

CORRELATIONS AMONG THE PROPERTIES OF NICKEL ON ALUMINA CATALYSTS AND THEIR PERFORMANCE IN THE HYDROGENATION OF UDEX RAFFINATE

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(Communicated by Prof. S. K. Bhattacharyya, F.N.A.)

(Received 29 November 1973; after revision 10 September 1974)

Several nickel on alumina catalysts including two commercial ones were characterised for their textural properties, chemical composition and reducibility in hydrogen. The influence of the temperature of calcination of the alumina supports and their sodium content on the reducibility of the finished catalysts is shown. The catalysts were tested in a micro-reactor for the hydrogenation of trace olefins in udex raffinate and were found to have high initial activity. Most of them, however, lacked activity-stability. Of different factors which may be responsible for the lack of activity-stability of the catalyst, it is likely that oxygen impurities (as glycol and water are used in the udex process) present in the raffinate slowly poison the nickel sites, thereby bringing down the activity of the catalyst.

INTRODUCTION

After extraction of aromatics from catalytic reformat by the Udex process (cf. Grote 1958; and Owan 1962), the raffinate contains paraffins and small amounts of cycloparaffins and olefins. This udex raffinate from an industrial plant was found to contain about 2.5 to 3.0 per cent olefins corresponding to a bromine number of 5.0 to 5.8 (or bromine index of 5000–5800). A selected cut of this can be used as food-grade hexane solvent, if its olefin content could be reduced to less than 0.5 per cent by hydrogenation.

Supported noble metal catalysts (Pt or Pd catalysts), sulphided Co-Mo catalysts and reduced nickel catalysts are the three important catalyst systems well-known in literature for such hydrogenation. The noble metal catalysts are costly and the sulphided Co-Mo catalysts require higher temperature (250–350°C) of operation. The latter also require the presence of sulphur compound in the feed to maintain the sulphided state of the catalyst. Supported nickel catalysts, on the other hand, are cheaper and are known to operate at low temperatures for such hydrogenation (Bond 1962). Studies were, therefore, carried out with several nickel catalysts to hydrogenate this small amount of olefin in udex raffinate.

EXPERIMENTAL

(a) *Catalyst preparation* : Catalytic activity of supported nickel catalysts varies with the kind of carrier and the method of preparation. In this study, the catalysts used were all nickel on alumina type. These included two commercial catalysts used

in other hydrogenation reactions and several samples prepared in the authors' laboratory. In preparing the samples three aspects were considered : (i) conditioning the alumina support at proper calcination temperature, (ii) maintaining optimum sodium content to facilitate reduction, and (iii) dispersion of nickel salt and its conversion to an easily reducible state.

The alumina supports were prepared by neutralizing sodium aluminate with dilute nitric acid, extruding them in drying gel state and then calcining in muffle furnace at appropriate temperatures. Variation in physico-chemical properties was achieved by controlling several preparation parameters such as temperature of mixing, pH of the mixture, agitation time, ageing time, washing etc. The support was then impregnated with nickel nitrate solution to obtain a nickel content of 9–12 per cent by weight in the finished catalyst.

(b) *Physico-chemical characteristics* : Surface area of the samples was determined from nitrogen adsorption isotherm at liquid nitrogen temperature by BET method. Combining the data available from the total nitrogen adsorption-desorption isotherm and 1000 kg—pressure mercury porosimeter, the total pore volume and the distribution of this volume among pores of different diameters were computed.

Reducibility to metallic nickel was determined by the Fischer thermogravimetric analyzer (1 mg/mV full scale recorder deflection). A linear heating rate of 5°C/min. and a hydrogen flow rate of 50 ml/min. were maintained throughout. Blank runs were done under identical conditions without the flow of hydrogen to account for any loss of weight due to thermal decomposition of salts or hydroxides. Reducibility is expressed as percentage of the total nickel oxide reduced to metallic nickel at any temperature.

Nickel content of the samples was estimated by conventional dimethyl glyoxime method and sodium estimation was done in a flame photometer.

