EFFECT OF CALCINATION TEMPERATURE ON NICKEL/ALUMINA CATALYSTS

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Alumina-supported nickel catalysts prepared by the methods of impregnation and coprecipitation and heated at four different temperatures showed that the optimal calcination temperature for both types of catalysts lies in the region of 623 – 673 K. Crystallite size measurements by XRD revealed that coprecipitated samples have larger crystallites than the impregnated samples. The total surface areas measured by nitrogen adsorption and the results of metal area measurements made by hydrogen adsorption are in agreement with the crystallite size results.

Nickel metal dispersed on an oxide support such as alumina is used in various industrial processes as a hydrogenation catalyst. When the catalyst is made, the nickel is present as nickel oxide which is reduced in the plant with hydrogen.

Different preparation variables which can have an effect on the properties of the catalyst are: method of preparation (impregnation, precipitation or coprecipitation); calcination temperature and time; temperature and duration of reduction; presence of chloride or sulfide ions; compounding the conventionally used support, alumina, with other basic oxides.

Bridger and Woodward[1] investigated the basic requirements for the production of a satisfactory nickel-based catalyst. They studied the effect of calcination temperature on the methanation activity of Al_2O_3/MgO supported impregnated nickel catalysts reduced at 300 °C. They found that maximum activity was obtained for a catalyst calcined at 250 °C and the activity decreased with increasing calcination temperature. Kruissink et al.[2] examined the preparation and pretreatment of a series of coprecipitated nickel/alumina catalysts for methanation at high temperature. They studied the effect of the following variables on the properties of the final catalyst: Ni/Al ratio, the pH of precipitation, the type of metal salt used and temperature of reduction. They concluded

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that the Ni/Al ratio in the final catalyst should be between 2 and 3 and that the pH of precipitation should be between 6 – 7. They also noted that the optimal temperature of calcination is 723 K.

Despite the above mentioned studies of preparation variables of the nickel hydrogenation catalyst, need for further research in this area is strongly felt.

The scope of the present work is the characterization of the catalysts prepared by impregnation and precipitation and subjected to different calcination temperatures. The properties evaluated are BET and metal surface areas and the crystallite size of nickel oxide.

EXPERIMENTAL

Materials

Gamma-alumina was obtained from Merck; nickel and aluminium nitrates and sodium carbonate were obtained from BDH. Nitrogen from Bangladesh Oxygen Ltd. was of high purity (99.9+%) and moisture free. He and H_2 from Air Products, U.S.A. were of 99.5+% purity.

Catalyst Preparation

Two methods were used to prepare the supported nickel catalysts. The concentration of nickel in both types of catalysts was 10% by weight.

1) Wet impregnation. The support was suspended in an aqueous solution of nickel nitrate. The slurry was stirred continuously, its temperature being maintained at 343 K. After the surface water had evaporated, the preparation was dried at 393 K for 2 h.

2) Coprecipitation. Aqueous solutions of nickel and aluminium nitrates were mixed in the relative amounts necessary to obtain the desired nickel loading in the final catalysts. To this solution, an aqueous sodium carbonate solution was added dropwise at room temperature with constant and uniform stirring. The amount of Na_2CO_3 added corresponded to that necessary to have a final pH of about 7. After standing for 24 h at room temperature, the hydrogel obtained was filtered and washed repeatedly with deionized water to remove residual Na^+ ions. The precipitate was dried at 393 K for 2 h.

Dried precipitates and impregnated supports were calcined in air for 16 h at different temperatures, ranging from 523 K to 673 K. The temperature was always gradually increased taking 1 h up to 523 K and further 30 – 60 min up to the final temperature. Finally, the calcined catalysts were allowed to cool to room temperature in a flow of air.

Catalyst Characterization

Eight separate catalysts were obtained by the above two methods of preparation at four calcination temperatures. Each catalyst was characterized by the following methods.

A) X-Ray diffraction measurement. Diffraction patterns of all the catalysts have been recorded after their calcination in air at respective calcination temperatures. X-Ray powder patterns were recorded using CuKα (λ = 0.154 nm) radiation generated at 30 kV and 15 mA on a Philips JA-12191 X-ray diffractometer. The crystallite size of nickel oxide in the catalysts was calculated from the diffraction patterns.

B) Surface area measurement. The BET surface areas of the catalysts were measured using a dynamic method of nitrogen adsorption at 77 K employing Flowsorb-II 2300 of Micromeritics, U.S.A. The value of the cross-sectional area of adsorbed N_2 molecule was taken as 0.162 nm^2.

C) Nickel surface area. Nickel surface areas of the catalysts were measured by hydrogen chemisorption at 370 K using the pulse technique. About 100 – 200 mg of each catalyst were weighed accurately in a U-shaped tube and loaded into the Flowsorb apparatus. The temperature was raised to 673 K in He flow and held for 15 min. The catalyst was then reduced in hydrogen flow for 6 h. Helium was then passed over the catalyst again for 15 min, and the sample was cooled to room temperature in a flow of He. The flow rate of 20 cm^3 min^{-1} was used for both the gases. Measurement was started soon after cooling. Pulses of hydrogen (0.5 ml) were injected via an injector valve with an interval between 2 and 3 min until the amount of exit H_2 as shown by the thermal conductivity detector (TCD) output reached a steady value; two more pulses were injected to confirm the steady value. Integration of TCD output signal determined the total H_2 uptake by the catalyst, from which the metal surface area was calculated taking a value of 0.065 nm^2 for the cross-sectional area of adsorbed atom of hydrogen and a stoichiometry of H : Ni = 1 : 1. Calibration of the injection volume was achieved by injecting the pulses of known volume of H_2 into the gas upstream of the detector.

