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# Basic Behavior of Alumina in the Presence of Strong Acids

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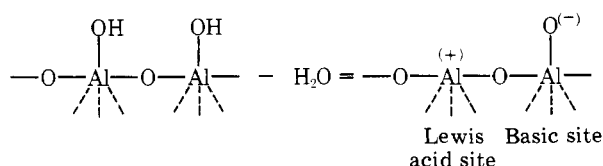
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The basic property of alumina surface, when treated with strong acids, such as hydrochloric and hexachloroplatinic, has been studied. Hydrochloric acid in the gaseous phase reacts with hydroxyls by forming water. Hexachloroplatinic acid is adsorbed from the aqueous solution on the alumina and the amounts of adsorbed platinum vary for several calcination temperatures of the alumina. There is a similar trend in the amounts of adsorbed platinum and the acidity of the alumina surface as functions of the calcination temperature. This fact suggests a correlation between the number of Lewis sites before water treatment and the number of basic ones after impregnation. Therefore an acid-base couple would be responsible for the adsorption of strong acids.

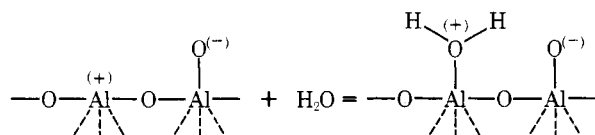
The choice of the support in the preparation and use of supported metallic catalysts, is important. The surface of the support is important both during the preparation of catalysts, because it can affect the impregnation process and during its use it can reveal a synergistic effect on the catalysis.

Many papers deal with the acid-base properties of alumina surfaces. The acidic properties of alumina surfaces have been extensively examined. This subject has been recently reviewed by Tanabe (1970). The influence of the calcination temperature of alumina on the acid character of its surface has been reported by Tanabe (1970) and Cornelius (1955).

Despite this wide treatment in the literature of the acidity of alumina, very few papers have considered the presence of basic sites on alumina. In this regard, Schwab (1964) has shown the existence of basic sites on alumina surface and Yamadaya (1965) has pointed out that the basic properties of alumina arise when alumina surface comes into contact with a sufficient quantity of water. In this case Lewis acid sites are transformed into Brönsted acid sites, which are very weak. According to Pines (1966), there must be either acid or basic sites formed on alumina as in the scheme:



The water treatment of calcinated alumina gives place to Brönsted acid sites:



The basic sites are located on a negatively charged oxygen atom. According to Peri (1965), there must be basic sites of different strength according to the chemical surrounding of the negatively charged oxygen atoms.

The Pines scheme suggests the existence of a basic site for each acid site. Therefore any acid characteristic of alumina must be related to its basic one. This observation is one of the subjects of this paper, in which the behavior of an alumina surface treated with strong acids (as HCl and H<sub>2</sub>PtCl<sub>6</sub>) is examined.

## Experimental Section and Discussion

The alumina employed in the experimental runs is  $\gamma$ -alumina prepared, according to Pines (1960), through the precipitation of aluminium isopropoxide and its calcination at 600 °C, for 6 h. This alumina is practically free from potassium and sodium. The surface area, measured with the classical BET method, was 177 m<sup>2</sup>/g.

The alumina was first thermogravimetrically examined by thermobalance (Figure 1). The diagram shown in Figure 1 allows the determination of the number of hydroxyls present on the surface.

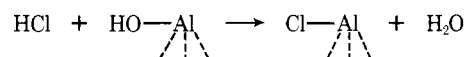
As we can observe from the figure, the alumina easily recovers the moisture lost during the calcination; the water lost between 230 and 600 °C, can be attributed mainly to the moisture adsorbed in the alumina manipulation and storage. This adsorbed water can eliminate or reduce Lewis acid sites, transforming them into Brönsted sites, but it cannot affect the number of acid and basic sites.

In Table I the number of the presumed or actual hydroxyls lost during the heating from 230 to 600 °C and the ones lost from 600 to 1025 °C is given. In the same table the covered surface area from each hydroxyl group is also reported.