(c) *Activity tests* : Activity screening of the catalysts was carried out in a micro catalytic reactor of 10 mm diameter, having a bed length of 9 cm. Catalyst particles of size 16–20 mesh (~1 mm) were packed to a volume of about 7 ml in the reactor. A flow-sheet of the microunit is given in Fig. 1. Characteristics of udex raffinate used as feed material are given in Table I. The initial activity tests and the longer runs were conducted at 15 kg pressure, at LHSV of 5 hr⁻¹ and at a temperature of 150°C with gas to oil ratio of 100 l/l. The effect of temperature on activity was studied in the range of 75–150°C. The extent of hydrogenation of the olefins was determined through estimation of the bromine index of the product.

RESULTS AND DISCUSSION

The textural properties such as surface area and total pore volume of the support aluminas are given in Table II. Results on reducibility and catalytic activity along with the nickel and sodium contents in each catalyst sample are presented in Table III.

Some influence of the method of preparation of the support on properties is evident from Tables II and III. Presence of sodium in alumina is well known to bring about marked changes in the texture of the catalyst (Plank & Drake 1947) Considering the series 202 B to 202 D, where the temperature of calcination was

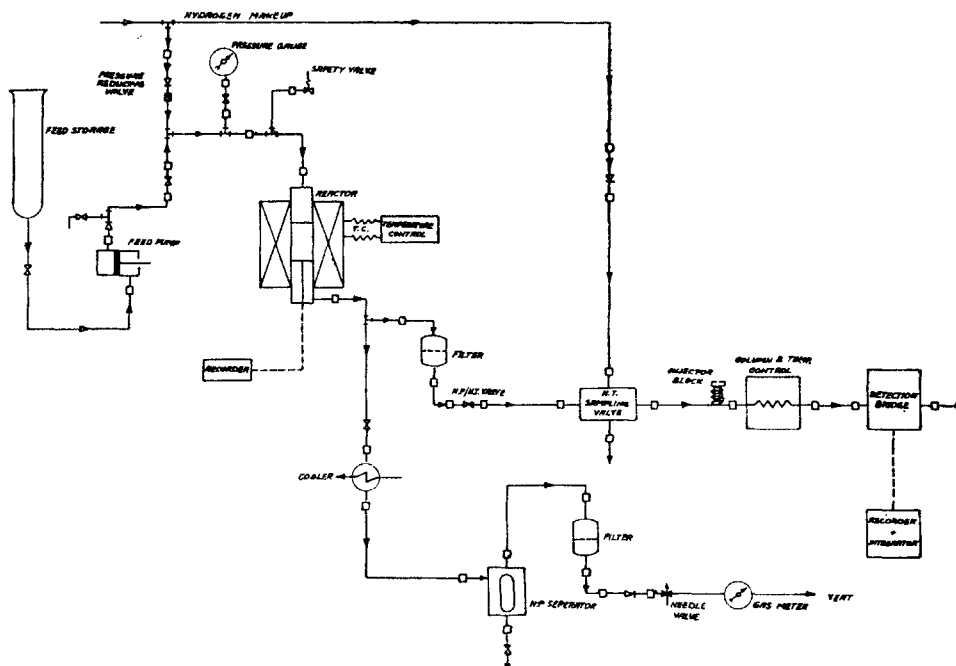


FIG. 1. Flow-sheet of Microunit used for the dehydrogenation studies.

TABLE I

Characteristics of feed material used

Density at 20°C	: 0.6726 g/ml
Sulphur	: 9 ppm
Bromine index	: 5800
Boiling range	: 54 — 80°C
<i>Component analysis</i>	<i>% vol. by G.C.</i>
(a) Saturates	: 99.12
(b) Aromatics	: 0.88
Existing gum (Air jet)	: 0.0005 g/100 ml.

maintained at 700°C, a decrease in the total pore volume from 0.49 to 0.24 ml/g was observed as the sodium concentration in the support was reduced from 0.62 to 0.014 per cent by weight. Fig. 2 shows the cumulative pore volume distribution according to pore size of the samples. The fall in total pore volume was found to be actually due to a fall in the macro pore volume (pores of 150 Å diameter and above) from 0.34 to 0.06 ml/g (Table II). The same effect is observed for samples 182 B and 182 C also. The amount of sodium in the catalyst was controlled at the time of washing of the gel. Removal of sodium during washing causes peptization of the

