

Structural and textural properties of some supported nickel catalysts

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Received 22 September 1992; revised and accepted 29 July 1993

Nickel/alumina, nickel/alumina-chromia and nickel/chromia supported catalysts have been prepared by impregnation method. The DTA and X-ray techniques have been used to investigate the influence of the support on the formation of the active phase. It is found that alumina, alumina-chromia and chromia affect the formation of nickel oxide and/or nickel metal. The surface areas and pore structures have been determined using low temperature nitrogen adsorption technique. The results indicate that the addition of nickel to alumina, alumina-chromia and chromia changes the textural properties of the supports. Nickel promotes both activation and sintering of the supports.

The surface properties of heterogeneous catalysts have been studied extensively¹⁻³. However, the surface state of an impregnation catalyst which has important effects on the catalytic activity, selectivity and reaction mechanism is in general complex and still indefinite: the nature of the catalyst surface strongly depends upon the kind of support^{4,5}, the method of preparation of the catalyst⁶ and the preparation conditions⁷.

Supported metal catalysts are technologically an extremely important class of catalysts^{8,9}. The primary aim in the preparation of these catalysts is to achieve maximum dispersion of the active phase on the support material and to stabilize this dispersion during heat treatment and catalytic conditions. Supported nickel catalysts are effective catalysts in hydrogenation - dehydrogenation reactions¹⁰ as well as in the hydrogenolysis of alkanes¹¹. The earlier works¹³⁻¹⁵ presented studies of structural and catalytic properties of some supported nickel catalysts, but relatively little work has been devoted to the effect of the kind of oxide support on the textural and catalytic properties of supported nickel catalysts and hence the title investigation.

Materials and Methods

Pure alumina gel was prepared by precipitation with dropwise addition of ammonium hydroxide (1M) and hydrated aluminium nitrate (1M) at pH 8 and temp. 70°C. The precipitated gel was washed thoroughly until it was free from nitrate ions. The same procedure was followed for the preparation of

pure chromia from chromium nitrate. Coprecipitated Al₂O₃-Cr₂O₃ support containing 50% wt Cr₂O₃ was prepared from the mixed aluminium nitrate and chromium nitrate solutions under the same conditions as those for pure oxide preparation.

Ni/Al₂O₃, Ni/Al₂O₃-Cr₂O₃ and Ni/Cr₂O₃ catalysts with different nickel content were prepared by impregnating the gel with nickel nitrate solution. The resulting slurry was evaporated and dried at 110°C for 10h. The solid was then pulverized and screened to particles of size 0.762 cm. The powder was compressed to tablets which were calcined at 500°C for 2h. The calcined solids were reduced by hydrogen at 500°C for 6h at a flow rate of 6 L.h⁻¹.

The differential thermal analysis was carried out using an automatically recording Shimadzu (Model 30-H) analyser.

The X-ray study was carried out using Philips apparatus of the type 1050 PW. The characteristic spacings and the relative intensities were compared with the data in the ASTM cards. The adsorption-desorption isotherms of nitrogen were determined at -196°C using a conventional volumetric apparatus.

In designating the various samples A, AC, C and N stand for alumina, alumina-chromia, chromia and nickel respectively. The arabic numbers 1, 2, 3, 4 and 5 directly following the letter N indicate the nickel contents, 5, 10, 20, 30 and 40 wt % nickel respectively. Thus for example, the designation ACN2 indicates alumina-chromia containing 10% wt nickel.

Results and Discussion

The differential thermal analyses of the samples investigated revealed that physisorbed water is

