Homogenizing Metal Oxide Catalysts

Charles U. Pittman Jr.[a]; Edwin H. Lewis[a]; Mohammad Habib[a]

[a] Department of Chemistry, University of Alabama University, AL

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Charles U. Pittman, Jr.,   Edwin H. Lewis
and Mohammad Habib

Department of Chemistry
University of Alabama
University, AL   35486

ABSTRACT

Metal oxide particles have been prepared which are
"soluble" in hydrocarbon solvents. The reaction of either
a metal (or its metal oxide) with water, mineral spirits,
and a mixture of carboxylic acids can result in hydrocarbon-
miscible metal oxide core particles of 20-1000Å diameter
sizes which are coated with a layer of hydrophobic carboxy-
lates. This will only occur if the metal:acid ratio ex-
ceeds one. The particle size increases as the metal:acid
ratio increases. The surface carboxylate groups are in
equilibrium, preventing the use of colligative property
measurements in determining molecular weights. Sedimentation
velocity studies confirmed that particle aggregation equili-
bria occur which are solvent dependent. Aggregation is more
serious in polar solvents. The distribution of carboxylic
acids used did not effect the particle size. Cobalt and
manganese oxide particles have been used in oxidations
of cyclohexane, toluene, and xylenes. Cobalt oxides were

used in hydroformylations of 1-pentene. Nickel oxide catalysts
were tested in hydrogenations of 1-pentene, polybutadiene, poly-
isoprene, and aromatic compounds, The nickel oxides were much
more active upon addition of Et_3Al. Cobalt oxide systems were
active in the syndiotactic 1,2-polymerization of butadiene.
The oxide particles could be coated onto supports such as
silica, alumina, and kieselguhr followed by oxidation to
give supported metal oxides. Reduction with hydrogen or
metal hydrides or Et_3Al gave supported metal catalysts. The
activity of these supported catalysts were investigated.

                              INTRODUCTION

        The area of heterogenizing homogeneous catalyst has
been an active research topic for the past few years.
Homogeneous transition metal complexes, for example, have
been immobilized onto crosslinked polymers and silica [1-3].
These heterogenized systems can then be used in fixed catalyst
beds.   However, the idea of homogenizing a heterogeneous
catalyst has largely been overlooked. Consider metal
oxide catalysts. How could one "homogenize" a metal oxide?
Could a metal oxide be prepared that was "soluble" in a
hydrocarbon solvent? It was this goal which was the basis
of the work described in this paper.
        Soluble metal carboxylate salts (soaps) have been used
as catalysts for paint drying, oxidation of p-xylene to
teraphthalic acid, and combustion, They have been prepared
from metals or metal oxides in the presence of an equivalent
of carboxylic acid [4]. However, what would happen if a
metal oxide was reacted with a limited amount of carboxylic
acid in a similar fashion (ie, if the metal/acid equivalent
ratio is kept greater than one)? If an insufficient quantit-
ies of acid were available to stoichiometrically form the
carboxylate salts, would a mixture of metal oxides and
metal carboxylates result? Anthony Alkaitis and Paul Cells,
working at Mooney Chemical Co., Inc. [5], pioneered such
reactions in 1977. The procedure is illustrated in Figure 1.
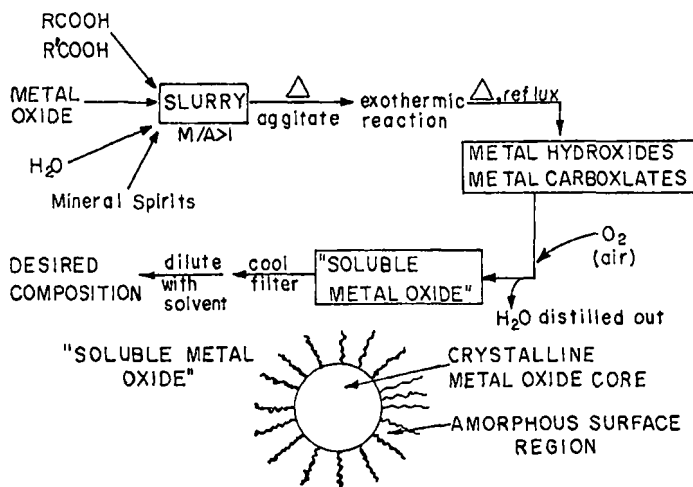
FIG. 1.

