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Activity and Selectivity of Homogeneous Ziegler-Type Hydrogenation Catalysts. I

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Various aspects of aluminumalkyl reduced hydrocarbon soluble non-noble metal hydrogenation catalysts were investigated. Activity comparisons were made between soluble iron, cobalt, and nickel catalysts. The subsequent more detailed studies were carried out with the cobalt system which proved to be the most active one. It was found that modification of the catalyst by stoichiometric amounts of Lewis base is the best technique to obtain highest activities and reproducibility under practical conditions. Further on it could be shown that contrary to previous reports the catalyst can be used in weakly acidic solvents. With regard to selectivity in olefin hydrogenation it could be established that terminal olefins are substantially faster hydrogenated than internal ones. The possibility of double bond isomerization with these catalysts is briefly discussed.

INTRODUCTION

It is well known that the reaction of transition metal halides with aluminumalkyls gives catalysts (Ziegler catalysts or A.M. catalysts) for the dimerization and polymerization of olefins. This has been investigated especially for titanium halides where the active catalyst is believed to be a complex involving a lower valent state of the metal. The treatment of cobalt or nickel acetylacetonate with trialkylaluminum in large excess leads to the formation of the so-called displacement catalyst (*3*). This catalyst has been described in the literature as consisting of colloidal transition metal. It affects the low-temperature equilibration of olefins with trialkylaluminums. Since the presence of colloidal metal was suggested it seemed worthwhile to try these systems for hydrogenation reactions. This led to our studies of aluminumalkyl reduced hydrogenation catalysts (*1, 2*). In the meantime, recent publications in this area came out especially those of Sloan *et al.* (*4*), Lapporte and Schuett (*6*), and Kalechits and Schmidt (*5*). Sloan *et al.* (*4*) reported that the reduction of transition metal chelates gave homogeneous, hydrocarbon-soluble hydrogenation catalysts. The isolation or structural identification of the actual catalyst has not been reported.

EXPERIMENTAL METHODS

Materials

All solvents and all olefins (Phillips pure grade or Phillips research grade) used in this study were purified either by degassing and percolating over molecular sieve and subsequent drying over sodium wire or by distillation over calcium hydride in argon atmosphere. The tri-isobutylaluminum was obtained from Texas Alkyls and was used without further purification as its analysis indicated sufficient purity. The cobalt, iron, and nickel acetylacetonates were obtained from Mackenzie Chem. Corp. They were recrystallized and dried up to 80°C in high vacuum. Subsequent elementary analysis indicated sufficiently high purity. The hydrogen used for the hydrogenations was "electrolytic grade" which was further purified by a "deoxo" unit and a molecular sieve drier.

Catalyst Preparation

The catalyst preparations (as well as the other operations) were carried out under a blanket of inert gas. In most cases a nitrogen dry box was used. The transition metal acetylacetonate is dissolved in benzene. At ambient temperature a dilute solution of tri-isobutylaluminum is added in the desired molar ratio with stirring. Usually the catalyst is aged overnight to allow for reproducible activity data. In some cases the reduction was carried out by the tri-isobutylaluminum *p*-dioxane 1:1 complex. This complex was prepared by adding to a 1 M solution of tri-isobutylaluminum in benzene the equimolar amount of a 1 M solution of *p*-dioxane in benzene with cooling and stirring. The reduced catalyst solutions are in all cases deep colored. No solids could be detected by using an ultracentrifuge or by looking for a possible Tyndall effect. The catalyst solutions could be stored over a long period of time (several months) without any deterioration. In general the catalyst concentrations for olefin hydrogenations at <50 psi and ambient temperature were 10^{-2} to 10^{-3} M (with regard to transition metal).