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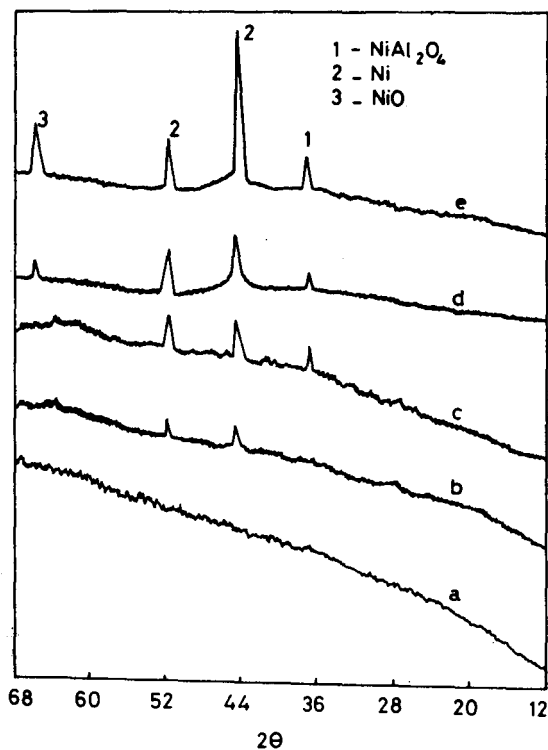


Fig. 1—X-ray diffraction patterns of (a) CN5, (b) ACN2, (c) ACN5, (d) and (e) AN5

removed in the temperature range 90-150°C via endothermic peaks with their minima located around 120°C. Another endothermic effect related to the decomposition of nickel nitrate and removal of water of crystallization was reported in the temperature range 230-260°C. The areas of these particular endotherms depend on the nickel content or on the amount of nickel nitrate used in the impregnation process. The third endothermic effect in the temperature range 300-340°C was assigned to the formation of nickel oxide and partial dehydroxylation of the gels. The dehydroxylation is expected to predominate at relatively higher temperatures. Upto 550°C, no exothermic effects were reported to account for new phase changes. However, this does not imply the absence of new phase formation. Nickel aluminate (low concentration) may start to form 500°C, as indicated from X-ray diffraction patterns. Being of slightly low concentration, undetected thermal changes are expected.

Figure 1 show the X-ray diffraction patterns of some supported nickel catalysts. It is evident, that (i) chromia inhibited crystallization of NiO and/or Ni metal even when the latter is existing in as much as 40% wt, (ii) alumina as a support did not inhibit the crystallization of NiO. The figure shows characteristic lines of NiO and metallic Ni formed on reduction with hydrogen. Moreover, the lines

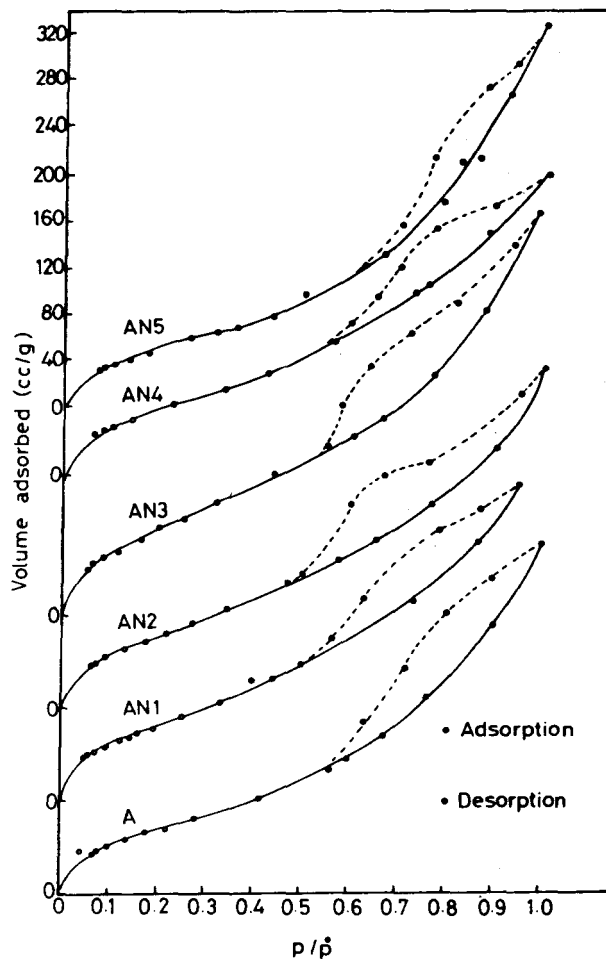


Fig. 2—Adsorption - desorption isotherms of nitrogen at -196°C on Ni/alumina catalysis

characterising nickel aluminate are also found indicating the solid reaction between the two oxides below 500°C. For $\text{Ni}/\text{Al}_2\text{O}_3\text{-Cr}_2\text{O}_3$ catalysts, an intermediate behaviour was found. Thus less intense lines corresponding to NiO, nickel metal and nickel aluminate are existing.

