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Studies on Nickel-Alumina Hydrogenation Catalyst Impregnated with Europium Oxide: I-Surface Area and Pore Structure

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Abstract: The effect of europium oxide on the resulting catalyst is investigated. Structural and textural changes were followed using XR diffraction and DTA techniques. The various texture parameters of nickel-alumina and impregnated with europium oxide samples were computed from the data on nitrogen adsorption at 77K.

Impregnation of nickel-alumina caalyst with europium oxide (catalyst I-IV) with drying at 383 over night and thermal decomposition at 773K for 24 hours produced non-crystalline catalysts. Differential thermal analysis of the mixed carbonates indicates the presence of only one asymmetric endothermic peak at 501 K which marks the decomposition of the carbonate to yield the oxide.

The dissolution of trivalent europium ions in nickel-alumina lattice at ≅ 1% europium oxide was accompanied by marked decrease in the surface area, total pore volume and pore radius of the catalyst. In contrst impregnating with ≅ 2% europium oxide led to a marked increase in the specific surface are as well as the other parameters of nickle-alumina catalyst this attained a maximum value, then decreases with increasing the amount of dopant oxide. The total pore volume and pore radius have the same trend as the specific surface area of all the pure and impregnated samples with europium oxide. Measurements before and after loading showed marked changes in total pore volume and pore size, in the range of 54-166 Å.

Introduction

It is well known that the texture of catalyst, which may be significantly affected by the method of preparation and treatment, must be known in order to obtain a better understanding of their function.

Even though the role of the surface in adsorption and catalysis was recognized a long time ago, little attention was paid recently to the importance of the location of the surface. If the adsorbing surface of an adsorbant or a catalyst is located in very narrow pores, it is expected that diffusion into or out of these pores may become the rate determining step in adsorption or catalysis. was recognized a long time ago, little attention wa spaid recently to the importance of the locationof the surface. If the adsorbing surface of an adsorbant or a catalyst is located in very narrow pores, it is expected that diffusion into or out of these pores may become the rate determining step in adsorption or catalysis.

Also, the energetics of the adsorption process on a surface located in a narrow pore would be different from that in a wide pore. The sizes of the pores can influence both the poisoning characteristics of the surface for one reaction compared with another and the extent to which a porous solid can build up temperature and pressure gradients in the case of catalytic reactions. It is therefore essential to define the surface of a catalyst by at least two parameters, namely the surface area and pore structure. A convenient tool for the investigation of pore structure and pore production during the preparation of active solids is provided by nitrogen adsorption isotherms measured at liquid nitrogen temperature [1, 57-105]. Quantitative textural data concerning the pore volume and the mean pore radius can be obtained from a sorption isotherm. Moreover, qualitative information concerning the shape of pores can also be obtained [2].

It is well known that the textural characteristics of a catalyst are influenced by the method of preparation [3]. These characteristics may also be affected by the introduction of a small amount of foreign ions into the lattice of a solid catalyst [4]. The homogeneous distribution of the foreign ions in the whole mass of the catalyst requires thermal treatment at elevated temperatures which leads, unfortunately, to sintering of the impregnated catalyst [5]. However, the dissolution of foreign ions in the outermost surface layers of a catalyst may occur at relatively low temperatures [6]. The addition of Al_2O_3 which is catalytically inactive for these reactions (hydrogenation), to nickel metal improves the surface properties of nickle by increasing its degree of dispresion, thus inhibiting its sintering [7, 8]. The increase in surface area of nickel metal due to the presence of $Al_2 O_3$ might be accompanied by an increase in the chemisorptive and catalytic activities of nickel.

In this investigation the surface area of unimpregnated Ni-Al_2O_3 and impregnated with europium oxide catalysts is studied. The surface area was computed by the Brunauer-Emmett-Teller (BET) equation [9].

The detection of porosity and of the existence of micropores or mesopores was carried out using the t-method offered by de-Boer and co-workers [10], using the notation of Dubinin [11, 12] for the classification of the pore systems into micropores with a diameter less than 20 A, mesopores with diameters in the range 20-300 A, and macropores with diameters larger than 300 A°. Macropores are outside the scope of the present investigation since they are less accurately determined by the adsorption method.

