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Textural properties of prepared alumina, stania and iron oxide catalysts

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Abstract

Aluminum, Iron and Tin oxides were prepared by precipitation method using ammonia solution. The prepared gels were dried and calcined for three hours at 873 K to give the appropriate metal oxides Al_2O_3 , Fe_2O_3 and SnO_2 . These samples have been characterized by means of nitrogen adsorption at 77 K. Textural data obtained from N_2 adsorption show that alumina has higher surface area than other oxides indicating the presence of small particle size in alumina samples. Moreover, these oxides have mixed porosity ranging from micro and mesopores. The analysis of t - and α_S curves shows the agreement between the values of specific surface area, S_{BET} , S_t and S_s .

Keywords: Alumina; Stania; Iron oxide; Texture; Porosity.

Introduction

Historically, oxide catalysts have been used primarily for vapor phase reaction in the petroleum and petrochemical industries. Recent work, however, has shown that these catalysts can also be effective in promoting a number of synthetically useful reactions. While simple oxides show activity for some oxidations, they are more commonly used as solid acids or bases. Complex oxides can act as acids or bases as well as oxidation catalysts. Complex oxide can range in composition from

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the simple, amorphous, binary oxides to the more complex ternary and quaternary systems.

Solid acid catalysts have found widespread applications in many catalytic reactions with reference to hydrocarbons e.g. isomerization, alkylation, oligomerization and cracking. These acid catalyzed reactions are large-scale industrial processes that play a most important role in the petroleum and petrochemical industries (Hua et al., 2001). Solid acids of metal oxides have been investigated for their use as environmentally friendly catalysts in many organic reactions (Sakthivel et al., 2003; Arata 1990). To control the properties of the oxides, some metals can lead to more catalysts that are active and more resistant against deactivation (Yadav and Nair, 1999). Therefore, several metals such as platinum, palladium, aluminum, nickel, cobalt and manganese have been added to sulfated metal oxides, producing active and selective catalysts (Pereira et al, 2008).

Gas reactions catalyzed by solid materials could occur at the exterior and interior surface of the porous solid catalysts. When a catalytic reaction takes place on a surface, the rate of the reaction increases in proportion to the surface area, if transport restrictions are negligible. Therefore, the optimum form of a catalyst is usually a porous solid that has a high internal surface area. Industrial catalysts typically have internal surface areas of hundreds of square meters per gram (Thomas and Thomas, 1996). Many metal oxides are readily prepared in the form of high surface area solids. Some other metal oxide catalysts exhibit low surface area that might be increased either by dispersion as minute particles on a sturdy high – surface area support or through chemical treatments. Either such treatments may increase the surface area available for adsorption and subsequent reaction or it may increase the catalytic activity per unit surface area (Scooneheydt, 1984). Hence, surface area measurement is an important expedient in predicting catalyst performance and determining the role, which the catalyst surface plays in any heterogeneous gas reaction. Surface area is by no means the only physical property, which determines the extent of adsorption and catalytic reaction. Equally important is the pore structure of the catalyst material or support, which, although contributing to the total surface area, must be regarded as a separate factor. This is because the distribution of the pore size in a given catalyst preparation may be such that some of the internal surface is completely inaccessible to large reactant molecules and, furthermore, may restrict the rate of conversion to products by impeding the diffusion of reactants and products throughout the porous medium. Accordingly, it is an advantage to investigate the pore structure of a catalyst.

The study of the catalyst texture is extremely important in characterizing the surface features of the catalysts. Catalytic activity is closely associated with the surface area and porosity available for the adsorption of the reactant. The more typical solid catalytic materials include metals, metal oxides, and metal sulfides, sometimes used in combination with each other (Gates, 1992). These solids are porous but the pores are nonuniform. To understand surface catalysis, it is helpful to study the catalyst texture.

The present study aims to exploring the textural properties including surface area, porosity and pore size distribution for some metal oxides that used as catalysts. These oxides are alumina, stania and iron oxide catalysts.