The low temperature adsorption-isotherms were measured for all the samples investigated, namely, pure alumina, pure alumina-chromia, pure chromia, Ni/alumina, Ni/alumina-chromia and Ni/chromia catalysts containing 5, 10, 20, 30 and 40 (%wt) nickel. The adsorption of nitrogen at -196°C was measured on these samples after calcination in air at 500°C and then reduction in hydrogen. Figure 2 shows representative adsorption-desorption isotherms of nitrogen on Ni/alumina-chromia catalysts. Most of the isotherms are type II of Brunauer's classification¹⁶ but in some cases isotherms intermediate between types II and IV were obtained. The desorption branch met the adsorption one at some intermediate relative pressure. The

Table 1—Surface characteristics of the samples

| Sample | S_{BET} m ² /g | S_t m ² /g | S_{cum} m ² /g | S_m m ² /g | S_w m ² /g | V_m ml/g | V_w ml/g | V_{cum} ml/g | V_T ml/g | r Å |
|--------|---------------------------------------|----------------------------|---------------------------------------|----------------------------|----------------------------|---------------|---------------|--------------------------|---------------|----------|
| A | 239.8 | 248.6 | 242.8 | 42.6 | 200.2 | 0.0718 | 0.3384 | 0.0102 | 0.4082 | 34.1 |
| AN1 | 275.2 | 276.0 | 279.8 | 68.3 | 211.5 | 0.1046 | 0.3239 | 0.4285 | 0.4238 | 30.8 |
| AN2 | 290.1 | 288.4 | 287.9 | 74.3 | 213.7 | 0.1053 | 0.3045 | 0.4098 | 0.4179 | 28.8 |
| AN3 | 322.8 | 324.3 | 324.9 | 109.2 | 215.7 | 0.1445 | 0.2857 | 0.4302 | 0.4286 | 26.6 |
| AN4 | 240.8 | 248.7 | 243.5 | 64.0 | 179.5 | 0.0961 | 0.2693 | 0.3654 | 0.3646 | 30.3 |
| AN5 | 208.6 | 211.9 | 215.8 | 44.5 | 171.3 | 0.0851 | 0.3281 | 0.4132 | 0.4113 | 39.4 |
| AC | 212.1 | 210.6 | 215.6 | 174.9 | 215.6 | 0.0812 | 0.3483 | 0.4295 | 0.4294 | 40.5 |
| ACN1 | 232.8 | 236.1 | 235.4 | 106.9 | 235.4 | 0.1985 | 0.1650 | 0.3635 | 0.3555 | 30.5 |
| ACN2 | 206.6 | 206.2 | 218.1 | 142.2 | 218.1 | 0.1079 | 0.2023 | 0.3102 | 0.3223 | 31.2 |
| ACN3 | 198.6 | 191.9 | 188.4 | 141.5 | 188.4 | 0.0809 | 0.2314 | 0.3123 | 0.3134 | 31.6 |
| ACN4 | 175.9 | 173.8 | 174.4 | 136.9 | 174.4 | 0.0625 | 0.2283 | 0.2908 | 0.2877 | 32.7 |
| ACN5 | 164.9 | 168.3 | 165.4 | 135.0 | 165.4 | 0.0655 | 0.2907 | 0.3563 | 0.3584 | 43.5 |
| C | 101.6 | 99.9 | 105.2 | 35.6 | 96.6 | 0.0952 | 0.1862 | 0.2815 | 0.2804 | 55.2 |
| CN1 | 72.1 | 73.3 | 74.4 | 20.1 | 54.3 | 0.0323 | 0.0874 | 0.1197 | 0.1212 | 33.6 |
| CN2 | 50.1 | 49.9 | 48.2 | 11.1 | 37.1 | 0.0196 | 0.0653 | 0.0849 | 0.0857 | 43.2 |
| CN3 | 36.9 | 35.5 | 36.4 | 6.3 | 30.1 | 0.0118 | 0.0563 | 0.0683 | 0.0670 | 36.3 |
| CN4 | 27.3 | 28.1 | 29.5 | 3.6 | 25.9 | 0.0062 | 0.0447 | 0.0509 | 0.0515 | 37.3 |
| CN5 | 16.8 | 17.5 | 18.5 | 1.6 | 16.9 | 0.0031 | 0.0330 | 0.0361 | 0.0358 | 43.4 |

S_m , surface area of micropores, S_w , surface area of wide pores; V_m , volume of micropores and V_w , volume of wide pore.