Heating metal oxides, water and a mixture of car-
boxylic acids, which were slurried in mineral spirits
(or other solvents), led to an exothermic reaction giving
metal hydroxides and carboxylates [5]. Air oxidation and
distillation of water gave "soluble" metal oxides [5]. For
example, stable hydrocarbon "solutions" of Mn_3O_4, CoO, or
NiO could be made that were 60% by weight metal. Other suc-
cessful preparations of Fe_2O_3 and CuO, as well as bimetallic
systems such as Mn_3O_4/CoO, Mn_3O_4/BaO and Mn_3O_4/ZnO were
made [5].

EXPERIMENTAL

The detailed synthesis of the "soluble" metal oxide
particles is described by Alkaitis and Cells in their 1979
patent [5]. Thus, the syntheses will not be further
described here. Sedimentation velcocity and equilibrium ex-
periments will be described in the following paper.

Homogeneous Reactions
        Homogeneous oxidations of cyclohexane, toluene, or
xylenes were carried out in 100cc or 250cc stainless steel
autoclaves under various oxygen/nitrogen partial pressures.
For example, a typical cyclohexane oxidation in benzene
involved charging cyclohexane (59 mmol), benzene (250 mmol),
and cyclohexanone (0.48 mmol, an initiator) into the auto-
clave. Then the cobalt oxide complex (0.13 mmol) and the
manganese oxide complex (0.44 mmol) were added, followed by
pressurization with oxygen or oxygen and nitrogen. The
reactor vessel was vigorously shaken while heated (115-160°)
with an external oil bath for the prescribed time followed
by cooling and analysis of glc. Similar straightforward
procedures were used in hydroformylations (CO/H_2 atmosphere),
and hydrogenations (H_2 atmosphere).

Supported Catalysts
        The preparation of the supported heterogeneous
catalysts from the "soluble" metal oxides followed the
following general method. The support (Al_2O_3, SiO_2, kieselguhr)
was thoroughly dried by heating at 500-600°C under a con-
tinuous nitrogen flow. Then under nitrogen or in vacuo, the
support was treated with a "solution" of the overbased
Mooney complexes to form a slurry which was thoroughly mixed.
The solvent was removed in vacuo. The supported catalysts
were then heated to 400-500° under a flow of oxygen to insure
the oxidation of any organic compounds on the surface and to
effect surface binding. In many cases reduction was then
effected using $NaBH_4$ or $AlEt_3$ or by heating in a hydrogen
atmosphere.

        As a general example, the preparation and use of
alumina-supported NiO and Ni for studies of the demethylation
of 1-methylnaphthalene is given. Alumina tablets (1/8") from
Calcicat, having a pore volume of 0.5cc/g and a surface area
of 200m^2/g were dried at 500°C for 3 hrs. under a continuous
nitrogen purge. After cooling, 106g of the support was
treated with a hexane solution (200ml) of the nickel oxide
particles (122Å diameter in mineral spirits, Ni/acid = 33,

acid distribution: 20%C_3, 50%C_8, 15%neoC_{10} and 15%C_{18})
containing 21.2g of the nickel complex (to give theoreti-
cally a 9% wt. Ni catalyst). The nickel complex was in-
jected; then nitrogen was introducted at 1 atm. and the
slurry was mixed for 10 hrs. The solvent was evaporated to
give dark tablets which were dried in a steel tube at 400°C
for 1 hr. under nitrogen and then an additional 2 hrs. at
400°C under oxygen. This catalyst was designated Al_2O_3-NiO.

The supported nickel oxide (just described) (60g) was
reduced with a 0.5M aqueous solution of $NaBH_4$ (3.2g, 0.085 mol).
After the evolution of gas stopped (~8hrs.) the catalyst had
turned green. The catalyst was washed with distilled water
three times and dried in vacuo. The tablets were heated
under a nitrogen flow for 2 hrs. at 400°C and then des-
ignated Al_2O_3-Ni.

