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Nanoscale skeletal nickel catalysts prepared via 'bottom up' method

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NiAl nanoparticles are of considerable importance because of interest in examining the effects of size, surface area, and composition on their physical and catalytic properties. Recently, a new method for the 'bottom up' wet chemical preparation of nickel aluminides has been reported. The ability to leach the aluminum from this system provides an entrance to the preparation of skeletal-type metal catalysts similar to those produced in Raney-type systems. Furthermore, it is believed that these nanoparticulate catalysts should provide high surface areas and high activities, while the presence of aluminum within the bulk of these catalysts provides additional stability. Here, we present the results of studies conducted on this system which compare their properties and behavior with traditional bulk Raney nickel systems. Additionally, we show that we are able to alter the properties of these nanoparticles by changing the stoichiometric ratio of nickel and aluminum. The properties of all systems have been analyzed through the use of nitrogen adsorption, X-ray diffraction, and elemental analysis. Finally, the catalysts generated have been compared for their activity in the hydrogenation of butyronitrile. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: nanoparticles; catalysts; hydrogenation; nickel; Raney; skeletal

INTRODUCTION

In 1924 Raney-type catalysts were first developed by Murray Raney when he produced a 50% nickel–silicon alloy.[1,2] He subsequently treated this alloy with aqueous sodium hydroxide, which produced a hydrogenation catalyst five times more active than the best catalyst available at the time. He next prepared a nickel catalyst by leaching a 50 wt% NiAl with an aqueous sodium hydroxide solution, yielding an even more active catalyst for which he filed a patent. This discovery founded the basis for the class of materials are metal aluminides from which the aluminum is leached to form the active catalyst, generally referred to as 'skeletal', 'sponge' or 'Raney' catalysts. This class of catalysts now includes iron, cobalt, copper, platinum, ruthenium, and palladium. In addition, small amounts of a third metal, such as chromium, molybdenum, or zinc, have been added to promote catalytic activity. The application of these catalysts has spread across a wide range of reactions, which includes numerous types of hydrogenation, ammonolysis, and methanations.

These alloys are traditionally prepared in the laboratory and commercially by melting the active metal and aluminum in a crucible and quenching. The resulting melt is then crushed and screened to yield the desired particle size range. Variations in the leaching conditions have been shown to yield catalysts of different texture, composition, and activities. Typically, these catalysts have high activity due to their high BET surface area ($\sim$100 $m^2 g^{-1}$ for nickel and 30 $m^2 g^{-1}$ for copper). Further analysis of traditional skeletal catalysts has shown that these systems contain a much higher concentration of low-coordinate sites, kinks, and edges that also contribute to their activity.

The alloy composition is extremely important, as different phases leach quite differently and, therefore, lead to different products. The metallography of the resulting alloy is a consequence not only of the composition, but also of the rate of cooling. The Raney nickel system, for example, contains the phases NiAl, Ni_2Al_3, $NiAl_3$, and eutectic. It is now well known that it is very easy to leach aluminum from the eutectic and $NiAl_3$ phases, whereas it is considerably more difficult to leach Ni_2Al_3 and nearly impossible to remove aluminum from the NiAl phase. For industrial applications,

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Table 1. Preparation of NiAl catalyst precursors

Sample	Initial Al/Ni ratio	Alkylaluminum	Ni product (wt%)	Al product (wt%)	Product Al/Ni ratio
Al	2	$AlEt_3$	49.9	41.6	1.8
A2	3	$AlEt_3$	43.6	43	2.2
A3[a]	3	$AlEt_3$	28.8	35	2.7
A4	3	$AlMe_3$	29.1	35	2.6
Ai5	3	$AlEt_3$			
Ai6	1	$AlEt_3$			
A7	3	$AlEt_3$	36.2	51.5	3.1
A8	1	$AlEt_3$	65	29	1

[a] Prepared using $Ni(acac)_2$ as starting material. Note: acac = acetylacetonate.

usually a 50 wt% nickel alloy is employed because it is a compromise between the readily leached $NiAl_3$ and the more mechanically strong Ni_2Al_3. The effects of composition and leaching conditions on the physical properties of skeletal-type catalysts has been the focus of numerous investigations.[3–11]

In this paper we present a new 'bottom up' synthetic approach to skeletal-type catalyst systems. Of particular importance with this approach is that by adjusting the stoichiometry of the starting materials the composition of the product formed can be controlled. Thus, it provides a method to overcome the phase diagram of metal aluminides, which is a major hindrance to melt preparations.

