°C, the surface acidity always markedly increases^{3–5}. From the results of IR studies of the adsorbed pyridine it was concluded that the acidity of alumina is due to the presence of Lewis acid sites^{6,7} formed by surface dehydration. On the other hand, the surfaces of silica-alumina and promoted aluminas contain both the Lewis and Brønsted sites, the mutual proportion of which depends on activation temperature^{8,9}. The determination of the acidity of these catalysts meets with some difficulties, since the often used sorption techniques without IR specification yield only the total number of sites. The choice of the sorbate and the technique to be applied determine also the detected H_0 region of the acid strength of sites. This makes the comparison of the results of different authors difficult. Thus, for example, Hirschler and Schneider⁵ found that the rehydrated and dried (120°C) silica-alumina catalyst (11% Al_2O_3) has the higher total concentration of acid sites ($H_0 \leq 3.3$) than the one activated at 500°C. In another study¹⁰ it was reported that the dehydration of silica-alumina (25% Al_2O_3), induced by the change of the activation temperature in the range 100–600°C, does not affect the concentration of acid sites of the strength $H_0 \leq -3$. The gas-phase sorption of 1-butylamine¹¹ on silica-alumina (13% Al_2O_3) activated from 100 to 500°C indicates, however, the increase in the total acidity. While the increased acidity of alumina resulting from surface dehydration was proved unambiguously, the effect of dehydration on the acidity of silica-aluminas or other mixed oxide catalysts has so far been little studied.

The aim of this work was to compare the effect of surface dehydration on the acidity of mixed metal oxide commercial catalysts and alumina. Besides the concentration

of acid sites determined by the pyridine adsorption, the acidity of the catalysts was characterized by their catalytic activity in two reactions having different demands on the strength of acid sites. This made it possible to get further information about individual regions of the acid strength of sites.

EXPERIMENTAL

Catalysts and Chemicals

Commercial catalysts studied were alumina Cherox 3300, cobalt-molybdenum-alumina catalyst Cherox 3601 containing 3.55% CoO and 14.1% MoO₃ (both catalysts produced by CHZ ČSSP Litvínov, Czechoslovakia) and a silica-alumina cracking catalyst containing 11% Al₂O₃ and 0.1% Cr₂O₃ (Petrochemical Works, Grozny, USSR). The sample of Cherox 3300 alumina was rehydrated by water during treatment¹². The other catalysts were used as received after storage in air. Prior to measurements, the catalysts (particle size 0.04–0.125 mm) were activated by drying in a stream of dry nitrogen for 1 h at a given temperature (90–550°C). The specific surface areas were determined by nitrogen adsorption, using Nelsen-Eggertsen method¹³. Surface hydroxyl groups concentration, c_{OH} , were determined by pulse method^{14,15} based on the reaction of gaseous dimethylzinc-tetrahydrofuranate with active hydrogen. Only the concentration of hydroxyl groups of the silica-alumina activated at 90°C was calculated from the c_{OH} value corresponding to the activation temperature 130°C and the amount of water released during activation between 90–130°C.

Cumene (Fluka AG, *purum*) was distilled before using. The other chemicals were reported elsewhere¹².

Determination of Acid Sites Concentrations of Catalysts

Surface concentrations of acid sites were determined by the sorption method reported earlier^{12,16}. The catalyst (approx. 0.4 g) was activated in a stainless steel column and *in situ* cooled to room temperature. Then, 0.0025M solution of pyridine in cyclohexane was passed through the catalyst until surface saturation was achieved. Weakly sorbed pyridine was eluted by 200 ml of cyclohexane and the fraction of strongly bonded pyridine was displaced by 0.05M solution of 1-butylamine in cyclohexane. During measurements, the concentration of pyridine on the column effluent was measured by UV detector (254 nm) connected to a linear recorder. It was assumed that the amount of pyridine displaced from the catalyst surface by 1-butylamine corresponds to the acid sites concentration c_A .

Testing of Catalytic Activity

For testing the acidity of the catalysts, two reactions with different requirements on the strength of acid sites were chosen; the depolymerisation of paraldehyde¹⁷ proceeding on the sites of the strength $H_0 \leq -3$ and the cracking of cumene, for which the greater acid strength of sites ($H_R \leq -13.3$) is needed¹⁸.

