Derivatized, High Surface Area, Supported Nickel Catalysts

A new and general procedure for preparing high surface area, supported intermetallic compound and alloy catalysts is described. In this technique, the volatile Group IIIA and IVA organometallic compounds SiH_4, Me_6Si_2, Me_6Ge_2, $BH_3 \cdot Et_3N$, and Et_3Al are decomposed thermally on high surface area nickel, supported on either SiO_2 or Al_2O_3, to yield, directly, mixed metal catalysts of varied composition and structure. Using the competitive dehydrogenation and hydrogenolysis of cyclohexane as model reactions, the effects of intermetallic compound formation on catalytic activity are described.

INTRODUCTION

Intermetallic compounds have been receiving increasing interest as catalysts (or catalyst precursors) during the past few years (1). The work of Wallace and others has shown that these materials are effective catalysts in ammonia synthesis (2), CO methanation (3, 4), ethylene hydrogenation (5), and hydrocarbon isomerization (6). While their selectivity can be extremely high, these catalysts, generally prepared by pulverizing the bulk material, have surface areas of at least an order of magnitude lower than those of oxide supported transition metal catalysts, and are thus of limited commercial utility.

We describe here a new and general procedure for preparing high surface area, supported, intermetallic compound and alloy catalysts (7). In this procedure, a volatile Group IIIA or IVA organometallic compound is decomposed thermally on high surface area nickel supported on either SiO_2 or Al_2O_3 to yield, directly, mixed metal catalysts of varied structure and stoichiometry. Using the competitive dehydrogenation and hydrogenolysis of cyclohexane as model reactions, the effects of intermetallic compound formation on catalytic activity are described (9). In particular, we find that the addition of main group metal atoms increases the selectivity of nickel for cyclohexane dehydrogenation, even under conditions of high hydrogen partial pressures. We also find that the overall activity of these new materials can be significantly higher than that of the starting nickel catalyst.

EXPERIMENTAL

The catalyst samples were prepared by stirring a methanol solution of $Ni(NO_3)_2 \cdot 6H_2O$, in which was suspended either SiO_2 or Al_2O_3 (~ 300 m²/g surface area) overnight and then evaporating the resulting slurry to dryness. Samples were then loaded into a pulsed, quartz microreactor and reduced at $\sim 600°C$ in flowing hydrogen (20 sccm total flow, 50% H_2 in He) for > 20 hr (12). Product analysis was carried out on a gas chromatograph equipped with a 6-ft, 10% Carbowax on Chrom W column and a thermal conductivity detector. It was noted that the activity and product distributions found for these catalysts prior to derivatization (see below) were sensitive to both the nickel loading and the reduction temperature used. Under the conditions employed in this study, the choice of support (Al_2O_3 or SiO_2) did not significantly influence the catalytic activity of the system. With our reactor design, 0.25-g samples with 10% Ni by weight gave catalysts whose activity at $\sim 300°C$ could be conveniently followed and, as such, were employed throughout this study. In a typical reaction, 2 μl of cyclohexane was injected into the reactor

Ni(NO$_3$)$_2$- Support $\xrightarrow[600\ C]{H_2}$ Ni- Support
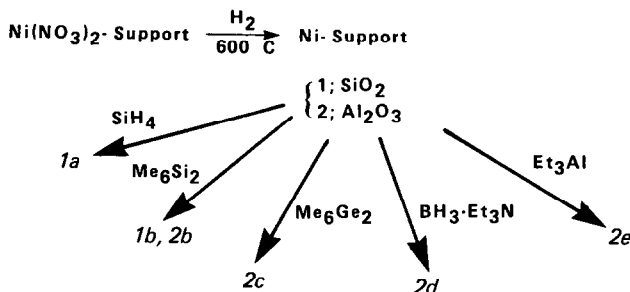
SCHEME 1. Modification of supported nickel catalysts.

with hydrogen flow rates varying between 0.4 and 10 sccm. The total flow rate was held constant at 20 sccm, the balance being helium.