RESULTS AND DISCUSSION

Catalyst preparation

Recently, a wet chemical method for the production of NiAl has been developed.[12] This method consists of the reaction between $Ni(COD)_2$ (where COD = cycloocta-1,5-diene) and $Al(ethyl)_3$ in toluene, which yields a black–brown dispersion. Hydrogen is used in this reaction as a means to hydrogenate the olefinic compounds of COD and ethylene. Drying under vacuum and heat treatment (130 °C) under a hydrogen pressure of 50 bar yields a black powder that consists of nickel aluminide. The particles were found to form aggregates of 100–500 nm; these were found to be comprised of

Table 2. NiAl catalysts prepared by leaching of different starting materials

Sample	Preparation	Precursor	Ni (wt%)	Al (wt%)	BET SSA ($m^2\ g^{-1}$)
Initial (1:1)					
B1	3 h reflux, 5 M NaOH	A8	73.75	16.01	
B2	3 h reflux, 3 M NaOH	A8	74.43	17.91	20
B3	24 h reflux, 5 M NaOH	A8	77.38	14.4	19
B4	18 h wash with EtOH/NaOH 25 °C	A8	69.78	20.59	40
B5	3 h reflux with EtOH/NaOH	A8	71.62	13.65	
B6	Consecutive washings NaOH/EtOH, 5 M NaOH	A8	70.82	19.73	
B7	NaOH reflux, then H_2O reflux	A8	69.8	23.43	
B8	3 h sonication with 5 M NaOH	A8	73.5	15.52	6
B9	3 h reflux with 5 M KOH	A8	69.07	16.38	
From 1:1 intermediate					
B10	3 h reflux, 5 M NaOH	Ai6	65.8	3.93	149
B11	24 h reflux, 5 M NaOH	Ai6	85	1.84	46.7
B12	18 h stirring 25 °C, 5 M NaOH	Ai6	77.38	14.4	88.6
B13	3 h stirring 25 °C, 5 M NaOH	Ai6			125.24
From $NiAl_x$					
B14	12 h stirring 25 °C, 5 M NaOH	A1	81.7	16.4	149
B15	12 h stirring 25 °C, 5 M NaOH	A7	80.44	10.84	77
From $NiAl_x$ intermediate					
B16	12 h stirring 25 °C, 5 M NaOH	Ai5			28

