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# Clustering of Metal Atoms in Organic Media. 11. Effect of Support on Nickel Catalysts Prepared by Solvated Metal Atom Dispersion (SMAD)

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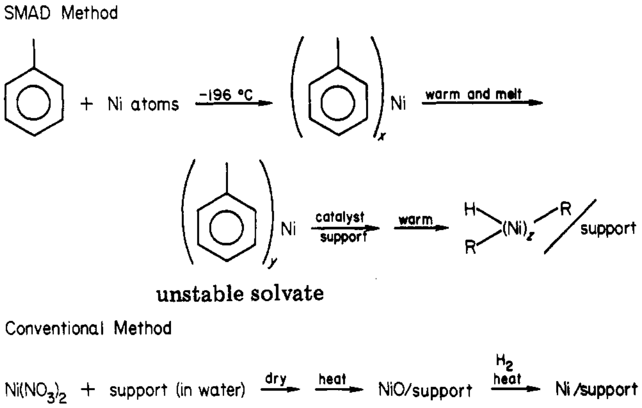
Highly dispersed Ni/support catalysts were prepared from toluene-solvated nickel atoms (solvated metal atom dispersed or SMAD). Catalysts were prepared on MgO, $Al_2O_3$, $SiO_2$, and carbon, and their activities were tested for hydrogenolysis of methylcyclopentane, hydrogenation of toluene, dehydrogenation of isopropyl alcohol, and methanation of carbon monoxide. Conventional catalysts were also studied and compared with the SMAD systems. The effect of the support on SMAD catalyst activities was minimal for hydrogenolysis of methylcyclopentane, hydrogenation of toluene, and dehydration of isopropyl alcohol. However, conventional catalysts showed a significant effect of support when these reactions were studied. This difference between SMAD and conventional catalysts is attributed to the presence of an insulating layer of carbonaceous species between Ni and the support in the SMAD systems. Conversely, catalyst activity for methanation of carbon monoxide was significantly affected by support, especially MgO. This phenomenon reflects a synergistic effect of MgO when Ni is present, where CO can be adsorbed readily on MgO which apparently aids in the initial CO reduction step. The SMAD method in combination with high surface area supports yields highly dispersed catalysts with very small particle sizes. Carbon, a support with a particularly high surface area, allows formation of the smallest particle sizes, and this phenomenon is believed to indicate a direct dependency of metal particle size on the surface area of the support. The implications of this finding on the mechanism of particle formation are discussed, as well as the observation of optimum nickel particle size effects for the reactions studied.

In previous papers[1-5] we have demonstrated that the use of metal vapors for preparing highly dispersed Ni/unsupported and Ni/supported catalysts is an effective catalyst preparative procedure. The catalysts prepared have shown extremely high activities in a variety of reactions. For supported catalysts, the metal vapor technique employs an unstable metal atom solvate ($\pi$-arene organometallic complex) which is allowed to permiate the catalyst support. Upon being warmed, the solvate decomposes, depositing small metal particles/atoms on the support. Thus the term "solvated metal atom dispersed" or SMAD catalyst is applied.

Since these catalysts have some interesting properties and potential usefulness, we decided to investigate the effect of supports on catalyst activities and properties and to compare support effects for the SMAD systems vs. conventionally prepared systems (see Scheme I). This appeared to be a particularly interesting study since the SMAD method produces catalysts in a reduced, dispersed state directly, and the SMAD catalyst preparations have been successful for all supports studied so far. However, a conventional preparative method requires that the $Ni^{2+}$ salts be reduced after deposition on the support, and the support can have a profound effect on this reduction step.[6,7] This is particularly true for basic supports such as MgO where solid solutions with NiO can form, which greatly inhibit the $H_2$ reduction step.

In assessing support interactions,[8] it is important to consider both electronic effects where the support can donate or extract charge density from the catalytically active metal particle,[9,10] and bifunctional effects where the support and metal particle act somewhat independently on the incoming reactant, but overall have a synergistic effect on the catalytic reaction (for example in hydrocarbon reforming).[11,12]

Scheme I



It should be noted at this juncture that the SMAD catalysts contain a significant amount of carbonaceous material, which is the result of low temperature cleavage of the organic solvent by the extremely reactive forming metal particles.[2] Does this carbonaceous material have an effect on the Ni - support interactions as discussed above?

## Experimental Section

**Catalysts.** Catalysts were prepared by the metal vapor SMAD method with toluene as the solvating medium. This procedure has already been described in detail in previous papers.[1,2,4,5] The catalyst supports used in this work are listed as follows. (1) MgO: Powdered MgO was produced by calcination of $Mg(NO_3)_2{\cdot}6H_2O$ (analytical grade from MallincKrodt Chemical) at 500 °C followed by washing with distilled and deionized water, drying at 110 °C, and heat treating at 800 °C under vacuum (3 × $10^{-5}$ mmHg). The surface area of MgO powder prepared in this way was 90 $m^2$/g.

