JOURNAL OF CATALYSIS 55, 213–227 (1978)

Clustering of Metal Atoms in Organic Media

VI. Solvated Metal Atoms Used for the Low Temperature Preparation of Highly Dispersed Zero Valent Metal Catalysts[1]

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Received March 15, 1978; revised July 27, 1978

Metal atoms dispersed in weakly complexing solvents yield "solvated metal atoms." Catalyst supports have been permeated with varying amounts of these solutions. Warmup of the solution-support slurry allows metal atoms and/or small crystallites of metal to de deposited in the catalyst support. This method serves as a new way of preparing zero-valent highly dispersed catalysts at low temperatures in the absence of H_2O or O_2, and no H_2 reduction step is used.

Optimum percentage of metal dispersions have been determined to be about 0.4% Ni/Al_2O_3. Heat treatment of the catalysts causes an increase in activity, apparently due to desorption of adsorbed materials, up to the point of gross sintering at 600°C, at which point activity falls off drastically.

INTRODUCTION

Recently we reported that deposition of metal atoms (vapors), into low temperature weakly complexing organic media (such as toluene, tetrahydrofuran, pentane, or similar organics) sometimes allows the formation of pseudo-stable metal atom solutions (solvated metal atoms) (*2*). Warming of these solutions to $> -80°C$ causes the formation of very small metal crystallites which have shown high reactivity in catalysis and in other interesting chemical processes (*1*). We also reported preliminarily on the deposition of small metal crystallites in catalyst supports by allowing the metal atom solution to permeate the support material followed by slow warming, subsequent decomposition of the weak M-solvent complex, and metal deposition (*2*).

The potential of this method for preparation of very highly dispersed zero-valent metal catalysts, perhaps atomically dispersed, is high for several reasons: (a) a host of different organic dispersants are available for each metal studied (as opposed to normal organometallic deposition procedures), (b) we have shown that catalysts of varying activities and selectivities can be prepared with the same metal simply by varying the organic dispersant (*1*, *2*). We do not yet know if this is due to the formation of varying crystal faces, or due to varying degrees of adsorption of organic fragments, (c) the catalysts can be prepared at very low temperature

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[1] Part V, Ref. (*1*).

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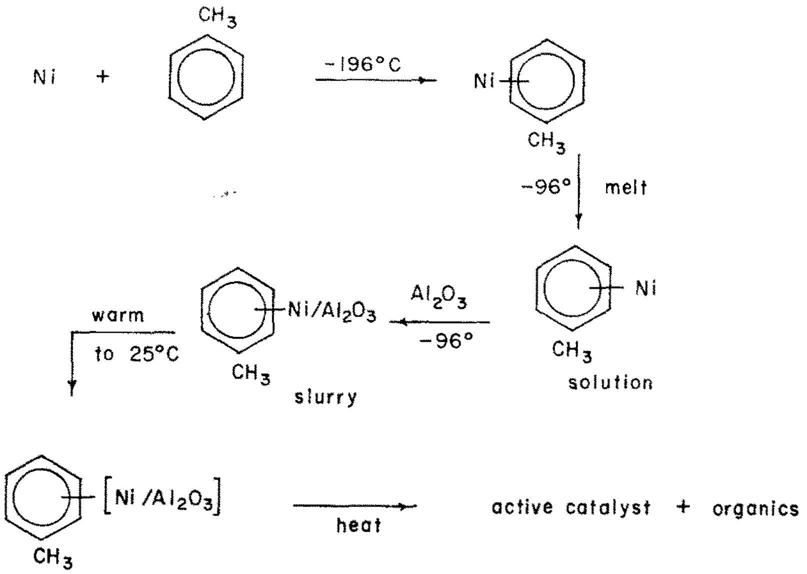
in the absence of water, (d) large scale processes appear feasible (*3*).



EXPERIMENTAL METHODS

Equipment and experimental details have been reported previously (*1*), for preparation of Ni-solvent slurries and catalysts. Very similar procedures were used here but with Al_2O_3 or SiO_2 supports present, and either Ni, Pd, Pt, or Ag vaporized.

Typical Example of a Catalyst Preparation: Preparation of 6.8% Ni/Al_2O_3

A piece of Ni shot was loaded into a Sylvania Emissive Products Integral W-Al_2O_3 crucible (CS-1008), weighed, and placed in position in a metal atom-vapor reactor (*4*).

Harshaw Al-0102P Al_2O_3 was calcined in air for 3 hr at 600°C using a Haskins tube furnace, after which 3.00 g of the Al_2O_3 powder was placed in the bottom of a metal vapor (atom) reactor, along with a magnetic stirring bar. The reactor was then sealed and slowly (pumpdown of several min is necessary to avoid splatter of Al_2O_3 with degassing) evacuated down to 1×10^{-4} Torr.

After pumpdown (about 6–8 hr) the crucible was degassed at a dull red heat, the reactor cooled in liquid N_2, and degassed purified toluene (*1*) vapor inletted. After coating the reactor walls with about 5 ml toluene, the crucible was warmed to a white heat and Ni vaporization was begun. Nickel vapor and toluene were cocondensed for 1 hr and 50 min yielding a brown-yellow matrix at −196°C. A total of 0.2179 g Ni (3.71 mg/atoms) and 25 ml toluene (235 mmoles) were inletted. After completion of the reaction the reactor was isolated from vacuum and the liquid N_2 Dewar was removed. The matrix slowly warmed and melted. Upon meltdown the dark brown solution permeated the Al_2O_3 support while vigorous magnetic stirring was commenced. During the warmup period of about 1 hr the Ni deposited in the Al_2O_3 (deposition at about −50°C), and a black Ni-toluene/Al_2O_3 slurry was obtained. The slurry was removed under N_2 flush via syringe using a wide 3 ft Teflon needle, and placed in Schlenk airless glassware (*5*). The colorless excess toluene was removed by syringe, and the Ni-toluene/Al_2O_3 catalyst was dried under vacuum at room temperature for several hours at 10^{-3} Torr. About 90% recovery of Ni vaporized and Al_2O_3 originally loaded is realized. The dry powder was handled under nitrogen in a Vacuum Atmospheres inert atmosphere box (<5 ppm O_2).

X-Ray Powder Sintering Studies

The Ni or Ag catalysts were loaded into 0.5 mm capillary tubes under inert atmosphere after being previously heat treated on the vacuum line at the desired temperature for 0.5 hr with 1 hr warmup, waxed, and later flame sealed. Then the capillaries were individually exposed to X-rays for 6 hr using a Siemann's powder camera on a conventional X-ray diffraction apparatus powered by a Norelco generator using a Cu source with Ni filter to obtain Cu$K\alpha$ radiation using 48 kV and 20 mA. When Ni bands were observable, the width of the 111 line was carefully measured, and crystallite size calculations were carried out by normal methods (*6*).