The change of the specific surface area of Ni-Al_2O_3 hydrogenation catalysts has been the subject of earlier studies [13-18], [19; pp. 136-153]. For the hydrogenation reaction over nickel-alumina catalysts, the factors that contribute significantly to the reaction are usually the texture of the solid substrate, the availability of the various reactants to reach active sites, and the implication of diffusion [20, pp. 934-946] and retardation of the reactants or products in certain pores. The effect of impregnating with

Europium oxide on the surface area and the pore structure of Nickel-Alumina catalyst are reported in the present investigation.

Experimental

Catalyst preparation

The method of homogeneous precipitation as described by van Dilllon *et al.* and others [21, 22, 23].

The amount of nickel nitrate, aluminium nitrate and europium oxalate in the above mentioned procedure was so arranged that nickel is about 10% of the Ni-Eu_2O_3-Al_2O_3. Catalyst after the nickel oxide was reduced to nickel metal and the europium oxide varied between ≅1-4% (W/W). The mixed nitrate solution by using 1 M ammonium carbonate at 343K, then the samples which had been dried at 383 K for 12 hours, crushed to 30-40 mesh, then heated in dinitrogen atmosphere at 773°C overnight.

All the catalysts were reduced at 773K in flowing dihydrogen at a space velocity of 0.2 s^{-1} for 24 hours. This temperature was chosen because it was found to give the highest extent of reduction without resulting in nickel crystal growth [22, 24-28], the compositions of different Ni-Eu_2O_3-Al_2O_3 catalysts prepared by this method and their designations are given in Table 1.

Table 1. Composition of different Ni-Eu_2O_3-Al_2O_3 catalysts

Catalysts designation	Catalyst	Ni content % w/w	Eu_2O_3 content % w/w	Al_2O_3 content % w/w
S	$Ni-Al_2O_3$	10.00	-	90.00
I	$Ni-Eu_2O_3-Al_2O_3$	9.90	0.99	89.11
II	$Ni-Eu_2O_3-Al_2O_3$	9.80	1.98	88.22
III	$Ni-Eu_2O_3-Al_2O_3$	9.71	2.92	87.37
IV	$Ni-Eu_2O_3-Al_2O_3$	9.62	3.85	86.53

Apparatus

Adsorption isotherms were measured by the conventional volumetric technique employing the apparatus shown in Fig. 1. A heater for out-gassing samples was a furnace hold around the adsorbent vessel. The temperature was controlled by a platinum resistance thermometer and sensor and a versatherm proportional temperature controller. Reduced samples were transferred to the adsorption apparatus under dinitrogen in a controlled environment chamber. High purity of dihydrogen and dinitrogen gases were used in reduction studies, adsorption determination and the dead space calibrations.

