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Catalytic Aluminas

III. Physical and Catalytic Properties of Nickel and Platinum Impregnated Eta and Gamma Alumina

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Previous papers have described the differences in certain surface and catalytic properties of two well-characterized samples of eta (η) and gamma (γ) alumina. This paper deals with the examination of several physical and catalytic properties of eta and gamma aluminas impregnated with nickel and platinum salts. For the nickel-impregnated catalysts there were pronounced differences in physical appearance, nickel surface area, the amount of nickel removable as nickel carbonyl, and cyclohexane dehydrogenation activity. There were no pronounced differences between the platinum–eta- and platinum–gamma-alumina catalysts. The data obtained on the nickel-alumina catalysts were compared to data obtained on nickel-silica, nickel–Davison eta-alumina, and nickel–silica-alumina catalysts.

INTRODUCTION

Previous papers (*1*, *2*) have described the differences in certain surface and catalytic properties of two well-characterized samples of eta (η) and gamma (γ) alumina. Gamma alumina differed from eta alumina in that the water content of gamma alumina was greater than that of eta alumina. In general, eta alumina was more active than gamma alumina for the isomerization of *p*-xylene, the double-bond and skeletal isomerization of 1-pentene and the cracking of 2,4-dimethylpentane.

This paper deals with examination of several physical and catalytic properties of the same eta and gamma aluminas impregnated with nickel and platinum salts.

EXPERIMENTAL

The samples of eta and gamma alumina employed in the present work were from the same batches used in the previous work (*1*, *2*). The nickel- and platinum-alumina catalysts were prepared by impregnating the supports with aqueous solutions of nickel nitrate hexahydrate (Fisher Certified) and chloroplatinic acid (Fisher), respectively, to the point of incipient wetness. The catalysts were dried at 110°C for 24 hr and then calcined in air at 500°C for 20 hr. The other nickel catalysts were prepared by impregnating American Cyanamid Triple A silica-alumina (nominally 25% Al_2O_3–75% SiO_2), Davison eta alumina, and Davison grade 70 silica gel using the same procedure described above.

The nickel and platinum metal areas were measured in an apparatus used for the hydrogen chemisorption work. (*3*). The hydrogen was obtained from the Air Reduction Company and was purified by passing it successively through a "Deoxo" unit, a magnesium perchlorate drying tower, and an activated charcoal trap at −195°C. In both cases 2-g samples were used. The samples were reduced with hydrogen at 500°C for 2 hr and then evacuated overnight (~16 hr) at 500°C to a pressure of 10^{-6} Torr.

Hydrogen was then chemisorbed on the

nickel samples at 0°C and at 1 atm for 2 hr. The nickel areas were calculated on the basis that each nickel atom adsorbs one hydrogen atom and that each hydrogen atom occupies 6.5 Å^2 (*4*, *5*). Hydrogen was chemisorbed on the platinum catalysts at 250°C and at 300 mm for 2 hr. The platinum areas were calculated using the assumption previously reported. (*6*).

The surface areas of the catalysts were determined by the BET method using a nitrogen adsorbate.

Metallic nickel was removed from the catalysts by flowing carbon monoxide at a space velocity of 300 over the reduced samples at 80°C. The amount of nickel removed was determined by decomposing the carbonyl at 300°C in a glass tube which was weighed before and after the carbonyl was decomposed. The carbon monoxide was C.P. grade, obtained from the Matheson Company, and was dried by passing it over thoroughly dried molecular sieves.

The optical spectra were obtained with a Beckman DK-1 spectrophotometer equipped with a reflectance attachment. The samples were held in aluminum containers equipped with quartz windows. A gamma- or eta-alumina sample was used as the reference. The spectrophotometer automatically compared the light reflected from both the sample and the reference and recorded the reflectivity.