Thermal Decomposition of Materials from Ni-Toluene/Al_2O_3 Catalyst

The dry Ni-toluene/Al_2O_3 catalyst was weighed under N_2 into a small glass vessel with provision for attachment to a vacuum line. About 0.50 g was used for each trial. The vessel was evacuated and then heated to the desired temperature using a 1 hr heating period and 0.5 hr at each temperature employing a Haskins tube furnace equipped with a thermocouple for monitoring temperature. As materials were desorbed they were collected in a -196°C trap. This trap was not open to the pumping system so that non-cocondensibles were saved as well. All products were analyzed by VPC. Noncondensibles were analyzed using a 5 Å molecular sieve column with He carrier gas at a flow of 60 ml/min. Since the thermal conductivities of H_2 and He are similar, the amount of H_2 present was determined indirectly. A CH_4 external standard was used to determine amounts of all other noncondensibles, thereby requiring that the amount unaccounted for in relation to the total millimoles determined by ideal gas calculations be the millimoles of H_2. Condensible materials were measured first for total amount by pressure and volume measurements, then separated as to volatile and nonvolatile components with pressure and volume measurements also being made on each of these. The less volatile components were isolated in a CO_2–isopropanol slush trap and the volatiles were trapped in a liquid N_2 trap. The less volatile components were then stored in a sample bulb with 10 to 15 μl of mesitylene added to form a solution. If two phases formed in the solution (indicative of H_2O presence) the two were separated and analyzed separately. The solution was analyzed using a 5 ft Carbowax column on a Varian Aerograph VPC with a 60 ml/min He flow. The volatile materials were also analyzed, but by use of a VPC system hooked into the vacuum line with isolating stopcocks. An HMPA column with 60 ml/min He flow was used for separation of the volatile materials.

Desorption of Organics from Ni-Toluene/Al_2O_3 Catalyst by Treatment with Hydrogen

The above procedures were employed here also except that at 25 and 250°C, 120 mm of H_2 was inletted and left in contact with the catalyst over a 4 hr period at each temperature. During this time a -196°C trap was present to hold any desorbed condensible materials. Analysis of condensibles and less volatiles were carried out in the same way as for pyrolysis.

Static High Pressure Hydrogenation Rate Studies on Toluene (typical example)

In an inert atmospheres box, a 128 ml Hastelloy C pressure vessel (Parr Instrument Co.) was charged with a stirring bar, 4.3% Ni-toluene/Al_2O_3 catalyst (0.4570 g) and 188 mmole of deoxygenated toluene. The vessel was then sealed, removed from the box and pressurized to 50 psig with H_2, flushed, and finally pressurized to 250 psig. The apparatus was connected to a ballast tank to maintain constant pressure, and the bomb was heated with constant vigorous magnetic stirring at 160°C for 16 hr. The vessel was then cooled, depressurized, and the contents were examined by VPC using a 5 ft Carbowax column with 60 ml/min He flow showing methylcyclohexane as product (0.003 mmole min^{-1}/g of Ni), and no benzene or cyclohexane generated.

Closed Recirculation Reactor Hydrogenation and Isomerization Studies on 1-Butene and 1,3-Butadiene

See Ref. (*1*).

Al_2O_3 Used

Powdered Al-0102P Al_2O_3 (Harshaw, surface area = 140–150 m^2/g), which was calcined prior to use at 600°C in air for 3 hr.

SiO_2 Used

Powdered SiO_2 (Cab-O-Sil HS-5 from Cabot Corp.) was calcined prior to use at 600°C in air for 3 hr.

RESULTS AND DISCUSSION

We report here some recent results concerning these catalyst preparation procedures for depositing Ni, Pd, Pt, Ag, on Al_2O_3 or SiO_2, and in particular catalytic work and electron microscopy work on Ni/Al_2O_3.

In a typical procedure, in the bottom of a metal atom reactor (*4*) is placed 1 to 10 g of calcined (600°C) Al_2O_3 or SiO_2 powder or pellets. Then metal vapor (ca. 0.5 g) is deposited with a high excess of solvent (ca. 50-fold excess) at −196°C. The dark matrix is then allowed to melt and flow down onto the support while under vacuum so that the M atom solution permeates the pores of the support. Then with vigorous stirring the slurry is allowed to slowly warm from the melting temperature of the solvent to 25°C. Metal deposits in the support usually about −40 to −90°C. The gray slurry is then removed under N_2 usually by syringe using a 3 ft Teflon needle, and moved to Schlenk airless glassware where the solvent is removed under vacuum.

1. Metals and Solvents Employed for Catalyst Preparations

Table 1 lists the catalysts we have prepared with qualitative comments. Note that toluene, trifluoromethylbenzene and THF all work well for Ni dispersion. However, for Ag dispersion only THF was acceptable, but even this was not entirely satisfactory. For Pd and Pt toluene works reasonably well. Pentane however did not yield a well-dispersed Ni catalyst.

Qualitatively we can say that low melting arene solvents work best for Ni, Pd, and Pt because relatively stable ($> -80°$ stability) π-arene complexes form with these metals, yielding good homogeneous metal atom solutions on meltdown. For Ag, however, more polar ether solvents are needed since the Ag-etherate appears to be more thermally stable than Ag–π-arene complexes.

As expected, higher metal loadings yield larger metal crystallites in the final catalyst. For normal loadings of 0.01 to 9% Ni, Ni crystallites are well below 40 Å, as determined by X-ray powder patterns. More exact determinations of crystallite sizes have not yet been possible since with these high dispersions, the X-ray studies show only very broad lines.

2. Electron Microscopy Studies

A 17% Ni-toluene/Al_2O_3 sample was examined by selected area diffraction in

TABLE 1

Catalysts Prepared

Metal/support[a]	Dispersing[b] solvent	% Ni Loading	Color	Approx. cryst. size (Å) by X ray[c]	Dispersion of Ni (visual)
Ni/Al_2O_3	$C_6H_5CH_3$	0.01	Faint gray		Excellent
	$C_6H_5CH_3$	0.32	Light gray	<40	Excellent
	$C_6H_5CH_3$	0.63	Gray		Excellent
	$C_6H_5CH_3$	2.2	Gray		Excellent
	$C_6H_5CH_3$	2.9	Gray		Excellent
	$C_6H_5CH_3$	3.1	Gray		Excellent
	$C_6H_5CH_3$	4.3	Gray	<40[d]	Excellent
	$C_6H_5CH_3$	5.6	Gray		Excellent
	$C_6H_5CH_3$	6.8	Gray	<40	Excellent
	$C_6H_5CH_3$	9.0	Black	<40	Excellent
	$C_6H_5CH_3$	17	Black		Good
	$C_6H_5CH_3$	23	Black	40–100	Good
	n-C_5H_{12}	16	Pepper[e]		Poor
	$C_6H_5CF_3$	19	Black		Excellent
	THF	17	Black		Good
Ni/SiO_2	$C_6H_5CH_3$	1.7	Gray		Good
	$C_6H_5CH_3$	2.0	Gray		Good
	$C_6H_5CH_3$	2.6	Gray		Good
Ag/Al_2O_3	$C_6H_5CH_3$	0.8	Light gray		Fair
	$C_6H_5CH_3$	1.0	Light gray		Fair
	$C_6H_5CH_3$	1.9	Light gray		Fair
Ag/SiO_2	$C_6H_5CH_3$	2.4	Light gray		Fair
	$C_6H_5CH_3$	4.6	Gray		Fair
	$C_6H_5CH_3$	13	Gray		Poor
Pd/Al_2O_3	$C_6H_5CH_3$	4.0	Gray		Good
	$C_6H_5CH_3$	~0.3	Light gray		Good

[a] cf. Experimental Section for details on supports used.