Experimental

Materials:

Pure alumina, was obtained from alumina gel by calcination at 873 K for 3 h. The gel was prepared according to (Khalaf et al., 2007) by a dropwise addition of a (1:1) solution of NH_4OH (AR-grade Prolabo product) to a 0.1 M solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR-grade, BDH product).

Tin oxide gel was prepared by a slow dropwise addition of a 1:1 ammonium hydroxide solution to a 0.3 M aqueous solution of tin (IV) chloride ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) AR grade, BDH product (England), with a continuous stirring till pH 8 is reached. The white precipitate was left over-night before being filtered and washed thoroughly with 2% $\text{CH}_3\text{COONH}_4$ solution until all chloride was eliminated (silver nitrate test), and then dried at 383 K till constant weight. The dried material was ground to 250 mesh size and kept dry over P_2O_5 desciator. Pure tin oxide, SnO_2 , was obtained from the dried gel by calcination at 873 for 3 h.

Iron oxide was prepared from a 0.3 M aqueous solution of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma, minimum purity 98%) by dropwise addition of ammonia solution (Carlo Erba, 30% solution) 1:1 up to pH = 9 under vigorous stirring for 1 h. The precipitate was aged in the mother liquor overnight, then carefully washed with distilled water till nitrate-free, and dried overnight at 383 K to obtain a fine $\text{Fe}(\text{OH})_3$ powder. Calcination of $\text{Fe}(\text{OH})_3$ at 873 K for 3 hours gives pure iron oxide.

Apparatus and techniques:

Nitrogen adsorption isotherm measurement:

Full nitrogen adsorption/desorption isotherms at 77 K were obtained using a NOVA 2200, version 6.10 high-speed gas sorption analyzer (Quantachrome Corporation USA). The calcined samples were first outgases at 470 K for 1 h. Twenty four-point adsorption and desorption isotherms were obtained, from which BET surface areas were derived using standard and well-established methods (Webb and Orr, 1997; Sing et al., 1985).

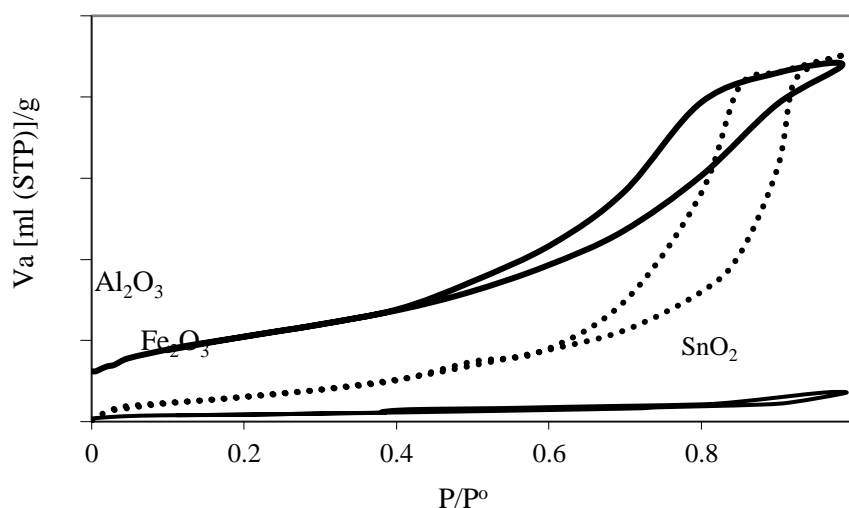


Figure 1. Nitrogen adsorption-desorption isotherms for the indicated metal oxides (Al_2O_3 , Fe_2O_3 and SnO_2)

The shape of the isotherms and the presence of hysteresis loop at high relative pressure, suggest that the samples exhibit porous surfaces in the meso-range (Sing et al., 1985). The hysteresis loop exhibited is most likely of type H3 according to the IUPAC classification, indicating that the pores contained are slit-shaped (Gregg and Sing, 1982). The higher inception point of the hysteresis loops may infer that the monolayer is completed slowly and multilayer formation is restricted.