Another alumina sample has been subjected, after the calcination at 600 °C, to a stream of gaseous HCl at 230 °C, in the thermobalance. The HCl used was produced by the SIAD Co. (title 99.995%).

An increase of 2.2% in its weight has been observed. Subsequently, the sample has been washed with a stream of helium and a decrease in the weight of 0.7% has been observed. This means that hydrochloric acid has been partially adsorbed in reversible form and partially in irreversible form.

The analysis of chlorine made on the alumina sample, treated as previously described, revealed the presence of 2.8% in weight of hydrochloric acid. This apparent discrepancy in the results can be explained if we accept that hydrochloric acid reacts with the hydroxyls of alumina in order to form water, which is removed from the system during the HCl washing, according the reaction:



During the helium treatment, on the contrary, the hydrochloric acid reversibly adsorbed (0.7%) has been removed, so the hydrochloric acid adsorbed in irreversible form (2.8%) is about twofold the increase in alumina weight, registered at

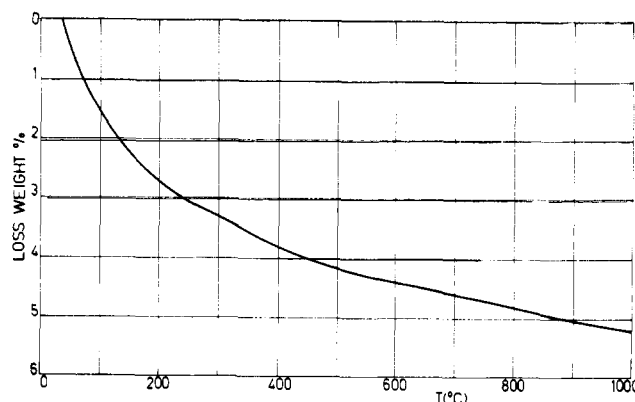


Figure 1. Thermogravimetric analysis of alumina.

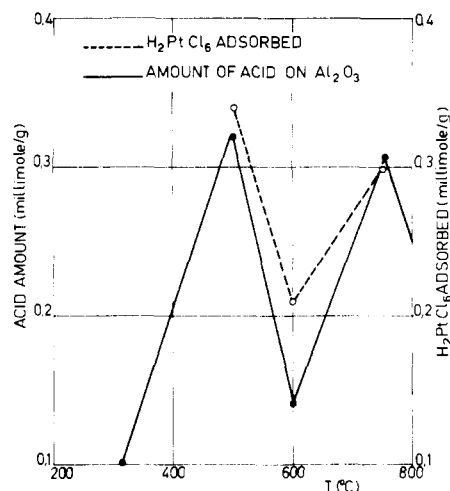
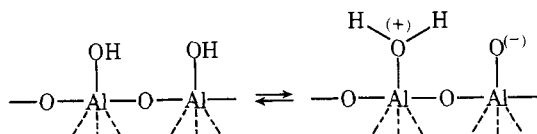


Figure 2. Comparison between the acid behavior of alumina (see Tanabe (1970)) calcinated at various temperatures and the amounts of the adsorbed chloroplatinic acid for the same types of alumina.

the thermobalance, minus the amount of hydrochloric acid reversibly adsorbed (2.2 - 0.7).

If we consider the difference in the atomic weight of the adsorbed chlorine and the molecular weight of the water removed, the discrepancy mentioned becomes very small. In Table I the number of HCl molecules that irreversibly react with the support is also reported. As we can observe, only a limited number of hydroxyls react with HCl and, if we consider exclusively the hydroxyls present on the surface, at 600 °C (the temperature of calcination), the number of reacting hydroxyls is half of the total. This fact suggests that HCl reacts with a couple of hydroxyls, which behaves as an acid-base couple, according to the scheme:



Let us now consider another aspect of the basic behavior of the alumina. As we have briefly mentioned, the direct contact of alumina with water produces the transformation of Lewis acid sites into Brönsted sites. On the other hand, if alumina is directly put in contact with a solution of a strong acid, for example, hexachloroplatinic acid, a simultaneous chemical attack with dissolution of alumina and adsorption of the hexachloroplatinic acid will occur. Aluminum in solution can be easily hydrolyzed and the hydroxyl group of the hydrolyzed aluminum salt can give place to an exchange with the support which is responsible for the adsorption.