[b] Generally a ~50:1 excess of solvent to Ni was employed. Experimentally this ratio can be easily varied as desired up to ~500:1.

[c] For some samples, approximate crystallite sizes have been determined by the method of Klug and Alexander (*6*).

[d] 40–100 Å after pyrolysis at 500°C.

[e] Metal particles interspersed with Al_2O_3 particles.

conjunction with transmission electron microscopy to determine particle size and shape. Figure 1 shows two photographs, one of the supporting Al_2O_3 and the other of a Ni particle/Al_2O_3 both at magnification ×37,000. Note the spherical nature of the Ni particles which are agglomerated into a very porous Ni skeleton. This finding is similar to the spherical particles formed directly from a Ni-toluene solution without Al_2O_3 support (*2*). However, in the Ni-toluene supported case the diameter of the individual spherical particles is approximately 0.03 μm (300 Å) while in the unsupported Ni-toluene case they are about 0.7 μm. The crystallite sizes in both cases are quite small in the neighborhood of 30 to 80 Å. It is interesting to note that the overall length of the individual Ni particle in Fig. 1 is about 0.8 μm (8000 Å), essentially the same as the spherical particles observed in the unsupported

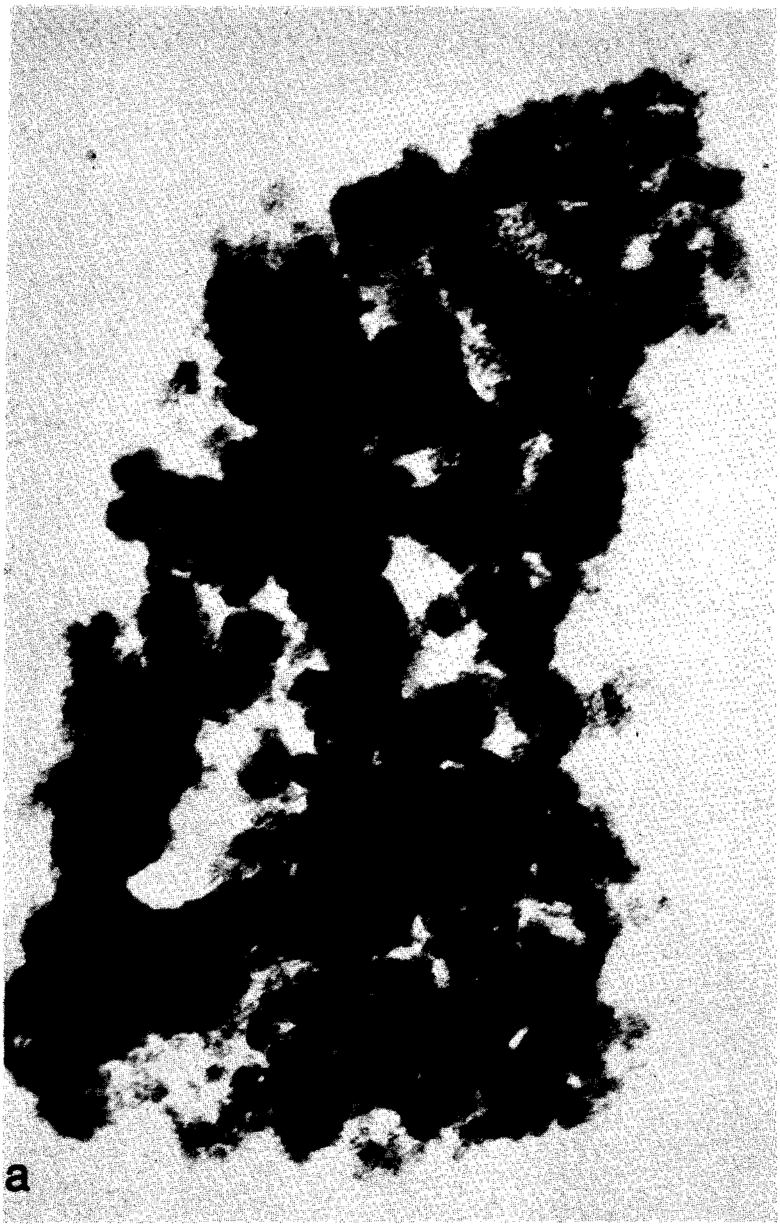
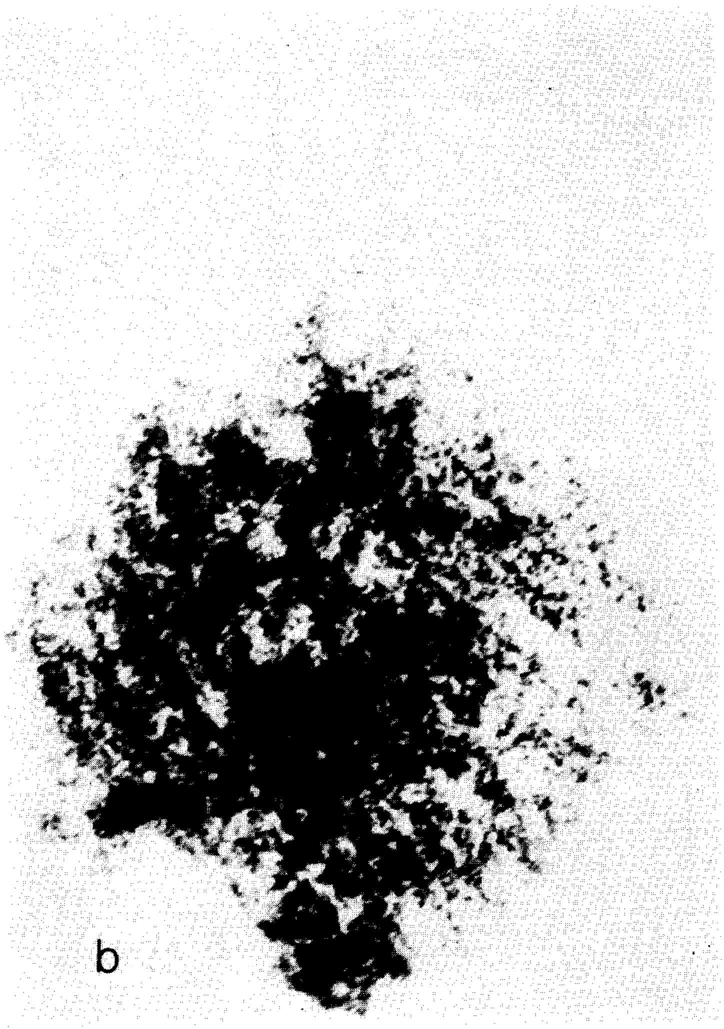