Depolymerisation of paraldehyde was carried out in a batch reactor in liquid phase¹². The activity of the silica-alumina catalyst was measured at 70°C, while for the less active alumina and cobalt-molybdenum-alumina catalyst, the temperature needed was 105°C. Initial reaction rates r_{PA}^0 were determined from the decrease in the concentration of paraldehyde with respect to the internal standard.

Cumene cracking was carried out in a differential-flow reactor in the gas phase at 330°C. The space velocity of cumene was $0.185 \text{ mol g}^{-1} \text{ h}^{-1}$ and the partial pressure of cumene in hydrogen was 0.03 MPa. The reaction mixtures were analysed by gas chromatography at 140°C, using the column packed with 4% PEGA on Rysorb. Initial reaction rates r_C^0 were determined from the concentration of benzene in the product.

RESULTS AND DISCUSSION

Surface hydroxyl groups concentrations c_{OH} are affected to a great extent by activation temperatures of the catalysts (Fig. 1). The concentration of hydroxyl groups of alumina at 140°C corresponds roughly to the monolayer and by increasing the activation temperature to 550°C the concentration decreases to about 25 per cent of the initial value¹². The cobalt-molybdenum-alumina catalyst has somewhat lower hydroxyl groups concentration at temperatures above 140°C, likely due to the partial coverage of alumina surface by molybdate species⁹. By contrast to the above two catalysts, the surface of silica-alumina is considerably dehydrated at 130°C. The low hydroxyl groups concentration above this temperature is characteristic for amorphous silica-alumina catalysts¹⁵.

In the case of alumina and cobalt-molybdenum-alumina catalysts, the increase in activation temperature leads to the formation of acid sites. The most marked is the increase in the c_A concentration for alumina (Fig. 2). On the other hand, after activa-

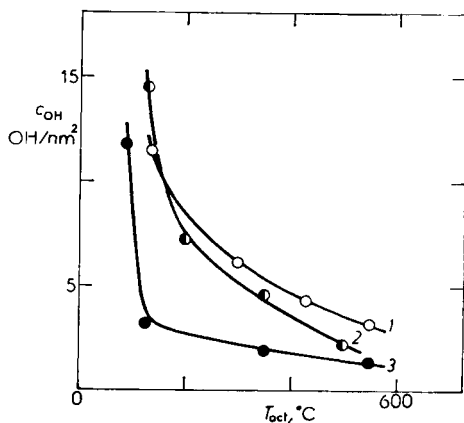


FIG. 1

The effect of activation temperature on the surface concentrations of hydroxyl groups of the catalysts. ○ Alumina, ◐ cobalt-molybdenum-alumina, ● silica-alumina

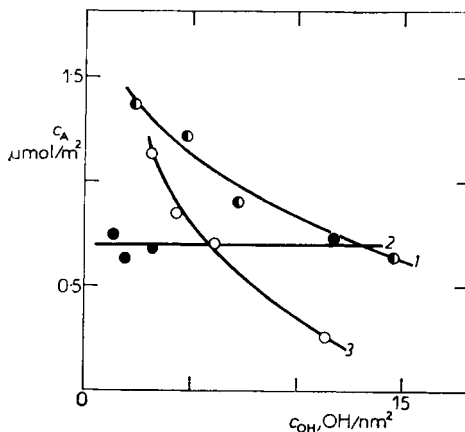


FIG. 2

The effect of surface dehydration on the concentration of acid sites of the catalysts. ○ Alumina, ◐ cobalt-molybdenum-alumina, ● silica-alumina

tion at 90–550°C, the concentration of acid sites of the silica-alumina remains constant within experimental errors, in accordance with the study by Furuyama and coworkers¹⁰. These differences can be closely related to the different acidity of hydroxyl groups of individual catalysts. With regard to the negligible acidity of the hydroxyl groups of alumina^{2,6}, one can assume that the strong adsorption of pyridine takes place only on Lewis acid sites formed by surface dehydration. This assumption is supported also by the good agreement between the c_A values for alumina activated at 500°C and the concentration of Lewis acid sites found by IR spectroscopy⁷ which equals to $0.95 \mu\text{mol m}^{-2}$. The cobalt-molybdenum-alumina catalyst shows the higher c_A value than does alumina at the same degree of dehydration, since a certain portion of pyridine can be held by more acidic OH groups¹⁹. The greater amount of chemisorbed pyridine on cobalt-molybdenum-alumina catalyst as compared to alumina was observed also earlier²⁰. Finally, the strong interaction of pyridine with both Lewis and Brönsted sites can explain the exceptional behaviour of the silica-alumina catalyst. The loss of Brönsted acidity caused by dehydration is compensated by the increase in Lewis acidity and, therefore, the total number of sites remains constant^{7,8}. Information about the acidity of catalysts in the region of the acid strength $H_0 \leq -3$ was obtained by means of the paraldehyde depolymerisation as a test reaction. The effect of surface hydroxyl groups concentrations on the activity of the catalysts is shown in Fig. 3. While the activities of alumina and cobalt-molybdenum-alumina catalysts increase significantly with increasing surface dehydration, the silica-alumina shows relatively high activity even in the fully hydrated state (after activation at 90°C) and this activity increases only slightly on further treatment. It becomes evident that in paraldehyde depolymerisation, the catalyst activity changes parallel to the acid sites concentration. Hence,