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(2) $Al_2O_3$: Fibrillar Alumina (ALBES FE) from Showa Tansan Kaisha, Ltd., was heat treated at 500 °C under vacuum. The final $Al_2O_3$ powder had a surface area of 110 $m^2/g$. (3) $SiO_2$: Silica gel S-157 (28–200 mesh) from Fisher Scientific Co. was employed; 60–200-mesh particles of the silica gel were collected by sieving. This $SiO_2$ was washed with distilled and deionized water, dried at 110 °C for 5 h, and heat treated at 500 °C under vacuum. The surface of the resultant powder was 190 $m^2/g$. (4) Activated carbon: DARCO-G-60 activated carbon from Atlas Chemical Industries was heat treated at 500 °C under vacuum. The surface area of this powder was 600 $m^2/g$.

These supports were transferred carefully to the bottom of the metal vapor reactor in a stream of dry, deoxygenated nitrogen gas.

Conventional catalysts were prepared by a salt-impregnation method; the supports prepared as mentioned above were impregnated with an aqueous solution of nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$, reagent grade from Allied Chemical] followed by drying at 110 °C and slow reduction in a $H_2$ stream.[13] The final temperature of reduction was 480 °C for $Al_2O_3$-, $SiO_2$-, and carbon-supported catalysts and 550 °C for MgO-supported catalysts.[1]

BET surface areas of supports were determined by the adsorption of nitrogen gas at -196 °C. The surface area of Ni metal was determined by $H_2$ chemisorption at room temperature, with the assumption that $H_2$ chemisorbs dissociatively on the surface of Ni atoms in a H/Ni ratio of 1, and the area of one Ni atom is 6.77 Å.[2,13] CO chemisorption at 0 °C and $O_2$ titration at 430 °C were also carried out to help characterize the catalysts.

Ni contents of the catalysts were determined by EDTA titration of 80 °C with 1-[(2-pyridyl)azo]-2-napthol as indicator at pH 4.[14] In the case of the $Al_2O_3$-supported catalyst, $Al^{3+}$ dissolved in acid solution disturbed the titration of the Ni metal. Hence, another procedure was necessary to avoid this problem; $Ni^{2+}$ in the solution was separated from $Al^{3+}$ by forming a Ni–DMG (dimethylglyoxime) complex at pH 4–10 followed by extraction of the Ni–DMG complex with chloroform and decomposition of the complex in acid solution.

**Catalytic Activity Measurements and Analyses of Products.** Catalytic activities were measured in a conventional pulse microreactor connected to a gas chromatograph. The reactions studied were hydrogenolysis of methyl cyclopentane (MCP), hydrogenation of toluene (TOL), methanation of carbon monoxide (CO), and dehydrogenation of isopropyl alcohol (IPA). The former three reactions were carried out in a hydrogen stream (60 $cm^3/min$), and the last reaction was done in a helium stream (60 $cm^3/min$). Both carrier gases, hydrogen and helium, were used after purification with 5-Å molecular sieve at -196 °C. The detailed procedures for the activity measurements were already mentioned in a previous paper.[1]

**Infrared Studies.** Sample disks for infrared spectral analyses were prepared by using a 23-mm Disc Maker made of stainless steel. Manipulations were carried out in a Vacuum Atmospheres inert atmosphere box under nitrogen. The Disc Maker was sealed with plastic tape in the box, removed, and pressed at 16000–24000 psi for 0.5 h. The disks were placed in a special cell (Figure 1), evacuated to $10^{-5}$ torr followed by heat treatment at 400 °C. During the heatup 100 torr of $H_2$ gas was inletted at 300 °C for 10 min and at 400 °C for 10 min to insure that the surface was as clean of carbonaceous species as possible. After cooling, the disk was moved to the NaCl window area, an IR spectrum recorded, and then 100 torr of CO added followed by IR spectral studies (Perkin-Elmer Model 180).