Surface area:

The Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938) is the most widely used procedure for the determination of the surface area of solid materials and involves the use of the BET equation (1).

$$\frac{P/P_o}{V_a(1-P/P_o)} = \frac{1}{V_m \cdot C} + \frac{C-1 \cdot P/P_o}{V_m \cdot C} \dots\dots\dots(1)$$

This equation demands a linear relationship between $P/P_o / V_a (1-P/P_o)$ and P/P_o (known as the BET-plot) where: P and P_o are the equilibrium and saturation vapour pressures, respectively, V_a represents the amount adsorbed of gas at pressure P , and C represents a constant including the ratio between adsorption time of the molecules in the first layer and that of second following layers, thus, the slope is become $C-1/V_m C$ and the intercept is $1/V_m C$.

By knowing the monolayer capacity (V_m), from the slope and intercept of the BET-plot, the surface area is computed according to the equation:

$$S_{BET} = 4.371 \times V_m \cdot m^2 g^{-1} \dots\dots\dots(2)$$

Data obtained from isotherms and BET-plots of the Al_2O_3 , Fe_2O_3 and SnO_2 samples are cited in Table 1. From these data, it is clear that tin oxide sample has the lowest specific surface area ($S_{BET} = 11 \text{ m}^2\text{g}^{-1}$) than other oxides which agree with previous data (Khalaf et al., 2010)]. The order of the S_{BET} values is $Al_2O_3 (187 \text{ m}^2/\text{g}) > Fe_2O_3 (61 \text{ m}^2/\text{g}) > SnO_2(11 \text{ m}^2/\text{g})$. These data are agree with the data obtained from X-ray diffraction results, which complied in Table 1 also, in which the alumina samples have smallest crystallite size (33 nm) that effect on the specific surface area (Khalaf et al., 2007).

Table 1. Textural data of metal oxides; Al_2O_3 , Fe_2O_3 and SnO_2 .

Sample	S_{BET} $m^2 g^{-1}$	C_{BET}	S_t	S_s	S_{cum}	$V_{p_{tot}}$ $cm^3 g^{-1}$	Aver. $r_p \text{ \AA}$	Particle Size(nm) ^a
			$m^2 g^{-1}$					

Al₂O₃	187	128	193	191	116	0.34	36.3	33
Fe₂O₃	61	39	60	59.5	48.8	0.35	14.8	45
SnO₂	11	14.7	10.3	10.8	6.9	0.032	17.5	185

^a These particle sizes obtained from literatures, see refs. (Khalaf, 2009; Khalaf et al, 2010; Khalaf et al, 2007).

Pore analysis:

In addition to specific surface area, pore structure is equally important of the catalyst, which although contributing to the total surface area, and must be regarded as a separate factor. Thus, it is advantageous to investigate the pore structure of the catalysts. The modifications observed of the surface texture are predicted by a pore analysis, using the t-method and α_s -method (Khalaf, 2005). The analysis facilitated detection and differentiation between the micropores and the mesopores.

Investigation of adsorption isotherm by t-method:

The experimental data concerning the amount of adsorbed nitrogen, which are measured as a function of the relative pressure P/P_0 , may be plotted with the aid of the t-curve according to the appropriate C_{BET} -value, as a function of the t-values. Then a straight line is obtained and passing through the origin. At higher P/P_0 deviations from the straight line may occur indicating certain porosity. By the aid of calculated C_{BET} values of the sample under study (128, 39 and 14.7 for Al₂O₃, Fe₂O₃ and SnO₂, respectively), t-plots are constructed (see Fig.2). From the resulting plots, one can deduce that all the catalysts under study show a positive (upward) deviation in the region corresponding to capillary condensation and hence indicating the presence of mesoporosity (Khalaf, 2005).