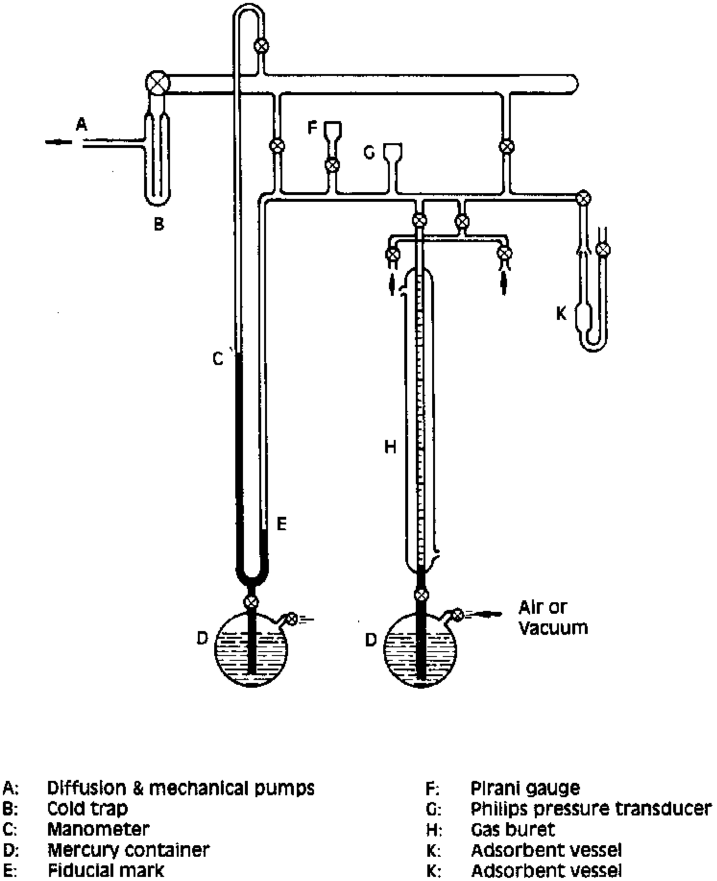

Fig. 1. Volumetric adsorption system.

A deoxohydrogen purifier and a gas drying unit was used in conjunction with the gas cylinder's in order to ensure removal of trace amounts of oxygen and water moisture.

Equilibrium adsorption isotherms were measured by standard methods, the Brunauer-Emmett-Teller (BET) method was used to determine the monolayer capacity and the specific surface area in the case of the nitrogen isotherms [29, pp. 171-235]. The BET equation was employed:

$$\boxed{\frac{P/P_o}{V(1-P/P_o)} = \frac{1}{V_m.C} + \frac{(C-1)}{V_m.C} \cdot \frac{P}{P_o}} \qquad (1)$$

where V is the amount of adsorbate per gram of catalyst at equilibrium pressure P, V_m is the amount of adsorbate per gram of catalyst at monolayer formation, C is a constant and P_o is the saturation vapor pressure of dinitrogen at liquid nitrogen temperature. In these studies molecular cross-sectional areas was taken to be 16.2 $Å^2$ [30, pp. 431-478].

Surface area were determined from

$$S.S.A. = N_M. S_o. N_A \qquad (2)$$

where N_A is Avogadro's Number, S is the cross sectional area of the adsorbed molecule and N_M is the number of moles of gas adsorbed per gram of catalyst at a monolayer formation.

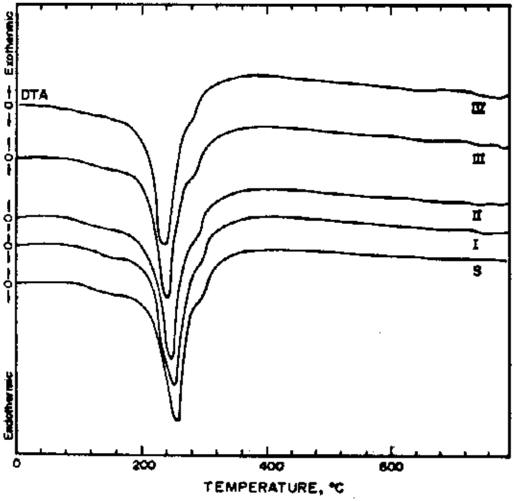

Fig. 2. Different thermal analysis curves for catalyst samples S, I, II, III and IV.

Differential Thermal Analysis (DTA) of basic mixed carbonate was carried out using a Metler (TA1) thermal analyzer. The rate of heating was 10 C min^{-1}.

An X-ray investigation of the catalysts was carried out using Siemens type D-5000 XR diffractometer. The diffraction angle 2θ was scanned at rate 2 min^{-1}.

Results and Discussion

Differential thermal analysis was carried out for pure nickel-alumina carbonate as well as of nickel-alumina carbonate impregnated with ≅1, 2, 3 and 4% (w/w) for Eu_2O_3. The data obtained is shown in Fig. 2.

The DTA curve for pure nickel-alumina carbonate indicates the presence of only one assymmetric endothermic peak at 498K which marks the decomposition of the carbonate to yield the oxide. For the impregnated samples, the general effect of impregnating is causing a very large decrease in the temperature of the endothermic peak, and as the concentration of the impregnate increases, the more significant is the lowering of the temperature of the endothermic peak.

The effect of dope cation is not only limited to the lowering of the temperature of thermal decomposition, but it may accelerate the rate of thermal decomposition, and also effect the extent and structure of the surface as well [31].