Procedure

The olefin solution and the catalyst solution were mixed immediately before the actual hydrogenation run and transferred with argon into a glass lined 250-ml Magne-Drive autoclave (Autoclave Engineers Co.). The autoclave was thermostated by means of a cooling coil (inside) and a constant temperature bath (outside) to ±1°C. The autoclave was outfitted with a gas inlet system which went almost to the bottom of the glass liner. The same inlet tube was used as a dip tube for withdrawing small amounts of samples which were quenched with a cold, aqueous solution containing 10% sulfuric acid and 10% methanol. The autoclave had a high speed stirrer (carbon steel) which was driven by rotating magnets. The hydrogenations were carried out at different stirring speeds to ascertain that the rates were not limited due to inefficient mixing. Most runs were made using a stirring speed of 1000 rpm using constant hydrogen pressure which was provided by a multistage hydrogen regulator. In one case the hydrogenation was carried out at falling hydrogen pressure (kinetic run). A large 200-psi range Heise gauge was used to determine the pressure at different times. The analysis of the samples (after the catalyst had been killed by above-mentioned treatment) was carried out by conventional gas chromatography.

RESULTS

The activity of reduced soluble catalysts for the low temperature, low pressure hydrogenation of cyclohexene was investigated as a function of the ratio of trialkylaluminum to transition metal acetylacetonate (Fig. 1). The trialkylaluminum used was tri-isobutylaluminum. The curves show a maximum in the 6:1 ratio for the divalent chelates, and around 8:1 to 10:1 for the trivalent iron chelate. At high ratios the trialkylaluminum acts as a strong poison. Although the poisoning effect can be partially eliminated by closely adjusting the ratio in the reduction step this is, from practical considerations, very difficult due to the low catalyst concentration commonly applied and due to small amounts of impurities (for instance oxygen, moisture) present in solvents and reactants even after careful purification.

If the reduction is carried out by using a Lewis base adduct of the trialkylaluminum, the ratio of aluminum to transition metal is no longer critical as long as a sufficient amount of reducing agent is present. In other words any excess of reducing agent is not a poison as long as it is present as Lewis base adduct (Table 1). The effect of the Lewis base remains the same whether used as stoichiometric adduct or as solvent.

Table 2 shows the effect of acidic compounds on a soluble cobalt hydrogenation catalyst. The reaction of the alcohols with the soluble catalyst occurs relatively fast with gas evolution. The resulting species are soluble and catalytically active for hydrogenations. The hydrogenation data of such

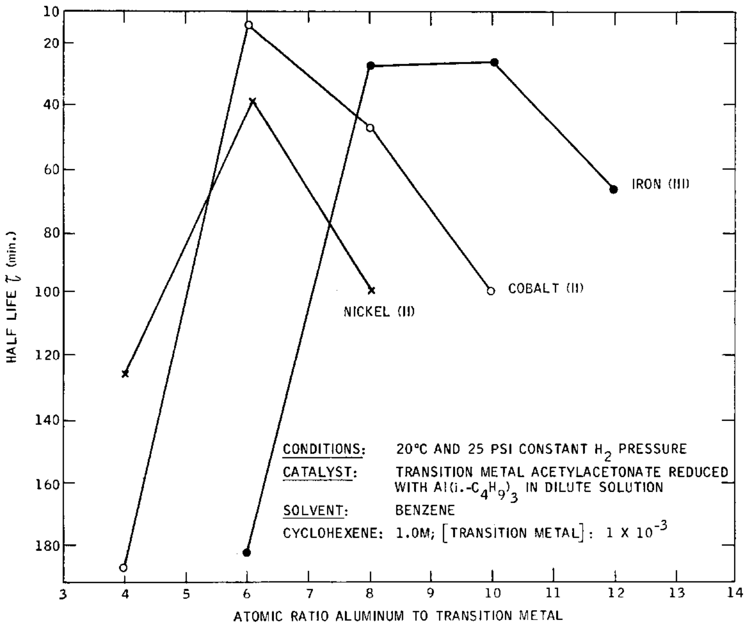


FIG. 1. Reduced, soluble transition metal catalysts in hydrogenation of cyclohexene.

alcohol-treated catalysts are reproducible. Interestingly in the case of *t*-butanol the catalyst activity is not changed when going from a small amount to a large excess.

