JOURNAL OF CATALYSIS 73, 216–227 (1982)

Clustering of Metal Atoms in Organic Media
9. High-Activity Ni/MgO Catalysts Prepared by Metal Vapor Methods. Surface Area and Particle Size Effects

KIYOTAKA MATSUO AND KENNETH J. KLABUNDE[1]

Department of Chemistry, Kansas State Unviersity, Manhattan, Kansas 66502

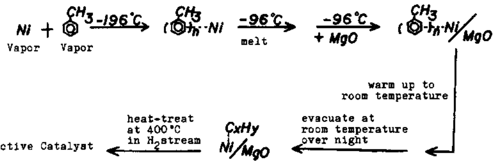
Received March 2, 1981; revised June 23, 1981

A metal vapor method was employed to prepare highly dispersed Ni metal catalysts (solvated metal atom dispersed = SMAD catalyst) supported on MgO. Compared with conventional Ni/MgO compositions, the SMAD catalysts showed much greater activities for all reactions studied (hydrogenolysis of methylcyclopentane, MCP; hydrogenation/hydrogenolysis of toluene, TOL; methanation of carbon monoxide, CO; dehydration of isopropyl alcohol, IPA). These high activities for the SMAD catalysts are attributed to the high surface area of Ni on MgO and the high percentage of this Ni in a zero-valent state ("reduction degree"). Conventional methods for preparing Ni/MgO catalysts did not yield nearly such favorable surface areas or reduction degrees. Nickel particle size effects were observed during hydrogenolysis studies of MCP and hydrogenation studies of TOL. These phenomena are explained by assuming the size of an active Ni particle to be largest for hydrogenolysis of MCP > hydrogenation of TOL > methanation of CO ≃ dehydrogenation of IPA.

INTRODUCTION

Over the past 12 years the field of "metal atom (vapor) chemistry" has become a well-established synthetic technique in inorganic and organometallic chemistry (*1*). In recent years this method of vaporizing metals and using the resultant atoms as synthetic reagents has been applied to prepare organometallic polymers and catalysts. Francis and Timms (*2*) "supported" metal atoms in siloxane polymers while Ozin *et al.* (*3*) have supported small clusters in similar media. Likewise we have been examining the clustering/reaction processes of metal atoms in organic solvent media at low temperatures (*4*). Fundamental information about metal atoms and cluster interactions/mobilities with organic and polymer media is being obtained through these studies.

Herein we report on the use of the metal atom-vapor method for the production of highly dispersed Ni/MgO catalysts (cf. Scheme 1). Since solvated metal atoms are employed as intermediates in these catalyst preparation schemes we have termed the catalysts "solvated metal atom dispersed" (SMAD) systems. The method is actually an extension of the work of Yermakov (*5*) and Ichikawa (*6*) where stable organometallic compounds are used as dispersing reagents. The use of organometallic complexes in low valent states allows the dispersion of the metal in low valent states. Thus, high-temperature reduction schemes are not necessary, as they are with the more conventional salt deposition/H_2 reduction methods. Of course the organometallic dispersion reagents depend on: (1) the availability of a suitable organometallic compound with appropriate solubility characteristics and the ability to bind to the



SCHEME 1. Sequence for the preparation of active Ni/MgO SMAD catalysts.

---

[1] To whom correspondence should be addressed.

0021-9517/82/020216-12$02.00/0

support, and (2) the ability of the dispersed organometallic to decompose under relatively mild conditions without migration so that fragments of the reagent (atoms or small particles) bind tightly to the support, and (3) the organic groups desorbed do not polymerize on the support surface or otherwise interfere with the active catalytic sites. In the case of Ni, there are a variety of stable low-valent organometallic complexes available that might be successfully employed (e.g., bis(cyclooctadiene)Ni(O), bis(allyl)Ni, $Ni(CO)_4$, tris(ethylene)Ni(O), or bis(cyclopentadienyl)Ni). However, these are very sensitive and toxic materials, and are not easy to prepare and work with. Also, when dealing with other metals, such as Fe, Co, Pd, or Pt such a variety of complexes is not available.

The SMAD method is a useful extension of the organometallic dispersing procedure since: (1) many metals can be employed, (2) relatively stable organic ligands can be employed such as toluene or tetrahydrofuran, (3) it is not necessary to isolate the intermediate organometallic (metal atom solvate), (4) the catalyst preparations can be carried out under very mild conditions (e.g., −50°C) under a vacuum or inert atmosphere, (5) a wide variety of organic dispersing solvents or mixtures of solvents can be employed which could lead to a "tailoring effect" on catalyst properties, and (6) large-scale preparations are feasible and necessary equipment is commercially available.

Previously we have reported on the SMAD procedure for preparing Ni/Al_2O_3, Pd/Al_2O_3, Ag/Al_2O_3 (*7*), and Ni/unsupported (*8*) systems. The present work deals in detail with a Ni/MgO system. Toluene was used exclusively as the solvating medium since for Ni/Al_2O_3 systems this was found to be the most effective (*9*).

The choice of the catalyst support is obviously crucial (*10*). Our current interest in MgO as a support is the result of several factors. First, the SMAD method should be of great advantage for MgO because on MgO it is quite difficult to reduce metal salts with H_2, apparently due to strong interactions of the metal cation with the basic surface (*11*). Hence, it is very difficult to obtain by classical methods highly reduced metal on MgO, and sintering during the reduction procedure is common. In the SMAD preparation no reduction step is necessary. Second, MgO has recently been shown to be active as the sole catalyst or as a promoter in hydrogenation of alkenes (*12, 13*), Fischer–Tropsch chemistry (*14*), and the water gas shift reaction (*15*). In addition, CO exhibits a fascinating chemistry on the surface of MgO (*16, 17*). In short, MgO and other alkaline earth oxides have proved to be quite versatile and interesting in recent years. It was our belief that the combination of high Ni surface area and a MgO support should generate some unusual catalytic properties, especially for CO reduction. However, we found a uniqueness in other reactions as well, and this work is reported fully herein.

