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The Structure of Raney Nickel

V. Partial Activation of the Catalyst

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The course of Raney nickel activation from nickel–aluminum alloys of 50 and 42 wt% of nickel (termed as alloy A and B, respectively) was followed by the controlled oxidation of aluminum in dilute aqueous NaOH at 50°C. The crystalline intermetallic phases, $NiAl_3$ and Ni_2Al_3, were identified in both alloys by X-ray diffraction, but the eutectic component was found in alloy B only. The removal of components of both alloys was reasonably uniform but the Ni_2Al_3 was the least reactive phase. Generation of surface area and pore volume per gram of original alloy per unit activation was reasonably constant for alloy A. For alloy B, large areas and pore volumes were produced initially, which decreased generally with increasing aluminum oxidation suggesting a collapse of the structure to that of the completely activated catalyst. The rate of activated surface nickel development different markedly in the two alloys and these results could be related to the nature and reactivities of alloy phases and to the amount of alumina trihydrate formed.

INTRODUCTION

The preparation of Raney nickel involves the removal of aluminum from a nickel–aluminum alloy by aqeuous alkali at elevated temperatures (*1*, *2*). The nickel–aluminum alloy, however, is not homogeneous but contains distinct phases, the nature and magnitude of which depend upon alloy composition (*3*) and other factors. Raney nickel is usually prepared from alloys containing 42–50 wt% of nickel. Alloys with nickel concentrations in excess of 50 wt% contain an NiAl phase that has been reported as insoluble in aqueous alkali (*4*). Those alloys of less than 42 wt% of nickel give correspondingly smaller yields of activated catalyst.

The mode of Raney nickel activation has been studied by X-ray diffraction (*5*), optical microscopy (*5–7*), and electron microprobe (*7*) techniques. In many cases, phase removal was not uniform, but the selectivity of which was governed by the concentration of alkali (*7*). No information, however, on the development of the catalyst pore structure as a function of aluminum oxidation has been reported. Consequently, the aim of this study was to follow, by X-ray diffraction, the phase changes that occur in alloys of different nickel composition under equivalent conditions of alkali treatment and to correlate bulk structural changes with that of the surface as examined by gas adsorption methods.

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TABLE 1

Phase Analysis of Raney Nickel Alloys (7)

Alloy	Ni (wt%)	Phases present (vol%)		
		Ni_2Al_3	$NiAl_3$	Eutectic
A	50.8	58	40	~2
B	40.5	30	45	25

EXPERIMENTAL

(a) *Partial Oxidation of the Aluminum Content in the Raney Nickel Alloy*

The bulk metal and phase compositions in the Raney nickel alloys used in this study have been reported previously (*7*) and are shown in Table 1. Alloy A has 50.5 wt% of nickel and alloy B 40.5 wt% of nickel, the difference in both cases being aluminum.

One problem associated with the partial oxidation of the aluminum lies in the hydrolysis of sodium aluminate (*8*).

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2 \quad (1)$$

$$2NaAlO_2 + 4H_2O \rightarrow Al_2O_3 \cdot 3H_2O\downarrow + 2NaOH \quad (2)$$

This reaction (2) regenerates sodium hydroxide for additional attack upon the alloy. Consequently, the aluminum oxidation is not determined by the amount of alkali used. We have chosen to use the volume of hydrogen evolved as a measure of aluminum oxidation and to stop the reaction when the desired amount of hydrogen was produced. Aqueous NaOH was added incrementally with stirring to alloy in water at 50°C so that hydrogen was evolved at a moderate rate. This procedure is similar to the Type II method (*9*), but less concentrated alkali was used.

Samples of alloys A and B with about 25, 50, and 75% of the aluminum oxidized were prepared by the addition of 20% aqueous NaOH to a given weight of alloy in 300 ml of distilled water at 50°C. When the amount of hydrogen liberated corresponded to a required extent of aluminum oxidation, the reaction was "quenched" by flushing the catalyst with large quantities of ice-cold water. The product was then thoroughly washed in absolute ethanol and stored in this medium at 0°C.

(b) *X-ray Analysis*

Samples of the parent alloy and of partly activated catalysts were analyzed under the same conditions of X-ray diffraction by means of a Philips horizontal goniometer. Specimen preparation and diffraction pattern recording techniques are discussed elsewhere (*10*). Each of the crystalline reflections was assigned to a particular phase, and a qualitative estimate of its concentration in a series of partly activated catalysts was obtained by a comparison of reflection intensities.