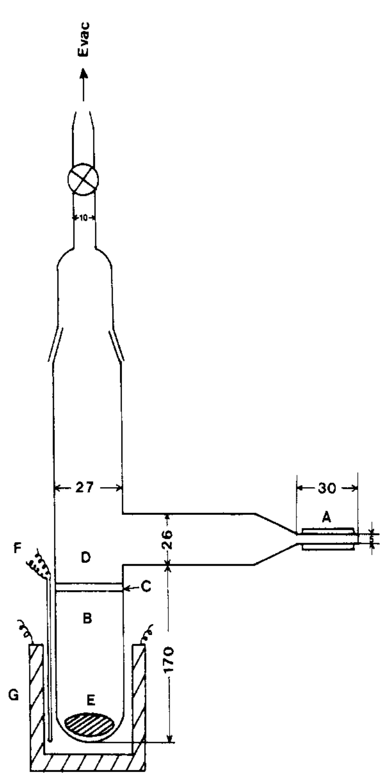

Figure 1. Infrared cell for CO adsorption studies: A = NaCl window, B = quartz glass, C = graduated seal, D = Pyrex glass, E = catalyst sample, F = thermocouple, and G = electric furnace. Dimensions are in millimeters,

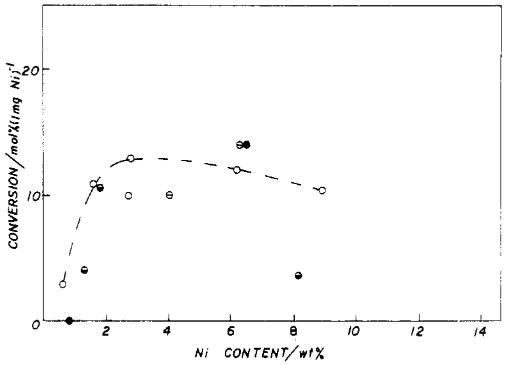

Figure 2. Percent conversions for hydrogenolysis of MCP for different loadings of Ni (all catalysts standardized to 1 mg of Ni): ○, Ni–MgO; ◒, Ni–$Al_2O_3$; ⊖, Ni–$SiO_2$; ● = Ni–carbon.

## Results

**(A) SMAD Catalyst Studies. (1) Hydrogenolysis of Methylcyclopentane (MCP).** Activities of the various catalysts plotted against Ni content, but normalized to 1 mg of Ni, are shown in Figure 2. The activities reflect the amount of catalytically active Ni available per milligram of Ni and should also reflect the influence of support on the MCP hydrogenolysis reaction (to yield a variety of acyclic hydrocarbons). Figure 2 demonstrates that the activities of SMAD systems Ni/MgO, Ni/$Al_2O_3$, and Ni/$SiO_2$ are very similar and that the MgO and $Al_2O_3$ systems exhibit the same tendency of very low loadings yielding less activity (on a normalized to 1 mg of Ni basis). Very high loadings always cause a lowering in activity whereas moderate loadings (1.5–7%) yield the highest activities. Since the only difference in preparative procedure for the different loadings is really the dilution of the $Ni(TOL)_x$ species in toluene, we assume that greater dilution will eventually yield greater dispersion and smaller average particle sizes. If this assumption is correct, then there apparently is an optimum particle size for MCP hydrogenolysis on Ni/MgO,[1] which is also the case in a very approximate way for Ni/$Al_2O_3$. For Ni/$SiO_2$ and Ni/C the data are too limited to make a conclusion. However, it is interesting that the Ni/MgO, Ni/$Al_2O_3$, and Ni/$SiO_2$ systems have similar activities as well as similar BET surface areas. In the case of Ni/C, which has a BET

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[13] C. H. Bartholomew and and R. B. Pannell, *J. Catal.*, **65**, 390 (1980); C. H. Bartholomew and R. J. Farauto, *ibid.*, **45**, 41 (1976).

[14] G. Schwarzenbach and H. Flascheka, "Complexometric Titrations", Methuen, London, 1969.

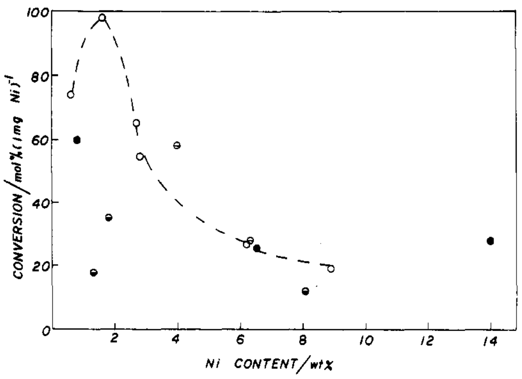

**Figure 3.** Percent conversions for hydrogenation of TOL for different loadings of Ni. Symbols are the same as those of Figure 2.

surface of 600 $m^2/g$, or several times higher than the MgO, $Al_2O_3$, or $SiO_2$ analogues, the MCP hydrogenolysis activity is essentially zero at 0.8% loading but jumps to one of the highest activities at 6% loadings. This might be explained by assuming that the size of the particles is dependent on the surface area of the support available for their deposition. Thus, an 0.8% Ni/C catalyst would have extremely small particles, and these may be ineffective for MCP hydrogenolysis. This reasoning seems logical since it is known that larger Ni particles are necessary for the alkane hydrogenolysis reactions.[15] More will be said about this later.