EXPERIMENTAL

Catalyst Preparations and Characterizations

Magnesium oxide was prepared by heat-treating magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$, analytical reagent from Mallinckrodt Chemical) in air at 500°C followed by washing with boiling, distilled water. Magnesium oxide (hydroxide) so prepared was dried at 110°C for 12 hr in air and then evacuated (3×10^{-5} mm Hg) at 800°C overnight. The BET surface area of the MgO powder was 90 m^2/g. Nickel was deposited on the prepared MgO by the metal vapor method (*7*) and a conventional method, as described below:

With the metal vapor method, a sphere of nickel metal (from Alfa Products) was loaded in an alumina-coated tungsten crucible in a 3000-cm^3 glass reactor which contained MgO powder prepared in the manner discussed above. The reactor was cooled with liquid nitrogen, as shown in Fig. 1. Nickel metal was vaporized under vacuum

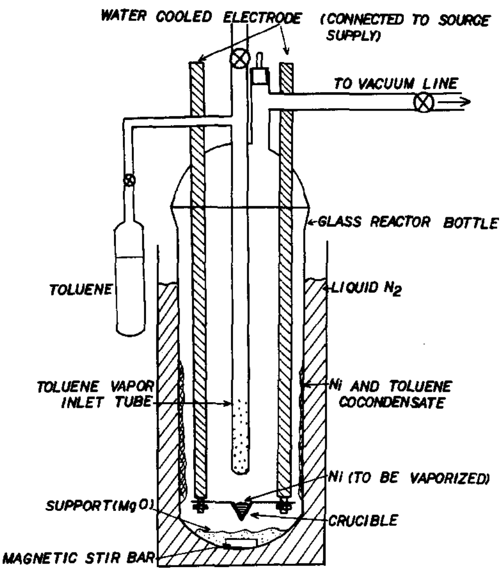


FIG. 1. Apparatus for catalyst preparation.

(1×10^{-3} mm Hg) and cocondensed with toluene vapor on the reactor wall kept at −196°C. In a typical experiment 0.05–0.4 g Ni would be cocondensed with 30–120 ml of toluene. After the cocondensation reaction, the reactor was warmed slowly to room temperature. During the warm-up period, nickel atoms/clusters solvated with toluene melted down to the reactor bottom and then were mixed with MgO powder by magnetic stirring. After slow warming and a 1-hr mixing at room temperature, the Ni–MgO solvated with toluene was evacuated overnight in order to remove excess toluene, and then it was transferred under N_2 to an inert atmosphere box (N_2). Loading of the catalyst into the reactor tube (made of stainless steel, ¼-in. o.d. × 1 ft long) was also done in the nitrogen-filled glove box (Vacuum Atmospheres, HE-493 DriTrain).

With the conventional impregnation method, MgO powder prepared as mentioned above was 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 then reduced carefully (*18*) in a H_2 stream. At the final stage of reduction the temperature was raised to 550°C, which was necessary to achieve better reduction of the Ni salt (*19*).

The BET surface area of the catalyst was measured by the adsorption of nitrogen gas at −196°C. The surface area of Ni metal was measured by hydrogen chemisorption at room temperature (*20*). CO chemisorption at 0°C and O_2 titration at 430°C were also carried out to characterize catalysts (*20*).

Ni metal contents of the catalysts were determined by an EDTA titration at 80°C using 1-(2-pyridylazo)-2-naphthol as indicator at pH 4 (*21*).

Catalytic Activity Measurements and Product Analysis

Catalytic activity measurements were carried out in a conventional pulse microreactor connected to a gas chromatograph. Pure hydrogen (99.8% pure, this gas was purified by passing it through molecular sieves kept at −196°C) was used as a carrier gas. A schematic diagram of the system is shown in Fig. 2. Catalyst loaded in the reactor was heat-treated at 400°C in a hydrogen stream (60 cm^3/min) for 2 hr, and then it was cooled down to the desired reaction temperature.

In the case of liquid samples, 1 μl of toluene (TOL) and methylcyclopentane (MCP) or 2 μl of isopropyl alcohol (IPA) was injected using a 10-μl syringe at intervals of 12 min (MCP and IPA) or 20 min (TOL). MCP and TOL used in this work were spectral-grade reagents from Eastmas Kodak, and IPA was a certified ACS reagent from Fisher Scientific Company. All of these were dried over molecular sieve 5A before use. Unreacted samples and reaction products were analyzed on a 25% SE-30 on Chromosorb P packed in an aluminum column (¼ in. o.d. × 15 ft long) at 85°C (for MCP) and 110°C (for TOL), and 20% Carbowax 20M on Chromosorb P packed in an aluminum column (¼ in. o.d. × 10 ft long) at 110°C (for IPA). In the case of a gas