Testing Al_2O_3-NiO and Al_2O_3-Ni
    Dried Al_2O_3-Ni (10g), cyclohexane (30ml), and 1-
methylnaphthalene (5g; 35.1mmol) were charged into a 300ml
autoclave which was pressurized to 850psi with hydrogen.
The reactor was heated to 320° (pressure increased to
1400psi) and held for 30min. Glc analysis (Hewlett Packard
Model 5710A with a model 3380A recorder integrator using
internal standard techniques) showed 1-methylnaphthalene
93.6%, naphthalene 3.8%, trans-1-methyldecalin 1.6%, trans-
decalin 0.5%, and cis-decalin 0.51%. After 17hrs at 320°
the product distribution was, respectively 0%, 1.9%, 11.6%,
11.0%, and 73.7%.

The Al_2O_3-NiO catalyst (20g) and 1-methylnaphthalene
(10g, 70.3mmol) were charged to an autoclave and reacted as
described above (740psi initial hydrogen pressure and 1250psi
at 320°). After 18hrs, glc analysis showed 1-methylnaphthalene
28.4%, naphthalene 14.2% cis-1-methyldecalin 5.7%, trans-1-
methyldecalin 7.8%, cis-decalin 10.7%, and trans-decalin 33.1%

RESULTS AND DISCUSSION

"Soluble" metal oxide systems were prepared in a
variety of concentrations. To characterize the particles,

the nature of the metal oxide core was studied by X-ray
analysis. A crystalline core domain was surrounded by an
amorphous region. The core phases were found to be Mn_3O_4
(spinel), CoO (cubic), Fe_3O_4 (spinel) and CuO (triclinic).
Where two different metals were used in the preparations
(ie Mn_3O_4/CoO etc.) the atoms of both were present in the
core. The amorphous outer region resulted from the dis-
similarily of the acid moieties and this confers the
high solubility in aromatic and aliphatic hydrocarbon
solvents. Electron microscopy ($2 \times 10^6 M$) of dried samples
revealed small spherical crystalline "ultimate core par-
ticles" (30-80Å diameter) which were aggregated into 200-
300Å clusters. Infrared and chemical analysis further
revealed a structure generalized in Figure 2. Carboxylic
acids are attached to the metal oxide particle surfaces.
Both carboxylate salt sites and hydrogen-bonded carboxylic
acid sites are present. Thus, during the preparation of
the core particles, metal oxide cores are formed and sur-
rounded by an amorphous carboxylic acid layer which renders

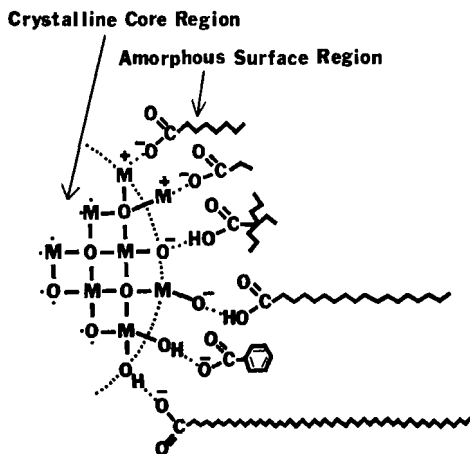**METAL OXIDE CARBOXYLATE PARTICLE STRUCTURE**

FIG. 2.

the core oxide particles "soluble" in such solvents as
mineral spirits, hexane, benzene, etc.

The solubility of these particles in a particular
solvent depends upon the distribution of carboxylic acids
used in the original preparation. Attempts to charac-
terize the solution behavior and structure of these par-
ticles caused much initial confusion. The particles'
molecular weights could not be obtained by gel permeation
chromatography due to association with the columns and
vapor pressure osmometry (VPO) gave molecular weights far
to low. This resulted because surface-attached carboxylic
acids were in equilibrium with the solution and the VPO
technique measures a colligative property. Figure 3 il-
lustrates this principle. Here a core particle, with a
molecular weight of 10^6 is in equilibrium with six dis-
sociated moleucles of carboxylic acid. Thus it will only
appear to have a molecular weight of $10^6/7$. Therefore,
ultracentrifugation was a perferable method to study the
solution behavior. Molecular weights from sedimentation
velocity experiments were in agreement with those from
sedimentation equilibrium experiments. However, the
dynamic equilibria which these core particles experience
in solution prevented the general application of sedimentation
equilibrium experiments.
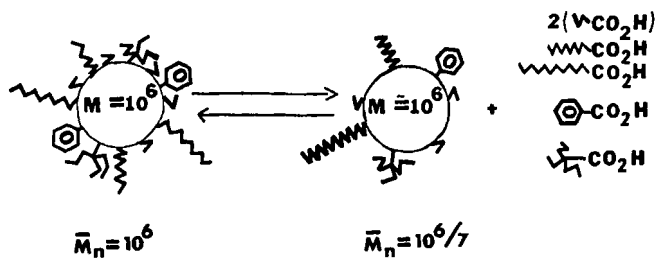
Particle Dissociation