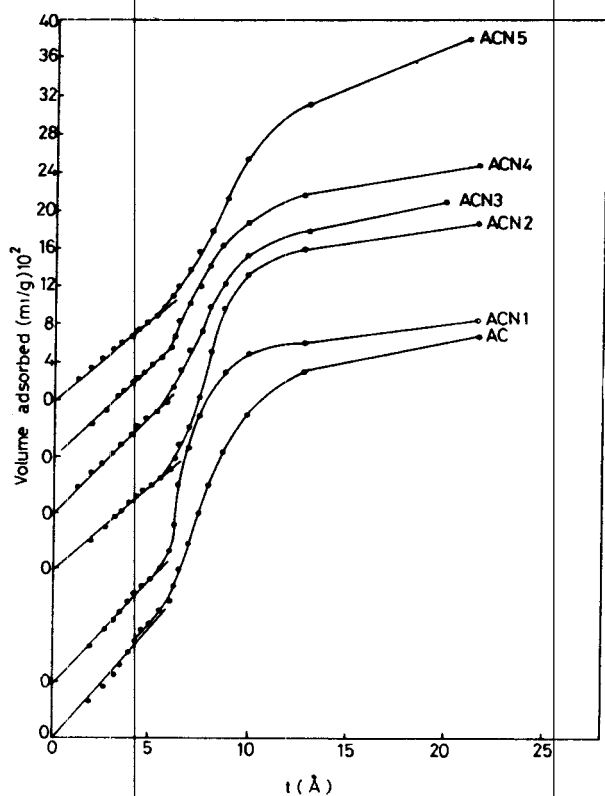


Fig. 3— V_t - t plots of nitrogen adsorbed on Ni/alumina-chromia catalysts

adsorption branches of the isotherms were interpreted in terms of the classical Brunauer-Emmett-Teller (BET) equation¹⁷ and the surface areas were calculated adopting the values of 16.2 Å² for the cross-sectional areas of nitrogen¹⁸. The BET areas are listed in Table 1.

The other two important textural parameters were obtained from the nitrogen adsorption isotherm. One of the two parameters is the total pore volume V_T (ml liquid/g), which is the volume of liquid nitrogen adsorbed at relative pressure very close to saturation. The total pore volume is a measure of total porosity of solid catalyst. The second textural parameter (r) is measured by the relation,

$$r = \frac{2 V_T(\text{ml/g}) \times 10^4}{S_{\text{BET}}(\text{m}^2/\text{g})}$$

where r is a measure of the mean pore radius, i.e., a measure of the average pore size. The values of V_T and r of the investigated samples are given in Table 1.

Some of the earlier workers¹⁹⁻²² have suggested reference t curves for the adsorption of nitrogen. The appropriate t curves for the adsorption of nitrogen on the samples studied were chosen on the basis of the BET-C constants, which in each case should be of the same order of magnitude for both the