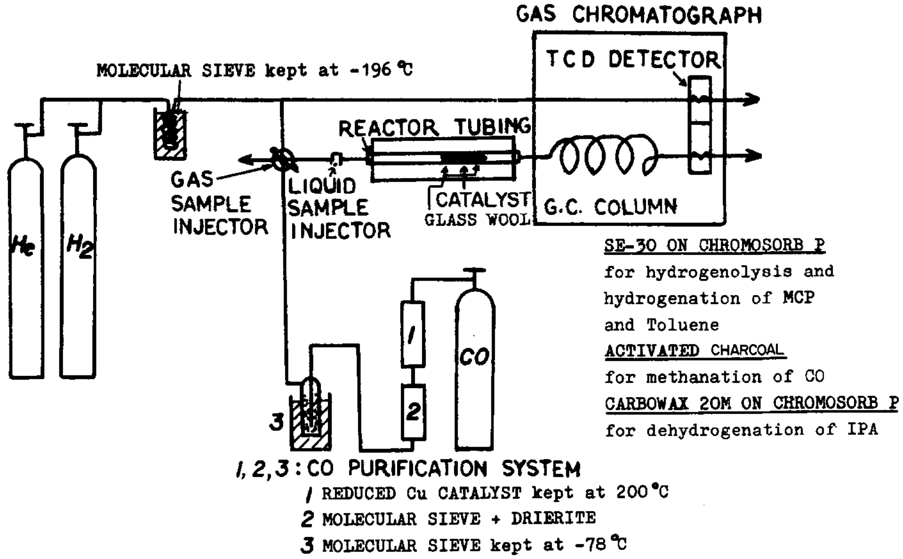


FIG. 2. Pulse microreactor system for catalytic activity measurements.

sample (carbon monoxide), 2.8 cm^3 of gas was injected by use of a gas sampling tube at intervals of 10 min. Carbon monoxide (99% pure, from Union Carbide Co.) was purified by passing it through a reduced copper catalyst at 180°C and then molecular sieves at −70°C, respectively. Gas analysis was carried out by use of an activated charcoal column (¼ in. o.d. × 10 ft long) at 100°C and a Chromosorb 102 column (¼ in. o.d. × 15 ft long) at 100°C.

RESULTS AND DISCUSSION

I. Catalytic Activities of SMAD Catalysts vs Conventional Catalysts

A. Hydrogenation of methylcyclopentane (MCP). Figure 3 indicates the extent of conversion of MCP observed over 2.8 wt% Ni SMAD and 4.5 wt% Ni conventional catalysts. In spite of the lower Ni content, the SMAD catalyst showed much higher activity, actually 13 times greater at 250°C (as later shown in Fig. 8). It was shown that the MgO support itself, having been treated with toluene and pretreated in the same way as the Ni/MgO catalyst, possessed no catalytic activity under the imposed conditions. Also, since Ni is well known as a hydrogenolysis catalyst (*22*), we conclude that Ni provides the main catalytically active site for this hydrogenolysis reaction. The great difference in activity between the SMAD and conventional catalysts is most likely simply due to a much greater dispersion degree and greater percentage of Ni in a zero-valent active state for the SMAD catalyst (this will be discussed more in Section III).

Products of the MCP reaction are C$_6$ (*n*-

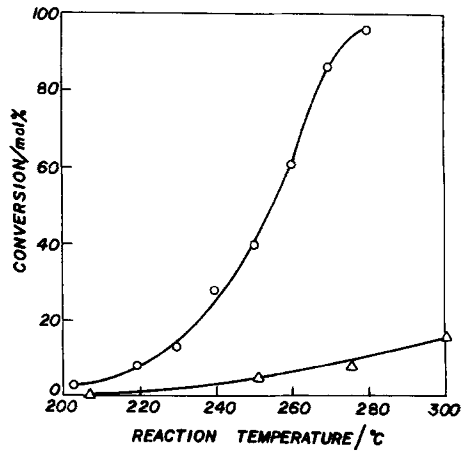
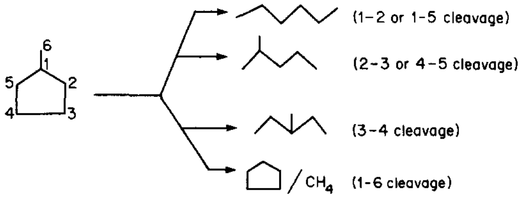


FIG. 3. Hydrogenolysis percentage conversions of MCP *vs* temperature. ○: 2.8 wt% SMAD catalyst, 100 mg. △: 4.5 wt% conventional catalyst, 100 mg.

hexane, 2-methylpentane, 3-methylpentane), cyclohexane, C_5 (*n*-pentane, 2-methylbutane), cyclopentane, C_4 (*n*-butane and 2-methylpropane), C_3 (propane), C_2 (ethane), and C_1 (methane). Cyclohexane was not observed with the SMAD catalyst. Product distributions are summarized in Fig. 4. The molar ratio of lower-molecular-weight products increased and the ratio of higher-molecular-weight products decreased with increasing conversion. The production of C_6 species and cyclopentane/methane required the cleavage of only one C–C bond in MCP:



Other hydrocarbons, of course, require the cleavage of at least two C–C bonds, either concertedly or successively (e.g., MCP → $C_6 \rightarrow C_5 + C_1 \rightarrow C_4 + 2C_1 \rightarrow 6C_1$). The increase in the amount of low-molecular-weight hydrocarbons with increasing conversion (Fig. 4) would suggest successive secondary reactions become important. Hence, we cannot be sure of what the primary product distribution is at high conversion. Therefore the plots in Fig. 4 were extrapolated back to zero conversion. The product distributions so calculated are shown in Table 1, and these represent the primary products for several SMAD catalysts and a conventional catalyst.