In conclusion, the most important finding is that the Ni/MgO, Ni/$Al_2O_3$, and Ni/$SiO_2$ catalysts exhibit similar activities, similar particle size effects, and similar MCP hydrogenolysis product distributions. Since these supports have widely varying acid–base properties, we conclude that there is no support effect for MCP hydrogenolysis with these SMAD catalysts (MgO, $Al_2O_3$, $SiO_2$). The differences in the Ni/C system can be attributed to an effect of surface area on Ni particle formation and not directly on an electronic support effect or bifunctional effect.

**(2) Hydrogenation of Toluene.** Figure 3 plots catalytic activities for toluene hydrogenation vs. Ni loadings. There is a clear dependency on particle size for the Ni/MgO catalyst. Also note that the 0.8% Ni/C catalyst exhibited significant activity for toluene hydrogenation (recall its zero activity for MCP hydrogenation). This may be further evidence that we are dealing with particle size effects since it is known that smaller particles can be effective in arene hydrogenations but not alkane hydrogenolysis processes.[1,15] Thus, the particles on 0.8% Ni/C are apparently large enough to be effective for toluene hydrogenation but too small to be effective for MCP hydrogenolysis.

Particle size effects concerning the Ni/$Al_2O_3$ and Ni/$SiO_2$ SMAD catalysts are not obvious from the existing data. However, it is clear that the overall activities are very similar for all the SMAD catalysts, and so an electronic or bifunctional support effect is definitely not present for toluene hydrogenation.

**(3) Dehydrogenation of Isopropyl Alcohol (IPA).** Catalytic activities of SMAD catalysts for dehydrogenation of IPA are illustrated in Figure 4. However, Ni/$Al_2O_3$ is not included since $Al_2O_3$ itself showed high activity for *dehydration* of IPA, which seriously interfered with dehydrogenation. The other supports (without Ni) showed no dehydration or dehydrogenation activities.

The results of these experiments can be interpreted in the same way as the toluene hydrogenation results. That is, the Ni/MgO, Ni/$SiO_2$, and Ni/C all have similar catalytic activities for similar Ni contents, and this means that no significant support effect is operative. Also note that the 0.8% low-loading Ni/C catalyst has high activity for IPA dehydrogenation, suggesting that its small Ni particles are large enough to be effective in this dehydrogenation reaction but not large enough for MCP hydrogenolysis (C–C cleavage).

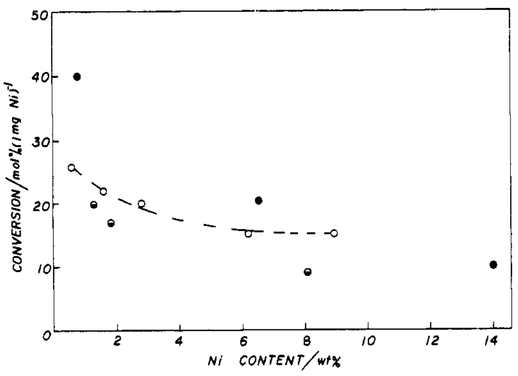

**Figure 4.** Percent conversions for dehydrogenation of IPA for different loadings of Ni. Symbols are the same as those of Figure 2.

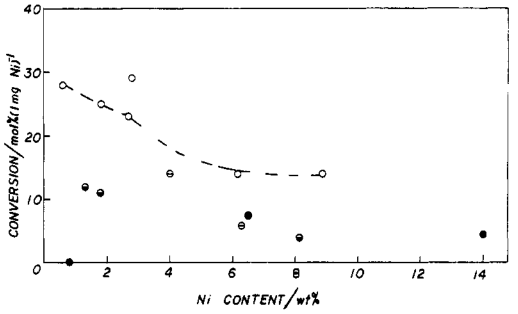

**Figure 5.** Percent conversions for methanation of CO for different loadings of Ni. Symbols are the same as those of Figure 2.

**(4) Methanation of Carbon Monoxide (CO).** In contrast to the previous reactions discussed, there is a substantial support effect for SMAD catalysts for the CO methanation reaction. Figure 5 illustrates this effect. The Ni/MgO catalyst is considerably more active than the Ni/$Al_2O_3$, Ni/$SiO_2$, or Ni/C SMAD systems. The complete inactivity of the 0.8% Ni/C is also noted, similar to the finding for MCP hydrogenolysis, which again suggests that the Ni particles on this catalyst are too small to be effective in the $CO \rightarrow CH_4$ reaction. Since this catalyst was effective in the toluene hydrogenation and IPA dehydrogenation, these results also imply that larger Ni particles are required for the CO methanation reaction (as well as MCP hydrogenolysis).