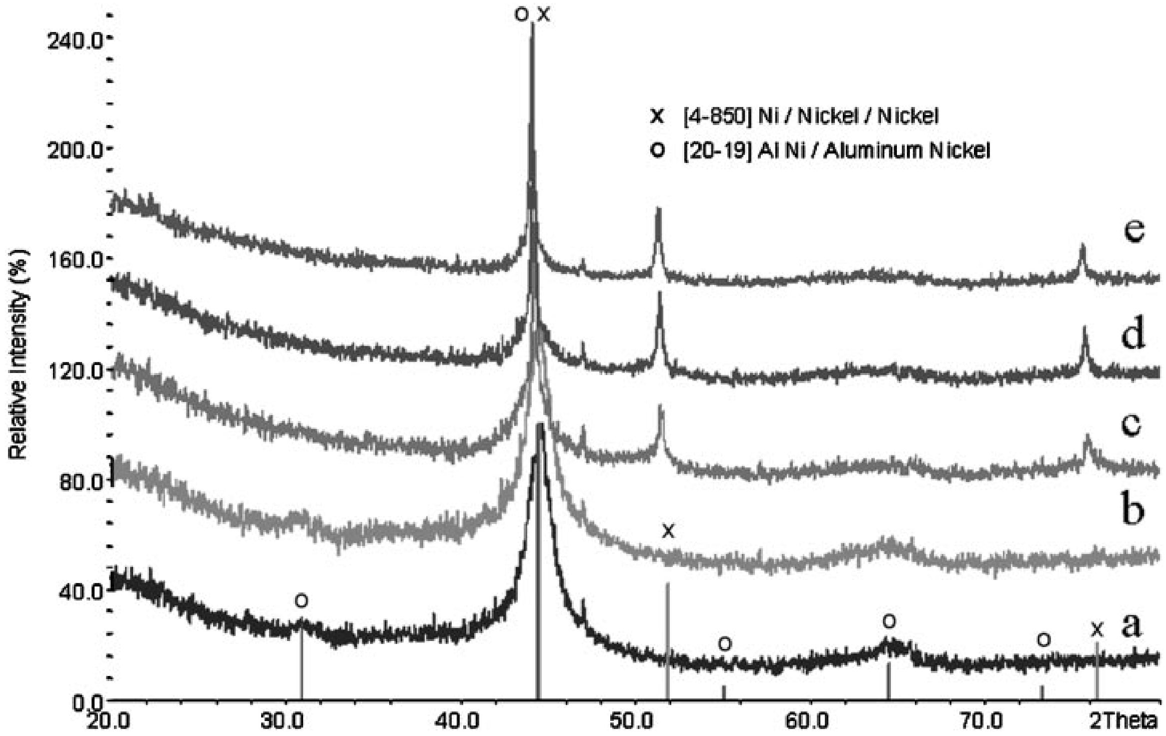

Figure 1. Temperature-programmed XRD of leached sample B14 prepared from NiAl precursor (A1) with the composition of $NiAl_{1.8}$: (a) 25 °C; (b) 100 °C; (c) 400 °C; (d) 500 °C; (e) 600 °C.

smaller particles of 5–7 nm (X-ray diffraction (XRD) via Scherrer equation) and 2–5 nm (transmission electron microscopy). This approach is especially attractive for the preparation of skeletal catalysts, because with $Ni(COD)_2$ the nickel is already reduced and the $Al(ethyl)_3$ is not used as reducing agent but rather as a reaction partner for the Ni(0) complex. As a consequence of this, the stoichiometry of the reaction is not limited to a specific ratio. This presents the opportunity to prepare nanoscale $NiAl_x$ catalysts in which the composition can be controlled by the stoichiometry of the starting nickel and aluminum components.

$$Ni(COD)_2 + xAlEt_3 \xrightarrow[\text{toluene}]{H_2} NiAl_x + \text{cyclooctane} + \text{ethane}$$

Ai

$$\xrightarrow[\text{16 h, 130°C}]{H_2} NiAl_x$$

A

It is well established that active skeletal catalysts require the leaching of the aluminum from the alloy, and it is known that this can only be done from the $NiAl_3$ and Ni_2Al_3 phases. Therefore, experiments were performed with the appropriate stoichiometric ratios of the starting materials (Ni $(COD)_2$ and $AlEt_3$) required to prepare these phases, as shown in Table 1.

These experiments have demonstrated the ability to extend this chemistry to prepare samples of Al/Ni in ratios ranging from 1 to 3. Samples A3 and A4 were prepared using alternative starting materials. Sample A3 (see Table 1) was prepared from $Ni(acac)_2$ in the place of $Ni(COD)_2$, where acac = acetylacetonate. Alternatively, sample A4 was prepared using $AlMe_3$ in place of $AlEt_3$. In both cases a much lower percentage of NiAl is observed in the final product. The samples Ai5 and Ai6 were taken in the form of their toluene solution prior to hydrogenation (intermediates and denoted Ai) and, therefore, no elemental analysis data are available. Samples A2 and A7 were prepared in the same manner with the exception of using fresh $AlEt_3$. It is believed that because of the high reactivity of the alkylaluminum compounds some activity may be lost during storage.

The precursors of varying compositions were then examined for the ability to leach the aluminum from the system with aqueous sodium hydroxide (NaOH). The experiments conducted are summarized in Table 2.

From Table 2 it can be seen that precursors of higher aluminum content produce catalysts with the highest weight percentage of nickel after leaching. Those samples reported as being leached from the intermediate of 1:1 precursors were produced by taking the precursor (Ai) prior to hydrogenation, drying under vacuum, then leaching. The samples leached from the precursor intermediates yield very low amounts of aluminum, and it is believed that this is a