(c) *Surface Study and Chemical Analysis*

Samples of partly activated catalysts were evacuated at 130°C for 24 hr, and the weight after this treatment was used in the determination of surface areas, pore volumes and chemical analyses. The first two of these parameters were evaluated from the adsorption of nitrogen at −195°C, and the methods of interpreting the data were the same as those used previously (*9*). The area of activated nickel on the surface, as a fraction of the BET surface area, was estimated from the chemisorption of carbon monoxide (*11*) with 13 $Å^2$ (*12*) and 16 $Å^2$ (*13*) being taken as cross-sectional areas.

Each of the partially activated catalysts was analyzed by standard chemical methods for total nickel and total aluminum by W. R. Grace and Co. The difference between the sample weight and its Ni plus Al content was assumed to be the "$O_3 \cdot 3H_2O$" component of alumina trihydrate (*10*). Consequently, the weight of unoxidized aluminum in the catalyst can be evaluated from the difference between the total aluminum in the catalyst and the weight of aluminum as the trihydrate. Assuming that there is no loss of nickel during catalyst activation, the original aluminum content can be calculated from the total nickel in the sample as the composition in the original alloy is known. The weight of aluminum oxidized is, therefore, the difference between the original and unoxidized aluminum weights, and this value is used as a check on that estimated by hydrogen evolution in any given catalyst preparation.

RESULTS

X-ray diffraction data on alloy A showed that all the alloy reflections could be assigned to either the $NiAl_3$ (β) or the Ni_2Al_3 (γ) phase. There was no evidence of elemental aluminum or any other intermetallic reflections. The partly activated catalysts displayed, in general, a decrease in the reflection intensities for both the β and γ phases, but the Ni_2Al_3 phase was, by far, the predominant one in the 75% aluminum-oxidized preparation. The gibbsite and bayerite types of alumina trihydrate had reflections which were much better defined in the 75% than in the 25% aluminum-oxidized alloy A. Crystallite development of Raney nickel became more clearly defined with increasing extent of aluminum oxidation, but only the (111) nickel reflection in the 75% activated preparation was sufficiently well defined to give an estimate of crystallite size, 35 Å, in keeping with that reported for the "completely activated" Type IIA (*10*).

The development of pore and surface structure for the alloy A activation sequence is given in Table 2. The surface area and pore volume increased regularly with an increasing extent of aluminum oxidation, whereas the mean pore diameter decreased. The fraction of the surface area as activated nickel increased to 50% aluminum oxidation then decreased before increasing to 63.0 or 72.6% for the "completely activated" alloy A (*11*).

Analytical data show that the extent of aluminum oxidation exceeds that from hydrogen evolution as given in Table 2. These differences could arise from retention of hydrogen in the Raney nickel and from failure to arrest the activation process instantaneously. Raney nickel of composition $NiH_{0.4}$ would result in the aluminum oxidation from hydrogen evolution being about 5% low. The nickel content increased with increasing aluminum oxidation, whereas the concentration of alumina trihydrate was greatest at 75% activation.

Partial oxidation of aluminum in alloy B results in bulk and pore structural changes markedly different from those for alloy A as shown in Table 3. X-ray diffraction analysis of alloy B revealed elemental aluminum as well as the $NiAl_3$ and Ni_2Al_3 reflections, which is in keeping with the

TABLE 2

Adsorption and Analytical Data[a] on the Partly Activated Alloy A Catalysts

Extent of activation (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)	CO chemisorption [cm^3 (STP)/g]	Surface nickel (%)[b]	Total nickel (wt%)	Aluminum (wt%)		$Al_2O_3 \cdot 3H_2O$ (wt%)	Aluminum oxidation (%)
							Total	Metallic		
25	18	0.015	33	0.73	17.8	53.52	40.7	37.6	8.85	27.4
50	46	0.030	26	6.33	59.6	63.66	30.9	28.0	8.3	54.5
75	73	0.042	23	5.38	38.55	70.27	19.9	14.7	15.0	78.4
"Complete"	87	0.054	25	15.7	72.6	83.79	9.0	5.3	10.9	93.45

[a] Adsorption and analytical data derived from the weight of catalyst after evacuation at 130°C for 24 hr.

[b] Assuming cross-sectional area of CO = 16 $Å^2$ (*13*).