To determine if the higher activity of the Ni/MgO SMAD catalyst was due to a unique electronic character of this SMAD system or due to a bifunctional effect of MgO, we carried out some mechanical mixing experiments. The Ni/MgO and Ni/C SMAD catalysts were each mixed separately under airless conditions with heat-treated MgO and C. Catalytic activities were measured, and Ni/C mixed with carbon showed no increase, but Ni/C mixed with MgO did (Table I). Ni/MgO mixed with carbon or MgO showed no significant changes. Since mechanical mixing would not be expected to yield an intimate Ni–support interaction, these results suggest that the unusual reactivity of the Ni/MgO SMAD system is due to a bifunctional effect. That is, Ni/C mixed with MgO should not yield a catalyst where the Ni particles are electronically affected by MgO but could yield a catalyst where MgO

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[15] J. A. Dalmon and G. A. Martin, *J. Catal.*, **66**, 214 (1980).

Table I. Carbon Monoxide Methanation Activities of Ni on Different Supports

| catalyst | conversion,[b] mol %/mg of Ni | catalyst | conversion,[b] mol %/mg of Ni |
|---|---|---|---|
| 6.2 wt % Ni-MgO | 14 | 14 wt % Ni-carbon + carbon[a] | 8.0 |
| 6.5 wt % Ni-carbon | 7.7 | 14 wt % Ni-carbon + MgO[a] | 14 |

[a] Mixture of 14 wt % Ni-carbon catalyst and carbon or MgO support. [b] Conversion at 350 °C.

Table II. Activities of Conventional Catalysts for Hydrogenolysis of MCP, Hydrogenation of TOL, Dehydrogenation of IPA, and Methanation of CO

| | conversion, mol %/ mg of Ni | | | |
|---|---|---|---|---|
| catalyst | MCP | TOL | IPA | CO |
| 4.5 wt % Ni-MgO | 1.0 | 2.4 | 5.6 | 2.2 |
| 4.7 wt % Ni-$Al_2O_3$ | 1.0 | 28 | | 9.7 |
| 5.1 wt % Ni-carbon | 0 | 9.7 | 13 | 4.8 |

Table III. Surface Area and Extent of Reduction of Ni on Different Supports

| catalyst | surface area,[a] $m^2/g$ of Ni | CO/H[b] ratio | extent of reduction,[c] % |
|---|---|---|---|
| 2.7 wt % Ni-MgO (SMAD) | 110 | 3.0 | 90 |
| 4.0 wt % Ni-$Al_2O_3$ (SMAD) | 37 | 2.5 | 100 |
| 1.8 wt % Ni-$SiO_2$ (SMAD) | 45 | 5.5 | 99 |
| 6.5 wt % Ni-carbon (SMAD) | | | 58 |
| 4.5 wt % Ni-MgO (conv) | 15 | 3.5 | 19 |
| 4.7 wt % Ni-$Al_2O_3$ (conv) | 30 | 3.8 | 50 |
| 5.1 wt % Ni-carbon (conv) | | | 21 |

[a] By hydrogen chemisorption. [b] By CO chemisorption. [c] By oxygen titration.

could serve to adsorb CO near a catalytically active Ni particle, and thus aid in the initial stages of the reduction. On consideration of the considerable propensity of MgO for CO adsorption, telomerization, electron transfer, etc.,[16,17] this seems to be a likely rationale.

It is also worthy of note that on a normalized to 1 mg of Ni basis, all of the Ni/MgO SMAD catalysts ranging in loading from 0.6 to 8.9 wt % of Ni exhibited high methanation activities. In fact, these activities were similar, falling only slightly as loading increased. Thus, good dispersion was obtained in each Ni/MgO SMAD preparation, and no optimal particle size effect was observed (for the MgO systems).

**(B) Conventional Catalyst Studies.** Three conventionally prepared catalysts were studied, and Table II summarizes the results. The general conclusions that can be drawn are as follows. (1) In all cases greatly decreased activities as compared with analogous SMAD catalysts were observed. This is apparently due to much poorer dispersion and larger particle sizes, and this was most striking in the Ni/MgO system.[1] With MgO as a support it is known that reduction of $Ni^{2+}$ to $Ni^0$ is extremely difficult owing to a very strong interaction between the support surface and $Ni^{2+}$.[7] Thus, high reduction temperatures are required, causing undesirable sintering. Our results confirm these earlier findings, and further results concerning reduction degree are found in the next section. (2) The support does have an effect on all four of the reactions studied (Table II). In some cases the support effect is large; for example, $Ni/Al_2O_3$ is very active for toluene hydrogenation. And, although our data is limited for the conventional catalysts, support effects are well-known phenomena in the field of heterogeneous catalysis[8] when dealing with conventionally prepared catalysts (cf. Discussion and Conclusions).

