



Synthesis and Characterization of Alumina-Zirconia Catalyst and Sulfate Loading Effect

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Abstract Samples of alumina and zirconia were prepared from which the alumina-zirconia sample was prepared by mechanical mixing of alumina and zirconia gels deposited (precipitated) from their aqueous solutions using ammonia solution as a precipitating agent. The mixture was left to subside repose for 24 hours. The prepared sample was filtered and washed with rainwater to completely remove the associated anions, and then dried at 120 °C for 24 hours. Then charging the sample prepared with sulfate ions in different proportions (5, 10) % by soaking (impregnation) using ammonium sulfate as a source of sulfate ions and the sample was left for 24 hours with stirring. The resulting sample was dried at 120 °C for 6 hours and then calcified at 550 °C for 3 hours. The tissue structure properties of the prepared sample were determined by processing the adsorption data of nitrogen gas at 77 K, and it was found that these properties change with the presence of loaded zirconia and sulfate. The strength and quantity of acidic centers were determined using the TPD.

Keywords Alumina - Zirconia, Sulphate loading, Adsorption, TPD

Introduction

Alumina is an important compound in many fields, and is widely used as a catalyst carrier due to the control of the structure and thermal stability of alumina, and the presence of certain additives from other compounds enhances this structure and improves its surface properties [1]. Zirconia is used as a catalyst loaded on alumina, which contributes to increase the durability of the alumina holder and its stability due to the dispersion of the crystalline shape of the zirconia within the alumina structure, especially if this scattering is homogeneous, which can be achieved through the method used in the preparation of the sentence Alumina_zirconia ($Al_2O_3-ZrO_2$), and Jelly Zol Method is considered one of the best preparation methods used to achieve this homogeneity [2]. The zirconia formula prepared by the Jelly Zolmethod is in the form or ZrO_nH_2O or $ZO(OH)_n$ which indicates the maximum supportive number of zirconium in the water state compared with anhydrous oxide. Zirconium hydroxide is present in several formulas which leads to the fact that zirconium forms different inorganic polymers that are linked together with hydroxyl groups [3].

The structure of zirconia prepared by precipitation is correlated with the mean PH value and Chen et.al shows that in the field of $pH = 7-10.5$ zirconia is in the form $[Zr(OH)_6]^{2-}$. It can be said that the mechanism of $Zr-OH$ correlation and the final form of this correlation depends mainly on the presence of hydroxyl groups, monomer structure, crystallization kinetics and the value of pH medium [4].



Sulfurized zirconia attracted the attention of researchers after it was first prepared by Hino and Arata in 1979, and this type of catalyst can be used in many organic reactions such as alkylation, acylation, saponification and some condensation reactions [5-6].

The presence of oxides such as alumina stabilizes the tetrahedral zirconia structure, which enhances the performance and effectiveness of the catalyst prepared in catalytic reactions, in addition to the fact that sulfate ions significantly increase the acidic surface properties [7].

Research Importance

The importance of this research is that it's an application to the sustainable development program of water resources to conduct periodic monitoring and evaluate the quality of the groundwater that surrounds the waste dump especially it irrigates most of the agricultural areas there, as well as drinking water and other uses.

Research Aims

The importance of this research is that it deals with solid acid catalysts sulfonated on the basis of common oxides that can be used in many industrial fields, especially petroleum industries and organic synthesis, in addition to the possibility of preparing these compounds locally and replacing imported materials and the great economic importance this has. The search aims to prepare the alumina-zirconia catalyst and study the surface properties of the catalyst and the effect of loading it with sulfate on these properties.

Research Methods and Materials

1- Alumina Preparation

A Concentrated solution of aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was prepared, then concentrated ammonia solution NH_4OH (30%) was gradually added to this solution with constant stirring until the gel was formed. The resulting gel was left for layer age (reposing) for 24 hours, then filtered and washed with distilled water until it was free from nitrate ions and dried in Drying oven at 120°C for 24 hours and then the product was grinded and divided into two parts:

The first is the dried at 120°C and called **A**

The second was calcified in the oven at 550°C for 6 hours and called **A (c)**.