Fig. 1. Selected area imaging and TEM on Ni-toluene/Al_2O_3 and Al_2O_3. Electron micrograph with X-ray flourescence attachment: can pick out nickel or Al_2O_3 (×37,000). (a) Ni particle; (b) Al_2O_3.

case (*2*). It would appear that the Ni-toluene matrix (about 1:50 ratio initially) upon warming allows crystallization to crystallite sizes of 30 to 80 Å, and these further agglomerate to spherical particles of about 300 Å. These can be trapped on Al_2O_3 (or loose agglomerations of these), or, if no support is present agglomerate further to about 8000 Å spheres which then are stable at room temperature.



3. *Materials Adsorbed on the Ni-Toluene/Al_2O_3 Catalyst*

During the catalyst preparation in toluene, significant amounts of organics become strongly bound to the Ni particles and Al_2O_3, and remain bound even after pumpdown to less than 10^{-3} Torr at 25°C. Figure 2 summarizes the products desorbed upon pyrolysis of the resultant powders at various temperatures for 4.3% Ni-toluene/Al_2O_3. At the lower temperatures organics were desorbed, such as toluene, and small amounts of benzene and methylcyclohexane. Water evolution began at 100°C and continued throughout the pyrolysis, with the bulk of water released in the 200 to 300°C range. Carbon dioxide evolution was continuous throughout, whereas hydrogen evolution began at 200°C and continued up to 600°C. Small amounts of methane were released at 300 and 400°C, but no other small hydrocarbons.

Our work on unsupported active catalysts has indicated that the organic material adsorbed is oxidized to CO_2 in an extremely facile manner over the catalyst. Since this active nickel is a very good oxygen scavenger, which then is converted to CO_2, some CO_2 is always observed even under the most stringent airless conditions. In

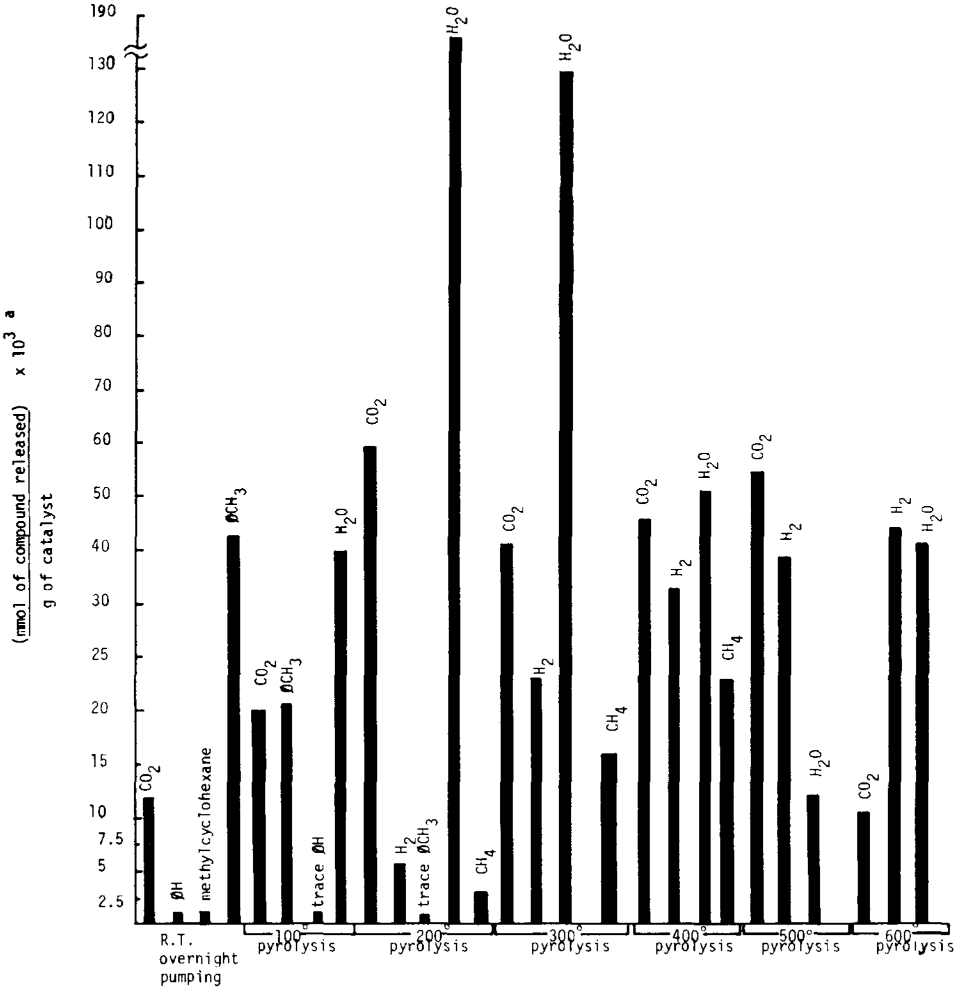


FIG. 2. CO_2, H_2O, H_2, and organics released upon pyrolysis of a Ni-toluene/Al_2O_3 catalyst. [a] Normal heating rate ≈1°/min but at faster rates slightly more CH_4 is observed. These are amounts released from one 4.3% Ni/Al_2O_3 sample heated progressively and samples taken off at the temperatures indicated.

the case of these supported catalysts, we believe similar oxidation of adsorbed carbon species occurs as the catalyst is heated. Some oxygen may also come from the Al_2O_3 support. The efficiency of this oxidation to CO_2 is striking in that only CO_2 is observed, no CO, alcohols or other intermediate products. In addition, Ni is necessary for this process since toluene-treated Al_2O_3 samples (blank experiments) yielded 10-fold less CO_2 on heating.

Figure 2 also indicates that some hydrogen is released upon pyrolysis. This probably indicates that carbonaceous species are formed on the surface of the Ni (organic $\xrightarrow{\Delta}$ H_2 + carbon). This process must only occur on Ni (not Al_2O_3) since toluene treated Al_2O_3 samples (blank experiments) indicated no formation of H_2 upon heating.

Methane formation occurs in comparable amounts whether Ni is present on the Al_2O_3 (blank experiments) or not.

Attempts to correlate catalytic activity with release of organics, H_2O, or CO_2 (cf. Catalytic Behavior section and Fig. 5) are not possible in a quantitative way. However, it is evident that large amounts of materials are desorbed in the temperature range where catalytic activities greatly increase. Thus, we believe loss of CO_2, H_2O, and H_2 with probable subsequent formation of some surface carbonaceous species is necessary for formation of the most active microcrystalline catalytic sites.