**(C) Surface Areas and Valence of Nickel on the Support.** Surface areas of Ni were determined by $H_2$ chemisorption, and the percent of Ni in the zero-valent state (reduction degree) was determined by $O_2$ titration, except in the case of Ni/C where a CO extraction of Ni(0) to form $Ni(CO)_4$ was employed.[13,14] Table III summarizes our findings which indicate that the SMAD catalysts possess much higher Ni surface areas and a higher percent of Ni in the catalytically active zero-valent state.

Although the Ni surface areas on these catalysts are large, they are not as high as we expected for either the SMAD or conventional systems. Therefore, we carried out CO adsorption studies. The CO/H ratio obtained can yield information concerning the accuracy of the $H_2$ chemisorption step. The CO/H ratio should be 1–3 theoretically,[13] with a value approaching 3 being found for highly dispersed Ni samples. However, we find values >3 and therefore believe that $H_2$ chemisorption must be suppressed, and so the surface areas calculated are *minimum* values. Actually the CO/H ratio should tend to increase with a decrease in Ni content because of a stronger interaction of small metal particles with the support.[13] However, the values of CO/H for the SMAD catalysts were smaller than those for conventional catalysts. Therefore the CO/H ratios shown in Table III add further evidence that the interaction between the Ni and the support is weaker in the SMAD systems.

**(D) Infrared Studies of CO Adsorption.** The position of $\nu_{C=O}$ for adsorbed CO should be indicative of the extent of Ni–support interaction.[10,18] Acidic supports should decrease the electron density of Ni, and therefore $\nu_{C=O}$ should increase, and vice versa for basic supports. Indeed, for conventional Ni/MgO several bands are observed below 2040 $cm^{-1}$ (cf. Table IV), and this clearly shows a strong electronic donating effect of MgO to Ni. Figueras and co-workers observed a similar phenomenon for CO adsorbed on Pd/MgO (2065 $cm^{-1}$) and Pd/$SiO_2$–$Al_2O_3$ (2100 $cm^{-1}$).[10] In the case of Ni/MgO SMAD, only one band was observed at 2055 $cm^{-1}$, which suggests a weak electronic MgO–Ni interaction. This conclusion is supported by the finding that $Ni/Al_2O_3$ SMAD and $Ni/SiO_2$ SMAD have $\nu_{C=O}$ absorptions at 2056 and 2055 $cm^{-1}$, respectively. However, conventional $Ni/Al_2O_3$ and $Ni/SiO_2$ systems also showed absorptions at 2056 and 2055 $cm^{-1}$,

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(16) A. Zecchina and F. S. Stone, *J. Chem. Soc., Chem. Commun.*, 582 (1974); A. Zecchina, M. G. Lofthouse, and F. S. Stone, *J. Chem. Soc., Faraday Trans. 1*, 71, 1476 (1975.

(17) R. M. Morris, R. A. Kaba. T. G. Groshens, K. J. Klabunde R. J. Baltisberger, N. F. Woolsey, and V. I. Stenberg, *J. Am. Chem. Soc.*, **102**, 3419 (1980).

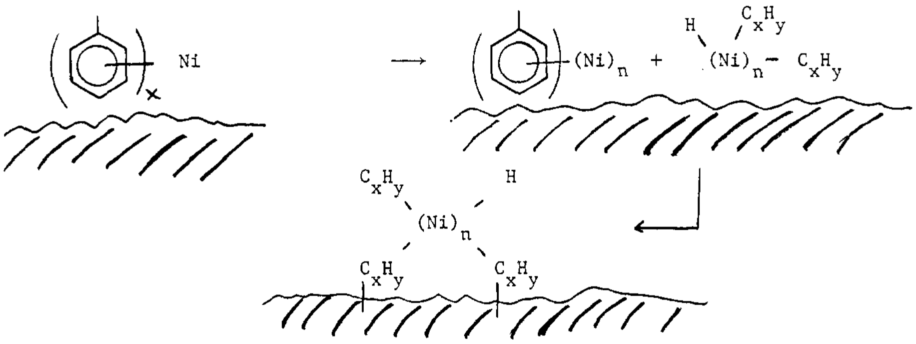
(18) L. H. Little, "Infrared Spectra on Adsorbed Species", Academic Press, London, 1966.