FIG. 3.

Sedimentation velocity studies revealed the observed molecular weight of a given preparation was a function of the solvent. This is the result of a solution aggregation equilibrium which is solvent dependent. Poor solvents gave the highest molecular weights as can be seen in Table 1. For example, a Mn_3O_4 sample, made with a metal/acid ratio of 18, was present as "ultimate particles " ($48\overset{o}{A}$ diameter) in the good solvent mineral spirits but aggregation of these core particles occured in poor solvents. In THF an average of 20 ultimate particles was present per aggregate. This nonspecific particle aggregation equilibrium is pictured in Figure 4. Thus, to measure the core particle's actual size requires that measurement be made in a good solvent. In a poor solvent the ultimate particles aggregate. By adding a good solvent, the equilibrium is reversed and the "ultimate particles" are again observed.

TABLE 1

Sedimentation Velocity Studies Confirm Aggregation
Equlibra Is Solvent Dependent

Sample	M/A	Solvent	Particle Dia -(A)	Molec. Weight	Ave. No. Of Ultimate Particles
40%Mn[A] (Mn_3O_4)	18	Min. Sp.	48	1.5×10^5	1.0
		Cyclohex.	72	5.0×10^5	3.3
		CCl_4	103	1.5×10^6	10.0
		Bz	111	1.9×10^6	13.0
		THF	128	3.0×10^6	20.0
50%Ni[B] (NiO)	33	Min. Sp.	122	3.1×10^6	
		Isooct.	132	4.1×10^6	
		CCl_4	286	40.0×10^6	
40%Co[C] (CoO)	24	Isooct.	86	9.0×10^5	
		CCl_4	160	5.7×10^6	

[A] 20% C_3, 40% C_8 [B] 20% C_3, 50% C_8 [C] 30% C_3, 55% neo C_{10}
   20% neo C_{10} 15% neo C_{10} 15% C_{18}
   20% C_{18} 15% C_{18}

Nonspecific Aggregation

Large aggregate

Ultimate particle

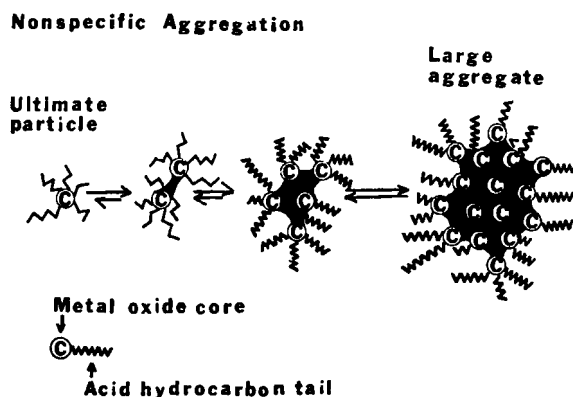**Metal oxide core**

Acid hydrocarbon tail

FIG. 4.

The size distribution of the core particles might be an important feature in their use as catalysts. Can a core particle's size be varied by changing the metal/acid ratio during preparation? The answer appears to be yes. In Table 2 one observes this trend. Other similar observa-

TABLE 2

Effect Of Metal/Acid Ratio On Particle Size

Sample	Metal Acid	Particle Dia., $\mathring{A}$	Molecular Weight	Solvent
Mn	6^A	35	6.3×10^4	Min. Sp.
(Mn_3O_4)	12^A	43	1.2×10^5	Min. Sp.
	18^A	48	1.5×10^5	Min. Sp.
Co	24^B	179	7.4×10^6	Min. Sp.
(CoO)	42^B	206	1.1×10^7	Min. Sp.