With supported SMAD catalysts the products are C_6, cyclopentane/C_1, and C_5/C_1 (the amount of C_1 produced is about the same as that of cyclopentane + other C_5 species, as would be predicted). On the other hand, a wider range of products is produced with the conventional catalyst and the *unsupported* Ni SMAD system. So on the supported Ni SMAD catalysts only one or two bond cleavages occur, whereas on conventional and unsupported SMAD systems multiple, concerted, bond cleavage is much more prevalent. This result is probably related to the size of the Ni particle on these different catalysts. Supported SMAD catalysts should contain smaller Ni particles whereas the conventional and unsupported SMAD systems should have larger particles (unsupported Ni SMAD sinters at 250–350°C) (*8*). According to Dalmon and Martin (*23*), in order for C–C cleavage to occur, certain size ensembles of surface Ni atoms are necessary. The required size is different for one, two, or three concerted bond cleavages; one C–C cleavage requires an ensemble of 12 Ni atoms, two cleavages require 17 Ni atoms, and three cleavages require 22 Ni atoms. (Dalmon and Martin were investigating *n*-alkane reactions; we are assuming that the results they obtained are qualitatively applicable to our studies of MCP.) Thus, we conclude that our MCP studies show that supported Ni SMAD catalysts possess considerably smaller, active

TABLE 1

Product Distributions (mole%) Observed for Hydrogenolysis of MCP over Different Catalysts

Catalyst	C_1	C_2	C_3	C_4	C_5	CP	C_6
0.6 wt% Ni/MgO SMAD	36	0	0	0	10	34	20
1.6 wt% Ni/MgO SMAD	40	0	0	0	10	35	15
2.7 wt% Ni/MgO SMAD	37	0	0	0	11	37	15
2.8 wt% Ni/MgO SMAD	34	0	0	0	12	36	18
6.2 wt% Ni/MgO SMAD	30	0	0	0	12	38	20
Ni SMAD (unsupported)	56	3	3	8	10	10	10
4.5 wt% Ni/MgO conventional	55	5	5	10	12	8	5

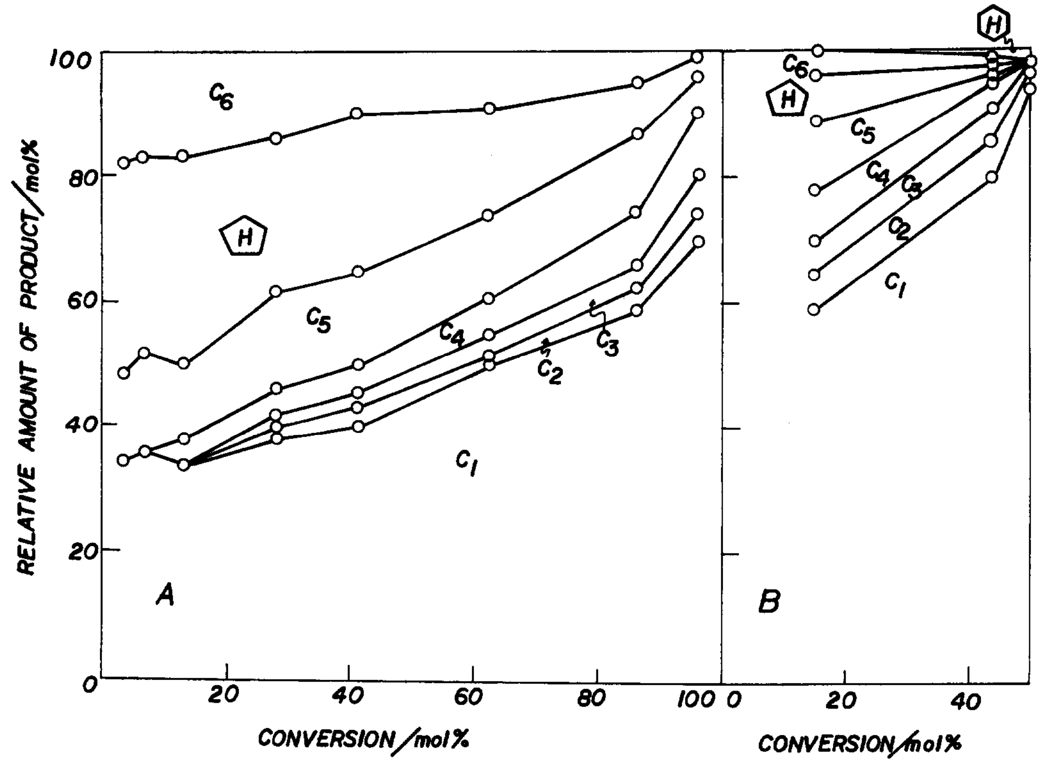
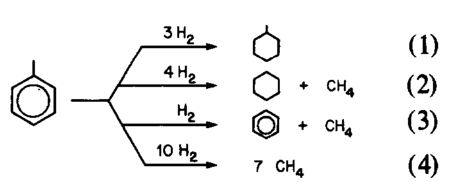


FIG. 4. Product distributions observed during MCP hydrogenolysis: (A) a 2.8 wt% Ni/MgO SMAD catalyst and (B) a 4.5 wt% Ni/MgO conventional catalyst.

Ni particles than the conventionally prepared catalyst.

B. Hydrogenation and hydrogenolysis of toluene (TOL). Figure 5 illustrates conversion and selectivity observed in the TOL + H_2 reaction over these catalysts. The reactions that took place are:



The conversion/temperature reaction curve has a maximum at 190–230°C, and a minimum at 290–320°C. Below 250°C only reaction (1) occurred. Above 250°C reactions (2), (3), and (4) also took place. As is demonstrated by Figs. 5 and 8 (which shows the maximum conversion at 190–230°C/1 mg Ni), the SMAD catalysts possessed much higher activities than the conventional catalyst. These high activities could again be attributed to the ultrahigh dispersion of Ni in the SMAD systems.