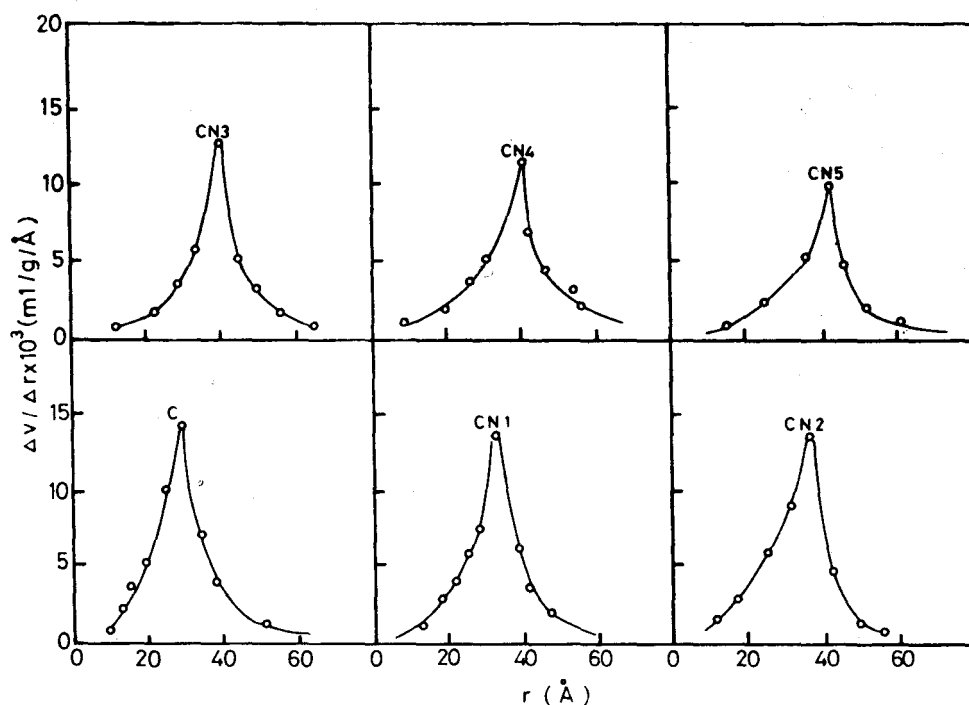


Fig. 4—Pore-volume distribution curves of Ni/chromia catalysts

reference t curve and the samples under investigation. The experimental adsorption curves were plotted as a function of the t values; hence $V_t = f(t)$ instead of $V = f(P/P)$, where V_t (ml g^{-1}) is the volume of nitrogen adsorbed and t (\AA) is the statistical thickness. The slope of the V_t - t plot passing through the origin gives the surface area S_t , according to the equation $S_t = 10^4(V_t/t)$. In addition, the nature of the pores, i.e. mesopores, micropores or a mixture of both, could be demonstrated by application of the V_t - t plots. Figure 3 shows the representative case of V_t - t plots for the Ni/alumina-chromia samples. The indication gained from the V_t - t plots is that all the investigated samples contain mostly mesopores. The V_t - t plots also indicate that these samples contain some microporosity as shown by their initial downward deviations. The microporosity which may exist differs from one sample to another. The percentage of microporosity changes with the chemical composition of the sample as discussed later. The S_t areas for all the investigated samples are shown in Table 1. The S_t and S_{BET} values are in good agreement in the majority of cases. This fact establishes the validity of the proposed t curves. The standard t curves of de Boer *et al.*^{21,23} and Mikhail *et al.*²² for non-porous solids were used.

The meso- and micropore analysis of all the samples under study was carried out using the corrected modelless method²⁴ and the micropore method²⁵ respectively. It was observed that the

parallel plate model can reasonably describe the shape of the pores. The data obtained from the pore structure analysis are also presented in Table 1, where S_{cum} and V_{cum} represent the cumulative surface area and the volume associated with the pores. The S_{cum} values calculated from the parallel plate model varies from the S_{BET} and S_t values. The same is also true for the cumulative pore volume, V_{cum} and the total pore volumes, V_T .

The data from Table 1 therefore revealed that all samples show micro- and mesoporosity. However the percentage surface area occupied by microporosity varies from one to another sample depending on the support and the metal content. For Ni/alumina samples the percentage of microporosity increases with nickel content up to 20% wt and then decreases with further increase in the nickel content. The addition of 5 wt % nickel to alumina-chromia was found to be associated with increase in the surface area and the fraction of microporosity. A further increase in the nickel content was found to cause a decrease in the surface area and microporosity. The situation for the chromia as a support is different. Impregnation with nickel decreased the surface area. The extent of this decrease goes parallel with the percentage of nickel.