TABLE II
Textural properties of support alumina

Catalyst sample	Temp. of calcination °C	Surface area m ² /g	Total pore vol. ml/g	micro-pore vol. ¹ ml/g	macro-pore Vol. ² ml/g
182 A	550	150	—	—	—
182 B	700	110	0.58	0.16	0.42
182 C	700	103	0.50	0.15	0.35
202 A	550	192	0.49	0.13	0.36
202 B	700	128	0.49	0.15	0.34
202 C	700	116	0.26	0.17	0.09
202 D	700	107	0.24	0.18	0.06
204	700	150	0.36	0.24	0.12
218	900	115	1.04	0.11	0.93
143	1100	17	0.34	0.05	0.29
Comm. I	—	45	0.45	0.05	0.40
Comm. II	—	50	0.20	0.08	0.12

¹Volume due to pores smaller than 150 Å dia.

²Volume due to pores of 150 Å dia. and above

TABLE III
Reducibility and catalytic activity

Catalyst sample	Amount wt% of		Reducibility % at		Br. Index	
	nickel	sodium	350°C	550°C	of product	%Activity
182 A	13.67	0.0094	3.6	19.6	—	—
182 B	12.13	0.65	17.1	95.4	190	96.7
182 C	10.9	0.0094	8.6	43.8	300	94.8
202 A	10.4	0.62	4.0	94.9	40	99.3
202 B	14.01	0.62	28.9	66.0	20	99.7
202 C	10.08	0.316	4.1	73.7	—	—
202 D	8.8	0.014	0.4	67.1	—	—
204	11.35	0.48	8.7	29.0	14	99.8
218	10.84	0.36	15.5	94.8	8	99.9
143	10.2	0.014	5.4	92.8	0	100.0
Comm. I	10.0	0.73	1.3	71.3	170	97.1
Comm. II	11.15	0.05	—	43.5	74	98.7

gel bringing the particle size to a lower level. This results in low pore volume due to close packing of the particles after calcination.

Reducibility studies show that at 550°C the reduction of nickel oxide is well over 40 per cent in most of the cases. The extent of reduction is varying from sample to sample with temperature as shown in Fig. 3. It is also seen from the figure that above 450°C there is a steep increase in the extent of reduction with temperature. What structural modification the catalyst has undergone after reduction is not clear. In these samples a distinct correlation between sodium concentration and reducibility at 550°C is not evident. It is possible that 550°C is too high a temperature, and hence a comparison may be difficult. The degree of reduction is more dependent on the distribution of nickel oxide in the alumina matrix and their availability in the macro-porous sites which are more accessible to hydrogen. It is, therefore, clear why any proportionality between the extent of reduction and the sodium content is not tenable when the method of preparation and calcination of the samples are different. Among the catalyst samples, only in a series (e.g., in 202 B to 202 D) where most of the preparation parameters were kept constant and only the sodium level in the catalyst was varied, did we observe some correlation. Detailed investigation on the kinetics of reduction (Banerjee *et al.*—*unpublished*) has shown that only below 450°C, the samples are comparable. Taking the reducibility values at 350°C for 202 B to 202 D series and for 182 B and 182 C (Table III, Fig. 3) it is seen that with decrease in the sodium content in the catalyst, the reducibility is low. The effect of sodium on the reducibility of nickel oxide thus follows a pattern compatible with the earlier reports (cf. Nowak & Koros 1967; Charcosset *et al.* 1971). Unlike Pt or Pd catalyzed reduction of supported nickel oxide, where the dissociative adsorption of hydrogen on Pt or Pd particles results in the enhancement of the rate of initiation of reduction (Nowak 1969), here sodium probably influences reducibility indirectly through the formation of some disordered superficial areas on nickel oxide presumably due to lesser interaction between the support and the metal oxide, as it is known that the presence of sodium restricts the interaction between nickel oxide and alumina.

The extent of reduction is also considerably influenced by the temperature of calcination of the support. Comparing 182 A with 182 C and also 202 A with 202 B in Table III (as the sodium content remains the same), it is seen that calcination of the support at higher temperatures viz., 700°C results in higher reducibility of nickel oxide phase in the finished catalyst, again the comparison being done on reducibility below 450°C (Fig. 3). Calcination of the support at a lower temperature (say, 550°C) renders its surface to be more amenable to react with the metal oxide, thereby decreasing the availability of nickel oxide for reduction. These studies indicate that the alumina support should be calcined at appropriate temperatures to suppress the interaction between the support and the metal oxide.