Derivatization of the nickel catalysts was carried out according to the procedure outlined in Scheme I. With all reagents, except silane, derivatization of the reduced, high surface area nickel catalysts was effected *in situ* by the sequential addition of pulses 2–10 μl of the reagent to a 20-sccm carrier stream flow of 10% H$_2$ in He with the reactor held at 300°C. In the case of silane (30% in argon), the gas was metered directly into the carrier flow. By suitable choice of reactants and experimental conditions, ma-terials of varied structure and composition can be prepared by these procedures (8).

RESULTS AND DISCUSSION

Catalytic Activity and Selectivity.

Table 1 shows a summary of the catalytic activity seen for the series of nickel catalysts outlined in Scheme I over the temperature range 300–320°C with a carrier gas flow of 10% H$_2$ in He (see Experimental). The results obtained for 1 and 2 are typical of standard supported nickel catalysts and show a conversion of cyclohexane (C) to benzene (B) of 10–20% along with a sub-

TABLE 1

Effects of Surface Derivatization on Cyclohexane Conversion Over Supported Nickel[a]

Catalyst treatment	Support material	% Total hydrocarbons[b]		
		Cyclohexane	Benzene	Hydrogenolysis products[c]
1 untreated	SiO$_2$	59 (76)[d]	15 (12)	26 (12)
1a silane	SiO$_2$	96 (97)[e]	4 (3)	0 (0)
1b hexamethyldisilane	SiO$_2$	36	64	0
2 untreated	Al$_2$O$_3$	54 (68)[d]	19 (14)	26 (18)
2b hexamethyldisilane	Al$_2$O$_3$	54 (50)[e]	46 (20)	0 (29)
2c hexamethyldigermane	Al$_2$O$_3$	82 (38)[e]	18 (62)	0 (0)
2d borane triethylamine	Al$_2$O$_3$	99	1	0
2e triethylaluminum	Al$_2$O$_3$	97	3	0

[a] $T = 300$–320°C, 10% H$_2$ in He (20 sccm).
[b] Values listed in parentheses are data for thermally aged catalysts.
[c] > 90% *n*-hexane.
[d] Temperature cycled to 1000°C under 10% H$_2$ in He.
[e] Temperature cycled to 600°C under 10% H$_2$ in He.

stantial yield of hydrogenolysis products (H). In general, the hydrogenolysis product mixture was complicated, containing quantities of hexane, methane, toluene (13), and hexenes which varied considerably from run to run. The total yield of these products, however, was reasonably constant with n-hexane always comprising >90% of the mixture. For simplicity of presentation, all of the hydrogenolysis products are combined in the n-hexane data (H).

Several general trends emerge from the data in Table 1. First, the prior addition of pulses of the Group IIIA and IVA compounds studied here yields nickel catalysts with dramatically altered selectivity in cyclohexane conversion as compared to the untreated materials. In all instances, pretreatment of the catalyst results in a significant increase in the selectivity for benzene production (14). Surprisingly, the total activity of the system can remain quite high compared to the untreated catalyst as evidenced by the results obtained for hexamethyldisilane treated nickel supported on either SiO_2 or Al_2O_3 (1b, 2b). In both cases the conversion of cyclohexane and the production of benzene increased upon treatment with hexamethyldisilane. On either support, three 5-μl pulses of Me_6Si_2 at 300°C were sufficient to completely suppress the hydrogenolysis activity of a reactor containing ~0.25 g of catalyst with 10% nickel loading. This effect persisted over a period of 24 hr, after which time some return of hydrogenolysis activity was noted. Increasing the reactor temperature increases the rate of return of hydrogenolysis activity. Subsequent retreatment with Me_6Si_2 restores the selectivity of the catalyst. The subsequent decay of the selectivity of this restored catalyst at 300°C is markedly slower than that witnessed for the initially treated sample. This trend was found to hold over three successive regenerations.