Subsequently we investigated the hydrogenation of different types of olefins. It had been reported (*4*) that homogeneous catalysts prepared by aluminumalkyl reduction of transition metal chelates can hydrogenate internal olefins faster than terminal ones. We have investigated the hydrogenation of individual terminal and internal olefins as well as the competitive hydrogenations of mixtures of both. The data obtained are shown in Table 3. Our data show clearly that the hydrogenation of terminal olefins is about 3.4 times faster than the hydrogenation of internal ones. No hydrogenation of the benzene occurs under these conditions.

These data were further confirmed by carrying out a competitive hydrogenation of equimolar amounts of hexene-1 and cyclohexene. Here the hexene-1 was hy-

TABLE 1

COMPARISON OF HOMOGENEOUS COBALT CATALYSTS IN HYDROGENATIONS[a]

Lewis base	$Al(iC_4)_3$:Co(II)	Half-life time for hydrogenation of cyclohexene (min)
+	8:1	12
–	10:1	99
–	8:1	47
–	6:1	15
–	4:1	Very slow

[a] Lewis base: *p*-dioxane; Solvent: benzene; (+) molar ratio $Co(ACAC)_2$:$Al(iC_4H_9)_3$:*p*-dioxane = 1:8:10; hydrogenation conditions: 20°C and 50 psi constant pressure; cyclohexene: 1.0 *M*; [Co]: 1 × 10^{-3} *M*. ACAC = acetylacetonate.

TABLE 2

EFFECT OF ALCOHOLS ON COBALT CATALYST USED FOR THE HYDROGENATION OF CYCLOHEXENE[a]

Molar ratio Co:Al:alcohol	Alcohol	Half-life time (min)
1:12:—	—	6
1:12:36	*t*-Butyl	16
1:12:2596	*t*-Butyl	16
1:12:36	*n*-Butyl	116
1:12:2695	*n*-Butyl	210

[a] Conditions: temp., 20°C; constant pressure of 25 psi; catalyst: Cobalt(II) acetylacetonate reduced with tri-isobutylaluminum-*p*-dioxane complex; solvent: benzene; cyclohexene: 1.0 *M*; [Co]: 1 × 10^{-3} *M*; Co:Al:*p*-dioxane; 1:12:15.

TABLE 3

Hydrogenation of Olefins Using a Soluble Cobalt Catalyst[a]

Olefin	Half-life time (min)
Hexene-1[b]	2.8
Cyclohexene	9.6

[a] Reaction conditions: solvent: benzene; cyclohexene: 1.0 M; [Co]: 1×10^{-3} M; catalyst: Cobalt-(II) acetylacetonate reduced with tri-isobutylaluminum-*p*-dioxane complex; atomic ratio Al:Co = 12:1; constant hydrogen pressure: 25 psi; constant temp. 20°C.

[b] Some isomerization occurs.

TABLE 4

Competitive Hydrogenations Using Soluble, Reduced Cobalt Catalyst

% (w/w) Solvent free		
Feed		Product
50 Hexene-1	$\xrightarrow{20°C/50\ psi}$	46 Hexane; 4 hexenes
50 Cyclohexene[a]		2 Cyclohexane; 48 cyclohexene
7 Phenylacetylene	$\xrightarrow{20°C/100\ psi}$	7 (Styrene + ethylbenzene)
93 Hexene-1[b]		Trace hexane; 92 hexene-1; trace hexene isomers

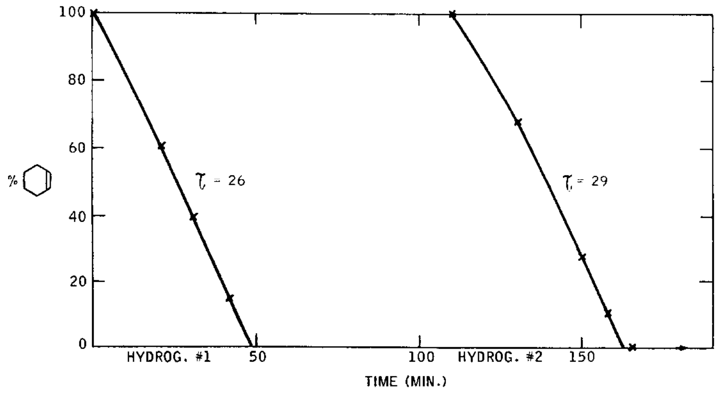
[a] Solvent: benzene; catalyst: 0.05 mM $Co(ACAC)_2$ + 0.6 mM $Al(i\text{-}C_4H_9)_3$ + 0.75 mM *p*-dioxane.