The procedure and apparatus used to record the wide-line proton nuclear magnetic resonance of the catalysts were described in previous publications. (*7*, *8*)

Catalysts were evaluated for dehydrogenation activity by using an atmospheric pressure bench-scale catalyst screening unit to convert cyclohexane to benzene under the following conditions:

Reaction temperature	300°C
Liquid hourly space velocity	2.36 hr^{-1}
Carrier flow	32 cc/min
Reaction time	1 hr
Carrier gas	H_2
Catalyst weight	1.0 g
Reactor bed volume	12 cc
Cyclohexane charge weight	2.36 g

Pure grade 99 mole % minimum cyclohexane was obtained from the Phillips Petroleum Company and was dried over Linde 5-A molecular sieves. The cyclohexane was injected into the feed gas stream by a positive displacement pump. The catalysts were pretreated with hydrogen at 500°C for 2 hr before the charge was introduced. The per cent conversion was calculated from the total moles of gaseous and liquid products collected. Products in the gas phase were analyzed by mass spectroscopy while the liquid collected was analyzed by gas chromatography.

RESULTS

Physical Properties

The objective of this work was to further examine the differences between well-characterized eta and gamma-alumina catalysts by studying their effect on impregnated metals. All of the catalysts that were studied and their surface areas are listed in Table 1.

The calcined, impregnated nickel catalysts differed considerably in physical appearance depending on the alumina support. The nickel–gamma-alumina catalysts were green while the nickel–eta-alumina catalysts were blue. The pronounced difference in physical appearance is illustrated by the diffuse reflectance spectra of these nickel catalysts shown in Fig. 1, in which the reflectivity is plotted versus wavelength. The spectra are shown only to illustrate the pronounced differences in physical appearance of the catalysts. A quantitative interpretation of the spectra is difficult because of the low intensity and breadth of the bands, variable scattering due to particle size effects, and the possibility of various forms of nickel ions existing. Examples of the latter are (1) the formation of Ni(II) ions in both octahedral and tetrahedral sites if nickel aluminate or a nickel aluminate-type compound is formed; (2) the creation of Ni(III) ions due to valence inductivity. (*10*)

The difference between the nickel–

TABLE 1

PHYSICAL AND CATALYTIC PROPERTIES

Sample	BET area (m²/g)	Nickel area (m²/g)	Platinum area (m²/g)	Hydrogen chemisorbed [cc(STP)/m² catalyst] × 10^4	% of the total nickel removed by CO	Cyclohexane dehydrogenation $\left(\frac{\% \text{ conversion}^a \pm 1}{\text{gram hour}}\right)$	Cyclohexane dehydrogenation $\left(\frac{\% \text{ conversion}}{\text{metal area hour}}\right)$
1. η-Al_2O_3	240.0	—	—	0.70	—	0.0	0.0
2. 2.57% Ni–η-Al_2O_3	195.2	—	—	1.60	1.4	0.0	0.0
3. 6.48% Ni–η-Al_2O_3	192.6	0.58	—	9.60	14.0	16.0 (3.5)[b]	27.6
4. 0.40% Pt–η-Al_2O_3	207.0	—	0.90	—	—	82.0	91.1
5. 0.78% Pt–η-Al_2O_3	219.3	—	2.30	—	—	83.0	36.1
6. γ-Al_2O_3	204.0	—	—	0.30	—	0.0	0.0
7. 2.56% Ni–γ-Al_2O_3	181.5	—	—	1.50	3.0	0.0	0.0
8. 6.00% Ni–γ-Al_2O_3	179.0	1.24	—	22.9	27.0	25.0–26.0 (4.5)[b]	20.2–21.0
9. 0.40% Pt–γ-Al_2O_3	207.0	—	1.10	—	—	82.0	74.5
10. 0.82% Pt–γ-Al_2O_3	202.2	—	2.33	—	—	82.0	35.2
11. 6.00% Ni–η-Al_2O_3	145.0	1.46	—	—	47.0	26.9	18.4
Davison commercial							
12. 6.00% Ni–silica-alumina	322.0	1.11	—	—	78.0	24.7	22.3
13. 6.00% Ni–silica gel	262.4	1.29	—	—	~100	13.3	10.3

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[a] All of the conversion was to benzene with the exception of sample 12 which had a selectivity of 85% to benzene; the remainder of the conversion was to methylcyclopentane.

[b] Activity after treating with carbon monoxide.

