HOKKAIDO UNIVERSITY

Title	TEXTURAL AND CATALYTIC PROPERTIES OF CHROMIA-ALUMINA CATALYSTS
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 28(2), 89-96
Issue Date	1981-02
Doc URL	https://hdl.handle.net/2115/25077
Type	departmental bulletin paper
File Information	28(2)_P89-96.pdf

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J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 28, No. 2, pp. 89 to 96 (1980)

TEXTURAL AND CATALYTIC PROPERTIES OF CHROMIA-ALUMINA CATALYSTS

By

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(Received January 14, 1980; in revised form March 7, 1980)

Abstract

Pure alumina, pure chromia and different chromia/alumina catalysts were prepared and their catalytic activities towards isopropanol were determined at 240°C. The textural properties of all the samples were also determined by nitrogen adsorption at −196°C.

The catalytic activity and the textural characteristics depend on the method of preparation, the chemical composition, the calcination temperature and the acidity of the catalyst. The % dehydration is related to the number of acid sites per unit area indicating that dehydration of isopropanol may take place via carbonium ion mechanism. On the other hand, the dehydrogenation of this alcohol is not related to the surface acidity and may occur without intervention of the acid sites.

1. Introduction

Chromia/alumina catalysts are important both in laboratory and industrial applications. They are particularly active in dehydration[1,8] petroleum cracking[2] reforming[3,4], isomerization[5~7], halogenation, catalytic decomposition[9] and reduction.[10]

In general, these catalysts are prepared by three techniques, mechanical mixing of chromia and alumina gels before drying, grinding and calcination, impregnation procedure in which a chromium salt is deposited on an alumina support from a suitable solvent and then decomposed to chromium oxide, and coprecipitation process in which the chromium and aluminium species are more or less simultaneously precipitated, dried and calcined to yield an intimate mixture of chromia and alumina.

The sorption and catalytic activity of mixed oxide catalysts are affected by some factors, namely, the chemical composition, the method of preparation, the calcination temperature and the chemistry of their surfaces which involves the number of acid sites on the surface. Although these factors have received separate attention, a study of their mutual effects received less attention.

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In the present investigation, various chromia/alumina samples were prepared by mechanical mixing, coprecipitation and by precipitating chromia on alumina surface. The last method is not a conventional method for the preparation of mixed oxide catalysts. Thermal products were obtained by the calcination of these samples at 400, 600, and 800°C. The obtained thermal products were characterized in terms of their surface area and porosity and in terms of their acidic characters. The textural properties were determined by the nitrogen adsorption technique and the catalytic activities towards isopropanol conversion were measured by the microcatalytic technique. This study will hopefully reveal the effect of some factors on the catalytic activity of the prepared samples. Conversion of isopropanol which involves dehydration and dehydrogenation reactions was selected for this purpose.

2. Experimental

2. 1. *Preparation of the mixed oxides*

Pure alumina gel was prepared by precipitation at pH 7.5 and 70°C, using 1 M ammomium hydroxide and 1 M hydrated aluminium nitrate. The dropwise addition of ammonium hydroxide was completed with continuous stirring. The precipitated gel was washed thoroughly, centrifuged and then dried at 110°C till constant weight. The same procedure was followed for the preparation of pure chromia from chromium nitrate. Mixed oxides containing 25, 50 and 75 mole% chromia were obtained by mechanical mixing. Coprecipitated gels containing 25 and 50 mole% chromia were prepared from the mixed nitrated solutions under the same conditions followed for pure oxide preparation. Precipitation of 25 and 50 mole% chromia on alumina was affected by shaking the alumina sample into bidistilled water and chromia is precipitated from chromium nitrate solution by slow addition of ammonium hydroxide, while the temperature is kept constant at 70°C and the pH at 7.5. The precipitation of chromia on alumina surface was followed by electrical conductivity techniques. Virtually complete precipitation of chromia was effected.

Pure chromia, pure alumina and the mixed oxide preparations received the same thermal treatment, namely calcination at 400, 600, and 800°C for 5 hr in a muffle furnace. In designating the samples here investigated, the letter A stands for pure alumina and the letter C for pure chromia. AC indicates mixed chromia/alumina samples. The Roman numbers I, II, and III beside "AC" indicate mechanical mixing, coprecipitation and coating, respectively. The numbers 25, 50 and 75 refer to mole % chromia in the

samples. The last number in each designation indicates the calcination temperature. Thus, *e.g.*, ACI-25-600 would indicate mechanically mixed chromia/alumina containing 25 mole % chromia and calcined at 600°C, while ACIII-50-800 would indicate chromia-coated alumina (50 mole % chromia), and calcined at 800°C.