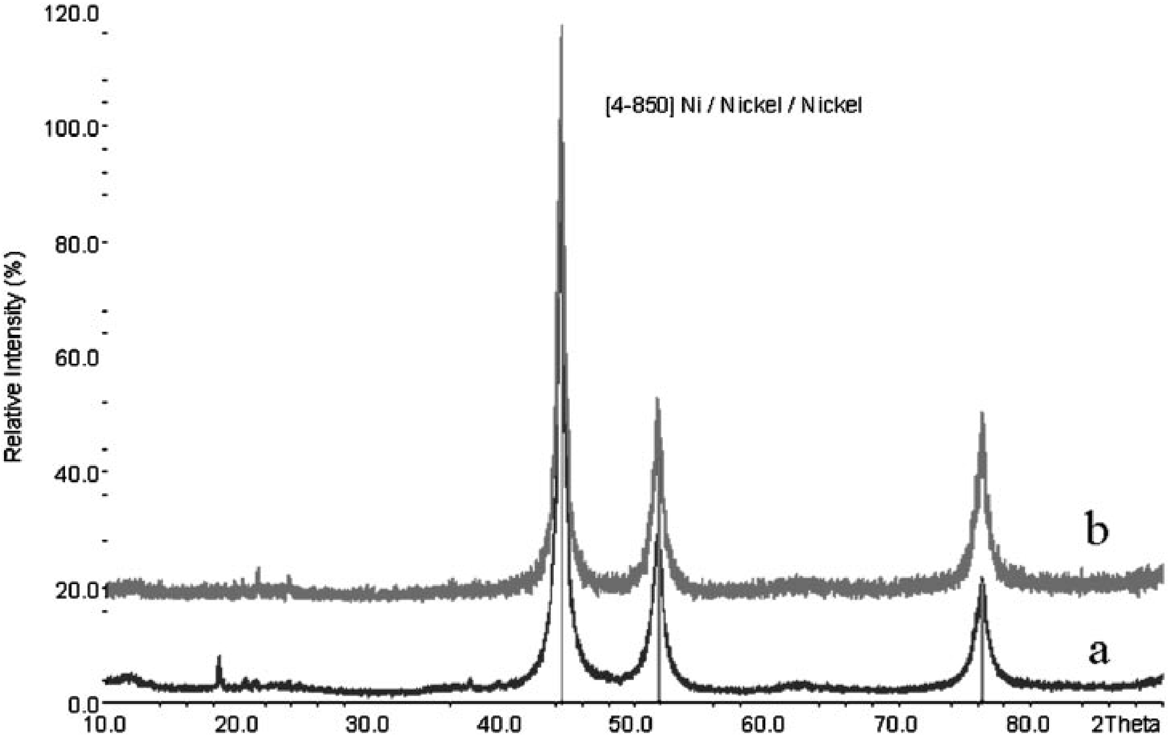

Figure 2. Powder XRD patterns of (a) commercial Raney nickel and (b) leached commercial Raney nickel.