The hydrogenation activity of the samples in terms of reduction of bromine index is also given in Table III. These initial activities of the samples were calculated from the bromine index of the catalysate collected after four hours of steady runs. High initial activity was observed in all the cases. It can be seen that observed reducibility does not appear to give any indication of the extent of activity of the

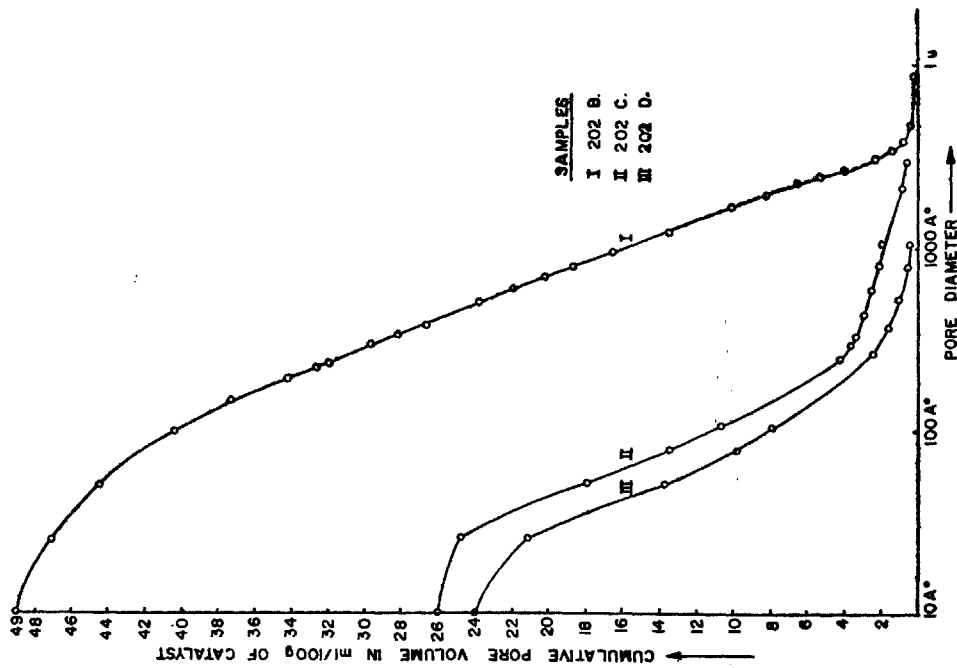


FIG. 2. Cumulative pore-size distribution in alumina supports.

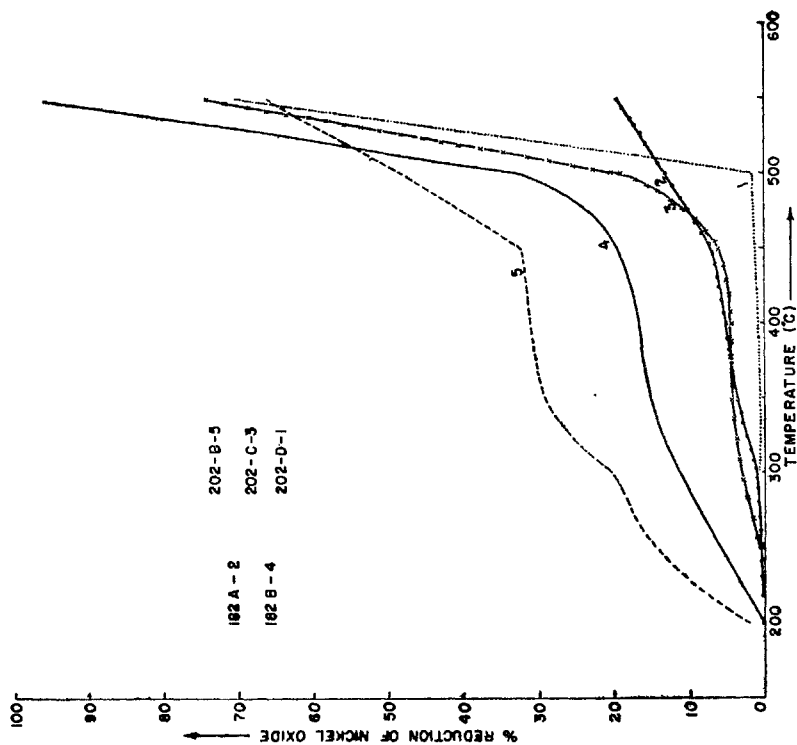


FIG. 3. Percentage reducibility of nickel oxide deposited on different alumina supports against temperature.