At 350°C, reaction (3), cleavage of one C–C bond, and reaction (4), cleavage of six C–C bonds, occurred simultaneously. The selectivity to reaction (3) using the SMAD catalysts was low compared with the conventional systems. However, we believe this apparent low selectivity is due to secondary reactions on the very active SMAD catalyst surfaces. If we compare SMAD and conventional catalysts at stages of similar conversions, higher selectivity to reaction (3) is observed for the SMAD systems. Again this could be rationalized by assuming much smaller particle sizes for the SMAD systems. Also, this points out the potential advantage of the metal vapor method for the preparation of more selective hydrogenolysis catalysts.

A H_2/temperature treatment of a SMAD

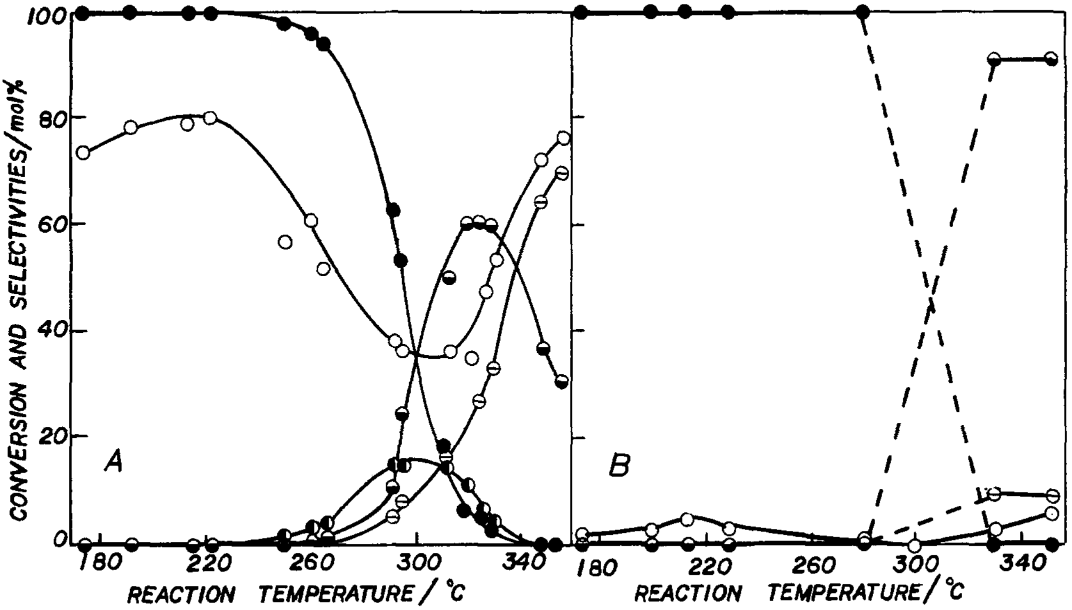


FIG. 5. Conversions and selectivities for hydrogenation/hydrogenolysis of TOL: (A) A 2.8 wt% Ni/MgO SMAD catalyst, 52 mg and (B) a 4.5 wt% Ni/MgO conventional catalyst, 100 mg. ○: Conversion. ●: Selectivity to reacton (1). ◐: Selectivity to reaction (2). ◒: Selectivity to reaction (3). ⊖: Selectivity to reaction (4).

catalyst was carried out in order to assess the thermal stability of the catalyst as well as the change in activity. The TOL + H_2 reaction was employed as the "detector" of change. Thus, Fig. 6 plots the conversion–selectivity *vs* heat treatment temperature of the Ni/MgO SMAD catalyst. During heat treatment a H_2 stream (60 cm^3/min) was passed over the catalyst. After heat treatment the catalyst was cooled to the desired temperature and toluene injected and conversion measured. As Fig. 6 demonstrates, the activity of the catalyst increased with heat treatment temperature up to about 400°C. This indicates that a surface cleaning process occurs in this range, probably involving the loss of carbonaceous groups (*24*). Little change in catalytic activity between 400 and 500°C heat treatment was observed, indicating that the cleaning process was completed and that the catalyst is stable toward sintering at least to 500°C.

C. Methanation of carbon monoxide (CO). Figure 7 compares the activity of a typical SMAD catalyst with a typical conventional catalyst for CO methanation. Although CH_4 was the only product over the less active conventional catalyst, CO_2 was also detected over the SMAD system when conversion exceeded 30 mole%. The formation of CO_2 could occur by reaction (6) or (7),

$$CO + 3H_2 \rightarrow CH_4 + H_2O, \qquad (5)$$

$$CO + H_2O \rightarrow CO_2 + H_2, \qquad (6)$$

or

$$2CO \rightarrow C + CO_2, \qquad (7)$$

although in the presence of excess H_2 (H_2 was the carrier gas) reaction (6) seems most likely. At low conversions the amount of H_2O available for reaction (6) is apparently not high enough to allow detection of CO_2.

When a larger amount of conventional catalyst was employed along with higher temperature, CO_2 formation was detectable. Therefore, there does not appear to be anything unique about the active sites of

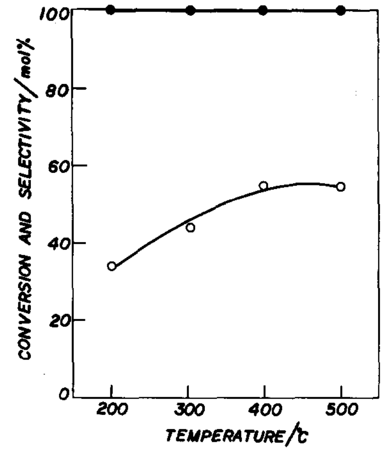


FIG. 6. TOL conversion *vs* preheat treatment temperature of 2.8 wt% Ni/MgO SMAD catalyst (50 mg). ○: Conversion. ●: Selectivity to reaction (1).

the SMAD catalysts, but they obviously possess much greater methanation activity than the conventionally prepared system.