A $25\%C_3$, $25\%C_{10}$, $15\%C_{18}$, 10%Benzoic

B $30\%C_3$, 55%neoC_{10}, $15\%C_{18}$

Conclusion. PARTICLE SIZE INCREASES AS M/A INCREASES

tions have been made in other solvents. By raising the
metal/acid ratios, larger particles are made. Does the
distribution of carboxylic acids, employed in synthesis,
change the particle size when the metal/acid ratio is
constant? In Table 3 we see the answer is no. The ultimate
particle size is independent of the acid distribution.
However, the acid distribution employed drastically effects the
solution aggregation equilibria's dependence on solvent.

From these results a general picture emerges. During the
oxidation stage of synthesis (Figure 1), metal hydroxides condense
into metal oxide particles and water is removed. The particles grow
until all available water is lost (complete M-O-M bond formation)
and their surfaces are covered by carboxylate functions.

Use of "Soluble Metal Oxides" as Homogeneous Catalysts

Metal carboxylates, $(RCO_2^-)_yM^{+y}$, have long been used
as soluble combustion catalysts for fuels and as driers
in paints and varnishes. Since the surfaces of the sol-
uble Mooney metal oxides have metal carboxylate sites,
it was of interest to see if these oxide complexes could
function homogeneously like metal carboxylates. Indeed,

TABLE 3

Effect Of Acid Distribution On Particle Size at Constant
Metal/Acid Ratio (In Mineral Spirits)

Metal (Oxide)	Metal Acid	S	Diameter Å	Molec. Weight
Mn (Mn_3O_4)	18^A	52.4	48	1.51×10^5
	18^B	51.3	47	1.47×10^5
	18^C	49.5	47	1.40×10^5
	18^D	52.5	48	1.53×10^5

A $25\%C_3$
   $25\%C_8$
   $25\%C_{10}$
   $15\%C_{18}$

B $35\%C_3$
   $35\%C_8$
   $10\%C_{10}$
   $5\%Benzoic$
   acid

C $50\%C_4$
   $40\%C_8$
   $10\%C_{18}$

D $40\%C_4$
   $40\%C_8$
 $20\%C_{18}$

Conclusion   Size is independent of acid distribution at
              constant M/A if solvent is a good one.

these complexes were successfully used as combustion
catalysts for heavy fuel oils.[6] The complexes, unlike
metal oxide powders which have also been used as fuel oil
combustion catalysts, are readily dispersed into the oil.
Furthermore, they do not agglomerate as metal oxide powders
do. Thus, they do not plug up furnace spray nozzles. We
report, here, several other attempts to use these complexes
homogeneously.

Cyclohexane Oxidation

Cobalt and manganese carboxylates are used commerically
to catalyze the oxidation of cyclohexane with oxygen at
$115-160^0$.[7] The special soluble particulate catalysts of
Mn_3O_4 and CoO also catalyze this reaction. The rates of
this oxidation when catalyzed by a soluble CoO complex
($Co/acid = 24$, $86\overset{0}{A}$ diameter in isooctane) were compared to
that when the catalyst was cobalt naphthenate at 115^0 and
300psi ($1/9$, O_2/N_2). The rates were approximately equal.
Similar comparisons were made of the Mn_3O_4 complex (Mn/
acid $=18$, $48\overset{0}{A}$ diameter in mineral spirits) to manganese
naphthanate at 140^0 and 170psi. Again the rates were
approximately equal. The reactions were carried out in
autoclaves shaken with a wristaction shaker; thus mass
transport (gas/liquid) considerations might be limiting.