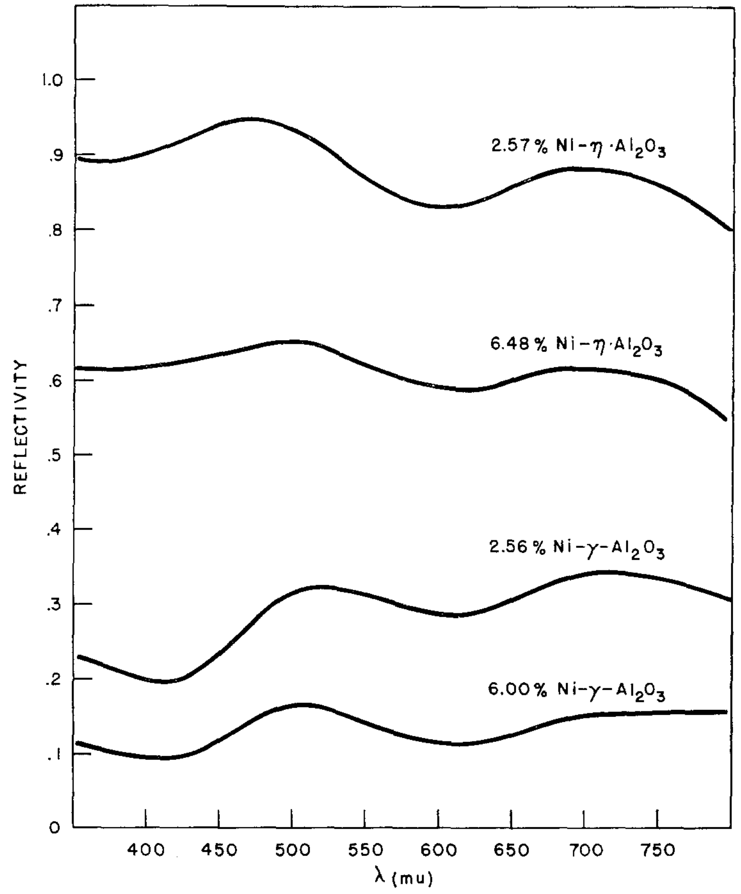

FIG. 1. Diffuse reflectance spectra of nickel-eta and -gamma alumina catalysts.

gamma-alumina and nickel–eta-alumina catalysts was further exemplified by the appearance of the reduced catalysts. Reduction of the catalysts had little effect on the physical appearance with the exception of the 6% nickel–gamma-alumina catalyst, which turned black.

From these observations, it appeared that the nickel in the 2% nickel–eta- and nickel–gamma-alumina catalysts and in the 6% nickel–eta-alumina catalyst was not readily reduced to the metallic state with hydrogen, whereas, a considerable amount of metallic nickel was formed in the reduced 6% nickel–gamma-alumina catalyst. To obtain more quantitative information about the state of the nickel in the reduced catalysts, hydrogen chemisorption and carbon monoxide extraction experiments were carried out. The results obtained were compared to data obtained from other nickel catalysts which were calcined and reduced under the same conditions.

Hydrogen chemisorption measurements were carried out on the reduced nickel–eta- and nickel–gamma-alumina catalysts at 100-mm pressure and at 0°C. The amount of hydrogen adsorbed per square meter of the nickel catalyst after 200 min is listed in Table 1. The 2% nickel–eta- and nickel–gamma-alumina catalysts adsorbed very little hydrogen, slightly more than the alumina supports. Both the 6% nickel–eta and -gamma-alumina catalysts adsorbed a considerable amount of hydrogen. However, the nickel–gamma-alumina catalyst adsorbed more than twice as much hydrogen as the nickel–eta-alumina catalyst.

Nickel surface areas were obtained on all of the 6% nickel catalysts from hydrogen chemisorption measurements. The nickel surface area of the 6% nickel–gamma-alumina catalyst was found to be approximately twice that of the 6% nickel–eta-alumina catalyst which was made from the "well-characterized alumina." It was interesting to find that the 6% nickel–gamma–alumina, 6% nickel–silica–alumina, 6% nickel–silica and 6% nickel–Davison eta alumina catalyst all had about the same nickel surface areas, approximately 1.2 m^2/g.