Table I. Hydroxyls Lost by Heating  $\gamma$ -Alumina. Hydrochloric Acid Adsorbed in Gas-Solid Phase

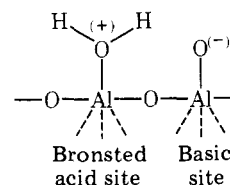
Temp, °C	Temp range, °C	OH molecules lost/g of support	HCl molecules adsorbed/g of support	Covered surface	
				by HCl in Å <sup>2</sup>	by OH in Å <sup>2</sup>
	230-600	$14.38 \times 10^{20}$	—	—	—
	600-1025	$10.35 \times 10^{20}$	—	—	—
230	—	—	$4.62 \times 10^{20}$	38	12
600	—	—	—	—	17

Table II. Comparison between the Acidity (see Tanabe (1970)) and Basicity of  $\gamma$ -Alumina Calcinated at Several Temperatures. The Basicity Is Expressed as a Function of the Amount of Chloroplatinic Acid Adsorbed

T, °C	Acidity of the surface, mol $\times 10^{-6}$ /g at $H_0 \leq 3.3$	Pt adsorbed, mol $\times 10^{-6}$ /g of support	Surface area of alumina, m <sup>2</sup> /g	Covered surface by H <sub>2</sub> PtCl <sub>6</sub> , Å <sup>2</sup>
500	470	344	220	106
600	210	216	205	157
750	490	304	165	90

Moreover, in the present paper we have observed that the temperature of alumina calcination strongly affects the amount of the adsorbed hexachloroplatinic acid. In fact if we place, for 3 h, three samples of 0.5 g of  $\gamma$ -alumina, calcinated at 500, 600, and 750 °C, respectively, in contact with 40 cm<sup>3</sup> of hexachloroplatinic acid solution ( $4 \times 10^{-2}$  M) at room temperature, the amounts of platinum adsorbed on the samples are quite different, as can be verified from the data reported in Table II. The platinum adsorbed on alumina has been evaluated by analyzing the solutions, after the adsorption, by the method suggested by Sandell (1959). More details of H<sub>2</sub>PtCl<sub>6</sub> adsorption are given in the preceding paper in this issue. It is useful to compare, in Table II and Figure 2, the data concerning the amount of platinum adsorbed on alumina, calcinated at various temperatures and the data reported by Tanabe (1970) for the acidity amounts of alumina in the same conditions.

It is possible to observe from Figure 2 that the trend is the same in both cases. This means that the basic sites are surely related with the acid ones and that the acid-base couple of the type:



is always responsible for the adsorption of strong acids. The conclusion, according to the Pines scheme, is that the basicity shown by alumina surface in the presence of strong acids is related to its Lewis acidity.

#### Acknowledgments

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# Kinetics of Ternary Nitric Oxide Reduction on Ruthenium

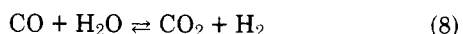
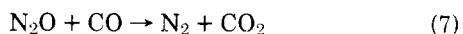
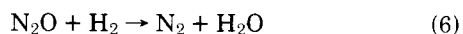
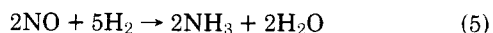
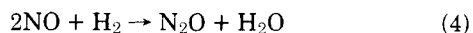
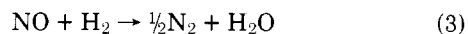
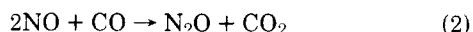
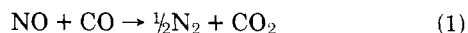
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The reduction of nitric and nitrous oxide by mixtures of carbon monoxide and hydrogen in helium over a fiber glass supported Ruthenium catalyst has been studied. The rate data from a differential tubular reactor, operating at atmospheric pressure and at temperatures ranging from 210 to 360 °C, were correlated with power law models. Feed concentrations of the NO and N<sub>2</sub>O were varied from 0.2 to 1.7 mol %, while those of the CO and H<sub>2</sub> were varied from 1.0 to 5.0 mol %. N<sub>2</sub>O was found to be a significant intermediate product of NO reduction at low conversions. The relative rates of reaction and the dependence of reaction rate upon feed concentration were in general agreement with previous studies of the same reaction systems using different supports.