Table IV. Positions of IR Bands of Adsorbed CO on Ni[a]

| catalyst | wave no. of bands of adsorbed CO, $cm^{-1}$ | catalyst | wave no. of bands of adsorbed CO, $cm^{-1}$ |
|---|---|---|---|
| 4.5 wt % Ni-MgO (conv) | 2040, 1970-1965, 1925 | 2.0 wt % $Ni-SiO_2$ (SMAD) | 2055 |
| 5.0 wt % $Ni-SiO_2$ (conv) | 2055 | 1.0 wt % and 4.4 wt % $Ni-Al_2O_3$ (SMAD) | 2056 |
| 4.7 wt % $Ni-Al_2O_3$ (conv) | 2056 | | |
| 1.1 wt % and 3.2 wt % Ni-MgO (SMAD) | 2055 | | |

[a] Pressure of gaseous CO is 100 torr.

Scheme II



respectively. Since these absorptions are in essentially the same position for gaseous $Ni(CO)_4$,[19] the overall conclusion is that there is no support effect on CO adsorption except for the Ni/MgO conventional catalyst.

Considering that the SMAD catalysts have smaller particles than the conventional systems, greater $\nu_{C=O}$ changes would be expected for the SMAD systems if any electronic Ni–support interaction were present. Therefore, the results concerning the SMAD catalysts are the most revealing.

## Discussion and Conclusions

**(A) Catalyst Activities.** The greater activities of the SMAD catalysts vs. the conventional catalysts can be rationalized by the fact that the SMAD catalysts have higher Ni surface areas (smaller particles) and a greater percent of Ni in the catalytically active zero-valent state. This is a natural consequence of the method of preparation and is especially important for the Ni/MgO system where it is extremely difficult to prepare a dispersed catalyst by conventional means.

**(B) Particle Size Effects and SMAD Catalysts.** The SMAD method employs an unstable π-arene–metal atom complex which can be regarded as a solution of solvated metal atoms. Upon being warmed, the complex decomposes to yield metal particles. In the presence of a catalyst support, the decomposition–deposition rate must be enhanced, or at least modified, since the final metal crystallites are smaller when supported. The data of Scott and co-workers[20] and our data[2,5] indicate that the crystallites are on the average less than 20 Å and that these can agglomerate and form chains of somewhat larger particles.

High surface area supports would be expected to yield catalysts containing the smallest particles. This is because the probability of the solvated metal atoms interacting with one another would be lowest as the organic Ni complex decomposes on slow warming, and Ni is being deposited. Thus, more surface would be available to accept atoms and small clusters before they have a chance to grow. High dilution of Ni atoms in the solvating medium should also lead to smaller Ni particles, by this reasoning.

In this work, evidence for optimal particles sizes was obtained by plotting catalysis reaction rates per milligram of Ni vs. the percent loading of Ni. For methylcyclopentane hydrogenolysis a particle size effect was noted for all the catalysts but was most striking in the Ni/MgO SMAD and Ni/C SMAD catalysts. For the Ni/C system, low Ni loadings (high dilution) and an extremely high surface area of C combined to yield a catalyst of such high dispersion that it was ineffective for methylcyclopentane hydrogenolysis. With increased loading, however, it became very effective. In contrast, for the SMAD Ni/MgO, $Ni/Al_2O_3$, and $Ni/SiO_2$ catalysts, where the supports have similar surface areas, the lower Ni loadings showed activity, but activity maximized in the 2–6% range. Thus, these data support our proposal that particle size can be controlled by Ni loading (solvated metal atom dilution) and support surface area. They also support the notion that optimal particle sizes are necessary for effective methylcyclopentane hydrogenolysis.

Similar phenomena were observed in the CO → $CH_4$ catalysis studies, indicating optimal particle sizes may be necessary and that the 0.8% Ni/C catalyst contains particles too small to be effective. For toluene hydrogenation particle size effects were also noted, but in this case the 0.8% Ni/C catalyst was active, suggesting that the optimal particle size is smaller for this reaction than for methanation or methylcyclopentane hydrogenolysis. And finally, no particle size effect was observed in the isopropyl alcohol dehydrogenation (all catalysts showed activity).

**(C) Support Effects.** Electronic interactions of the support surface with the attached metal cluster have been observed numerous times with conventionally prepared catalysts.[8] Sinfelt and co-workers observed varying ethane hydrogenolysis activities for Ni and Co supported on $SiO_2$, $Al_2O_3$, $SiO_2$–$Al_2O_3$, or carbon.[21,22] Likewise, O'Neill and

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Yates[23] and Figueras and co-workers[10] observed the effects of different supports ($Al_2O_3$, $SiO_2$, $TiO_2$, MgO, and zeolite) for CO adsorption on supported Ni.

In our comparative studies of SMAD vs. conventional Ni/support catalysts we have found that electronic support effects are minimal for the SMAD catalysts but are significant for the conventional systems. Thus, the Ni–support interactions are definitely different in the two systems.