The major drawback in these oxidations was the lack
of chemical stability of the soluble oxide complexes. As
the yield of cyclohexanol and cyclohexanone increased, the
catalysts precipitated as a black powder. Possibly, some
of the cores' surface acid groups are esterified, thus pro-
moting aggregation and precipitation. Alternatively, the
keto and hydroxyl groups could compete with carboxylic acids
for surface sites on the core particles.
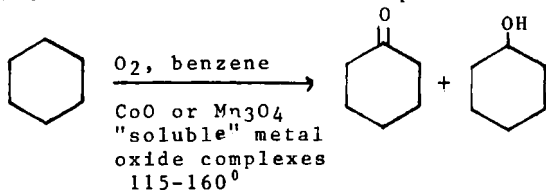
Oxidations of Toluene and p-Xylene

The oxidations of toluene to benzoic acid and p-xylene to p-toluic and terephthalic acids with O_2/N_2 mixtures were successfully catalyzed by the Mn_3O_4 and CoO soluble Mooney complexes at 160^0 and 120-200psi in benzene. Since surface sites must be involved in catalysis, it was not surprising that the core complexes were only about 1/10 as active per metal atom as the corresponding metal carboxylate salts. It would be interesting to see if the use of smaller CoO core particles would lead to an increase in rate.

$$\begin{array}{c} \\ \hline O_2/N_2 \\ \hline \text{CoO or } Mn_3O_4 \\ \text{complexes} \\ 160^0, \text{ 120-200psi} \end{array}$$
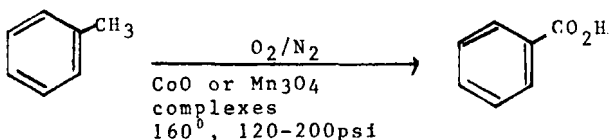
Hydroformylation.

The CoO complexes catalyzed 1-pentene hydroformylations. The soluble core complexes decomposed, in part. to $Co_2(CO)_8$ in these reactions. This was shown by demonstrating $Co_2(CO)_8$ and the CoO complex gave the same normal/branched aldehyde selectivities at a variety of temperatures. Thus cobalt carbonyl served as the true homogeneous catalyst in this case and one cannot view the soluble metal oxide as the catalyst.

$$\begin{array}{c} H_2/CO \\ \hline \\ 800-1300psi \\ 160^0 \\ \text{CoO complex} \end{array}$$

CHO + isomers
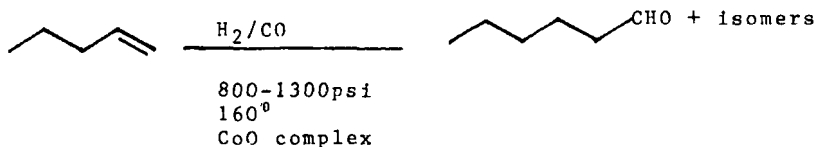
Polymerizations

Butadiene was selectively polymerized to 1,2-polybutadiene at temperatures from 20^0 to 70^0 using a catalyst system composed of an 80Å diameter CoO core complex, CS_2, and $AlEt_3$ (Al/Co:50). Benzene was used as the solvent and the resultant 1,2-polybutadiene had a high crystallinity and melting points ranged from 203-

213^0. The polymer was dissolved into hot o-dichloro-
benzene and precipateted into methanol. A strong IR
absorption at $660m^{-1}$ characterized the 1,2-mode of poly-
merization. No polymer was obtained in the absence of
CS_2. Typical reactions employed butadiene (5g), benzene
(30ml), cobalt complex (0.05mmol of Co), CS_2 (0.42mmol)
and $AlEt_3$ (2.5mmol). Under these conditions the polymer
yield was 40% at 20^0 after 24 hr. and 19% at 60^0 after
3.2 hr.

Apparently, Zeigler-Natta type catalyst sites are
formed on the surfaces of the soluble metal oxide com-
plexes. Similar catalyst systems prepared from homogeneous
cobalt octoacte were 10 to 20 times more active per cobalt
atom added. This is due to the fact that only metal atoms
at the surface of the particles are available as catalyst
sites whereas all the metal are available catalyst sites
with cobalt octoate.
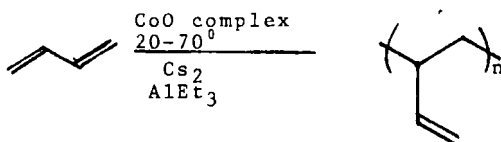
Hydrogenations

The soluble nickel oxide core particles (Ni/acid = 33,
diameter in mineral spirits = $122\overset{0}{A}$) were active catalysts
in the hydrogenation of olefins and polybutadiene if first
complexed with $AlEt_3$. Neither the NiO complex nor nickel
octoate was active without the presence of $AlEt_3$ unless
the reaction temperature exceeded 130^0. In example reactions
carried out at 100^0C and using $AlEt_3/Ni$ = 3.7, 1-pentene
was rapidly hydrogenated and isomerized in cyclohexane
using either the nickel oxide core particles or nickel
octoate. The activities were comparable. Table 4 sum-
marizes a few representative reactions.