2- Preparation of Zirconia

A concentrated solution of zirconium chloride ZrCl_4 was prepared and then a concentrated ammonia solution NH_4OH (30%) was gradually added to this solution with constant stirring until the formation of the gel. The resulting gel was left for layerage (reposing) for 24 hours, then a portion of the gel was filtered and washed with distilled water until it was free from chloride ions, then dried in a drying oven at 120°C for 24 hours and then grinded into two parts:

The first is the dried at 120°C and called **Zr**

The second was calcified in the oven at 550°C for 6 hours and called **Zr (c)**.

3-Preparation of alumina_ zirconia

The sample was prepared:

AZ1-0.1mole of alumina to 0.1 mole of zirconia

Preparation was performed after mixing the prepared alumina gel which was reposed for 24 hours as previously with the previously prepared zirconia gel and reposed for 24 hours ; after mixing it was stirred for 3 hours and then the gel was left to rest (repose) for 24 hours and then was filtered and washed with distilled water until the filtration was free from nitrate ions and chloride, and then dried in a drying oven at 120°C for 24 hours and then the product was grinded and divided into two parts:

The first the dried at 120°C and was called sample **AZ1-0.1**

The second was calcified in the oven at 550°C for 6 hours and called **AZ1-0.1 (C)**.



4- Loading:

The sample AZ1-0.1 was taken and was loaded with sulfate ions in two different rates by soaking method where the percentage of loaded sulfate was $X = 5.10\%$ by dissolving the appropriate amount of ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ in the lowest possible amount of distilled water and then adding this solution to the sample with constant stirring; the samples were left for 24 hours and then dried at $120\text{ }^\circ\text{C}$ for 6 hours and then calcified at $550\text{ }^\circ\text{C}$ for 3 hours and the sample was called **X- SO_4 /AZ1-0.1**

Where **X** is the percentage of sulfate loaded

Results and Discussion

1) Tissue (Textile)Structure:

Equal-grade adsorption curves for the presence of porous structure show samples and their variation from sample to sample in Figures (1) and (2):