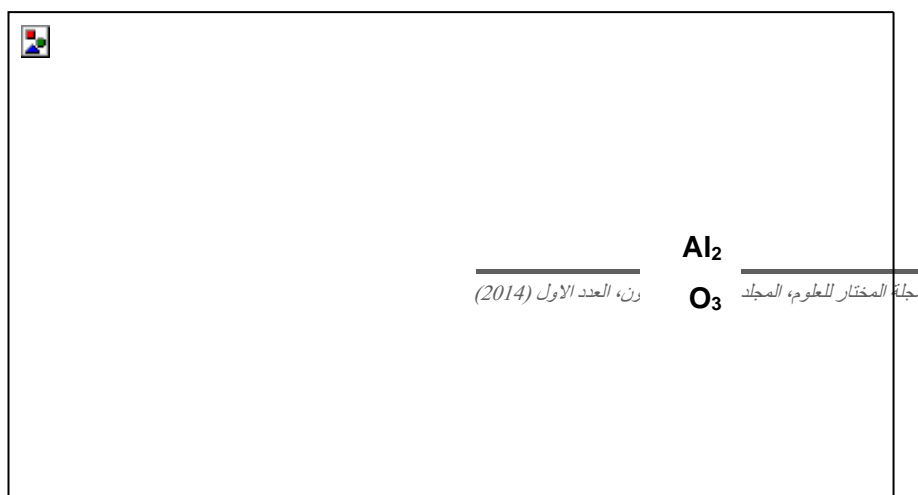


Figure 2. t-Plots for the indicated metal oxides (Al₂O₃, Fe₂O₃ and SnO₂).

This as mentioned above indicates the presence of mesoporosity. This can actually finds some support from the pore size distribution (PSD) curves (Fig. 4). Specific surface area of the samples can be determined from the slopes of the straight lines of Fig. 2 by using the following equation (3):

$$S_t = 3.54 \times V_a/V_m \dots\dots\dots (3)$$

Where: V_a is the amount of gas adsorbed.

The values obtained from this equation are designated S_t and these values are cited in table 1. From this table, the S_t values are 193, 60 and 10.3 m²g⁻¹ for Al₂O₃, Fe₂O₃ and SnO₂, respectively. On comparing the values of S_t with that of S_{BET} , it can be deduced that the two sets of values are in faire agreement. This agreement would mean the validity of the corrected t-curves.

Investigation of adsorption isotherm by α_s -method:

α_s -plots constructed by plotting the corresponding V_a ml (NTP) g⁻¹ against the α_s values. These plots, which called α_s -plots, are shown in Fig. 3.



Figure 3. α_S -Plots for the indicated metal oxides (Al_2O_3 , Fe_2O_3 and SnO_2)

On using equation (4), the surface area can be determined, and the resulting areas are designated S_s and cited in table 1. The calculated values of S_s are 191, 59.5 and 10.8 m^2g^{-1} for Al_2O_3 , Fe_2O_3 and SnO_2 , respectively, and by the comparison of these data with the data resulting from BET calculation S_{BET} , it is clear that there is an agreement between the two sets of values. This again indicates the appropriateness of the standard α_s curves used for constructing the α_s -plots. The mesoporous character of the catalysts is strongly sustained by the observed upward deviations of these α_s -plots as observed from Fig. 3. Hence, according to t- and α_s -plots the porosity of these catalysts under investigation lie in the mesoporous range. Some sort of restriction to the narrow range is to be empathized (Khalaf, 2005).

