BET Surface Area Analysis of Nickel Catalyst on Thoria Modified Silica Support

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Summary: BET surface area has been determined for 3% and 10% Ni catalyst on thoria modified silica support. The Th/Si mole ratios are 0, 0.0036, 0.0061, 0.0154, 0.031, 0.049 and 0.071. The BET area is calculated from nitrogen desorption method using a mixture of 30% nitrogen and 70% helium as a carrier gas in thermal conductivity detector of a gas chromatograph. The BET area of pure dried support is 239 m^2/g and that of thoria modified dried support ranges from 226 m^2/g to 167 m^2/g. The calcined ThO_2/SiO_2 support gives BET area from 231 m^2/g to 181 m^2/g. In 3% Ni loaded support the area ranges from 222 m^2/g to 164 m^2/g while in 10% Ni loaded support the area decreases from 208 to 156 m^2/g. 3% loaded Ni is a better catalyst.

Introduction

Catalyst versatility of nickel is well known [1-5]. Since most metals used in catalysis are costly like Pt, Pd, Rh etc., the catalyst is not used in pure metallic form, it is spread (dispersed) on an inert support to increase active area. This technique is also used with nickel for more catalytic area. The inert supports are usually alumina, charcoal, silica, zirconia etc. [1-5]. The metal is thus highly dispersed throughout the pore system of support. Catalytic rate primarily depends upon the available active surface [6-8]. Pore structure affects surface access, surface stability and resistance to poisoning and selectivity as well as to heat transfer [6,7]. Therefore a good understanding of catalyst behaviour should start from information with surface area and pore structure. Some time additives like rare earth and actinide metal oxides are often added in nickel, cobalt or iron based methanation and Fisher-Tropsch catalysts. Those additives change the properties of supported metal catalysts [9]. There are many methods of surface area determination, but the most popular and useful one is the use of BET equation [6,10]. The present work is concerned with BET surface area determination of nickel catalyst on thoria modified silica support. The measuring method consists of passing a mixture of nitrogen and helium through a glass cell containing the sample. The cell is immersed in liquid nitrogen which causes the nitrogen in the mixture to be adsorbed by the sample. When adsorption is complete, removal of sample from liquid nitrogen causes desorption to occur. The desorbed nitrogen produces a signal in thermal conductivity detector that is proportional to the volume of nitrogen that is desorbed. The signal is integrated in a digital integrator which has been previously calibrated.

Experimental

(a) Chemicals

(1) Aerosil 200: Degussa Corporation, Pigment Division, N.J., U.S.A. for silica support.

(2) Thorium nitrate $Th(NO_3)_2.\ 6H_2O$ and nickel nitrate $Ni(NO_3)_2.\ 6H_2O$, Fisher certified ACS for Ni catalyst.

(b) Preparation of Silica Support

The support was prepared in crucibles. The porcelain crucibles were obtained from Coors (Cat. No. 60110 with cover Cat. No. 60126) U.S.A. The crucibles were used ones and were cleaned by carbide paper. These were then washed with deionized and distilled water and dried in an oven. A small amount of Aerosil 200 was transferred to a crucible and enough amount of water was added to make a slurry. During slurry making the slurry was vigorously mixed and rubbed against the wall and bottom of crucible with a spatula till the paste was uniform and homogeneous. The process of addition of Aerosil 200 and water continued till the paste was uniform and homogeneous and crucible was filled to three-fourth of its capacity. Seven crucibles were prepared in this manner. These crucibles were dried for 24 hours in an oven at 100-120°C. The

material was then calcined at 500°C for 8 hours in a furnace. The calcined material was powdered thoroughly by spatula against the wall and bottom of crucible. This was a support material SiO_2.

(c) Modification of support

For modification of support the thorium contents were varied to produce Th/Ni atomic ratios which were chosen to correspond to those of the Ni_x Th_y intermetallic compounds which have been studied before [11]. For this purpose first Th/Si ratios were selected and samples were prepared according to Table 1.

Table 1: Amount of SiO_2 and $Th(NO_3)_4$. $4H_2O$ needed for different samples of thoria modified silica support.

Sample No.	Th/Si (moles)	SiO_2 g	$Th(NO_3)_4.4H_2O$ g
0	0	0	
1	0.0036	6.288	0.2080
2	0.0061	6.104	0.3424
3	0.0154	5.207	0.7368
4	0.0310	4.668	1.3299
5	0.0490	4.601	2.0718
6	0.0710	4.667	3.0448

For sample No. 1 pore volume (0.8 ml/g) was calculated which was (0.8 ml/g) x 6.288 = 5.0304 ml. 0.208 grams of $Th(NO_3)_4$. $4H_2O$ was weighed in a crucible and it was dissolved in 5 ml (5.0304 ml) of distilled and deionized water completely by constant stirring with spatula. 6.288 g of SiO_2 was then transferred to it and quick mixing was done. The time of mixing was rapid and duration of mixing was noted. It was 5 minute. This procedure was repeated for other samples (2 to 6 of Table 1). The samples were immediately transferred to oven after 5 minutes of mixing. These were dried in that oven for 24 hours.

The samples prepared in this manner were divided into 3 part as follows:

(i) One-third were kept for future reference.

(ii) The rest were calcined at 400°C in a furnace for 8 hours.

Calcined samples were further subdivided into equal parts for the following:

(i) 3% Ni loading

(ii) 10% Ni loading

(d) Loading of nickel catalyst on thoria modified support.

$Ni(NO_3)_2$. $6H_2O$ weight was calculated for 3% and 10% (by weight) Ni as catalyst. Pore volume was (0.8 g/ml). Table 2 and Table 3 give weight of $Ni(NO_3)_2$. $6H_2O$.