The X-ray diffraction pattern of the nickel-alumina with varying composition of Europium oxide calcined in dinitrogen at 773K were determined Fig. 3. The lines of crystallinity were not observed in any catalyst. It can be concluded that both Ni-Al_2O_3 and Eu_2O_3 exert a mutual effect on the crystallization process of each other. The interaction between Eu_2O_3 and Ni-Al_2O_3 to produce $EiEu_2Al_2O_6$ does not occur at an appreciable rate at 773K. Thus, higher temperatures might be required for the formation of the crystallization. A non-crystalline catalyst is also obtained when more europium oxide is added to the Ni-Al_2O_3 original sample. These results are in good agreement with those obtained by Samaane and Yoshitomi [7, 15].

Nitrogen adsorption on the impregnated Ni-Al_2O_3 mixed oxide prepared by coprecipitation of nickel carbonate, aluminium carbonate and europium carbonate.

The adsorption isotherms of dinitrogen were measured on Ni-Al_2O_3 -Al_2O_3 calcined in dinitrogen at temperature 773K and reduced by dihydrogen at the same temperature. These isotherms belong to types II and IV of Brunauer classification [32]. Figures 4, 5 and 6 show representive adsorption isotherms measured for samples S, I, II, III and IV. Adsorption of dinitrogen is irreversible and exhibits hysteresis loops of different areas depending on the chemical composition i.e. the percentage of Al_2O_3.

Inspection of the hysteresis loops obtained in this investigation for sample Ni-Al_2O_3 and its doped preparations, indicates that for samples S, II, and III, the hysteresis loops are almost type A of de-Boer's classification, while for samples I and IV the loops seem to be type E [33].

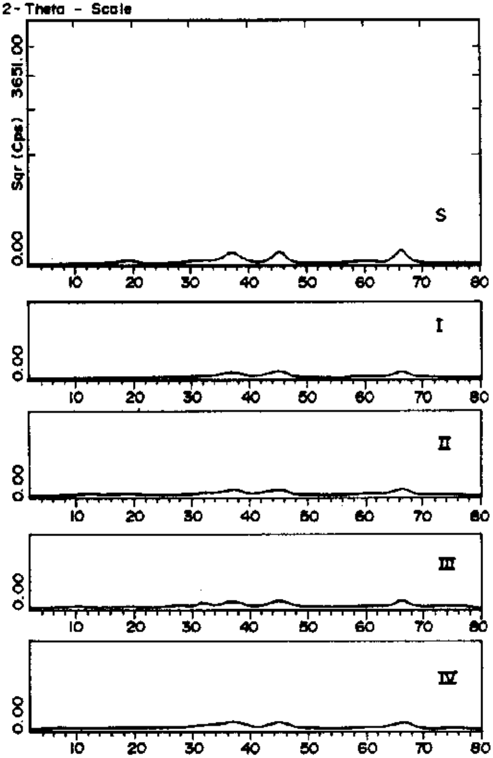

Fig. 3. X-ray diffraction patterns for catalyst series S, I-IV.

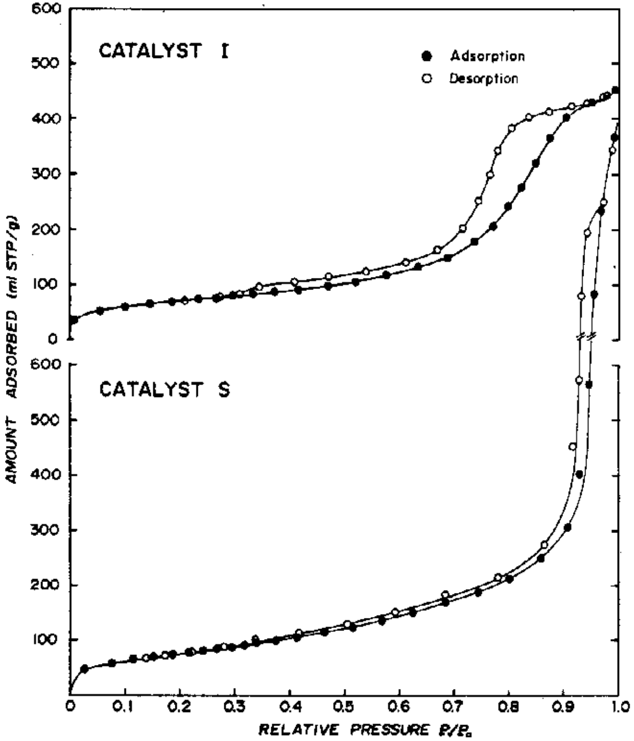

Fig. 4. Nitrogen isotherm at -195°C for catalysts S and I.