D. Dehydrogenation of isopropyl alcohol (*IPA*). Isopropyl alcohol is readily dehydrogenated over metal catalysts (*22*). We studied this reaction to gain further comparative data between Ni/MgO SMAD and conventionally prepared systems. The reaction was carried out by pulsing the alcohol over the catalyst at 150°C in a He stream. The support, MgO, had no activity under these conditions. The percentage dehydrogenation conversions/1 mg Ni did not change much for a series of different loadings of Ni on MgO (see Fig. 8). However, the conversions were very much higher (several times) for all the SMAD catalysts than for the conventional systems employed.

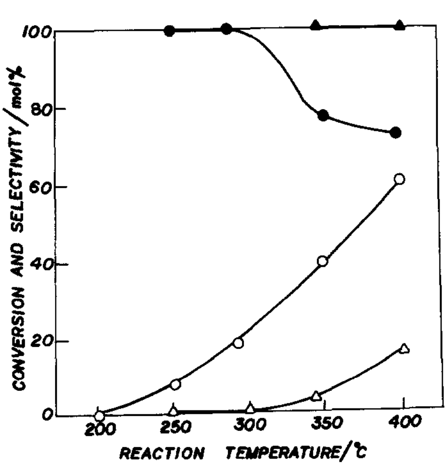


FIG. 7. Conversion and selectivity of CO to CH_4 (2.8 wt% Ni/MgO SMAD catalyst, 50 mg; 4.5 wt% conventional Ni/MgO catalyst, 90 mg).

II. Effect of Ni Loadings; Particle Size Effects

Figure 8 plots the conversions calculated for 1 mg Ni for a series of SMAD catalysts of varying loadings and for a conventional catalyst of 4.5 wt% Ni. Conversions of MCP are taken at 250°C reaction temperature, TOL at the maximum between 190 and 230°C, CO at 350°C, and IPA at 150°C.

As Fig. 8 indicates, MCP and TOL conversions showed maxima at approximately 2.7 and 1.6 wt% Ni, respectively, for the SMAD catalysts. We had observed this phenomenon before for TOL conversion over Ni/Al_2O_2 SMAD catalysts (*7*), and attributed it to the formation of optimum crystallite/particle sizes by employing special SMAD experimental methods. Thus, during preparation of the SMAD catalysts

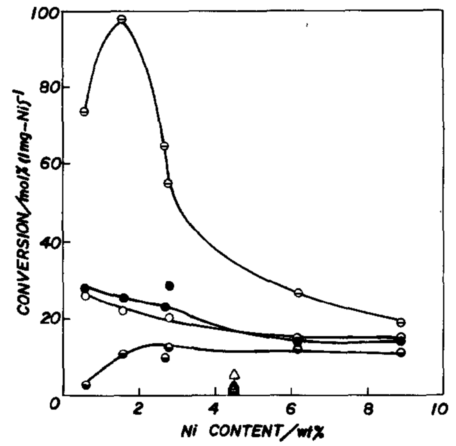


FIG. 8. Percentage conversions for TOL, CO, IPA, and MCP for different loadings of Ni on MgO (all catalysts; standardized to 1 mg Ni for each system). ⊖, △: Hydrogenation of TOL. ●, ▲: Methanation of CO. ○, △: Dehydrogenation of IPA. ◒, ▲: Hydrogenolysis of MCP. ⊖, ●, ○, ◒: SMAD catalyst. △, ▲, △, ▲: Conventional catalyst.

the amounts of dispersing solvent and catalyst support, and/or metal can be varied. It would be predicted that smaller metal particles would be deposited on the support under higher-dilution conditions and when small amounts of metal are employed (vaporized) (*25*). Heavier metal depositions would favor larger particles and, thus some of the metal would be lost to the inner reaches of the particles/crystallites. (Unfortunately the crystallites, even in the heavy-loading cases, are too small to measure accurately by X-ray techniques.) (*7*).

Thus, hydrogenolysis of MCP and hydrogenation of TOL apparently are affected by ensemble effects on the particles, and thereby are affected by particle/crystallite size. However, it is interesting that methanation of CO and dehydrogenation of IPA are not so affected. This seems reasonable since it would be expected that the active site for the CO or IPA reactions would probably not need to be large in terms of the ensemble of atoms on the surface. On the other hand, it is rather easy to imagine where MCP and TOL would require more Ni atoms in order to "sit down" on the active site.

Particle size effects on hydrogenation and hydrogenolysis have, of course, been studied by many very able investigators (*23, 26–28*). The work of Dalmon and Martin (*23*) on *n*-alkane hydrogenolysis is of particular recent interest, as mentioned before. In our studies, however, there is an added dimension. That is that the particles are deposited for each SMAD catalyst in the same exact way with no need for concern about sintering during metal reduction, salt crystallization effects during drying, or other complicating features bound to be encountered during conventional catalyst preparations. We believe our direct comparisons with different reactions and a series of SMAD catalysts convincingly show a strong particle size effect for TOL hydrogenation, a mild effect for MCP, and no recognizable effect for CO or IPA conversions.

Consideration of the similarity of percentage loadings optimum for MCP and TOL conversions would suggest that similar-sized particles are optimum for each. Furthermore, CO and IPA are converted efficiently even by very small Ni particles that would be present with the low loadings. However, this indicates that monatomic Ni must not be highly prevalent as a supported species, since it is believed that at least a small ensemble effect is necessary (*28*).