RESULTS AND DISCUSSION

Crystallite Size

Crystallite size of nickel oxide in the calcined samples of the impregnated and coprecipitated catalysts were obtained from X-ray diffraction line broadening and were ± 10% reproducible.

Table I shows that for catalysts of both types, the crystallite size of nickel oxide increases with calcination temperature up to 623 K. The crystallite size of both

TABLE I
Effect of calcination temperature on NiO crystallite size, BET (S_{BET}) and nickel surface area (S_{Ni})

Sample	Calcination temperature, K	Crystallite size, nm	S_{BET} m^2/g	S_{Ni} m^2/g
		Impregnated samples		
I-41	523	16.9	94.1	2.9
I-42	573	21.1	97.2	4.4
I-44	623	22.5	96.1	6.3
I-45	673	20.1	102.0	2.8
		Coprecipitated samples		
P-12	523	27.8	54.3	1.1
P-16	573	28.7	52.4	0.9
P-11	623	29.8	52.5	1.0
P-15	673	26.9	53.4	0.9

impregnated and coprecipitated catalysts calcined at 673 K is lower than that of the corresponding samples calcined at lower temperatures. This behaviour, although unexpected, points to the existence of an optimum calcination temperature for both types of the catalysts. Such an optimum temperature, seems to lie in the 623 – 673 K region. This kind of behaviour has not yet been reported in the literature. Bridger and Woodward[1] found increasing crystallite size on increasing the calcination temperature over 573 – 773 K for the nickel oxides supported on alumina either singly or compounded with magnesium oxide. Kruissink et al.[2] stated that the optimal tempe- rature was 723 K. However, it is not clear from their work whether the crystallite size of the samples calcined at higher temperatures was lower compared to those calcined at 723 K. The behaviour observed in this work can be explained by formation of $NiAl_2O_4$. The samples calcined at 673 K are likely to have a larger proportion of $NiAl_2O_4$ than the samples calcined at lower temperatures, since $NiAl_2O_4$ formation is favoured at the higher temperatures. It is well known that $NiAl_2O_4$ is more difficult to reduce than the oxide itself. This is because the nickel atoms in $NiAl_2O_4$ are surrounded by oxygens of the alumina lattice and hence rendered less reactive. By similar reasoning, $NiAl_2O_4$ can provide resistance to crystal growth. In such a case, with the larger fraction of $NiAl_2O_4$ in the catalyst, the average crystallite size as measured by X-ray diffraction would be lower than in the samples calcined at lower temperatures, in which the $NiAl_2O_4$ fraction is smaller. This may happen when $NiAl_2O_4$ is interspersed between the nickel oxide crystallites, thereby preventing coalescence of the latter. The degree of such resistance to sintering will be the higher, the larger the fraction of $NiAl_2O_4$ will be in the catalyst. The observed lower crystallite size for the samples calcined at the high temperature (673 K) then seems reasonable.

Table I further shows that coprecipitated samples have larger crystallites than the corresponding impregnated samples. This is consistent with the total surface area results presented below.

BET Measurements

Table I shows that the total surface areas of both types of the nickel oxide catalysts are virtually independent of the calcination temperature. The surface area of the copre- cipitated samples are about fifty per cent of those of the impregnated catalysts. This is not unexpected since in the impregnated catalyst the support material is highly porous whereas such a porous structure may not be readily obtained when employing the coprecipitation technique. Although the porous structure of the coprecipitated catalyst depends mainly on the conditions of precipitation and aging and can be controlled, no such measure was taken except for the pH of the solution which was maintained at 7. The total surface area results are consistent with the crystallite size data which show that the crystallite size of coprecipitated samples are about 1.5 times higher than those of the impregnated samples.

Clearly, the larger the crystallites of nickel oxide in the catalyst, the smaller the contribution of these oxides to the total surface area, for a given concentration of nickel in the catalyst.

Nickel Surface Area

It is seen from Table I that the impregnated sample calcined at 623 K (sample I-44) has the maximum metal surface area. This is consistent with data on crystallite size which show that the sample calcined at the higher temperature 673 K (sample I-45) has the lower average crystallite size. One can presume that the extent of formation of $NiAl_2O_4$ in I-45 is higher than in I-44 so that the latter sample has relatively lower fraction of NiO area available for the dispersion of the metal. As a result, the free metal area of the sample I-45 is lower than that of the sample I-44. The trend in metal areas for samples I-41 to I-44 in Table I is consistent with the crystallite size data. No such trend was observed for the coprecipitated samples, their metal surface areas being substantially lower than those of the impregnated samples. The nickel surface area measurements were reproducible to within ± 6%.

CONCLUSIONS

The results of the present study indicate that the optimum calcination temperature for the coprecipitated and impregnated nickel/alumina catalysts lies in the region of 623 – 673 K. The coprecipitated samples have larger crystallites and the smaller total and free-metal areas than the corresponding impregnated samples. The BET and metal area values are consistent with crystallite size data.

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