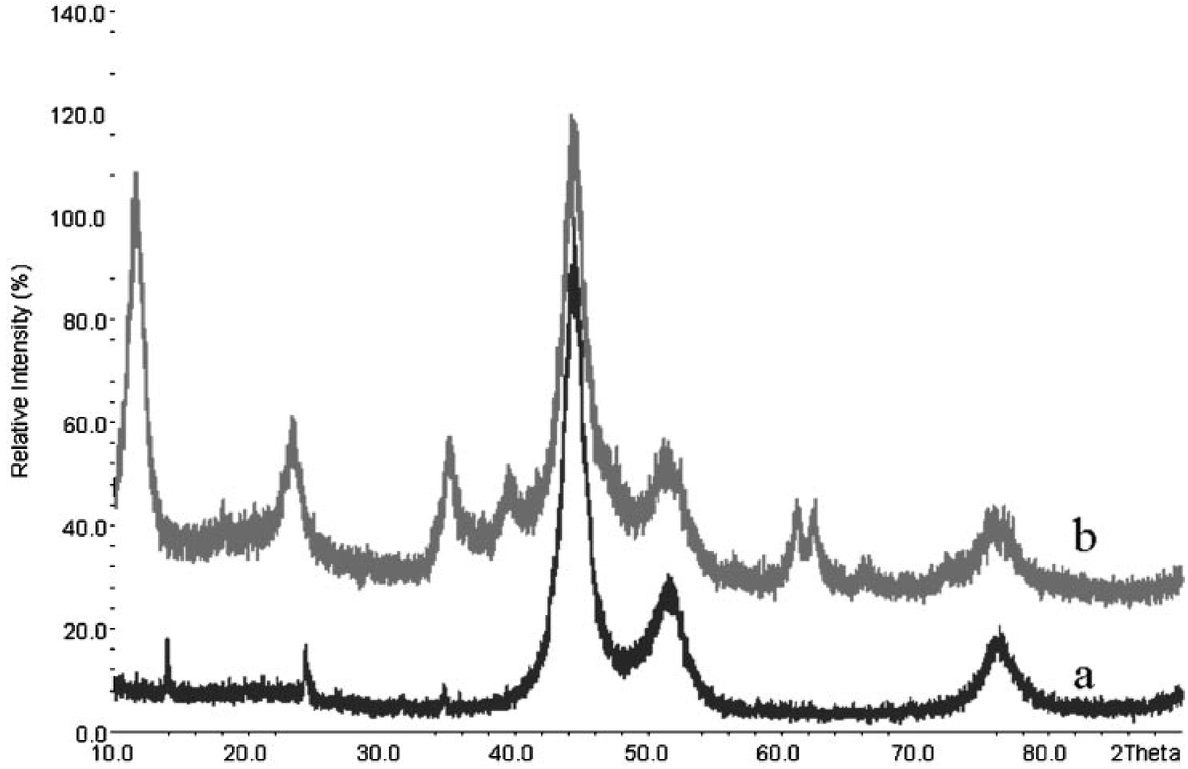

Figure 3. Powder XRD patterns of samples prepared from leaching intermediates (a) B10 and (b) B11.

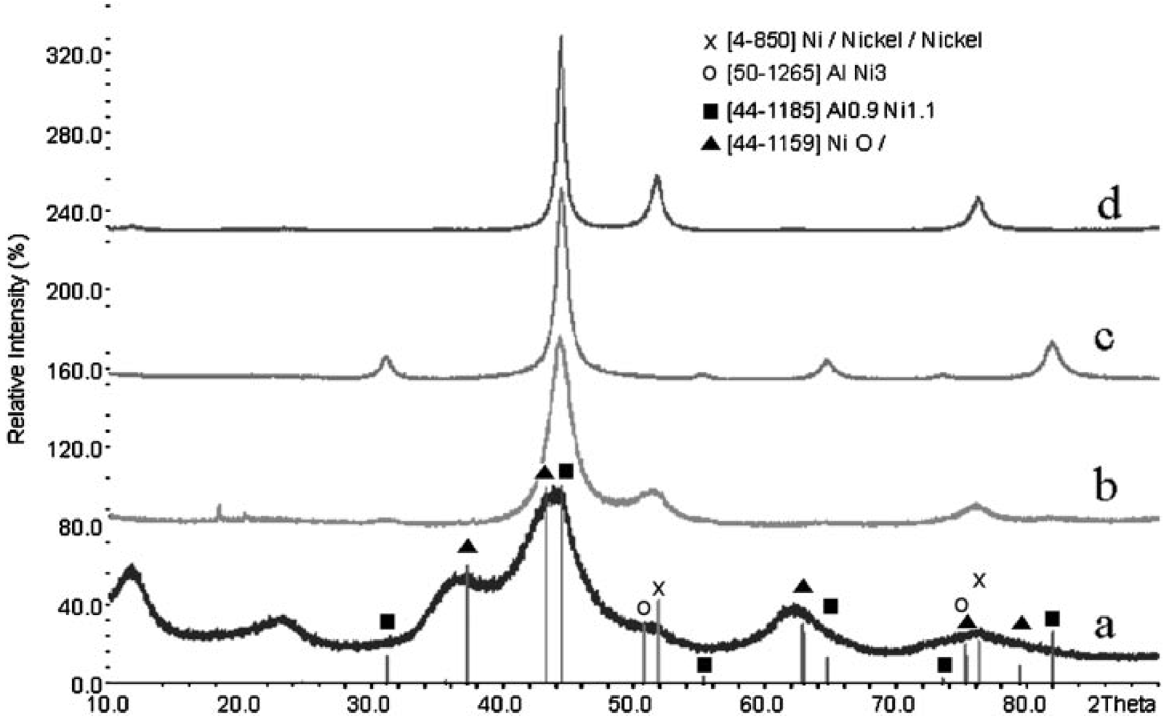

Figure 4. Powder XRD reflections of samples prepared from intermediates of $NiAl_x$, where $x = 1–2.4$: (a) B16; (b) B12; (c) B14; (d) commercial Raney nickel after leaching.

result of the incomplete reaction and alloying caused by foregoing the hydrogenation step. These samples also have very large amounts of oxide and carbon left in the catalyst, which are difficult to remove without destroying the desired skeletal architecture of the catalyst. Further examination of these systems by powder XRD yields even further information about the compositions of these systems.