2.2. *Techniques*

The adsorption isotherms of nitrogen were determined at −196°C using conventional volumetric apparatus.

Surface acidity was determined by the chemisorption of pyridine. Adsorption-desorption of pyridine was determined using quartz spring balances (sensitivity 75 mm/100 mg), and the system was fitted with greaseless stopcocks. Pyridine was admitted to the sample after being outgassed for 48 hr at 200°C, and the physically adsorbed pyridine was removed by heating the sample at 150°C under a reduced pressure of 10^{-5} mm Hg.

The catalytic measurements were carried out using the microcatalytic technique.[11,12] 2×10^{-3} mℓ of isopropanol was injected into the microreactor which contains 0.15 g catalyst, then the reaction products were directly transferred by an inert gas carrier (nitrogen 30 mℓ/min) to a gas liquid chromatograph (Pye Unicam model 104). A column of D. C. Silicon oil 550 over a chromasorb W, 25 feet length and 3.5 mm diameter was used. Good separation for all products at 130°C was detected by a flame ionization detector.

3. Results and Discussion

3.1. *Nitrogen adsorption (Surface area and pore structure)*

Low temperature nitrogen adsorption-desorption isotherms were measured for all samples at −196°C. The adsorption isotherms are Type II of Brunauer's classification,[13] and pronounced hysteresis loops closing at some intermediate relative pressure were exhibited by all samples.

Specific surface areas ($S_{BET}^{N_2}$, m^2/g) were estimated through the application of the BET equation (14) adopting a value of 16.2 Å^2 for the cross sectional area per nitrogen molecule. The values are shown in column 2 of Table 1. These values indicate that the surface areas of pure aluminas calcined at 400, 600, and 800°C are higher than those of pure chromias calcined at the same temperatures. Chromia/alumina catalysts measure intermediate surface areas. The only exceptional case was found with coprecipitated chromia/alumina samples where higher surface areas were measured for those containing 25 mole % chromia. It is also seen from column 22 of Table 1

TABLE 1. Textural properties, acidities and catalytic activities of the investigated samples

Sample	Surface area m^2/g	Most Probable pore radii Å	Total pore Vol. $m\ell/g$	$N_{acid}/cm^2 \times 10^{-13}$	% Dehydr-ation	% Dehydro-genation
A-400	147	21.5	0.1740	7.9	14.5	0
A-600	260	24.5	0.3562	15.0	34.0	0
A-800	170	34.6	0.3230	9.8	18.5	0
ACI-25-400	127	24.0	0.1750	7.4	12.2	10.5
ACI-25-600	227	26.0	0.3030	14.1	27.8	9.8
ACI-25-800	166	36.0	0.3250	9.6	16.9	8.7
ACII-25-400	185	16.8	0.1710	6.8	12.0	15.7
ACII-25-600	320	20.0	0.3600	13.1	25.0	14.5
ACII-25-800	209	25.8	0.3240	8.7	16.0	13.5
ACIII-25-400	110	27.6	0.1750	4.0	2.8	37.0
ACIII-25-600	217	30.8	0.3900	5.8	6.0	36.5
ACIII-25-800	161	41.0	0.3750	4.4	4.8	35.0
ACI-50-400	116	28.0	0.1920	6.3	9.5	20.5
ACI-50-600	210	30.8	0.3800	12.9	24.5	18.8
ACI-50-800	153	36.0	0.3250	8.8	15.7	17.0
ACII-50-400	125	20.0	0.1500	5.4	7.2	30.0
ACII-50-600	258	22.5	0.3605	6.8	15.5	29.0
ACII-50-800	158	27.9	0.2805	4.9	8.9	28.2
ACIII-50-400	93	30.0	0.1752	3.7	2.6	37.0
ACIII-50-600	181	33.8	0.3805	4.6	5.5	36.0
ACIII-50-800	133	39.0	0.3382	4.4	4.8	35.0
ACI-75-400	111	30.0	0.2172	5.4	6.8	28.8
ACI-75-600	170	34.5	0.3505	10.2	18.2	27.8
ACI-75-800	129	42.0	0.3452	6.8	10.3	26.0
C-400	90	29.8	0.1782	3.4	0	38.5
C-600	172	35.0	0.3752	3.0	0	36.5
C-800	125	43.8	0.3654	2.7	0	35.8

that the surface areas of pure alumina, pure chromia and chromia/alumina samples increase with the rise of the calcination temperature from 400° to 600°C indicating an activation process. Further rise of the calcination temperature to 800°C was found to cause a significant decrease in surface areas indicating sintering of these solids at this relatively high temperature. The activation and sintering processes are expected to be accompanied by variations in the pore structure.