When the Ni-toluene/Al_2O_3 was heated

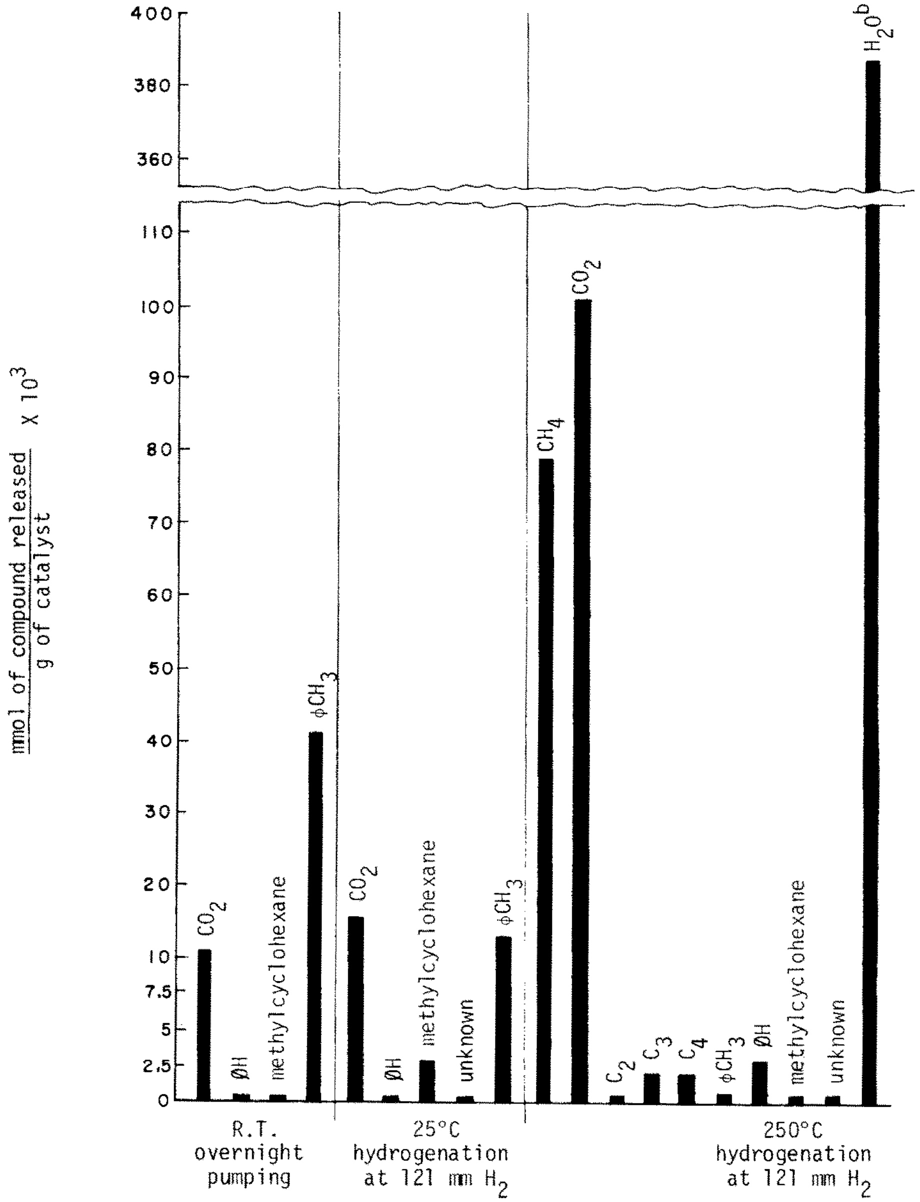


FIG. 3. CO_2, H_2O, and organics driven off by treatment of Ni-toluene/Al_2O_3 with H_2 at 25 and 250°C. [a] Done using 3.1% Ni-toluene/Al_2O_3. [b] Analyzed volumetrically; all others determined by VPC analysis.

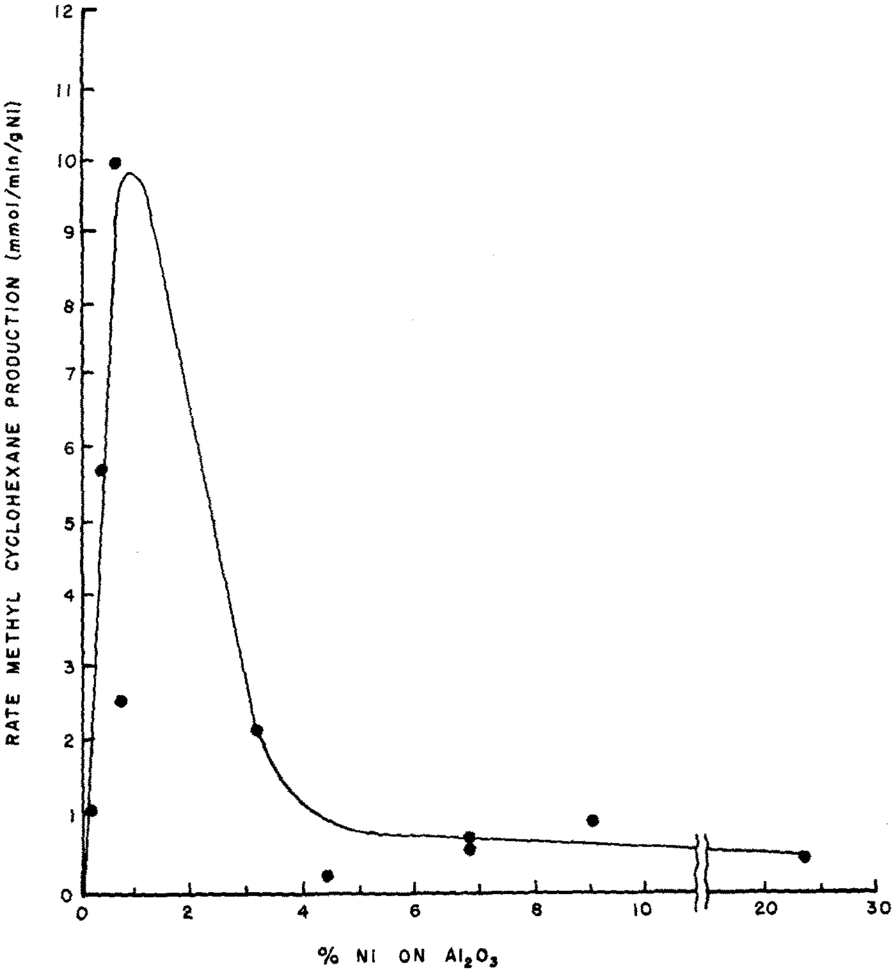


FIG. 4. Activities of Ni-toluene/Al_2O_3 in toluene hydrogenation with variance in Ni loading.

in the presence of excess hydrogen, organics, CO_2, and H_2O were again released (cf. Fig. 3). At lower temperatures most of the organics were released including, as expected, significant amounts of reduced products. At higher temperatures H_2O was the predominant product released, especially at 250°C where apparently surface oxygen is readily converted to H_2O.