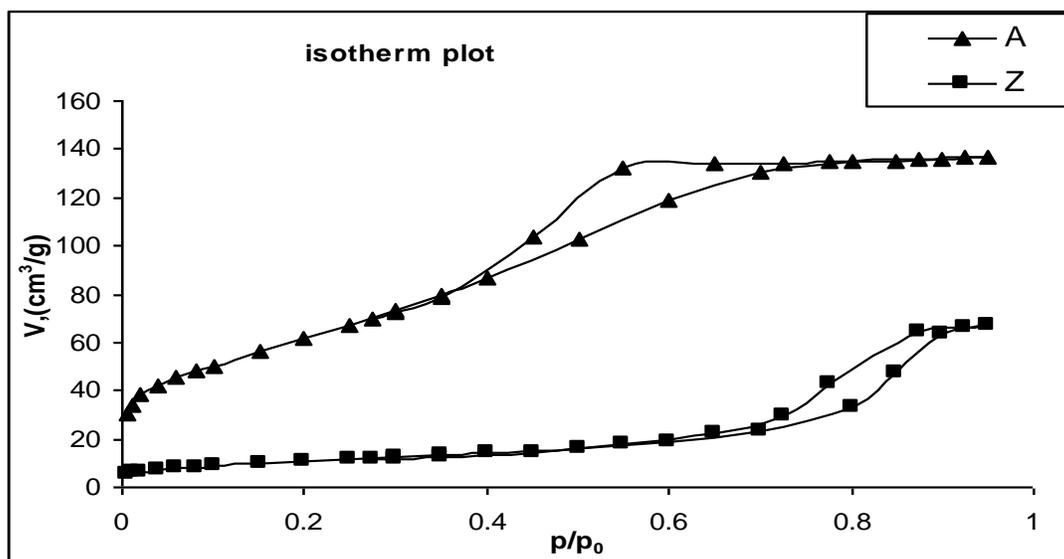


Figure 1: Nitrogen adsorption curves at 77K

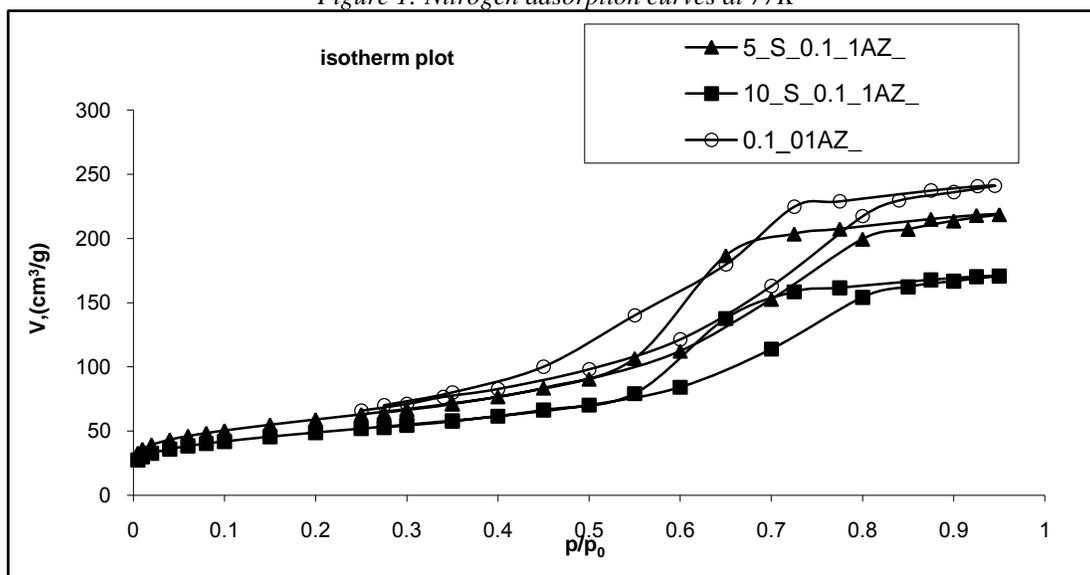


Figure 2: Nitrogen adsorption curves at 77K

Capillary condensation was observed in all samples due to the presence of the loop on the adsorption curves, indicating the presence of medium porosity and the presence of fine porosity, which is confirmed by the presence of a knee on the adsorption curves in the field of low relative pressure by analyzing the data of adsorption curves using the relationship DR, BET [5]. The histological structure factors of some prepared samples were determined as shown in Table (1).

Table 1: Histological Structure Factors of Prepared Samples

(V_c/V_p) %	E_0 (Kj/mol)	C_{BET}	V_c (ml/g)	V_P (ml/g)	V_P (ml/g)	S_{BET} (m ² /g)	Sample
36	14	58	0.078	0.211	0.211	229.8	A
12.6	14.14	83	0.013	0.103	0.103	38.1	Z
21.4	14.28	86	0.079	0.37	0.37	220.9	AZ(1:0.1)
22.9	15.28	169	0.077	0.338	0.338	208.6	AZ(1:0.1) 5S
24.3	15.5	239	0.064	0.264	0.264	170.5	AZ(1:0.1) 10S

The second column in Table (1) shows the change in specific surface area, where the specific surface area decreases from value 229 m²/g of sample A to 220.9 m²/g for sample AZ (1: 0.1) due to the fact that zirconium oxide Z has a weak porosity structure, and has a low specific surface area in comparison with alumina A as shown in the second column of Table (1) and therefore the increase of the percentage of zirconium can lead to the closure of some pores. This is reflected on the radius of the middle pore-column IV Table (1) while the change of the minute porosity ratio is different.

In the case of Sulfonatedoxide, we also note the specific surface area decrease along with increasing sulfate rate where the specific surface area decreases from 220.9 m²/g for sample AZ (1: 0.1) to 208.6 m²/g and value 170.5 m²/g for the two samples for AZ (1: 0.1) 5s and AZ (1: 0.1) 10s which indicates sulfate correlation.