Treatment of the starting nickel catalyst (1 or 2) with either SiH_4, Me_6Ge_2, $BH_3 \cdot Et_3N$, or Et_3Al enhances the selectivity of the catalyst at the expense of the overall activity of the system. Cyclohexane hydrogenolysis activity at ~300°C is completely suppressed, while the activity of these materials for benzene production is decreased by a factor of ~2–10. Unlike the results obtained above, heating a sample of 2c (treated with sufficient Me_6Ge_2 to eliminate hydrogenolysis activity) at 600°C for 1 hr does not result in a decrease in the selectivity of the catalyst for cyclohexane conversion at 300°C; the activity, however, increases by as much as a factor of 4 (see Table 1). This latter material was found to be remarkably stable; after heating at 600°C for an additional 24 hr in 10% flowing H_2, no return of hydrogenolysis activity at 300°C was observed. The increase in activity noted above was similarly stable. Such behavior implies that the intermetallic and/or mixed metallic–intermetallic surface phases which formed by this treatment at 300°C can be annealed to give new structures and/or stoichiometries with both higher total activity and comparable selectivity (15).

Dependence of Catalytic Activity on the Partial Pressure of Hydrogen.

As has been recently shown, intermetallic compounds of Group VIII metals (such as nickel with silicon) can exhibit strikingly different reactivity patterns than that exhibited by the pure metal (17). Of particular relevance was the observation that thin $NiSi_2$ films were inactive in dissociating H_2 under ultrahigh vacuum conditions. By extension, such a property is expected to greatly perturb the product distribution obtained from a reforming catalyst; in simple terms, decreasing the amount of surface bound hydrogen should promote dehydrogenation over hydrogenolysis. The untreated catalysts, 1 and 2, show the expected trends: the dehydrogenation of cyclohexane to benzene is inhibited by increasing the amount of hydrogen in the carrier feed while hydrogenolysis of the starting material, yielding hexane and other
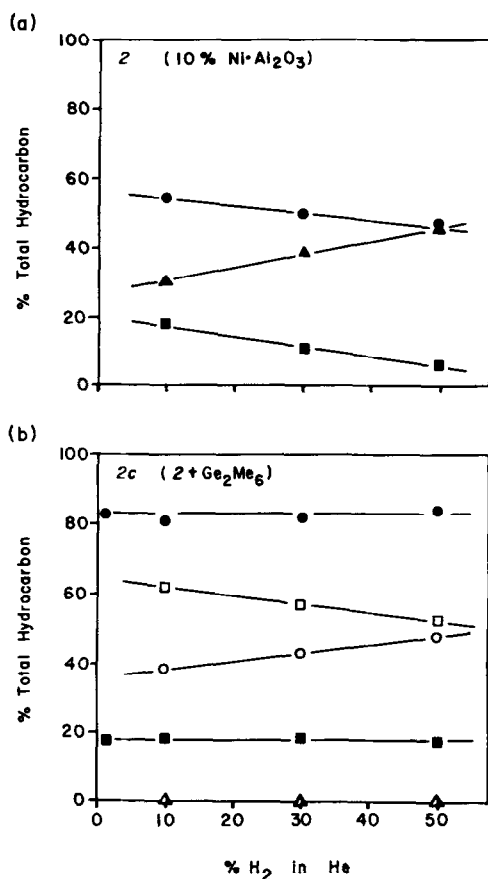
(a)

(b)

FIG. 1. Hydrogen partial pressure dependence of cyclohexane ($\bullet$, $\bigcirc$), conversion to benzene ($\blacksquare$, $\square$), and hexane ($\blacktriangle$, $\triangle$) over a 10% Ni/Al_2O_3 catalyst (2). After treating 2 with Ge_2Me_6 (2c), benzene is obtained as the sole product, the yield of which is independent of P_{H_2}. Heating 2c to 600°C results in an increase in catalyst activity at 300°C. While the selectivity is unchanged, the yield of benzene is now dependent on P_{H_2}. Open symbols represent the activity of 2c after cycling to 600°C. The error bars in (a) and (b) are of the size of figure symbols.

hydrogen addition products, is promoted (18). A representative example is shown in Fig. 1a which details the dependence of the conversion of cyclohexane on catalyst 2 as a function of the hydrogen content of the carrier flow.