Cis-polybutadiene was hydrogenated using catalyst systems
composed of the NiO particles reduced with $AlEt_3$ or nickel

TABLE 4

Hydrogenation of 1-Pentene Catalyzed by Soluble NiO-
Complexes Versus Nickel Octoate [a]

Catalyst	Temp ^0C	H_2 Pressure psig	Time hr.	n-Pentane %	2-Pentene %(cis/trans)
Nickel octoate[b]	100	450	3	0	0
NiO-particles[b]	98	450	16	0	0
NiO-particles[b]	160	475	110	100	
Nickel octoate	100	200	0.5	66	8/26
" "	"	"	12.0	100	0
NiO-particles	"	"	.33	52	6/21
" "	"	"	12	100	0
Nickel octoate	60	110	.25	24	57/17
NiO-particles	72	110	.25	51	40/9

[a] Reactions run in cyclohexane (15ml) using 1-pentene (2.0ml,
18.2 mmol), nickel species (0.98 mmol), and AlEt$_3$ (3.6mmol)
unless noted otherwise.
[b] No AlEt$_3$ added.

octoate/AlEt$_3$ (Al/Ni=3.5). Using 1.0mmol of Ni, the hydro-
genations were complete after 10hrs. at 120^0 and 110psi.
Nickel octoate/n-BuLi and nickel octoate/n-BuLi/phenol systems
were also active but n-BuLi or n-BuLi/phenol was unable to
activate the NiO core particles. Unlike cis-polybutadiene,
neither the NiO particle nor nickel octoate systems were able
to catalyze the hydrogenation of polyisoprene.
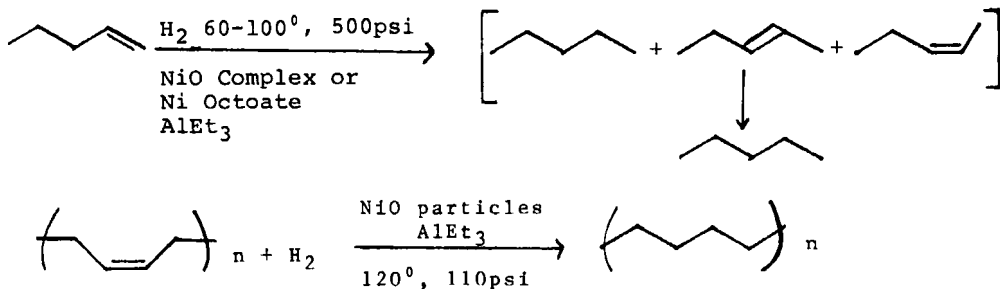
Preparation and Use of Supported Heterogeneous Catalysts from "Soluble" Metal Oxide Complexes

Supported metal oxide catalysts are usually prepared by impregnating support materials (Al_2O_3, SiO_2, Kieselguhr etc.) with aqueous solutions of metal salts followed by drying and oxidation (with O_2 at $400-800^0$) to the oxide. Reduction with hydrogen ($200-500^0$), or with metal hydrides, give the supported metals. We have shown that the soluble metal oxide particles can be used to prepare supported metal oxide or metal catalysts. The route is illustrated in Figure 5. One might be able to tailor the particle size of the supported metal oxide (or metal) by varying the size of the core complex employed or by using the aggregation equilibria (illustrated in Figure 4).