TABLE 3

Adsorption and Analytical Data[a] on the Partially Activated Alloy B Catalysts

Extent of activation (%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)	CO chemisorption [cm^3 (STP)/g]	Surface nickel (%)[b]	Total nickel (wt%)	Aluminum (wt%)		$Al_2O_3 \cdot 3H_2O$ (wt%)	Aluminum oxidation (%)
							Total	Metallic		
25	43	0.031	29	0.55	5.5	44.58	47.7	43.7	11.75	33.3
50	51	0.041	32	1.25	10.65	46.25	35.4	25.6	28.1	62.3
75	99	0.076	31	3.90	16.9	55.09	25.15	14.7	30.2	81.85
"Complete"	115	0.082	29	16.1	69.2	85.31	7.7	4.0	10.7	96.8

[a] Adsorption and analytical data derived from the weight of catalyst after evacuation at 130°C for 24 hr.

[b] Assuming cross-sectional area of CO = 16 $Å^2$ (*13*).

greater content of eutectic (95% aluminum) shown in the phase analysis data of Table 1. The concentrations of both the $NiAl_3$ and Ni_2Al_3 phases, as exhibited by reflection intensities, decreased with increasing extent of aluminum oxidation but the 75% aluminum-oxidized sample displayed residual $NiAl_3$ and aluminum reflections in contrast to the corresponding preparation from alloy A. Alumina trihydrate reflection intensities increased with increasing aluminum oxidation as did the degree of definition in the Raney nickel reflection. The detail of the latter did not, however, enable crystallite size estimates to be made.

Surface and pore structural development in catalysts partially activated from the alloy B are given in Table 3. As in the alloy A series, the surface area and pore volume increased with increasing aluminum oxidation, but the mean pore diameters varied in the opposite way. Carbon monoxide chemisorption estimates of the fraction of surface nickel exhibited a regular increase with aluminum oxidized, but these values were much smaller than those for the corresponding preparations from alloy A.

Analytical estimates of the extent of aluminum oxidation in the partly activated samples also exceeded those from hydrogen evolution data. The increase in the alumina trihydrate concentration with increasing aluminum oxidation up to 75% matched the trend revealed by X-ray diffraction.

Adsorption data given in Tables 2 and 3 were reported per gram of catalyst after evacuation at 130°C. These changes in area and volumes per gram of original alloy can be correlated better by dividing these quantities by the fraction of aluminum oxidized to give areas and volumes per gram of original alloy per unit activation. Results of these calculations are in Table 4. The generation of surface area and pore volume appears to be fairly uniform for the alloy A series but these quantities decrease with increasing activation in the early stages of alloy B activation.

DISCUSSION

Both alloys exhibited X-ray diffraction evidence of crystalline $NiAl_3$ and Ni_2Al_3 phases, but elemental aluminum reflections appeared only in the spectrum of the alloy B which is consistent with the phase analysis data in Table 1. A reasonably uniform removal of the original alloy phases was observed at different stages of Raney nickel activation from both alloy types with the $NiAl_3$ (β) component being more reactive, particularly in alloy A. The greater ease of aluminum oxidation from the β phase agrees with other findings (*4*, *7*, *17*, *18*), but the presence of eutectic in the later stages of alloy B activation does not (*7*).

The reactivity of phases in a multicomponent alloy has, however, been shown to be dependent upon the concentration of alkali (*7*). The aqueous NaOH solutions

TABLE 4

Catalyst Properties per Gram of Original Alloy and per Unit Oxidation

Fraction of Al oxidized	Per gram of original alloy				Per gram of original alloy per unit Al oxidation			
	$Al_2O_3 \cdot 3H_2O$ (g)	CO chemisorption [cm^3 (STP)]	Surface area (m^2)	Pore volume (cm^3)	$Al_2O_3 \cdot 3H_2O$ (g)	CO chemisorption [cm^3 (STP)]	Surface area (m^2)	Pore volume (cm^3)
Alloy A								
0.274	0.0835	0.69	17	0.014	0.304	2.52	62	0.052
0.545	0.066	5.02	36.5	0.024	0.121	9.21	67	0.044
0.784	0.1080	3.86	52.5	0.030	0.138	4.93	67	0.0385
0.9345	0.066	9.46	52	0.0325	0.070	10.13	56	0.035
Alloy B								
0.333	0.107	0.50	39	0.028	0.320	1.50	171	0.0845
0.623	0.246	1.09	45	0.036	0.395	1.76	72	0.058
0.8185	0.222	2.87	73	0.056	0.271	3.50	89	0.068
0.968	0.051	7.64	55	0.039	0.052	7.90	56	0.040

used in the present study were less concentrated than those of the Type II preparations and approached the concentrations used for the Type IVA (*9*) or I.G.T. preparations (*8*). In this case optical microscopy (*5*, *7*) and electron microprobe (*7*) data have demonstrated an equivalence in the rates of removal of the β and γ phases.