4. *Sintering Properties*

For a 4.3% Ni-toluene/Al_2O_3 sample heating cycles were carried out and the resultant samples were examined by X-ray powder techniques. No detection on *any crystallinity* was observed until the samples had been pyrolyzed at 500°C or higher. Some sintering obviously could have occurred below this temperature, but certainly not gross sintering. These results indicate, as expected, the Al_2O_3 support served to stabilize the small crystallites toward sintering, since we know that unsupported Ni-toluene sinters about 300°C (*1*).

5. *Catalytic Behavior*

Hydrogenation and olefin isomerization reactions were studied employing these Ni catalysts. Comparisons were made for activity per gram of Ni for different Ni loadings, and for different catalyst heat treatment temperatures.

Ni Loading Variations. Rates of hydrogenation of toluene to methylcyclohexane at various Ni loadings are plotted in Fig. 4. Note that the more highly dispersed catalysts allowed effective use of the Ni, as would be expected, and these data may reflect a simple Ni surface area effect. Very low Ni loadings, where higher dispersions must be important, did not show much activity however. Thus, note the abnormally low activity for a Ni loading of 0.01%. This indicates that there is a maximum activity at about 0.4% Ni. We do not have adequate data to allow clear explanation of these data. It does seem evident, however, that an optimum dispersion reflects an optimum crystallite or cluster size. It may be that at very low loadings the Ni clusters are so small that their support interaction becomes overwhelming, which affects catalytic activity.

Assuming an Al_2O_3 surface area of 150 m^2/g, a 0.4% Ni loading would give only

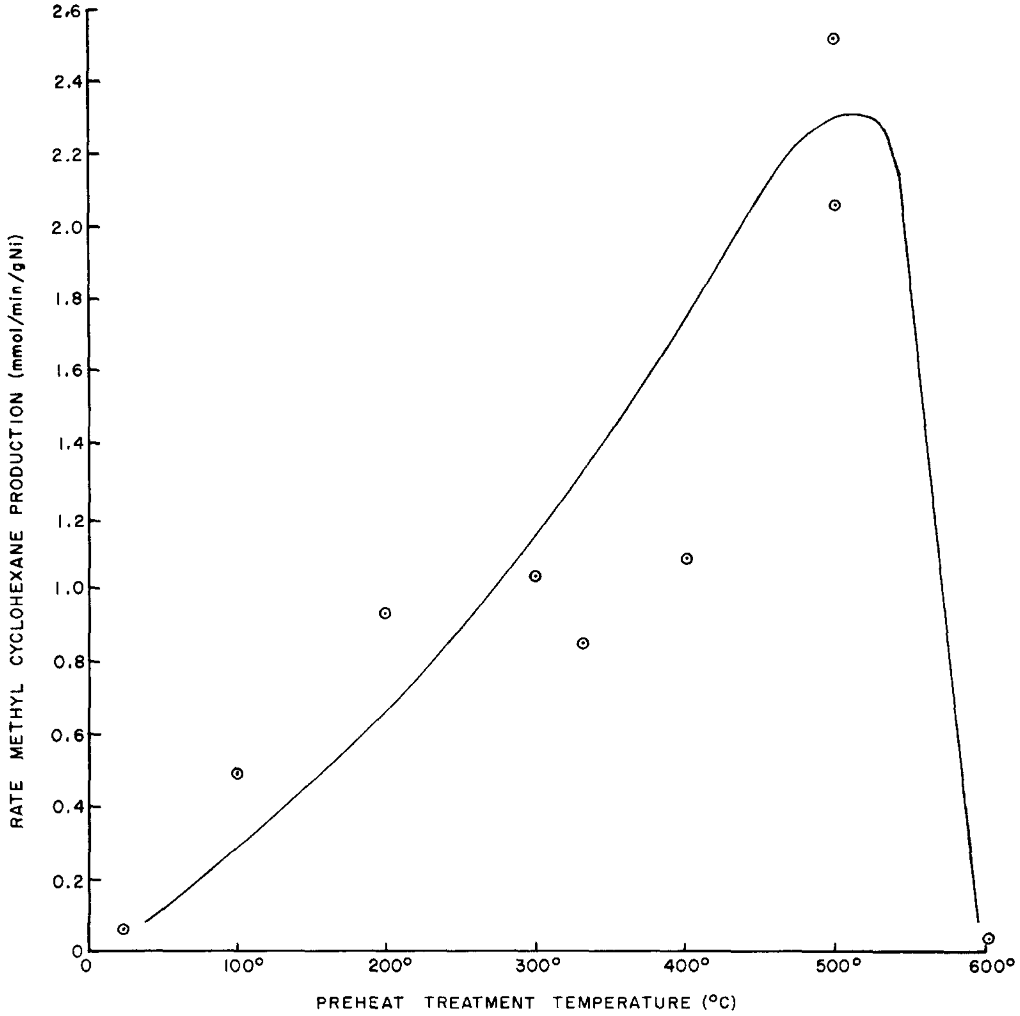


FIG. 5. Activity of 4.3% Ni-toluene/Al_2O_3 for toluene hydrogenation with variance in catalyst preheat treatment temperatures.