samples. In other words, an overall correlation between reducibility and hydrogenation activity is hardly perceived. Some samples with lower reducibility also showed remarkably high activity, e.g., sample 204. Probably only a fraction of the nickel surface, which are well accessible, is good enough for this hydrogenation of low concentration of olefins in the feed stream.

The effect of reaction temperature on product bromine index has been studied for five catalysts. The particles of the catalyst samples were very small and uniform; the flow rates were such that resistance to bulk diffusion was negligible. The conversions observed were also very high in these initial activity tests. In fact, variation of conversion in the temperature range of 95–150°C was very small. Under these conditions, Arrhenius plots showed apparent activation energies in the region of 0.1 to 0.5 kcal/mole, which is much lower than the values reported in literature, as summarized by Bond and Wells (1964). In majority of the samples investigated, the pore volume was above 0.4 ml/g. Under the conditions of this study diffusion resistance, both bulk and Knudsen in the macropores should be important. The pressure and flow of fluids, catalyst particle sizes and pore distributions suggest that the bulk diffusion would be negligible and Knudsen diffusion would be predominant. Estimation of diffusion coefficients by hydrogen under the reaction conditions, assuming a void volume of 40 per cent, pellet density of 0.9 g/ml, and the value between 1.5 and 2 for τ which is a factor to allow for both tortuosity and varying pore cross section, as done by Satterfield and Sherwood (1963) also confirmed this.

Though the initial activity was good in almost all the samples prepared, long run tests in the micro-reactor indicated that only a few catalysts retained the activity for over 60 hrs. The activities of five catalyst samples are shown in Fig. 4. Only samples 204 and 218 showed good activity-stability. However, these also fell after 100–150 hrs'. run. The fall in activity-stability of all these nickel-alumina catalysts

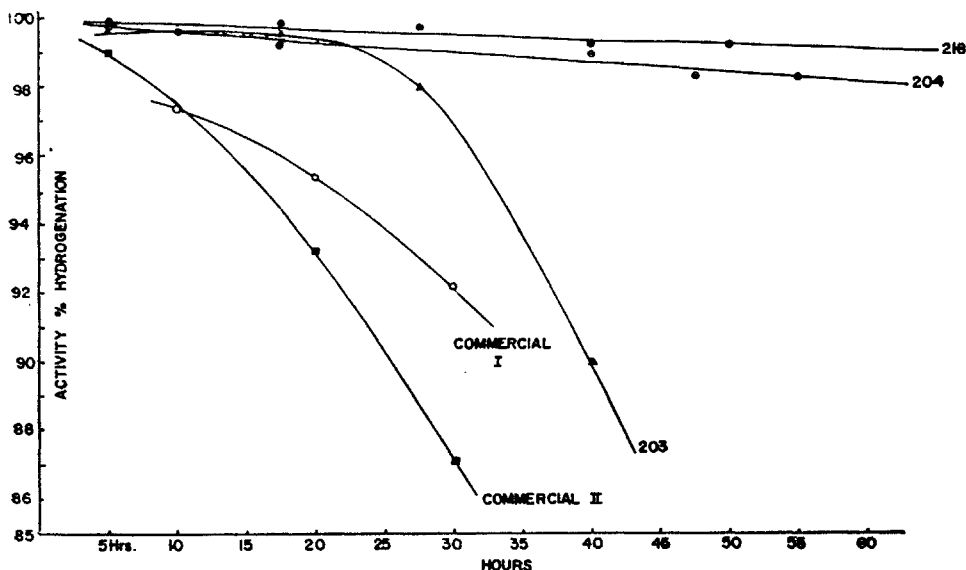


FIG. 4. Long run hydrogenation tests in microunit.