The nickel surface areas we obtained are much lower than those previously reported for nickel-impregnated catalysts. Nickel areas of 4.37 and 5.26 m^2/g have been reported for 10% nickel–silica catalysts which were calcined in air for 4 hr at 760° and 650°C, respectively. (*5*) Nickel areas of 13.3, 15.6 and 6.83 m^2/g of catalyst have been reported for 10% nickel–silica, nickel–alumina, and nickel–silica-alumina catalysts respectively. (*11*) The latter catalysts were not calcined but were dried at 110°C in air and then reduced with hydrogen at 370°C. The catalysts studied in this paper were all calcined at 500°C for approximately 20 hr, resulting in metal sintering. The calcined catalysts were studied mainly because any catalyst used commercially probably would eventually be subjected to a similar treatment on regeneration.

The reduced nickel-alumina catalysts were also treated with carbon monoxide at 80°C in order to determine the amount of nickel capable of being removed in the form of nickel carbonyl. The data listed in Table 1 were obtained from rate plots, four of which are shown in Fig. 2. The symbols represent experimentally determined points, whereas, the bars represent the variation that can be expected using this technique. A very small amount of nickel was removed from the 2% nickel–alumina catalysts, with slightly more being removed from the nickel–gamma-alumina catalyst (3%) than from the nickel–eta-alumina catalyst (1.4%). The difference in the amount of nickel removed from the catalysts containing 6% nickel is much more pronounced. About 27.5% of the total nickel content was found to be removed from the nickel–gamma-alumina catalyst in this case compared to 14.5% removed from the nickel–eta-alumina catalyst. As can be seen from the curves in Fig. 2 the majority of the nickel is removed during the first 2 hr.

The amounts of nickel removed from 6% nickel–silica, –silica-alumina, and –Davison eta-alumina catalysts (*12*) are listed in Table 1. These results are included to show that even though the nickel areas are the same the amount of nickel capable of extraction with carbon monoxide varies greatly. Only 14% of the total nickel content could be removed from the "well-characterized" eta-alumina catalyst compared to 47% from the nickel–Davison eta alumina. This difference is related to the differences in the BET surface areas. The low-area eta alumina would combine with less nickel, and therefore more nickel could be reduced to the metallic state and thus removed with carbon monoxide.

There were slight differences in the physical appearance of the calcined platinum–eta-alumina and platinum–gamma-alumina catalysts. The platinum–eta-alumina catalysts were white whereas, the platinum–gamma-alumina catalysts were pale yellow. Platinum metal area measurements were carried out to examine the state of the platinum in the reduced samples. The results are summarized in Table 1. From these results it can be reasonably concluded that the platinum areas are the same on the eta- and gamma-alumina supports for a given weight percent of platinum.

Catalyst Activities

In a previous paper it was reported that the eta and gamma aluminas are catalytically different. (*2*). The metal-impregnated aluminas were also found to be catalytically different for several types of reactions. In this paper data are presented for the dehydrogenation of cyclohexane to benzene. As anticipated it was found that