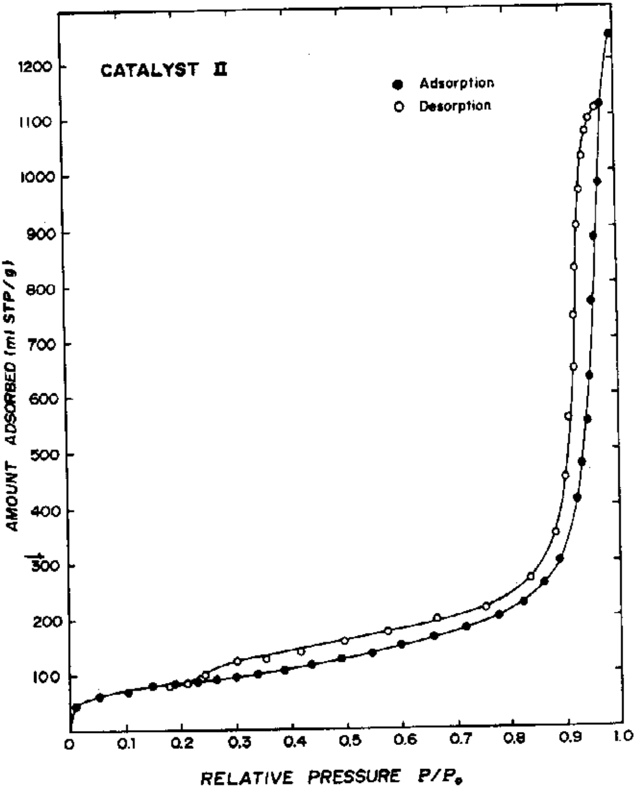

Fig. 5. Nitrogen isotherm at -195°C for catalyst II.

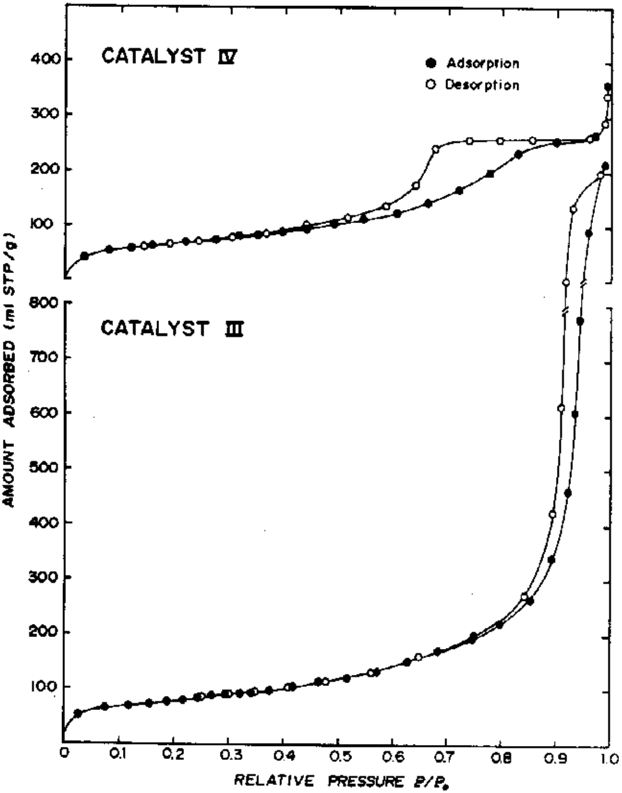

Fig. 6. Nitrogen isotherm at -195°C for catalysts III and IV.