[b] Solvent: *n*-heptane; catalyst: 0.9 mM $Co(ACAC)_2$ + 8 mM $Al(i\text{-}C_4H_9)_3$ + 53 mM 1,2-dimethoxyethane.

drogenated with high selectivity (see Table 4).

Other successful selective hydrogenations carried out include the hydrogenation of small amounts of acetylenes in presence of large amounts of hexene-1 or the selective hydrogenation of vinylcyclohexene to ethylcyclohexene.

The reproducibility of the hydrogenations is quite good. Figure 2 shows two successive runs using the same catalyst. The conversions were determined by frequent analysis of samples using gas chromatography. After the first run, more cyclohexene was added and the hydrogenation was continued. The second hydrogenation was carried out in more dilute solution and with less catalyst due to loss in sampling. Although the half-life time is about 10% longer, the reproducibility under these conditions is good. Table 5 shows a hydrogenation with falling pressure. The catalyst is a Lewis base modified reduced cobalt(II)



CATALYST: $Co(ACAC)_2$: 0.40 mM; $Al(iC_4H_9)_3$: 1.0 mM

SOLVENT: N-HEPTANE

CYCLOHEXENE: 95.9 mM

HYDROGENATION CONDITIONS: 100 PSI CONSTANT H_2 PRESSURE
22°C TEMPERATURE

Fig. 2. Reproducibility of hydrogenations with soluble cobalt catalyst (repeat runs with same catalyst).

TABLE 5
KINETICS OF HYDROGENATING CYCLOHEXENE WITH SOLUBLE CATALYST[a]

Time (min)	Pressure (psi)	log P_0/P	$10^2 \times k$ (min^{-1})
0	61.3	—	—
2	56.6	0.03463	4.0
3	54.2	0.05346	4.1
4	51.9	0.07225	4.2
5	49.5	0.09272	4.3
6	47.4	0.11160	4.3
7	45.5	0.12937	4.3
8	43.9	0.14489	4.2
9	42.1	0.16316	4.2
10	40.8	0.17667	4.1

[a] Temp.: 20°C; catalyst: Cobalt(II) acetylacetonate reduced with tri-isobutylaluminum–p-dioxane complex. solvent: benzene; cyclohexene: 1.0 *M*; [Co]: 1.06×10^{-3} *M*; Al:Co = 10:1.

acetylacetonate. The data show first-order kinetics up to fairly high conversions.

As these catalysts are extremely active we wanted to be sure that we were not measuring diffusion rates. Therefore we followed the hydrogenation rates of reduced divalent nickel and cobalt acetylacetonate at different temperatures (using a catalyst concentration of 90 ppm). On plotting the log of the rate data (obtained at different temperatures) versus $1/T$ we obtained straight lines (Fig. 3). This fairly well documents that our reaction is not diffusion controlled. These data also show clearly that the soluble cobalt catalyst is more active than the nickel catalyst over a sufficiently wide range of temperatures using the same ratio of trialkylaluminum to transition metal chelate.

It was mentioned earlier that some double-bond isomerization occurred in the hydrogenation of hexene-1. Table 6 presents data on the isomerization of hexene-1 under typical hydrogenation conditions (see also Table 3). The hexene-1 all disappeared after 5-min reaction time and a substantial amount of internal olefin (hexene-2) was formed. Because the isomerization reaction is not fast the amount of hexene-3 was very small. The hydrogenation rate of the hexene-2 mixture is slow compared with the hydrogenation rate of hexene-1 which observation is in agreement with the general picture obtained earlier from the hydrogenations of hexene-1 and cyclohexene (Tables 3 and 4). Interestingly enough the same catalyst does not cause any isomerization of hexene-1 at ambient temperature *without hydrogen* over a period of at least 1 hr.