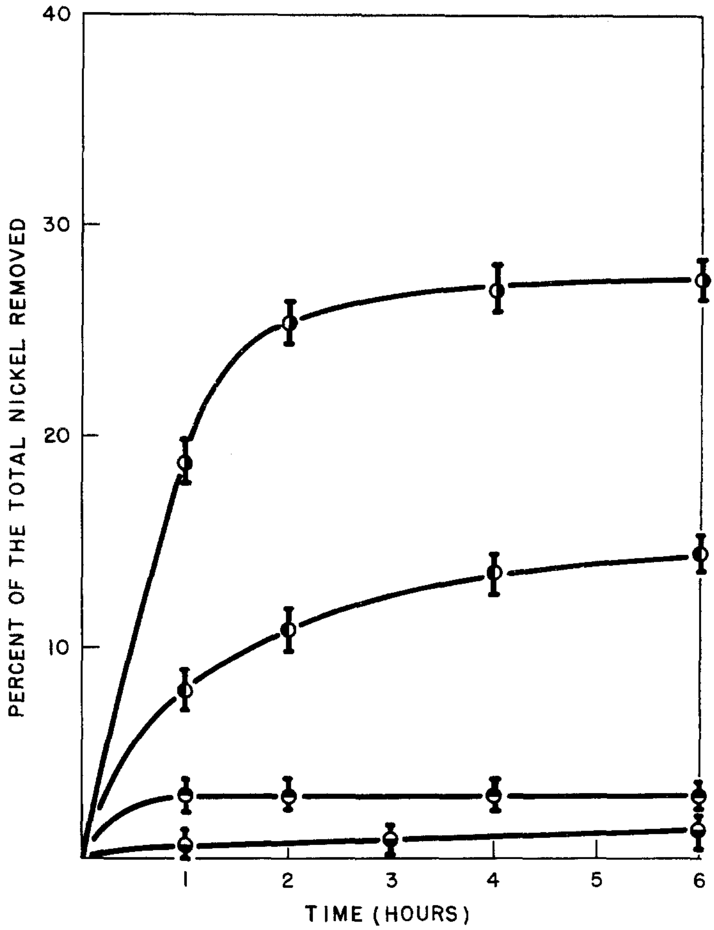

FIG. 2. Removal of nickel from nickel-alumina catalysts with carbon monoxide: ◑, 6.0% Ni–γ-Al_2O_3; ◐, 6.48% Ni–η-Al_2O_3; ◓, 2.56% Ni–γ-Al_2O_3; ◒, 2. 57% Ni–η-Al_2O_3.

the eta- and gamma-alumina supports and the 2% nickel–eta and –gamma-alumina catalysts resulted in no conversion to benzene under the conditions used. These results are also summarized in Table 1.

The cyclohexane conversion per gram of catalyst for the 6% nickel–gamma-alumina catalyst was found to be much greater than the conversion of the 6% nickel–eta-alumina catalyst. However, the specific conversion, that is, the conversion per unit metal area, was greater for the nickel–eta-alumina catalyst than for the nickel–gamma-alumina catalyst. The activities of the carbon monoxide-treated 6% nickel–eta and –gamma-alumina catalysts were very low, as shown in Table 1. These results were not surprising since Beuther and Larson (*13*) reported that the aromatic hydrogenation activity of carbon monoxide-treated nickel-alumina catalysts was very low. The activities of 6% nickel–silica, –silica-alumina, and Davison-eta alumina catalysts were also obtained for comparative purposes. On a conversion per gram basis the activity was found to decrease in the following order: nickel–Davison eta alumina > nickel–gamma alumina > nickel–silica-alumina > nickel–eta alumina > nickel–silica. The order of the specific activity is different with the activity decreasing in the order: nickel–eta alumina > nickel–silica-alumina > nickel–gamma alumina > nickel–Davison eta alumina > nickel–silica. In view of the assumptions and uncertainties involved in the measurement of the metal surface areas the differences between the specific activities of the nickel–silica-alumina, nickel–gamma-alumina, and nickel–eta-alumina catalysts may not be significant. However, it is believed that the difference between the activity of the nickel-silica catalyst and the alumina-supported nickel catalysts is significant and it will be discussed later.

The 0.4% platinum–eta-alumina and 0.4% platinum–gamma-alumina catalysts had the same activity. This would seem to indicate either that the support exerts no appreciable effect on the platinum or the reaction used was not sensitive to differences in the state of the metallic platinum.

DISCUSSION

The results of this investigation have shown that there are pronounced differences between nickel–gamma-alumina and nickel–eta-alumina catalysts. If it is assumed that all of the metallic nickel is removed from the nickel catalysts with carbon monoxide, then the results indicate that there is a considerable amount of nickel chemically associated with the aluminas and that more is associated with the eta alumina than with the gamma alumina. The chemical association is further demonstrated by the fact that the reduced 2% nickel catalysts contained very little nickel that was capable of being removed with carbon monoxide or capable of adsorbing hydrogen.