Pore size analysis was made by using the "corrected modelless" method developed for the analysis of mesopores[15] and by using the microporous "MP" method for the analysis of micropores.[16] The corrected modelless method was programmed and the computations were run on IBM 1130 computer.[17] The main conclusions drawn from pore volume distribution curves (not presented here), are summarized as follows: (i) Calcination products obtained at 400°C exhibit their most probable radii at relatively small r values (*cf.* column 3 of Table 1). The rise of the calcination temperature to 600°C is accompanied in all cases by an increase in the number of pores as well as in their size. Further rise of the calcination temperature to 800°C leads in all cases to a decrease in the number of pores but an increase in their size. (ii) At any calcination temperature, the most probable hydraulic radii are located at r values according to the order: coprecipitated chromia/alumina < pure alumina < mechanically mixed chromia/alumina < chromia-coated alumina < pure chromia. The total pore volumes of all the investigated samples (V_1, mℓ/g) are listed in column 4 of Table 1.

3. 2. *Factors affecting the catalytic dehydration*

The results presented so far show that the textural properties (surface area and porosity) change with both the calcination temperature and the method of preparation. Undoubtedly, these factors, among other factors, affect also the catalytic activity. The catalytic activity was tested through the conversion of isopropanol, which is considered as a simple reaction yielding mostly propylene as a dehydration product and acetone as a dehydrogenation product. Preliminary studies have shown that the optimum pretreatment temperature for the conversion of isopropanol is 400°C. Accordingly, the catalyst samples were heated in air at 400°C for 4 hr followed by nitrogen streaming. Also it was indicated from the preliminary experiments that highest conversion activities are obtained at 240°C. The % dehydration of isopropanol at 240°C for all the samples is listed in column 6 of Table 1, while the % dehydrogenation is listed in column 7.

It is seen from column 6 that the dehydration activities of the investigated catalysts calcined at a certain temperature follow the order: pure alumina > mechanically mixed chromia/alumina > coprecipitated chromia/alumina > chromia-coated alumina. The pure chromia catalysts calcined in the temperature range 400–800°C do not measure any dehydration activity. Also as a general trend the % dehydration decreases with the increase in chromia content. With regard to the effect of calcination temperature it is evident from Table 1 that the % dehydration increases with the rise of the calcination temperature from 400° to 600°C and then decreases with the further rise

of the calcination temperature to 800°C. This trend goes parallel with the effect of calcination temperature on the surface area indicating thus the importance of the extent of the surface in determining the dehydration activity.

It remains now to relate the % dehydration to the acidity of the surface. A trial was made to relate the number of acid sites per unit area (column 5 of Table 1), to the % dehydration. A straight line is obtained (Fig. 1), indicating that the number of acid sites on the surface of the catalyst is actually a predominant factor in determining the catalytic dehydration of isopropanol or possibly other alcohols as well. Apparently it seems that