DISCUSSION

This study shows clearly that the molar ratio of trialkylaluminum to transition metal chelate is very critical for obtaining high hydrogenation activity. At a large excess of reducing agent the catalyst is inactive for all practical purposes. In any case this dependence of hydrogenation rate data upon the ratio alumium to transition metal poses a real problem for a comparison of reduced soluble catalysts containing different transition metals. The most active catalyst (Fig. 1) seems to be the reduced

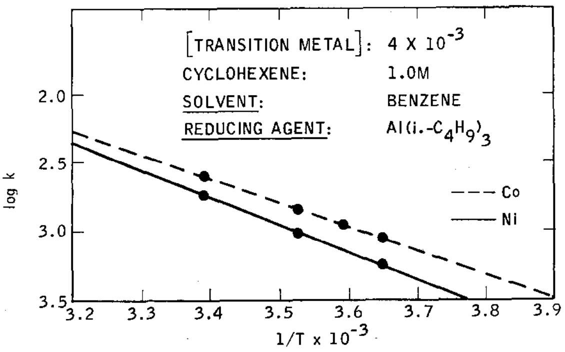


FIG. 3. Arrhenius plot for hydrogenation rates in hydrogenation of cyclohexene at 100 psi with soluble cobalt and nickel catalysts having a ratio of aluminum to transition metal as 2.5:1.

TABLE 6

HYDROGENATION AND ISOMERIZATION OF HEXENE-1 USING A SOLUBLE COBALT CATALYST[a]

Reaction time (min)	(% w) Hexane	Hexene-1	*cis-* + *trans-* Hexene-2	*cis-* + *trans-* Hexene-3
0	—	100	—	—
5.0	84.9	—	14.9	0.2
7.3	93.2	—	6.8	—

[a] Feed: 1 *M* hexene-1 in benzene; catalyst: cobalt(II) acetylacetonate reduced with tri-isobutylaluminum–*p*-dioxane complex; atomic ratio Al:Co = 12:1; olefin: 1.0 *M*; [Co]: 1×10^{-3} *M*; constant hydrogen pressure: 25 psi; constant temp.: 20°C.

cobalt catalyst followed by iron and nickel. This comparison is based on using equimolar amounts of transition metal ("specific activity") in the hydrogenation test. It is obviously difficult to pinpoint the exact location and the height (i.e., half-life time) of the maxima. The high activity of the reduced iron catalyst is truly remarkable if one recollects the poor performance of reduced supported iron catalysts in hydrogenations.

In subsequent hydrogenations the reduced cobalt and nickel catalysts were compared at different temperatures (Fig. 2). It appears that the "specific activity" of the reduced cobalt catalyst is greater measured over a substantial temperature range when using the same atomic ratio Al:transition metal of 2.5:1. Similar results were obtained later for the hydrogenation of aromatics where cobalt catalysts were always more active than nickel catalysts (*7*). This finding is interesting with regard to supported catalysts where the specific activity of a cobalt catalyst for benzene hydrogenation was found to be lower than that of a nickel catalyst (*8*).

As the optimum adjustment of a given soluble catalyst is difficult due to the abovementioned criticality and due to the presence of small amounts of impurities in the feed stream, we tried out several approaches to alleviate this problem. One solution utilizes our finding that some Lewis bases are not harmful to the soluble cobalt catalyst and that the adducts of the trialkylaluminum reducing agent with the same Lewis bases no longer affect the catalyst activity adversely. Therefore one can use an excess of the trialkylaluminum base adduct for obtaining maximum catalyst activity and at the same time for scavenging catalyst poisons.