The chemical association of the nickel with the aluminas is probably due to the formation of nickel aluminate or a nickel aluminate type of compound. Nickel aluminate spinel has been observed in nickel-alumina catalysts by X-ray diffraction (*14*), however, no evidence of nickel aluminate was observed by X-ray diffraction for the calcined nickel-alumina catalysts reported in this paper. The fact that nickel aluminate was not observed does not rule out its existence as a noncrystalline phase which would not exhibit an X-ray diffraction pattern.

The exact reason why the "well-characterized" eta alumina combines more extensively than the gamma alumina with nickel is not known, but it is certainly related to their physical and chemical differences. An attempt was made to obtain information on the "chemically associated" nickel in the calcined catalysts by using broad-line proton nuclear magnetic resonance. Such a technique has been employed to measure the hydroxyl concentration on the surface of silica (*7*), silica-alumina (*7*), and alumina (*8*) catalysts. We found that after a 200°C dehydration in vacuum for 2 hr that the eta-alumina and 6% nickel–eta-alumina catalysts contained the same number of protons ($\sim 2 \times 10^{+21}$ protons/g). These results indicate that the nickel combines with the alumina without significantly affecting the surface hydroxyl concentration. More detailed information about this phase could possibly be obtained from magnetic measurements. (*15*) This technique is also a more accurate method to determine the metallic nickel content than the carbon monoxide treatment.

The hydrogen reduction time of the nickel catalysts at a given temperature is important. For comparative purposes a standard reduction procedure was used in this work. It has been shown that the support strongly effects how readily ionic nickel can be reduced to the metallic state. (*15*) The ionic nickel-on-alumina catalysts have been reported to be especially resistant to reduction to metallic nickel. At the present time quantitative studies have not been carried out on the effect of prolonged hydrogen reduction times on the nickel catalysts studied in this paper.

The difference between the 6% nickel catalysts prepared with the "well-characterized" aluminas was also exemplified by the cyclohexane dehydrogenation results. The nickel–gamma-catalyst was found to be approximately twice as active as the eta-alumina catalyst on a per gram basis. It was interesting to find that the specific activities of the nickel catalysts containing alumina were much higher than the nickel-silica catalyst. Taylor, Yates, and

Sinfelt carried out a detailed kinetic study of the hydrogenolysis of ethane over supported nickel catalysts (*11*) and reported that the specific activity decreased in the order nickel-silica > nickel-alumina > nickel–silica-alumina and also that the reaction proceeded with approximately the same activation energy: 40.6, 41.5, and 39.2 kcal/mole, respectively. They concluded that some chemical or electronic interaction between metal and support was responsible for the results. The nature of this interaction was not discussed and the formation of an ionic nickel phase and the possible effect of this ionic nickel on the specific activity were not mentioned. From the results reported in this paper and a previous publication (*12*) it has definitely been shown that some nickel is held in the lattice. The amount of this ionic nickel increases as the alumina content of the support increases for a constant surface area. Therefore, for reduced nickel-alumina and nickel–silica-alumina catalysts metallic nickel is not only dispersed on the support but is also dispersed on the ionic nickel phase. The differences between the cyclohexane dehydrogenation activities of the nickel-silica catalyst and the nickel catalysts containing alumina may be due to the presence of the ionic nickel. The enhanced activity is not directly due to the ionic nickel since the 2% nickel–alumina catalysts were inactive for the cyclohexane dehydrogenation reaction, and the carbon monoxide-treated 6% nickel–gamma and –eta-alumina catalysts exhibited very low activities. The activities that these carbon monoxide-treated catalysts did exhibit is mainly due to metallic nickel which is formed after a second hydrogen reduction. The role of the ionic nickel may be that of accepting or donating electrons to the metallic nickel phase, thus affecting the catalytic nature of the metallic nickel. Blyholder (*16*) recently discussed such interactions where alumina supposedly donates electrons to the metallic phase in supported catalysts. It is assumed that the nickel-silica catalyst does not contain ionic nickel in this case since nearly all of the nickel was removed with carbon monoxide.

It does not appear from the limited data obtained that the state of the platinum on eta and gamma alumina is significantly different and that there is no chemical association of the platinum with the support as there appears to be with nickel.

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