Figure 1 demonstrates a typical XRD analysis of samples prepared from the leaching of $NiAl_x$ samples. The sample B14 was prepared from $Al(NiAl_{1.8})$. Temperature-programmed XRD shows that at low temperatures only reflections resulting from NiAl alloy are present. Upon heating to 400 °C, pure nickel reflections are observed, indicating that the nickel particles are too small or amorphous for detection by XRD at room temperature.

Figure 2 depicts the XRD patterns of commercial (CM)

Table 3. Catalyst activity towards butyronitrile hydrogenation

Sample	Preparation	Hydrogenation activity (N ml min^{-1})
CM Raney nickel		12.3
Prepared from 1:1 NiAl		
B3	NaOH reflux, 24 h	0
B4	EtOH/NaOH, Rt 18 h	4.8
Prepared from 1:1 NiAl intermediate		
B10	Reflux 3 h NaOH	9.9
B11	Reflux 24 h NaOH	6.2
B12	RT, 18 h stirring 5 M NaOH	1.2
B13	RT, 3 h stirring 5 M NaOH	0
Prepared from $NiAl_x$		
B14	RT, stirring 5 M NaOH	26
B15	RT, stirring 5 M NaOH	51
Prepared from $NiAl_x$ intermediate $x = 2.4$		
B16	RT, stirring 5 M NaOH (init. 1:3)	26

Raney nickel samples. The lower pattern is from a standard CM Raney nickel sample without any further treatment. The other spectrum is from the same commercial sample after refluxing in 3 M NaOH for 3 h. Both spectra show reflections corresponding to nickel, whereas the refluxed sample shows slightly more intense peaks that are most likely a result of an increase in crystallinity brought about by the heating.

The powder XRD patterns observed after leaching the intermediates are shown in Fig. 3. Both samples were prepared from the intermediate of the sample Ai6, which had a stoichiometry of 1:1. Sample B10 was refluxed for 3 h, in NaOH and has XRD 2θ reflections at 25, 35, 40, and 62° that correspond to NiAlOH. Sample B11 was refluxed for 24 h in NaOH and XRD showed all major peaks corresponding to nickel. From these results it can be seen that leaching the intermediates (Ai) requires very harsh conditions (i.e. refluxing) and results in a product that contains numerous oxides (including NiO and AlO). It is also clearly indicated that there are considerable differences between the commercial Raney samples and those of B10 and B11. This, however, is to be expected, because in the case of B10 and B11 we are starting with a 1:1 intermediate, which is not easily leached. Similar experiments conducted with the 1:1 product after heat treatment showed that only very small amounts of aluminum could be leached, even under the harshest conditions.

The samples prepared from the leaching of intermediates and products of $NiAl_x$ where $x > 1$ are shown in Fig. 4. Sample B16 was leached from Ai5 (1:3 intermediate) with excess 5 M NaOH for 48 hours at 25 °C. The XRD shows the presence of nickel, NiO, and NiAl phases. This is similar to what was observed in case of the 1:1 intermediates. Sample B12 was leached from Ai6 (1:1 intermediate) with excess 5 M NaOH for 48 h at 25 °C. The XRD of this sample shows only nickel and NiAl reflections somewhat similar to those of the commercial Raney system but much broader. Sample B14 was prepared by leaching A1 with excess 5 M NaOH at 25 °C. XRD of this sample shows reflections corresponding to Ni/Al with small amounts of nickel. For comparison, a commercial Raney nickel catalyst leached with 5 M NaOH is shown as (d). Here, only reflections corresponding to nickel can be observed.

The results of the hydrogenation activity measurements for several of the catalyst systems are reported in Table 3. Upon examining Table 3 it becomes apparent that the precursor used has a very significant effect upon the resulting catalytic activity. For those samples prepared from 1:1 NiAl the hydrogenation activity is very poor, as would be expected based upon the prior studies with commercial Raney systems. Using the leached intermediate of the 1:1 NiAl, a somewhat improved activity is observed; but this activity is still lower than that observed for commercial Raney nickel systems. However, when NiAl precursors of the form $NiAl_x$ (with $x > 1.5$) are leached with NaOH, the observed catalytic activity is considerably greater than that of commercial samples. The most significant improvement was observed in the catalyst prepared from $NiAl_3$. This behavior may be explained by the nanoscale structure of the precursors as well as the homogeneous nature of the samples prepared by the bottom-up route. Additional studies are currently under way to determine the structural and/or electronic properties of these active catalysts in an attempt to determine what differentiates them from the traditional systems. Furthermore, studies need be undertaken to determine the mechanical stability of these systems.