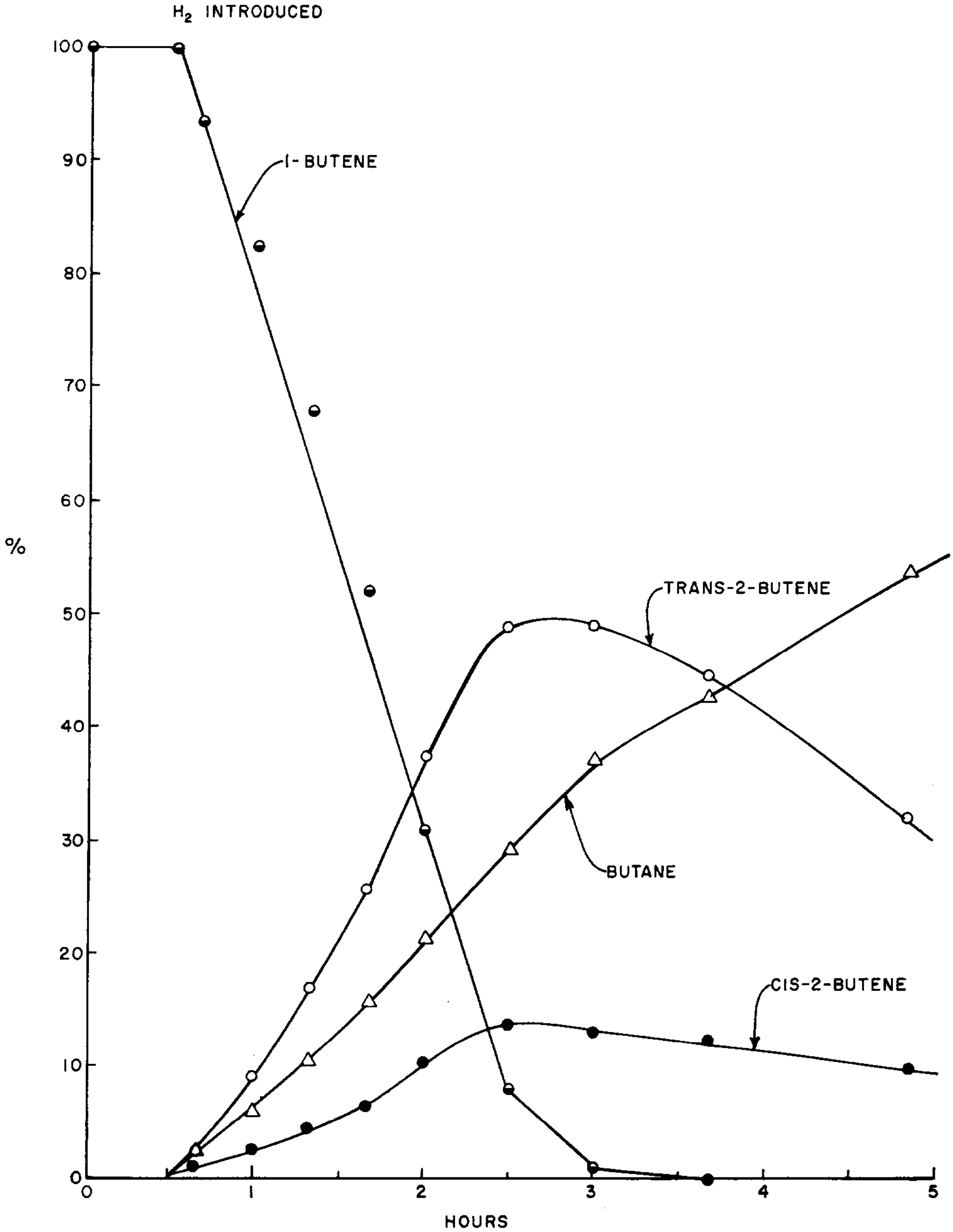


FIG. 6. Isomerization and hydrogenation of 1-butene over 6.8% Ni on Al_2O_3 (0.03969 g).

about 4.2% coverage as a monolayer of nickel (using Ni–Ni bond lengths as 2.49 Å[8]) (*7*). Since Ni is less catalytically efficient above 0.4% loading, it would appear that additional Ni simply serves to increase the cluster sizes, or is deposited in areas of the Al_2O_3 where catalysis can not be effective. Further work is needed in order to learn more about the Ni–Al_2O_3 interactions in the toluene system (what types of sites on Al_2O_3 are used up where Ni deposits, for example).

Heat treatment temperature variations. Portions of a 4.3% Ni-toluene (Al_2O_3

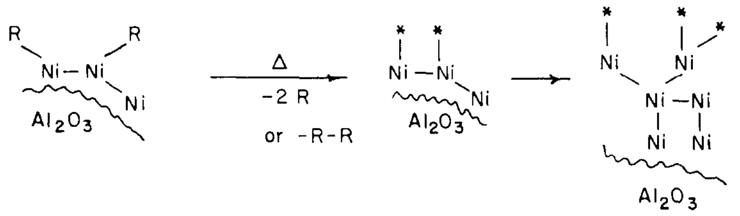
TABLE 2

Hydrogenation, Isomerization Rates for 1-Butene and 1,3-Butadiene Over Ni-Toluene/Al_2O_3 Catalysts and Ni-Toluene

Catalyst	Isomerization of 1-butene (mmol/min/g Ni)		Hydrogenation of 1-butene		Hydrogenation of 1,3-butadiene		Selectivity[a]
		rel. rate		rel. rate		rel. rate	
3.1% Ni-$\phi CH_3/Al_2O_3$	0.057	0.27	0.46	4.2	0.048	0.55	0
4.3% Ni-$\phi CH_3/Al_2O_3$	0.035	0.17	0.32	2.9	0.12	1.4	0
6.8% Ni-$\phi CH_3/Al_2O_3$	0.0	0.00	0.45	4.1	0.15	1.7	0
Ni-ϕCH_3[1]	0.21	(1.0)	0.11	(1.0)	0.088	(1.0)	0
Pure Al_2O_3 with ϕCH_3 treatment	0.0	0.0	0.0	0.0	0.0	0.0	—

[a] 0 = butane formed after 1,3-butadiene was completely consumed; X = butane was formed when 1,3-butadiene remained; Δ = intermediate between 0 and X.

catalyst were heat treated under dynamic vacuum at different temperatures, and the resultant catalysts were used in toluene hydrogenation studies. The purpose of these experiments was to: (a) determine at what temperature the Ni clusters sintered, and how this affected their activity in the toluene hydrogenation, and (b) to monitor the materials desorbed during the heat treatment procedure, and determine if the desorption process correlated with hydrogenation activity. The results of these studies turned out to be quite revealing, and are summarized in Fig. 5. The data clearly indicate a substantial and progressive increase in catalyst activity with catalyst preheating treatments up to 400°C. Then, a sharp increase of activity was observed at 500°C followed by a drastic loss of activity at 600°C pretreatment temperature. The falloff in activity correlates with gross sintering that occurs over 500°C. The steady increase in activity with increase in pretreatment temperature probably is due to desorption of materials (cf. Figs. 2 vs 5), with release of more active sites for the catalytic act. More work is needed to make clear actually what crystalline changes are occurring on organics desorption. Shown below is a possible representation of how more active sites might be generated on heating.



New microcrystalline faces? R = organic solvent or fragment molecule, CO_2, or H_2O; * = active site.