Table 2. Surface characteristics of S, I, II, III and IV

Catalyst sample	BEC C-constant	S_{BET} ($M^{-3}.g^{-1}$)	S_T ($m^2.g^{-1}$)	V_P ($ml.g^{-1}$)	r_H (A°)
S	65	275	272	1.7188	156
I	149	245	252	0.7030	70
II	100	291	290	1.9375	166
III	101	282	272	1.7188	152
IV	51	255	250	0.5625	55

The specific surface areas of various catalysts were calculated from the linear plots of the BET equation which was satisfactorily obeyed in P/P_0 range between 0.05-0.35. The data for S_{BET} obtained are given in Table 2. Also included in Table 2 are the total pore volume V_p which were calculated using equation (3) [33].

$$V_p = 15.47 \times 10^{-4}.\ V_{st} \tag{3}$$

where V_{st} is the volume of dinitrogen adsorbed at saturation; and the mean pore radius r_H of various catalysts was also calculated using [34. pp. 18-31].

$$r_H = 2.5\ \frac{V_P}{S_{BET}} \times\ 10^4 \tag{4}$$

For the detection of porosity, de-Boer and his co-workers [10] developed a method which they called the t-method. In this method, a plot between the volume V_1 ($ml.g^{-1}$) of liquid adsorbed, and the thickness t(A) of a non-porous reference sample should give a straight line passing through the origin, with a slope proportional to surface area $S_1(m^2.g^{-1})$ of the solid, according to the relation.

$$S_1\ =\ \frac{V_1}{t}\ \times\ 10^4 \tag{5}$$

De-Boer and co-workers have demonstrated that a deviation from the straight line is associated with the existence of pores in the solid. A downward deviation from the straight line (negative deviation) indicates the present of micropores; their filling by the adsorbate molecules cuts down their surface from further adsorption, while an upward deviation from the straight line (positive deviation) indicates the presence of mesopores in which capillary condensation can take place [35, pp. 189-202], causing the amount adsorbed to increase beyond the straight line in the V_1-t plots.

The S_t values of the catalysts were calculated from the slope of the V_1-t plots. The C-constant of the BET equation was calculated for different catalysts and found to be in the range of 65-149. So the t-curve of de-Boer [10] were used.

Typical Vl-t plots are shown in Fig. 7 for catalysts S, I, II, III and IV and the indicating gained from these plots is that all the catalysts contain mesopores. The comparison of st and SBET shows that these values are very close to each other which justifies the choice of the t-curve for the analysis, and also reveals the absence of ultramicropores.

The impregnation treatment of Ni-Al_2O_3 with ≅1% europium oxide caused a decrease in their adsorption capacities and the total pore volume decreases as well. In the case of catalyst II, the variations in the surface area and total pore volume were detected; this indicates a compensating effect between the pore vacations which leads to an increase in both surface area and total pore volume.