$$S_s = 2.89 V_a / \alpha_s \dots\dots\dots(4)$$

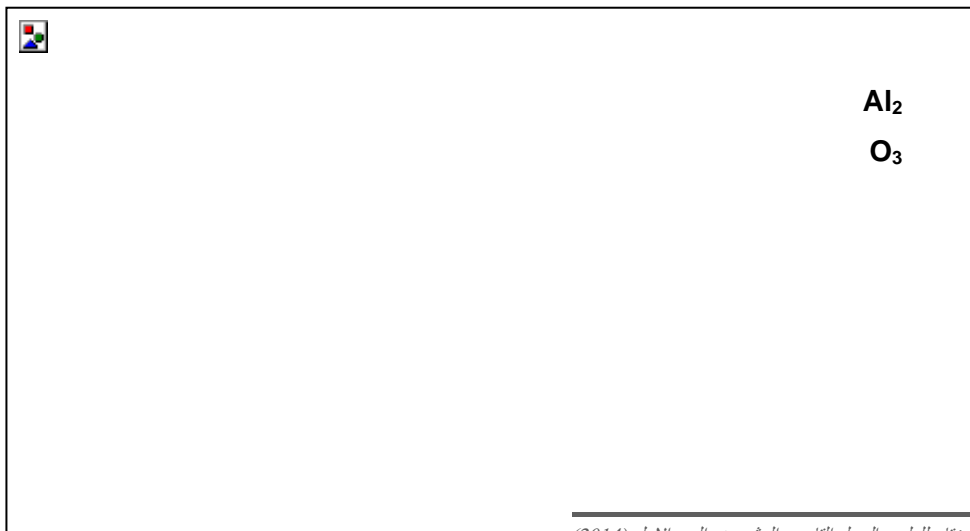


Figure 4. Pore size distribution for the indicated metal oxides (Al_2O_3 , Fe_2O_3 and SnO_2)

Pore Size Distribution:

The distribution of pore volume with respect to pore size is called a pore size distribution (PSD). Pore size distribution can be obtained by plotting $\Delta V_P / \Delta r_P$ against r_P , where ΔV_P is the change in pore volume and Δr_P is the change in pore radius. This plot will give the relative abundance of the pores of various radii in the solid.

The pore size distribution (PSD) curves of the tested samples are shown in Fig. 4. From these curves it is cleared that the PSD lies between 5- 100 Å. Four main peaks at ~12, ~15, 32 and 70 Å are observed. This means that the porosity of Al_2O_3 is mixed between mesopores and micropores in agreement with the findings of the t- and α_S -methods.

For Fe_2O_3 , the PSD curve shows four peaks at 17, 40, 50 and 100 Å (broad) indicating the presence of little micro and more mesopores. This is supported by t- and α_S -plots. Also, the PSD for SnO_2 shows peak at < 28 Å, which means that the porosity of SnO_2 is micropores in addition to little amount mesopores.

Conclusions

Nitrogen sorption isotherms at 77 K of $\gamma\text{-Al}_2\text{O}_3$, Fe_2O_3 and SnO_2 metal oxides are related to Type IV revealing a porous surface character and the hysteresis loops belong to H3-type indicating that the pores are mostly slit-shaped. The surface area of $\gamma\text{-Al}_2\text{O}_3$ is $187 \text{ m}^2\text{g}^{-1}$ and higher than other oxides, this is attributed to the small particle size (33 nm). In addition, the higher C_{BET} value of alumina sample (128) revealing higher interaction between the catalyst and the adsorbate in comparison with other oxides (Fe_2O_3 and SnO_2). The investigation of porosity by t-plots and α_S -methods show that all metal oxides have upward deviations indicating the presence of mesopores, which is supported by pore size distribution curves.

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خصائص التركيب النسيجي لمحفزات (الالومينا، أكسيد القصدير و أكسيد الحديد) المحضرة

جلال محمد المنفي

الملخص

تم في هذا البحث تحضير بعض أكاسيد الفلزات المستخدمة كعوامل حفازة مثل أكاسيد الألومنيوم، الحديد والقصدير عن طريق الترسيب بإستخدام محلول الأمونيا. الجل المتكون يتم تجفيفه حتي ثبات الوزن ثم حرقه عند 873 كلفن لمدة 3 ساعات للحصول علي الأكاسيد المقابلة (Al_2O_3 , Fe_2O_3 and SnO_2). للوقوف علي التركيب النسيجي لهذه العينات تم إستخدام تقنية امتزاز النتروجين الغازي عند درجة حرارة النتروجين السائل (77 كلفن). أظهرت النتائج المتحصل عليها أن أكسيد الألومنيوم (الأمونيا) يمتلك أكبر مساحة سطح مقارنة بأكسيد الحديد وأكسيد القصدير نليلاً علي وجود جسيمات صغيرة الحجم في الألومينا. علاوة علي ذلك فإن هذه الأكاسيد تمتلك مسام مختلطة ما بين مدي المسام الدقيقة (الميكرو) والمسام المتوسطة (الميزو) مما يؤهلها لخواص امتزاز عالية. أيضا أظهرت قياسات مساحة السطح توافق تام بين جميع القيم المقاسة بعدة طرق مختلفة.

مفتاح الكلمات: الالومينا، أكسيد القصدير، أكسيد الحديد، التركيب النسيجي، المسامية