In stark contrast to this, the activity of the high selectivity catalysts 1b, 2b, and 2c, treated so as to remove all hydrogenolysis activity, is found to be largely insensitive to the hydrogen content of the carrier feed

(representative data for 2c are shown in Fig. 1b). For all three catalysts, hydrogenolysis activity was absent with carrier flows containing as much as 50% H_2 (the most hydrogen rich carrier flow we tested). Over the same range, the activity of the catalyst for the dehydrogenation of cyclohexane to benzene was only minimally inhibited by increasing the hydrogen content of the carrier feed. Qualitative observations also indicated that 1b demonstrated increased resistance toward deactivation as compared to 1 when cyclohexane pulses were passed over the catalyst in the absence of hydrogen.

It is interesting to note that thermally aging the nickel-germanium bimetallic catalyst 2c (see above), while maintaining selectivity and promoting dehydrogenation activity, restores a strong inhibitatory hydrogen partial pressure dependence for cyclohexane conversion (see Fig. 1b). The origin of this effect is not understood.

CONCLUSIONS

The results presented above demonstrate that highly selective and potentially useful catalysts can be prepared by treating standard supported catalysts with certain volatile Group IIIA and IVA organometallic compounds. While many of the detailed aspects of this chemistry remain unclear, the trends in reactivity observed and the techniques developed detail new and useful additions to heterogeneous catalysis. We note, however, that derivatization of nickel represents but one example of a more generally applicable procedure (19). Thus, this technique may find applications in areas outside hydrocarbon catalysis (and presumably in geometries other than high surface area, supported materials). We will report on other developments in this area in future publications.

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7. In many instances it is hard to distinguish between intermetallic compound and alloy formation. In the case of reactions of nickel with SiH$_4$, strong evidence exists that the surface phases formed are discreet intermetallic compounds (*8*).
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9. In many respects, our results parallel those of Sinfelt and others on the effects of alloying on catalytic activity (*10, 11*).
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13. Although toluene, a minor product, is dehydrogenated with respect to cyclohexane, its formation still requires partial hydrogenolysis of the starting material.
14. It is thought that the most active sites on the catalyst surface are responsible for hydrogenolysis reactions and therefore one might argue that selective poisoning of these sites (i.e., by sulfur in the case of Pt/Al$_2$O$_3$ + CS$_2$) will enhance product selectivity. This will not explain, however, the increased activity of catalysts 1*b*, 2*b*, and 2*c* (heated to 600°C).
15. It should be emphasized that the untreated nickel catalysts, 1 and 2, did not display any thermal aging characteristics when cycled under flowing hydrogen to temperatures ≤ 800°C. At higher reduction temperatures some irreversible changes in selectivity were observed, namely a 50% decrease in cyclohexane hydrogenolysis activity under conditions comparable to those described in Table 1. A recent report in the literature has claimed that these same conditions produce "nickel–silicon alloys" (*16*). This alloy, if formed, is not the same as that obtained from the treatment of supported nickel with either silane or hexamethyldisilane, as both of these materials exhibit different physical and catalytic properties. Our BET surface area and H$_2$ and CO uptake data suggest that pure nickel catalysts reduced at high temperature (≥ 1000°C) are extensively sintered.
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18. At high hydrogen pressures, a negative rate dependence of the hydrogenolysis activity can be observed presumably due to the high hydrogen surface concentration.
19. For example, supported platinum and rhodium catalysts have been similarly modified (*20*).
20. Nuzzo, R. G., and Dubois, L. H., unpublished observations.

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