III. Surface Area and "Reduction Degree" of Ni

From the results above it is clear that the Ni/MgO SMAD catalysts exhibit much higher activity than analogous conventional catalysts. The high activity is apparently due to high dispersion, high percentage of Ni in the reduced zero-valent state, and in some cases, optimum particle sizes. Can we collect data to support these contentions?

In the recent past Ni metal surface areas have been measured by selective gas adsorptions, X-ray line broadening, electron microscopy, and related techniques (*29–31*). However, when very small Ni particles are supported, it becomes impossible to use X-ray methods, and exceedingly difficult to use electron microscopy methods. Also, chemisorption may not be reliable because of the suppression of chemisorption (especially H_2) by support effects on the electronic properties of the Ni (*20*). In an analogous way, CO chemisorption may not be accurate because the stoichiometry (Co : Ni) may change as the Ni particles become small and support effects become more dominant.

Thus, keeping in mind the possible errors involved, and realizing that trends would be useful anyway, we decided to proceed with chemisorption studies since, in our laboratory, we had no other practical approach to obtaining the data we wanted (*25*). Table 2 summarizes the surface areas of Ni on MgO that we determined by H_2 chemisorption assuming the ratio H (chemisorbed)/Ni (surface) is 1/1 and the surface area of one Ni atom is 6.77 Å^2 (*20*). The values obtained should be treated as minimum.

The results shown in Table 2 are quite interesting. Initial examination of the hydrogen chemisorption data would suggest that some property of the catalysts causes a great deal of scatter or unreliability in the data. This is certainly partially true and we have attributed this to the presence of significant amounts of carbonaceous species even after H_2 treatment at 400°C. However, the H_2 chemisorption values are reproducible for each catalyst, and, even more importantly, CO chemisorption follows the same trends. That is, if H_2 chemisorption is suppressed in one sample, CO chemisorption is also suppressed (mole H_2/g-atom Ni *vs* mole CO/g-atom Ni). But interestingly a plot of moles CO/moles H *vs* percentage Ni loading shows a smooth progression from very high values of CO/H for low Ni loadings to low CO/H ratios for high Ni loadings. Since this is a smooth progression and dependent on two different chemisorption experiments (CO and H_2), we conclude that whatever affects the efficiency of chemisorption, both CO and H_2 are affected similarly (not random), but since the CO/H values do decrease with increase in Ni loading, differences are accentuated by Ni particle size. We assume Ni particle sizes would be smallest for low Ni loadings. These particles are apparently covered by carbonaceous material or support surface atoms in such a way that H_2 chemisorption is severely suppressed while CO chemisorption is less severely suppressed. On going to higher Ni loadings (and supposedly larger particles) the CO/H ratio approaches unity, suggesting that CO and H_2 are chemisorbed with equal affinity, a result that does support our assumption that higher Ni loadings lead to larger particles and vice versa.

The large CO/H values clearly indicate that H_2 chemisorption is seriously suppressed, especially in the samples with low Ni loadings. Thus, the Ni surface areas for these SMAD catalysts are probably much higher than the chemisorption data indicate.

As expected, the SMAD catalysts showed high "reduction degrees" while the conventional system did not (cf. Table 2). These results reemphasize the problems involved in reducing Ni^{2+} on supports, especially MgO (*11*, *32*), and the usefulness of the SMAD method in such instances.

CONCLUSIONS

The metal vapor method is effective for

TABLE 2

Surface Area and Reduction Degree of Ni on MgO

Catalyst	Surface area[a] (m^2/g Ni)	Reduction degree[b] (%)	CO/H ratio[c]
0.4 wt% Ni/MgO (SMAD)	39	100	7.8
0.6 wt% Ni/MgO (SMAD)	67	100	8.8
1.6 wt% Ni/MgO (SMAD)	19	—	3.0
2.7 wt% Ni/MgO (SMAD)	110	90	3.0
2.8 wt% Ni/MgO (SMAD)	53	65	2.2
6.2 wt% Ni/MgO (SMAD)	145	62	1.7
8.9 wt% Ni/MgO (SMAD)	37	82	1.2
4.5 wt% Ni/MgO (conventional)	15	19	3.5

[a] Calculated from H_2 chemisorption data.

[b] Determined by O_2 titration at 430°C. Represents the percentage of Ni in the zero-valent state.

[c] The ratio of CO chemisorbed to H atoms chemisorbed.

preparing highly dispersed Ni/MgO catalysts. Since solvated metal atoms are intermediates in the process, the catalysts so prepared are termed "solvated metal atom dispersed" or SMAD. These catalysts possess high Ni surface areas and a high percentage of Ni in the zero-valent state. Conventionally prepared Ni/MgO catalysts, prepared by Ni^{2+} reduction, have much lower Ni surface areas and percentage of Ni in the zero-valent state (reduction degree). The catalytic activities of the SMAD catalysts outstrip by many times the activities for the conventional systems in methylcyclopentane (MCP) hydrogenolysis, toluene (TOL) hydrogenation and hydrogenolysis, carbon monoxide (CO) methanation, and isopropyl alcohol (IPA) dehydrogenation. In some cases their unique activities are due in part to MgO as the support. Furthermore, the MgO stabilizes the Ni particles toward sintering even as high as 500°C in a stream of H_2.

Particle size effects were observed for MCP and TOL reactions, but not CO and IPA reactions. For these studies, the optimum particle size effect was strongest for TOL hydrogenation. Our results would suggest that the preferred particle is largest for $MCP > TOL \gg CO \simeq IPA$. Thus, even very small particles are effective for CO methanation and IPA dehydrogenation.