Figure 4 gives the representative case of the pore volume distribution curves of Ni/chromia samples. The curves of all the samples are characterised by the presence of one maximum indicating the presence of a

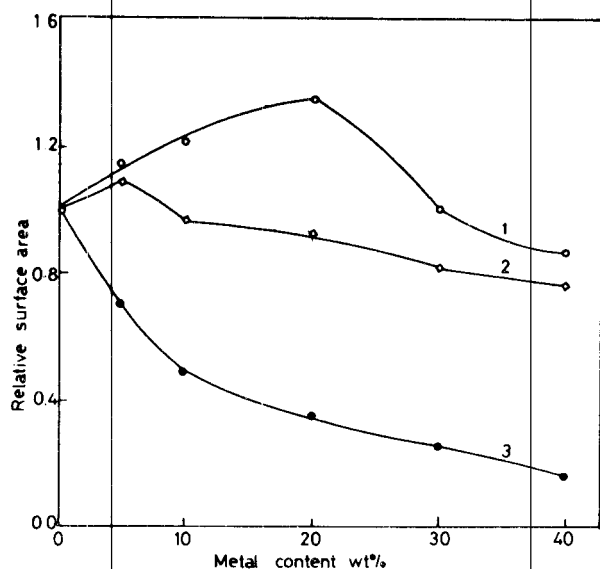


Fig. 5—Variation in the relative surface area with the nickel content: (1) Ni/Al₂O₃; (2) Ni/Al₂O₃-Cr₂O₃ and (3) Ni/Cr₂O₃

large number of pores in a certain size range. Inspection of the pore volume distribution curves could reveal several interesting points which can be summarized as follows:

It was found that the addition of nickel to alumina up to 20 wt % increases the number of pores as indicated from the increase in the height of the maximum. Also the maximum is shifted to lower pore radius values. A further increase in the nickel content is accompanied with a decrease in the number of pores and continuous pore widening.

For Ni/alumina-chromia catalysts with the exception of the catalyst containing 5 wt % Ni, the location of the maximum always shifts to high pore radius values as the nickel content increases from 10 to 40 wt % Ni. Also the height of the maximum was found to decrease with nickel content thus indicating, the decrease of the pore number.

The continuous pore widening and decreasing height of the maxima were the main characteristics of the pore volume distribution curves of Ni/chromia catalysts (Fig. 4).

The dimensions of the pores of all the samples investigated varied within a narrow limit which could not affect either the adsorption properties or the catalytic performance of these catalysts. However, the changes in the surface area brought about by impregnation seems more pronounced. These changes are clarified if we consider the relative surface area, which is expressed as the surface area of the impregnated catalyst divided by the surface area of the corresponding support. Figure 5 shows the relative surface area as a function of the nickel

content. It is evident that impregnation of alumina with nickel increases the surface area. The increase continues up to 20 wt % Ni content. It seems that nickel promotes the activation of alumina which predominates below 500°C. Above 20 wt % Ni, a considerable fraction of nickel reacts with alumina to form low surface area-nickel aluminate and the other parts may exist as NiO and/or Ni metal. The sintering of alumina which predominates above 500°C may be also affected by the presence of NiO and/or Ni metal. Most probably this oxide will also promote the sintering of alumina. This is because activation and sintering process of alumina are both material transport processes sensitive to any additive.

The activation process of chromia predominates at temperature lower than 500°C. The sintering which is associated with a lowering in surface area is expected to increase with the increase of nickel content (Fig. 5). The impregnation of alumina-chromia with nickel nitrate, followed by calcination at 500°C and reduction with hydrogen at the same temperature brought about a small change in the surface area of this mixed support. This is because the increase in the surface area of alumina due to the presence of nickel oxide and/or nickel is more or less balanced by the lowering in the surface area of chromia brought about by the same oxide and/or metal.

In supported metal catalysts, two processes take place during the catalyst treatment. These processes are activation which predominates at low metal content and sintering which predominates on a support with small surface area and/or when the support is highly loaded. The activation process is associated with an increase in microporosity, creation of new pores as evident from the change in S_m (Table 1), change in the pore volume distribution curves and consequently an increase in the surface area. The second process leads to a decrease in surface area. In addition, high metal content can also lead to some pore blocking as evident from the decrease in the height of the pore volume distribution curves of highly loaded metal catalyst. This is also true for supports with small surface areas (chromia).

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