We notice from the sixth column, Table 1 that the value of **BET** constant is relatively low which indicates a weak mutual effect between the surface of the samples and the adsorbed gas. The adsorption energy value E_0 is low and does not exceed 20 Kj/mol for all samples, indicating the physical adsorption nature of the adsorbent material on the surface of the samples.

We notice that these results correspond to many reference studies where the alumina prepared in different ways has a greater specific surface area of zirconia, and when zirconia is entered, it leads to a decrease in the specific surface area as noted in the reference studies the introduction of chromium, molybdenum and tungsten leads to a decrease in the specific surface area. Many researchers have also shown that the presence of surface sulfates leads to a reduction in surface area specific quality [7,8].

2) Determination of the quantity and strength of acid centers

This method is based on the determination of the amount of acidic centers based on the adsorption of a base on these centers and then heating the solid sample in a specific thermal field at a specific heating speed with an inert gas flow. The solid surface will then give up the adsorbent foundation and the inert gas will carry it out of the device. During the heating process, the base used gradually starts from the surface according to the strength of its association with the surface as the temperature increases.

In this research we used Triethylamine as a adsorbent, and samples were heated in the temperature range 25_650 °C at heating speed of 10 °C /min and with a flow of helium gas, and the curves show the distribution of weight loss or acidic centers at different temperatures.

The aforementioned figures generally show three thermal domains of the adsorbent amine and vary slightly from one sample to another, but they express the strength of the acidic centers. These domains are 110-250 °C, 280-330, 380-600. With some displacements from one sample to another which express the chemical adsorption of the amine used on weak, medium and strong centers respectively.

It appears from the above figures that alumina A and Z zirconia have lower acidic properties than the sample AZ_1_0.1, knowing that it has weak centers in the domain 110-250 °C, and medium in the domain 280-450 °C, and strong centers are few, while at sulfate loading the quantity of all centers increases. The amount of weak centers



is higher than the medium and strong, noting that when the sulfate percentage increases from 5% to 10%, the amount of weak and medium acidic centers decreases and the amount of strong centers increases.

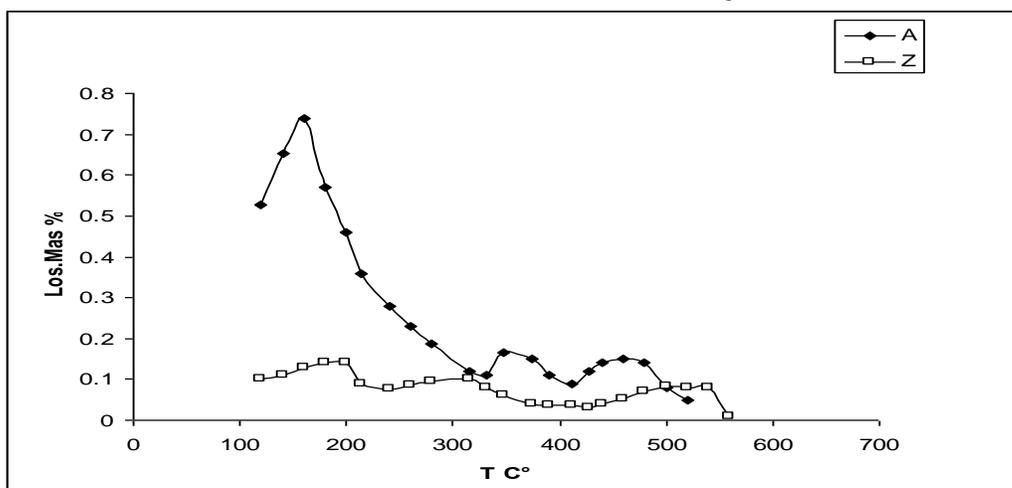


Figure 3: TPD curves for adsorption of Tri-Ethyl Amine (Triethylamine)