Generally, the SMAD catalyst production method yields high-activity catalysts because of (1) the achievement of extremely high dispersion and small particle size, (2) the high percentage of metal in the zero-valent state on the support, and (3) during the preparation the organic dispersant not only acts appropriately to prevent M atoms/clusters from growing large, but also to protect the surface of the supported atoms/clusters before actual catalyst use, at which time the organics can be removed from the surface bareing active sites (the organic moieties are fragments of the organic dispersant molecules and are bound tightly especially throughout the interior of the particles (*4*, *7*, *8*).

ACKNOWLEDGMENTS

We are grateful for the generous support of the National Science Foundation (CHE-7919587-01) and the Department of Energy (EX-76-C-01-2211). We also appreciate helpful discussions with Professors Baltisberger, Stenberg, and Woolsey of the University of North Dakota.

REFERENCES

1. (*a*) Klabunde, K. J., "Chemistry of Free Atoms and Particles." Academic Press, New York, 1980. (*b*) Blackborow, J. R., and Young, D., "Metal Vapor Synthesis in Organometallic Chemistry." Springer-Verlag, Berlin, 1979. (*c*) MosKovits, M., and Ozin, G. (Eds.), "Cryochemistry." Wiley–Interscience, New York, 1976.

2. Francis, C. G., and Timms, P. L., *J. Chem. Soc. Chem. Commun.*, 466 (1977).

3. Francis, C. G., Huber, H., and Ozin, G. A., *Inorg. Chem.* **19**, 219 (1980).

4. Davis, S. C., and Klabunde, K. J., *J. Amer. Chem. Soc.* **100**, 5973 (1978); Davis, S. C., Severson, S., and Klabunde, K. J., *J. Amer. Chem. Soc.* **103**, 3024 (1981).

5. Yermakov, Y., *Catal. Rev. Sci. Eng.* **13**, 77 (1976).

6. Ichikawa, M., *J. Chem. Soc. Chem. Commun.*, 26 (1976).

7. Klabunde, K. J., Ralston, D. H., Zoellner, R. W., Hattori, H., and Tanaka, Y., *J. Catal.* **55**, 213 (1978).

8. Klabunde, K. J., Davis, S. C., Hattori, H., and Tanaka, Y., *J. Catal.* **54**, 254 (1978).

9. Ralston, D. H., and Klabunde, K. J., submitted for publication.

10. Taylor, W. F., Yates, D. J. C., and Sinfelt, J. H., *J. Phys. Chem.* **68**, 2962 (1964); Yates, D. J. C., Sinfelt, J. H., and Taylor, W. F., *Trans. Faraday Soc.* **61**, 2044 (1965).

11. Vedrine, J. C., Hollingen, G., and Duc, T. M., *J. Phys. Chem.* **88**, 1515 (1978).

12. Hattori, H., Tanaka, Y., and Tanabe, K., *J. Amer. Chem. Soc.* **98**, 4652 (1976).

13. Kijenski, J., and Malinowski, S., *React. Kinet. Catal. Lett.* **10**, 233 (1979).

14. Shah, Y. T., and Perrotta, A. J., *Ind. Eng. Chem. Prod. Res. Dev.* **15**, 123 (1976); Hanrici-Olive, G., and Olive, S., *Angew. Chem. Int. Ed. Engl.* **15**, 136 (1976).

15. Oliver, R. B., British Patent 1,099,802 (1968); *Chem. Abstr.* **68**, 53839r (1968); Atroschenko, V. I., Bibr, B., Zhidkov, B. A., Zasorin, A. P., and Ivanova, L. N., *Nauchn. Osn. Podbora Proizvod. Katal. Acad. Nauk SSSR Sibirsk. Otd.*, **177** (1964); *Chem. Abstr.* **68**, 4991f (1965).

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

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

18. Bartholomew, C. H., and Farrauto, R. J., *J. Catal.* **45,** 41 (1976).

19. This is based on our own findings. Bartholomew and Farrauto (*18*) report that 480°C is adequate for Ni/Al_2O_3 systems, but we find this is not adequate for Ni/MgO using H_2 as the reducing medium.

20. Bartholomew, C. H., and Pannell, R. B., *J. Catal.* **65,** 390 (1980).

21. Schwarzenbach, G., and Flascheka, H., "Complexometric Titrations." Methuen, London, 1969.

22. Bond, G. C., "Catalysis by Metals." Academic Press, New York, 1962.

23. Dalmon, J. A., and Martin, G. A., *J. Catal.* **66,** 214 (1980).

24. We have studied this behavior before for Ni/Al_2O_3 SMAD catalysts (see Ref. (*7*)).

25. The surface areas of the SMAD Ni/MgO catalysts are shown in Table 2. There are problems involved in that H_2 chemisorption is severely suppressed especially for the smaller Ni particles. This is apparently due to the presence of carbonaceous species (see later discussion).

26. Boudart, M., *in* "Proceedings, 6th International Congress on Catalysis London, 1976" (G. C. Bonds, P. B. Wells and F. C. Tompkins, Eds.), p. 1. The Chemical Society, London, 1977.

27. Sinfelt, J. H., Carter, J. L., and Yates, D. J. C., *J. Catal.* **24,** 283 (1972).

28. Ponec, N., *Catal. Rev.* **18,** 151 (1978).

29. Whyte, T. E., *Catal. Rev.* **8,** 117 (1973).

30. Wanke, S. E., and Flynn, P. C., *Catal. Rev.* **12,** 93 (1975).

31. Parkash, S., CHEMTECH **10,** 572 (1980).

32. Nikolajenko, V., Basacek, V., and Danes, V. L., *J. Catal.* **2,** 127 (1963).