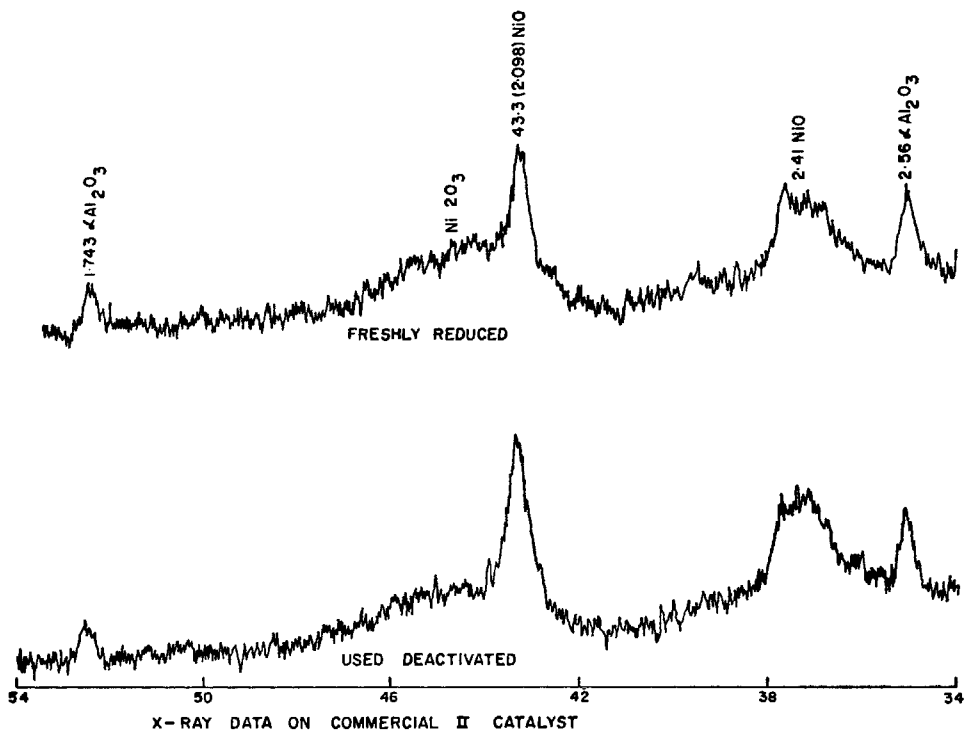


FIG. 5. X-ray diffractogram of fresh and used Ni-alumina (Commercial II) catalyst.

may be due to three factors either individually or collectively viz., (a) some carbonaceous matter formed during the course of long runs might have poisoned the surface active sites—In two cases it was observed that the refractive index of the material collected during purging after a long run had high values which is indicative of the presence of some polymeric species. Estimation of carbon in one spent catalyst (after 150 hrs.' run) showed it to contain 4.79 per cent carbon. This might be due to diffusional restrictions, but more probably is due to undesirable, but unavoidable temperature conditions in a micro-reactor owing to high surface to volume ratio, (b) growth of nickel crystallites responsible for the fall in activity (Under the conditions of reaction studied, this appeared to be unlikely), and (c) poisoning of active nickel sites by oxygen impurities that could not be ruled out. The feed was a raffinate-cut after extraction with ethylene glycol and water. Traces of oxygen containing impurities from glycol or water in the feed could compete for active nickel sites and bring about slow deactivation. X-ray data on freshly reduced and used-deactivated samples from these tests are shown in Fig. 5. This indicates an increase in the concentration of nickel oxide phase in the used catalyst. Poisoning by oxygen impurities present in the feed, therefore, appeared to be the most probable reason.

CONCLUSION

The importance of having optimum sodium concentration in and calcination at suitable temperature of alumina support to get fairly good reducibility and texture for nickel-alumina catalyst is indicated. In the hydrogenation of traces of olefins present in the udex raffinate, only a part of reduced nickel present in such catalysts contributes to the overall, satisfactory activity. Hence, the activity of these nickel catalysts does not appear to depend on the extent of reducibility. The activity-stability of these catalysts was low. This appeared most probably due to oxygen containing impurities present in the feed.

ACKNOWLEDGEMENT

The authors are thankful to Messrs. H. R. Sharma and S. M. Dhir for their assistance in the experimental work, and to Mr. S. S. Roy for analysis. We are also grateful to Dr. M. G. Krishna, Director, IIP for encouragement and support.

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