6. Catalyst Selectivities

Although we have employed toluene hydrogenation rates as a general measure of catalyst activity, selectivity and activity studies of olefin and dienes hydrogenation were also carried out. A recirculation flow reactor was employed (*1*) for hydrogenation of 1-butene to butane, and 1,3-butadiene to butane. It was found that 6.8% Ni-toluene/Al_2O_3 was a highly active

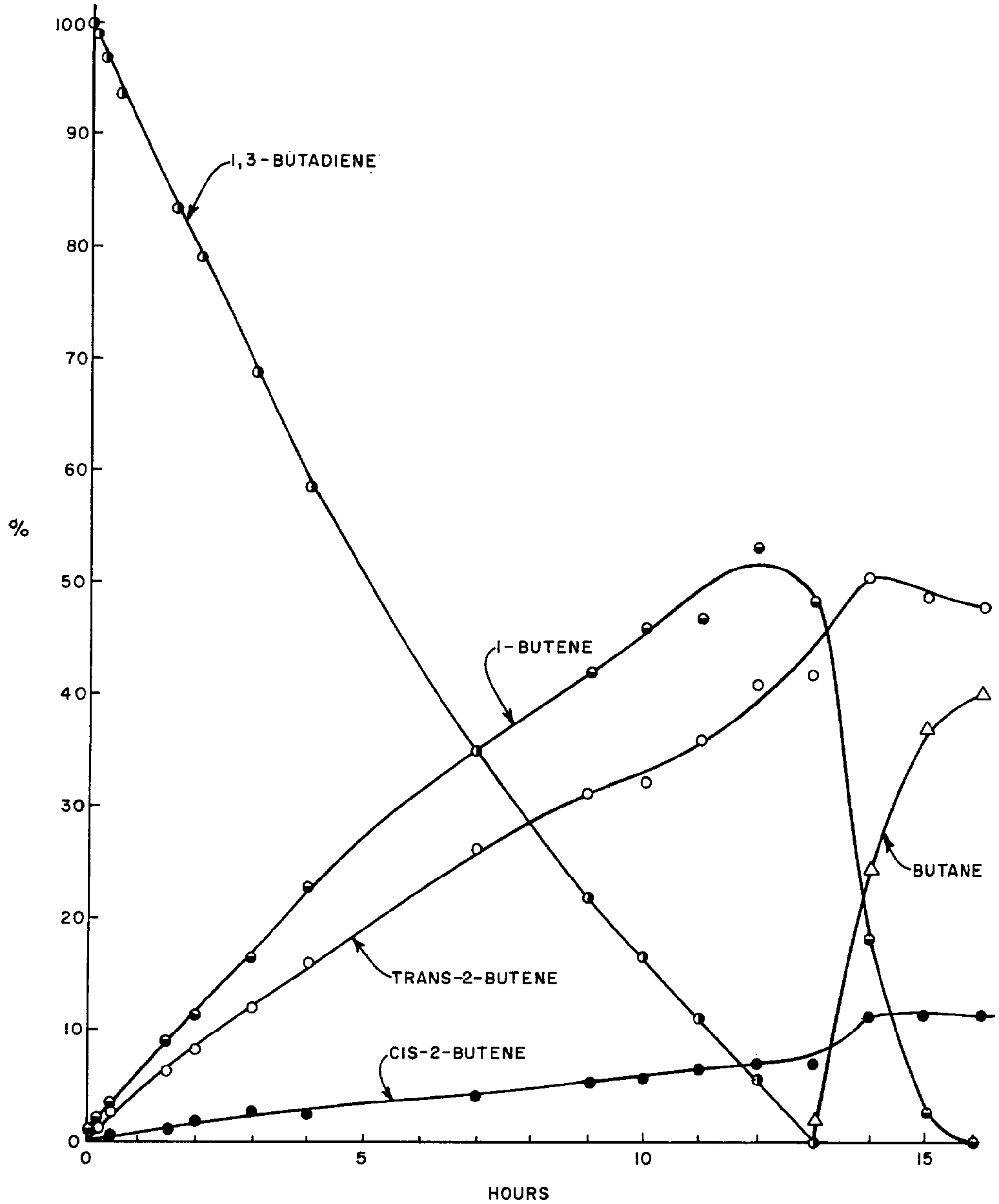


FIG. 7. Hydrogenation of 1,3-butadiene over 6.8% Ni on Al_2O_3 (0.06548 g).

catalyst/g Ni for the 1-butene → butane conversion, more active than Ni-toluene itself (*1*). However, this Ni-toluene/Al_2O_3 catalyst was ineffective as 1-butene isomerization catalyst in the absence of H_2 (cf. Fig. 5). This is in contrast to our findings with Ni-toluene as a catalyst by itself (*1*) (cf. Table 2), and shows that Al_2O_3 definitely affects the hydrogenation mechanism. On the other hand, the Ni-toluene/Al_2O_3 catalyst behaved quite similar to Ni-toluene (*1*) *after H_2 introduction,* and 1-butene was extensively isomerized as well as hydrogenated during the experiment time (Fig. 5). Thus, the Al_2O_3 hinders isomerization in the absence of H_2, but not in the presence of H_2.

Hydrogenation of 1,3-butadiene over 6.8% Ni-toluene/Al_2O_3 occurred in a fashion very similar to that occurring over Ni-toluene (*1*). Thus, extensive hydrogenation to butenes, especially 1-butene, took place before butane formation. The diene was only hydrogenated partially on the Ni surface, released, and then later 1-butene preferentially converted to butane (cf. Fig. 6).

In both the 1-butene and 1,3-butadiene work, the Ni-toluene/Al_2O_3 and Ni-toluene catalysts behaved similarly, but in both cases greater reactivity/g Ni was observed with the Al_2O_3 dispersed catalyst.

Comparison of different percentage of Ni loadings were also carried out, and the results are shown on Table 2. These data reemphasize that Ni-toluene/Al_2O_3 is a poorer 1-butene isomerization catalyst than Ni-toluene without support. However, straight hydrogenation of 1-butene to butane is somewhat more Ni efficient when Al_2O_3 supported. Hydrogenations of 1,3-butadiene (Fig. 7) are very similar in rate, and both the supported and nonsupported catalysts allow first only partial hydrogenation (to butenes, mainly 1-butene) *followed by* butene conversion to butane. Possible reasons for such behavior in these systems has been discussed previously, and probably involve competition for active sites by adsorbed organics (from toluene) with 1-butene or 1,3-butadiene, or the formation of very characteristic active sites when the Ni-toluene catalyst system is formed (*1*). Work is in progress which will hopefully clarify the system further.

CONCLUSIONS

Highly dispersed Ni, Pd, Pt, Ag-Al_2O_3, SiO_2 catalysts can be prepared by the metal vapor-solvent codeposition technique. For Ni/Al_2O_3, catalyst activities increase with increasing dispersion until a loading of about 0.4% is reached where activity falls off quickly. Thermal desorption of bound molecules (possibly with concomitant formation of new Ni crystallites) increases catalyst activity steadily until Ni sintering occurs. The Ni-toluene/Al_2O_3 catalyst shows similar selectivities compared with an unsupported Ni-toluene catalyst (*1*). Particle appearances are also similar for these catalysts showing the particles to be tiny spheres. These spheres are much smaller when dispersed on Al_2O_3 however. Crystallite sizes are in the 30–80 Å range.

ACKNOWLEDGMENTS

We are extremely grateful to Professor Galen Stucky and Dr. Ian Ward of the University of Illinois for transmission electron microscopy experiments and helpful discussions. Also, we thank Professor Kozo Tanabe of Hokkaido University for helpful discussions and preliminary study of some of these catalysts. We are grateful to the National Science Foundation for financial support in the form of a general research grant (CHE-7402713) and an NSF Energy Related Traineeship (to D.R.).

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