Sloan *et al.* (*4*) mentioned that the homogeneous catalyst was killed by addition of alcohol or acetone. This was used as an argument against the presence of colloidal metal. However, we found that stoichiometric amounts, as well as an excess of alcohol (degassed, oxygen free), did not kill the homogeneous cobalt catalyst (Table 2). These data are reproducible and mean that by addition of alcohol new, soluble catalysts are prepared with less activity. Especially interesting are the data obtained with stoichiometric amounts or with excess *t*-butyl alcohol. They indicate that a new catalyst species is formed and that no solvent effect is observed. We postulated earlier (*2*) that the active catalyst species involves a complex between a reduced transition metal species and an organoaluminum compound as stabilizer and solubilizer. The data obtained with Lewis bases and alcohols give additional valuable information on the active catalyst species which matter will be discussed in a subsequent paper. The existence and stability of soluble hydrogenation catalysts in the presence of compounds with acidic hydrogen makes it possible then to carry out hydrogenations in which the unsaturated starting material, the intermediates or the end products have acidic hydrogen. One example is the hydrogenation of benzonitrile to benzylamine (*1*) practically without side reactions as commonly encountered over heterogeneous catalysts.

In hydrogenations with most heterogeneous and other catalyst systems it has been established that terminal olefins are faster hydrogenated than internal ones *(9)*. Recently it was reported *(4)* that with homogeneous, hydrocarbon soluble hydrogenation catalysts the reverse is the case. Therefore it seemed of interest to us to investigate this question further. We found (Table 3) contrary to above reference that terminal olefins are hydrogenated about three times faster than internal ones. Subsequently co-hydrogenations of different unsaturated hydrocarbons were carried out. Of course the selectivity in such hydrogenations cannot be predicted from the reaction rates of hydrogenation of the individual compounds *(10)*. The co-hydrogenation of equimolar amounts of hexene-1 and cyclohexene was carried out using the same soluble cobalt catalyst (Table 4). The hexene-1 was hydrogenated with high selectivity. Similarly, 4-vinylcyclohexene-1 was hydrogenated selectivity to 4-ethylcyclohexene-1. Numerous other examples are available from our studies as, for instance, the selective hydrogenation of cyclopentadiene to cyclopentene, or the selective hydrogenation of phenylacetylene in the presence of large amounts of hexene-1 *(1, 7)*.

The data in Table 6 show that the hydrogenation of hexene-1 is accompanied by double-bond isomerization. Although the isomerization of terminal olefins over certain Ziegler-type catalysts *in the absence* of hydrogen was observed earlier *(3)*, there were no data available on the extent of isomerization *during* hydrogenations with soluble catalysts as described above. The occurrence of the isomerization reaction complicates rate studies with terminal olefins because the isomerized olefins give the same saturated hydrocarbon upon hydrogenation. No *immediate* isomerization is observed in such mixtures containing hexene-1 and the catalyst at ambient temperature unless hydrogen is added. This "hydrogen effect" upon the isomerization can best be explained by assuming that a hydride form of the reduced catalyst is formed as schematically indicated in Fig. 4. The first step in the catalyst preparation gives the reduced catalyst which can absorb hydrogen, thus converting to the hydride form. The latter can easily perform the isomerization of the olefin by repeated addition and elimination reactions.

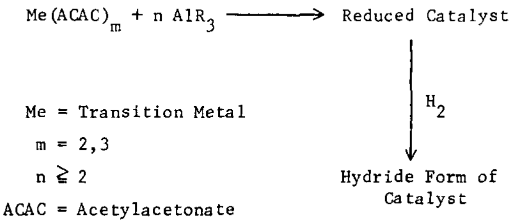


FIG. 4. Isomerization scheme.

The exact structures of the reduced catalyst and of the hydride form of the catalyst are not known because the isolation and characterization has not been successful due to instability. In a subsequent publication we will discuss experimental results which will allow us to suggest structures for the reduced and the hydride form of the catalyst. This in turn will explain the poisoning effect of excess free trialkylaluminum, the effect of Lewis bases and the effect of *t*-butyl alcohol on the hydrogenation catalyst. The above non-noble metal, soluble systems are truly remarkable because of their high activity and selectivity for hydrogenations under mild conditions and low catalyst concentrations.

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