Conclusion

In conclusion, we have demonstrated that nanoscale NiAl catalysts can be prepared by a 'bottom up' wet chemical synthesis. Further, the phases of these catalyst precursors can be tailored by altering the stoichiometric ratio of the starting materials. The aluminum can then be leached with aqueous NaOH from the systems prepared via the bottom-up method and demonstrates the same leaching behavior as commercially produced Raney nickel. Upon leaching the aluminum from these systems a very pyrophoric catalyst is formed. This catalyst has demonstrated catalytic activity for the hydrogenation of butyronitrile two to three times higher than commercial Raney nickel samples.

EXPERIMENTAL

Preparation of $NiAl_x$

The preparation of NiAl precursors was undertaken according to previously published procedures.[12] Two samples presented in Table 1 were prepared according to a general procedure in which only the stoichiometry of the starting materials was altered. The only exceptions to this were samples A3 and A4. In the case of A3, $Ni(acac)_2$ (Aldrich) was used instead of $Ni(COD)_2$. Sample A4 was prepared using $AlMe_3$ in place of $AlEt_3$. The general procedure is as follows. To 100 ml toluene, $Ni(COD)_2$ (8.24 g, 30 mmol) was added under an inert atmosphere. An equimolar (in the case of 1:1 NiAl) amount of $AlEt_3$ (3.42 g, 30 mmol) (Witco Inc.) was then added. The solution was then transferred to an autoclave and hydrogen added to a pressure of (5–10 MPa) and the reaction stirred at room temperature for 72 h. This process yielded a clear solution with a solid precipitate. This precipitate was then placed under high vacuum (10^{-2} Pa) to evaporate solvent and dry the product, and resulted in a black, air-sensitive product (referred to in the tables as the 'intermediate' Ai). This black powder was then treated under a pressure of 50 bar hydrogen for 16 h at 130 °C. The resulting air-sensitive, black powder was referred to as the final NiAl precursor.

Aluminum leaching

Experiments for leaching aluminum from the NiAl were all conducted using standard Schlenck techniques to eliminate air exposure. Aqueous NaOH solutions were prepared from and washed with UHQ water, which was degassed three times using freeze–thaw techniques in order to minimize reaction variables. Unless specified otherwise, experiments were performed using a static argon atmosphere.

XRD analysis

XRD studies were carried out with a Stoe STADIP diffractometer equipped with a linear position selective detector in transmission geometry using Cu $K\alpha_1$ (1.540 598 Å radiation and allowing 2θ angles down to 1.0° to be measured. All samples were measured in 0.5 mm quartz or glass capillary tubes.

Surface area measurements

All surface area measurements were taken on a Micromeritics ASAP 2010 apparatus. Samples were activated by heating to 100 °C under vacuum for 2 h prior to measurement. The surface areas reported were determined using standard nitrogen adsorption measurements and BET data analysis.

Determination of hydrogenation activity (butyronitrile test)

The hydrogenation apparatus used consists of a dropping funnel for the catalyst, a temperature-controlled reaction chamber, a self-aspirating mechanical stirrer, and a mercury-sealed precision gas burette. Typical experiments involved placing a quantity of catalyst (100–200 mg) in the dropping funnel and connecting to the reactor. The reactor and burette were filled with hydrogen and evacuated several times. The catalyst in the dropping funnel was suspended in 50 ml ethanol (air-free, DAB 7) and then introduced to the reactor. The dropping funnel was subsequently washed with an additional 50 ml ethanol. The catalyst suspension was treated in the presence of hydrogen for 5 min, equilibrated at 40 °C, and stirred at 2000 rpm. To the reactor, 10 ml of butyronitrile was added and the system closed. The reactor was closed to hydrogen flow and the connection to the mercury-sealed precision gas burette was opened. The stirring at 2000 rpm was resumed and the volume of hydrogen in the burette recorded at 1 min intervals. The hydrogen consumption was then converted to N milliliters H_2 per minute.

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