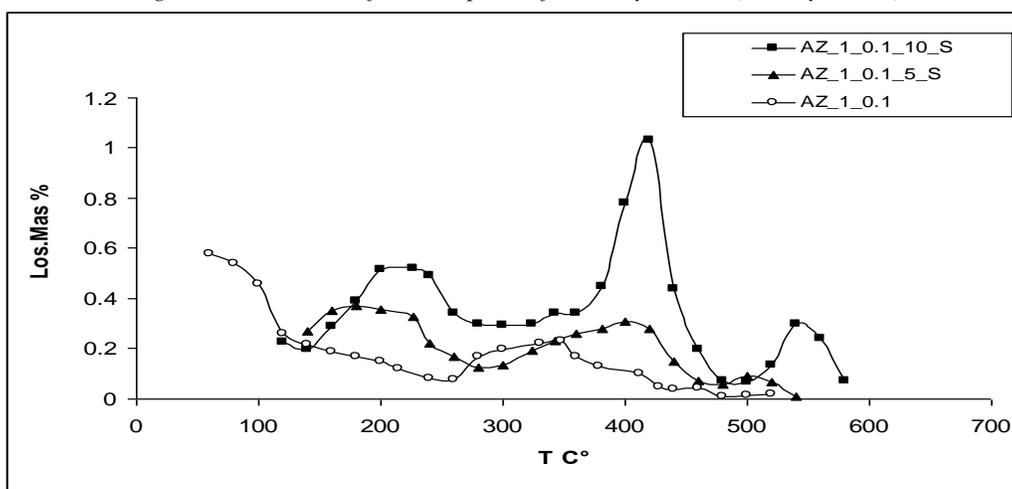


Figure 4: TPD curves for adsorption of Tri-Ethyl Amine (Triethylamine)

The distribution curves of the acidic centers of samples AZ-1: 0.1-S-5 and AZ-1: 0.1-S-10 also show that there are acidic centers whose quantities increase after 500 °C as the adsorbent amine remains bound on the surface to [9]. 500 °C which indicates the presence of very strong acid centers or what is called Super Acid.

By TG curves shown in the figures, the total weight loss of the adsorbent amine was calculated in the temperature range 110-600 °C, which represents the total amount of acidic centers of the prepared samples shown in Table 2:

Table 2: Total amount of acidic centers of the prepared samples

Acidity m.mol/g	Sample
0.084	A-550°C
0.107	Z-550°C
0.373	AZ-1:0.1
0.504	AZ-1:0.1-S-5
0.770	AZ-1:0.1-S-10

We observe from Table (2), the increase of the surface acidity of the prepared samples after being loaded with sulfate compared with the non-loaded alumina and zirconia, for it increases as for the sample AZ-1: 0.1 from 0.373m.mol/g to 0.770 m.mol/g which means that the sulfate ions lead to an increase in the amount of acidic centers.

We conclude that sulfate ions can lead to generating strong acidic centers when correlated (bonded) to the alumina-zirconia catalyst surface, and the sulfate groups themselves form Lewis acid centers or by accepting electrons they form Lewis acid centers on the oxide surface. The distribution of acidic centers on the surface of the loaded oxide varies depending on the method of preparation where there can be a shift in the peaks that indicate the distribution of acidic centers, but all researches indicate the generation of strong acidic centers [10]

Conclusions

- ✓ The Prepared samples (specimens) have good tissue structure to be used in heterogeneous (Disproportionate) catalytic processes depending on the nature of the reaction and the purpose of this reaction.
- ✓ Loading alumina-zirconia with sulfate ions leads to a slight decrease in the value of the specific surface area, and this decrease is increased by increasing the proportion of sulfates from 5% to 10%.
- ✓ Sulfate loading leads to the presence of strong acid centers (**Super Acid**).
- ✓ The surface acidity of the samples (specimens) increases by increasing the sulfate rate from 5% to 10% .

Recommendations

- ✓ Studying the catalytic activity of the prepared samples.
- ✓ Studying the effect of loading other elements on surface properties and catalytic activity.

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