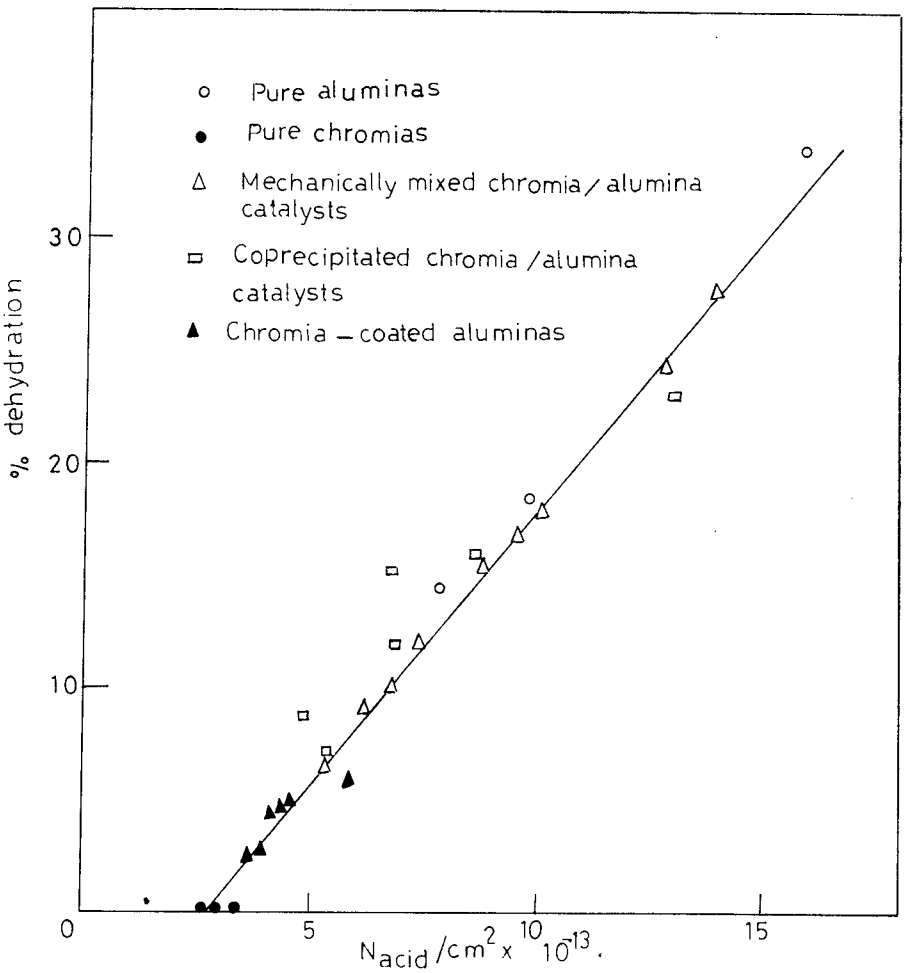

Fig. 1. Variation of % dehydration with N_{acid}/cm^2.

dehydration occurs via carbonium ion mechanism[18] in which the acid sites are involved. However the great deal of scatter shown in Fig. 1 indicates that the number of acid sites is not the only factor determining the catalytic dehydration of alcohols. Moreover, the straight line in Fig. 1 intersects the ordinate at some small number of acid sites per unit area, indicating that not all the acid sites are involved in the dehydration of isopropanol, or a critical number of acid sites should be present in order to exhibit a measurable dehydration activity.

3.3. *Factors affecting the catalytic dehydrogenation*

The results shown in Table 1 indicate that pure chromia catalysts measure the highest dehydrogenation activities while pure alumina samples are totally inactive for dehydrogenation. Chromia/alumina samples exhibit dehydrogenation activities depending on the chromia content. However, in the case of chromia-coated aluminas high dehydrogenation activities comparable to the activities of pure chromia catalysts are measured. This may indicate that in these particular mixed oxides alumina acts as a support for the chromia. The dehydrogenation of isopropanol depends also on the method of the preparation of the chromia/alumina catalyst. Thus for the same chromia content the catalyst prepared by precipitating chromia on alumina measures higher dehydrogenation activity as compared with the catalyst prepared by the mechanical mixing technique. The catalysts prepared by coprecipitation measure intermediate dehydrogenation activities compared to those containing the same percent of chromia and prepared by different techniques. It is also evident from Table 1 that regardless the method of preparation the catalysts calcined at 400°C are more active for dehydrogenation of isopropanol than those calcined either at 600° or 800°C. This may be attributed to the partial formation at relatively high calcination temperatures of the less active stoichiometric Cr_2O_3.[19] Table 1 indicates also that the number of acid sites per unit area of the catalyst bears no relation to the catalytic dehydrogenation of isopropanol. The dehydrogenation reaction may occur without the intervention of acidic sites. It has been reported in a previous investigation[20] in which nickel (II) oxide-titanium oxide catalysts were used that dehydrogenation of isopropanol occurs through a complex with coordinate bonding at Ni atoms of the phase of free NiO. The mutual effects of more than one factor on the textural and catalytic properties of mixed oxides necessiate more extensive studies. Hopefully, this will be achieved in this laboratory and/or other laboratories.

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