## Introduction

Recently Schleppy and Shah (1976a) presented a kinetic study of nitric oxide reduction by carbon monoxide and hydrogen in binary mixtures over fiber glass supported ruthenium and platinum catalysts. At low conversions it was found that the NO was reduced primarily to both N<sub>2</sub> and N<sub>2</sub>O. NH<sub>3</sub> formation was generally less than 10% except for NO-H<sub>2</sub>/Pt which was not investigated. The low conversion data were correlated into power law rate expressions. Attempts to find a Langmuir-Hinshelwood type expression which would successfully correlate the data were unsuccessful. The present paper will extend that study to include the kinetics of NO reduction over a fiber glass supported Ru catalyst in a ternary mixture (NO-CO-H<sub>2</sub>). Also considered are the kinetics of N<sub>2</sub>O reduction, the inclusion of which will provide some explanation for the N<sub>2</sub>O intermediacy phenomena. The principal reactions occurring in a catalytic converter between NO, CO, H<sub>2</sub>, and N<sub>2</sub>O are



Literature not cited in the previous work includes a study of the dual state behavior of Ru catalysts by Voorhoeve and Trimble (1975). The primary difference they noted between the two states during NO reduction was in the amount of NH<sub>3</sub> formed. Only small differences were observed in any of the reactions considered in this work. Sugi et al. (1975) studied N<sub>2</sub>O intermediacy in the reduction of NO by CO over an Fe<sub>2</sub>O<sub>3</sub>

catalyst. Their data indicated that the NO was much more strongly adsorbed than the N<sub>2</sub>O, thereby displacing the newly formed N<sub>2</sub>O from the catalyst surface before it had time to react with the CO. At higher temperatures, however, the N<sub>2</sub>O did show an increasing tendency to react before being displaced.

Studies of NO reduction in multicomponent systems over noble metal catalysts contain some interesting observations. Kobylinski and Taylor (1974) report that H<sub>2</sub> is the predominant reducing agent in the H<sub>2</sub>-CO-NO/Ru system, but that the overall rate of reduction is closer to that of the CO-NO/Ru binary system. Klimisch and Barnes (1972) claim that the H<sub>2</sub>O present in the exhaust gas reacts with the CO via the water gas shift reaction to produce H<sub>2</sub> which thereby becomes the dominant reducing species. Voorhoeve and Trimble (1975) note that CO is the main reducing agent at low temperatures in the H<sub>2</sub>-CO-NO-H<sub>2</sub>O-CO<sub>2</sub>/Ru system, whereas H<sub>2</sub> tends to predominate at higher temperatures. According to Taylor and Klimisch (1973) this is due to the fact that the H<sub>2</sub>-NO reaction is faster at higher temperatures than the CO-NO reaction.

Bauerle and Nobe (1974) found that the presence of H<sub>2</sub>O reduced the selectivity of Ru toward N<sub>2</sub>. Bauerle et al. (1972), Klimisch and Taylor (1973), and Shelef and Gandhi (1972) in separate studies on the effects of O<sub>2</sub> on NO reduction all agree that although the presence of O<sub>2</sub> slightly reduces the amount of NH<sub>3</sub> produced, it has little effect on the overall NO reduction rate provided that a significant excess of reducing agent is present.

## Experimental Section

Details of the equipment used, a description of the catalyst, and the experimental procedure are given by Schleppy and Shah (1976a). During the present study two different Ru catalyst beds were used. No reduction was carried out over a bed made up of 28 0.4% Ru impregnated fiber glass cloth disks (2.35 g, 2.6 cm) "sandwiched" out with neutral fiber glass to a final bed length of 5.9 cm. For the N<sub>2</sub>O reduction runs an