The crystallinity of the intermetallic components was maintained at all stages of catalyst activation, which suggests that aluminum oxidation and removal do not alter the structure of the remaining alloy phase. This finding supports the observation, from optical microscopy, that the phase removal takes place by an "advancing interface" mechanism in which the reaction does not proceed with the formation of intermediates or by the progressive removal of aluminum over the particle as a whole (*7*). Only Raney nickel and residual alloy phase reflections were observed in the later stages of catalyst activation, a feature consistent with other data reported in the literature (*4*).

If there were a uniform generation of surface area and pore volume from the alloy grains during catalyst activation, the magnitude of these quantities per gram of original alloy per unit activation should be constant. Reasonable constancy was found for the alloy A series, except for lower values for the "completely" activated samples (Table 4). For alloy B preparations, surface areas and pore volumes per unit activation decreased with increasing activation except for the sample with 82% oxidation of Al. These results suggest sintering or collapse of the catalyst structure during the last stages of the activation. Completely activated preparations from both alloys, however, had nearly the same area and pore volume per gram of original alloy.

As relatively dilute alkali was used in these preparations, the attack of the alloy components would be expected to be essentially the same (*7*). In support of this postulate, all of the alloy phases were detected by X-ray diffraction in the partly activated alloy B samples, and the nearly uniform generation of pore structure in the alloy A series can also be explained in this way.

The average pore diameters of catalysts activated at 50°C from alloy A were about 25 Å and from alloys B and C (*9*) about 30 Å. In most instances, the pore diameter was independent of the degree of activation and the aluminum content of the catalyst. Larger pore diameters were generally found for catalysts from aluminum-rich alloys.

Possibly for alloy, B alkali attack of the eutectic leads initially to a high area structure of lower nickel content than the Raney nickel produced from the β and γ phases. The X-ray diffraction data give no particular support to this argument, but the presence of a different high area phase, however, would not be expected to be easily detectable in these samples because of its inherently low crystallite size.

As the conditions of Raney nickel activation from the different precursors were equivalent, the resulting pore and nickel surface structure should be dependent upon the nature, concentration, and reactivity of the phases in the original alloy. Because of no marked selectivity in phase removal from both types of alloy, under the aluminum oxidation conditions used, the original phase composition should strongly affect the development of catalyst structure.

X-ray diffraction has shown crystalline aluminum (the eutectic component) even in the 75% aluminum-oxidized alloy B. This eutectic could be crucial in determining the extent of surface nickel activation for, having a nickel content of only about 5%, the eutectic must not be expected to contribute significantly to the final catalyst structure. The eutectic has a dendritic structure and on dissolution leaves voids (*7*, *18*). Hence, partial or complete removal of eutectic at a given point in the catalyst preparation may lead to a high area porous structure or at least a roughened surface that would increase total area to a greater extent than nickel area. Partly activated catalysts from alloy B contained larger amounts of alumina than corresponding preparations from alloy A. This alumina, probably a low area trihydrate, has been postulated to fill and block pores and to make some of the nickel inaccessible (*9–11*). Scanning electron microscopy has shown crystalline alumina on the external surface and in larger pores of Raney nickel (*20*). Catalysts with high alumina trihydrate contents, e.g., the Type IV preparations, chemisorbed less CO than completely activated Type II samples (*11*). Blocking of the nickel surface by alumina may account for the low chemisorptions observed for the partly activated alloy B series but this does not explain other aspects of the adsorption data, such as larger surface areas and pore volumes. For both series of catalysts the fraction of nickel on the surface varied inversely with the alumina content.

The marked development of surface nickel during the last stages of catalyst activation from both alloy types may be related to attack on the less active Ni_2Al_3 phase, as shown by the X-ray diffraction data. This phase, having less aluminum per unit weight of nickel should generate a greater amount of the Raney catalyst per unit aluminum oxidation. In addition, in the last part of the extraction the concentration of alkali is larger and most of the alumina is dissolved.

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