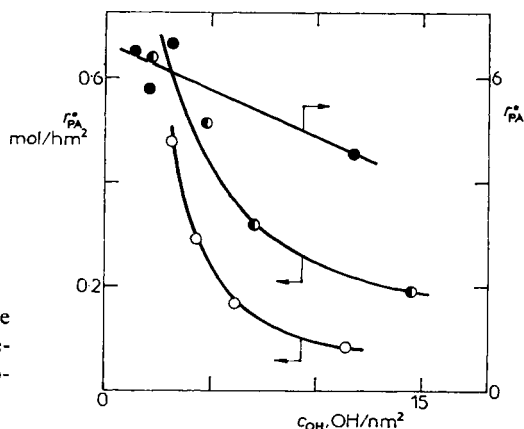


FIG. 3

The effect of surface dehydration on the activity of the catalysts in paraldehyde depolymerization. ○ Alumina, ◐ cobalt-molybdenum-alumina, ● silica-alumina

good correlations between both quantities were obtained for alumina and the cobalt–molybdenum–alumina catalyst (Fig. 4).

From the above results it can be concluded that the sorbed water on the surface of the catalysts affects their acidity to a different extent. The relatively most sensitive is alumina alone, the acid sites of which are firmly occupied by water. The high sensitivity to the amount of sorbed water shows also the cobalt–molybdenum–alumina catalyst, where the alumina support plays probably a significant role. Both catalysts exhibit the highest acidity after activation at 500–550°C when water desorption leads to the release of the largest portions of acid sites. Compared to these catalysts, the silica–alumina is much less sensitive to the presence of water, as already observed⁵. As a result of the strong acidity of present OH groups, the considerable surface acidity is developed at the low activation temperature around 100°C.

Further information concerning only the region of the most acidic sites ($H_R \leq -13.3$) was obtained by means of cumene cracking. Under the experimental conditions used, only the silica–alumina catalyst was active. This confirms the presence of very strong sites on its surface, in contrast to alumina and the cobalt–molybdenum–alumina catalyst. The cracking activity of the silica–alumina activated at 500°C was, however, only one fifth of that obtained after activation at 330°C. This activity decrease indicates the elimination of a part of the most acidic sites that are most likely of Brönsted type. The results obtained by both test reactions speak for the more complicated change in the acid sites distribution of the silica–alumina during thermal treatment. While the region of the acid strength $H_0 \leq -3$ remains essentially unaffected by surface dehydration above 130°C, the fraction of the most acidic sites diminishes markedly at higher temperatures.

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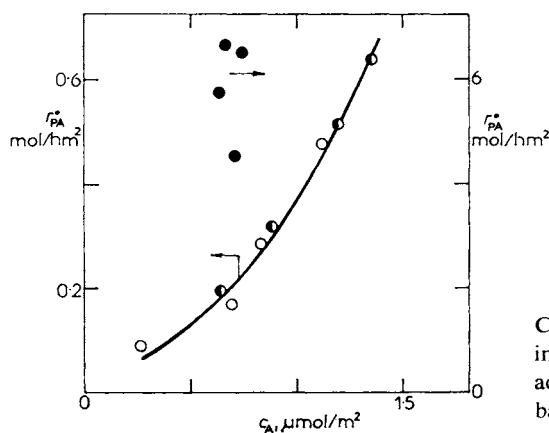


FIG. 4
Correlation of the activity of the catalysts in paraldehyde depolymerisation with their acid sites concentrations. ○ Alumina, ◐ cobalt–molybdenum–alumina, ● silica–alumina

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