Table 2: Weight of $Ni(NO_3)_3$. $6H_2O$ for 3% nickel on thoria modified silica support.

Sample No.	Sample ThO_2+SiO_2 g	SiO_2 g	Pore volume ml	$Ni(NO_3)_2.6H_2O$ g
0	1.6620	1.6620	1.4	0.2470
1	1.7645	1.7372	1.4	0.2581
2	1.6300	1.5875	1.3	0.2359
3	1.2537	1.1742	1.0	0.1745
4	1.1679	1.0279	0.9	0.1527
5	1.3522	1.1127	1.1	0.1653
6	2.0600	1.5701	1.7	0.2333

Table 3: Weight of Ni $(NO_3)_2$. $6H_2O$. for 10% Ni catalyst on thoria modified support.

Sample No.	Sample ThO_2+SiO_2 g	SiO_2 g	Pore volume ml	$Ni(NO_3)_2.6H_2O$ g
0	2.3426	2.3426	1.9	1.1605
1	2.1350	2.1019	1.7	1.0413
2	1.9380	1.8874	1.6	0.0413
3	1.5872	1.4866	1.3	0.7365
4	1.3950	1.2277	1.1	0.6082
5	1.7525	1.4421	1.4	0.7144
6	1.0900	0.8308	0.9	0.4116

For sample No. 0 for 3% Ni from Table 2. 0.2470 g of $Ni(NO_3)_2.6H_2O$ was dissolved in pore volume of 1.4 ml of distilled and deionized water in a crucible by stirring with a spatula. 1.6620 g of sample of SiO_2 was then mixed with $Ni(NO_3)_2$. $6H_2O$ solution. The mixing was immediate, vigorous and continued for 6 minutes. The sample was then put in oven for 24 hours at 110 - 120°C. This process was repeated for all 3% Ni samples. The samples were then calcined at 400°C in a furnace for 8 hours. Similar procedure was then repeated for 10% Ni samples.

BET area measurements

The apparatus used was Beta Scientific Corporation Automatic Surface Area Analyser Model 4200. This instrument uses a mixture of 30% nitrogen and 70% helium as carrier gas. About 0.1g of sample is taken in a cell which is heated to 300°C for about 30 minutes to remove any dissolved gas. The cell is then cooled in liquid nitrogen and

nitrogen (30%) of carrier gas is adsorbed in it for 60 s. The meter which is calibrated by standard γ-alumina sample gives adsorbed area. In desorbed mode the sample is removed from liquid nitrogen temperature and is allowed to warm up. Nitrogen is desorbed at room temperature. 60s wait time is needed for desorb signal to appear on meter. Actually the surface area is desorbed area. Specific surface area or BET area is calculated from formula.

$$\text{Specific surface area} = \frac{\text{Desorbed surface area of meter}}{\text{weight of sample}} \quad \ldots\ldots (1)$$

Results and Discussion

The results of BET area of 3% Ni and 10% Ni on thoria modified silica support using Beta Scientific Corporation Model 4200 Automatic Surface Area Analyser and Eq. (1) are given in Table-4.

Table 4: BET surface area of 3% and 10% Ni catalyst on thoria modified silica suppot.

Sample No.	Th/Si ratio	Dried* ThO_2/SiO_2	Calcined** ThO_2/SiO_2	BET Area m^2/g 3% Ni on** ThO_2/SiO_2 #	10% Ni on** ThO_2/SiO #
0	0	239	231***	222	208
1	0.0036	226	216	214	196
2	0.0061	219	211	208	192
3	0.0154	204	202	193	180
4	0.0310	197	190	180	174
5	0.0490	175	184	171	165
6	0.0710	167	181	164	156

* These samples were dried at 110-120°C for 24 hours.

** These samples were calcined at 400°C for 8 hours.

*** The support (non-modified) samples were calcined at 500°C for 8 hours.

These contain NiO a catalyst in oxide form.

The result of calcined support, 3% Ni loaded, 10% Ni loaded on calcined thoria modified support are shown in Fig. 1. In dried support the maximum area is 239 m^2/g for silica support and it decreases as thorium content is increased. In calcined support the maximum area is 231 m^2/g and it decreases less slowly as thorium content is increased. Calcination has some effect on pore size. Besides these drying

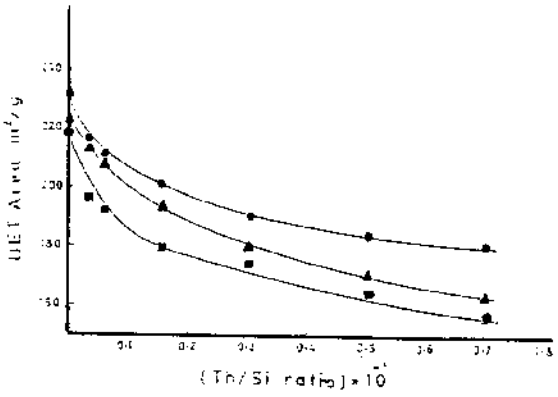

Fig.1: BET area m^2/g) against Th/Si mole ratio for (●) thoria modified calcined silica support; (▲) 3% Ni loaded on thoria modified silica support; (■) 10% Ni loaded on thoria modified silica support.

in fact does not produce pure ThO_2 and SiO_2. Some $Th(NO_3)_4$ and hydrated silica remains and this is the main reason of abrupt decrease in area as thorium content is increased. The area decreases further as 3% Ni is loaded on the modified support from 222 m^2/g to 164 m^2. 10% Ni loading further decreases the area from 208 to 156 m^2/g. 10% Ni is in fact not a good composition for this catalyst. Its behaviour is not that of monolayer as is seen from X-ray and ESCA studies [12]. From the area measurements 3% Ni appears to be better catalyst than 10% Ni loaded catalyst.

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