For an explanation of this difference, recall that during low-temperature clustering of nickel atoms in organic media a competition exists between Ni–Ni bond formation (cluster growth) and reaction of the forming clusters with the organic medium. This process leads to extensive C–C and C–H cleavage of alkanes at temperatures even as low as $-130$ °C,[2] and a great deal of carbonaceous material is incorporated into the final clusters. Scott and co-workers[20] and we[2] have demonstrated that the final Ni clusters are surrounded by a protective carbonaceous layer.

Arenes react similarly to alkanes with the bare Ni clusters. However, at low temperatures ($<-50$ °C) formation of a stable $\pi$-arene–Ni complex prevents much cluster formation, and so C–C and C–H bond cleavage probably does not occur until the $\pi$-arene complex starts to decompose ($>-50$ °C). At this time the catalyst support is present in the melted Ni–arene solution. Thus, as decomposition of the $\pi$-arene–Ni complex occurs, Ni clusters begin to form and can react with the excess arene and thereby incorporate carbonaceous residues. These residues or arene fragments could serve as a mode of attachment of the Ni clusters to the surface of the support (see Scheme II). It is possible that this would lead to a robust Ni–support attachment but would also serve to insulate the Ni clusters from electronic effects of the support. That such a sequence of reactions takes place seems likely on the basis of our previous work and the current data.

In support of the above explanation, we have determined that after treatment of a 8.9 wt % of Ni/MgO SMAD catalyst wth $H_2$ at 400 °C some of the incorporated carbon remains. The final value was 0.33 wt % of carbon (Ni/C molar ratio of 5.5), and this would likely be the carbon buried under the metal cluster and in close proximity to the support surface. It is not likely that this remaining carbon is dispersed over the support surface since the Ni/$Al_2O_3$ catalyst still exhibited acidic character (IPA dehydration activity), and the Ni/MgO catalyst still exhibited basic character (bifunctional CO methanation activity). Therefore, the active support sites not containing Ni do still exist after the SMAD treatment.

The available data lead us to conclude that the SMAD catalysts consist of very small Ni clusters probably attached to the support through carbonaceous residues. This mode of attachment precludes electronic support effects but still allows bifunctional catalysis to occur, as is the case with methanation over the Ni/MgO SMAD catalyst. In the future we hope to obtain further information through surface spectroscopic studies as well as high-resolution transmission electron microscopy.

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**Registry No.** Nickel, 7440-02-0; methylcyclopentane, 96-37-7; toluene, 108-88-3; isopropyl alcohol, 67-63-0; carbon monoxide, 630-08-0.

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# Synthesis and Thermal Isomerization of Tricyclo[4.2.2.0$^{1,6}$]dec-7-ene ([4.2.2]Propell-7-ene) to 3,8-Dimethylenecyclooctene

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Tricyclo[4.2.2.0$^{1,6}$]dec-7-ene ([4.2.2]propell-7-ene ([4.2.2]propell-7-ene; **1**) has been prepared from *cis*-4-cyclohexene-1,2-dicarboxylic anhydride through a conventional 12-step reaction sequence by way of bicyclo[4.2.0]oct-1(6)-ene and tricyclo[4.2.1.0$^{1,6}$]nonane-9-carboxaldehyde tosylhydrazone. It is isomerized thermally to 3,8-dimethylenecyclooctene (**2**) with activation parameters $E_a = 35.8 \pm 1.3$ kcal mol$^{-1}$ and log $A = 12.6 \pm 0.6$. Two possible explanations for the isomerization are considered: reaction by way of a short-lived bicyclo[4.2.2]deca-1(8),6-diene intermediate or direct cleavage of C(1)–C(6) and C(9)–C(10) simultaneously.

Bicyclo[2.2.0]hex-2-ene[1] isomerizes thermally to give 1,3-cyclohexadiene.[2-4] This electrocyclic reaction must be disrotatory and thus orbital symmetry forbidden; nevertheless, it is favored kinetically over alternative modes of rearrangement such as cyclobutane cleavage, degenerate [1,3] sigmatropic carbon shift, and retro-ene reaction.

5-Methylenebicyclo[2.2.0]hex-2-ene[5] and 5,6-dimethylenebicyclo[2.2.0]hex-2-ene[6] react similarly, giving 1-methylene-2,4-cyclohexadiene and 1,2-dimethylene-3,5-cyclohexadiene (*o*-xylylene), respectively.

*cis*-1,3,5-Hexatriene is not an important intermediate in the bicyclo[2.2.0]hex-2-ene isomerization to 1,3-cyclohexadiene; were it formed, it would be detected, for its rate of isomerization to cyclohexadiene is comparatively slow.[7,8]

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