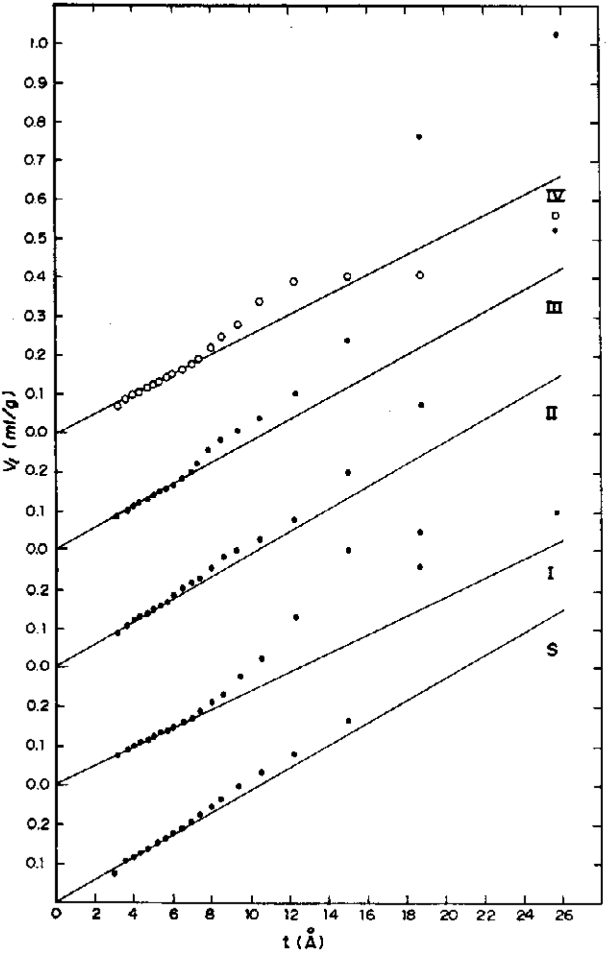

Fig. 7. V_lt plots from N_2 adsorption on catalyst sample 0–4% Eu_2O_3 doped on Ni-Al_2O_3.

When the europium oxide content increases catalysts III and IV, a continuous decrease in both surface area and total pore volume was obtained Fig. 8. It is apparent that impregnating accelerates the rate of loss of both surface area and pore volume.

The main conclusions drawn from pore structure analysis on nickel-alumina catalysts doped with europium oxide is, when the sample is mostly mesopores, the blocking of certain pores (or pore entrance), especially when the sample exhibits a type IV adsorption isotherm, lead to a decrease in the total pore volume so in the mean pore radius Fig. 8.

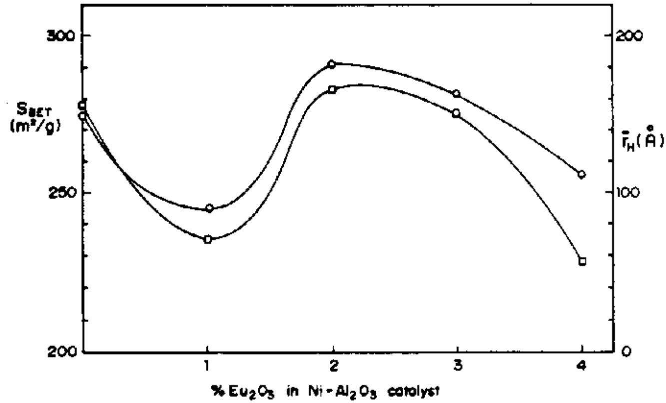

Fig. 8. Variation of S_{BET} and r_H with the percentage of doping of Eu_2O_3 on Ni-Al_2O_3 catalyst.

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دراسات على حافز النيكل ـ الألومنيوم للهدرجة المغمور بأكسيد اليوروبيوم
١ ـ مساحة السطح والتركيب المسامي

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(سُلِّم في ٤ صفر ١٤١٥هـ؛ وقُبل للنشر في ١٥ محرم ١٤١٦هـ)

ملخص البحث. دُرس أثر أكسيد اليوروبيوم على الحافز المستعمل واستعملت كل من الأشعة السينية والتحليل الحراري التفاضلي، وحُسبت القياسات التركيبية من نتائج امتزاز النيتروجين على السطح عند ٧٧ كلفن.

وأمكن الحصول على حوافز غير متبلورة نتيجة غمر حافز النيكل ـ الألومنيوم بأكسيد اليوروبيوم وتجفيفه عند ٣٨٣ كلفن، ومن تحليله حراريًا عند ٧٧٣ كلفن. ودلّت نتائج التحليل الحراري التفاضلي لخليط الكربونات على حدوث تفكك إلى أكاسيد ماصة للحرارة.

وأدى ذوبان اليوروبيوم الثلاثي في شبكة الحافز عند نسبة من الأكسيد حوالي ١٪ إلى انخفاض ملحوظ في المساحة السطحية، وحجوم المسامات وأقطارها، في حين حدث عكس ذلك عند حوالي ٢٪، ووُجد أن أثر الانخفاض يحدث مرة أخرى عند النسب الأعلى من هذه النسبة. وتأخذ حجوم المسامات وأقطارها اتجاه المساحة السطحية نفسه لكل هذه الحوافز سواءً المغمورة أو غير المغمورة. وأظهرت القياسات قبل الغمر وبعده تغيرات واضحة في معدّل أقطار المسامات تراوحت بين ٥٤ و ١٦٦ انجستروم.