The metal oxide complexes were deposited on support surfaces from an organic solvent. After removal of the solvent, oxidation with O_2 at $400-700^0$ gave the supported metal oxide. Reduction with H_2, $NaBH_4$ or $AlEt_3$ gave the

USE OF "SOLUBLE METAL OXIDE CORES" TO PREPARE HETEREGENEOUS CATALYSTS

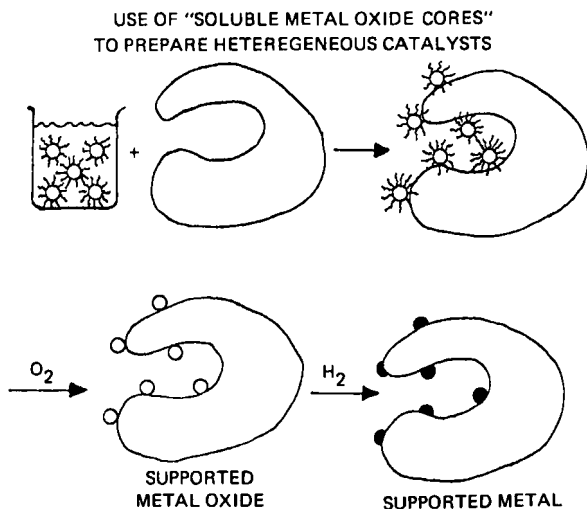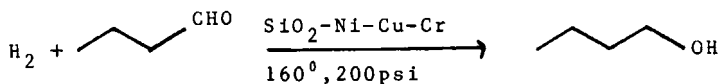SUPPORTED METAL OXIDE   SUPPORTED METAL

FIG. 5.

supported metal. Supported oxides (CoO, NiO, Fe_2O_3, and
$CoO-Fe_2O_3$) were prepared on alumina and kieselguhr. After
reduction with $AlEt_3$ all these systems were very active
hydrogenation catalysts for aromatic systems. These are
described in the next chapter in more detail.

Hydrogenation of Aldehydes to Alcohols

A reduced $SiO_2-Ni-Cu-Cr-$ catalyst was prepared and used
in the hydrogenation of aliphatic and aromatic aldehydes to
alcohols. These reactions were patterned after those des-
cribed in US Patent 3,803,055 which used a silica-supported
catalyst prepared by the classic salt impregnation tech-
niques. Silica (8-12mesh, $300m^2/g$, pore volume = 1cc/g)
was treated with aqueous NaOH to bring its pH to 8.2. After
washing and drying (120^0 in vacuo and 500^0, 4hrs., under
nitrogen flow), the silica was treated with pentane solutions
of both the soluble NiO (Ni/acid = 33, $122\overset{0}{A}$ diameter) and
CuO (Cu/acid = 19, $280\overset{0}{A}$ diameter in CCl_4) and chromium
octoate, followed by drying in vacumn. The resulting solid
was heated for 2 hrs. at 500^0 in oxygen to give a supported
metal oxide catalyst analyzing for 8%Cu, 2.7%Ni and 0.4%Cr.
The oxide catalyst was reduced by heating in a hydrogen
atmosphere at 200^0 (1hr.) and 300^0 (1.5hr.)

$$H_2 + \quad \diagup\!\diagdown\!\diagup^{CHO} \quad \xrightarrow[160^0,200psi]{SiO_2-Ni-Cu-Cr} \quad \diagup\!\diagdown\!\diagup\!\diagdown_{OH}$$

Butanal was readily hydrogenated to butanol at 160^0
and 200psi using this supported catalyst. The reaction
was completed in 20hrs. and the catalyst was recycled
several times without loss of activity. Under the same
conditions benzaldehyde was reduced to benzylalcohol at
about one half the rate of butanal. Cyclohexanecarboxa-
ldehyde, contaminated with 15% of cyclohexane carboxylic
acid, was reduced to cyclohexylcarbinol at a rate com-
parable to the benzaldehyde reductions.

Demethylation of 1-Methylnaphthalene

The alumina-supported Ni and NiO catalysts (des-
cribed in the experimental section) were prepared by
deposition of soluble NiO particles on Al_2O_3 followed
by oxidation (O_2, 400°) and reaction with $NaBH_4$. They
were active in the demethylation of 1-methylnaphthalene
at 320° and 1400psi. Not only did demethylation occur,
but hydrogenation of the naphthalene ring system occurred
in competition with demethylation. Product distributions
as a function of time showed that the hydrogenation was
independent of demethylation and that naphthalene produced
by demethylation was sequentially reduced to cis and trans
decalin. The Al_2O_3-Ni catalyst was substantially more
active than Al_2O_3-NiO.
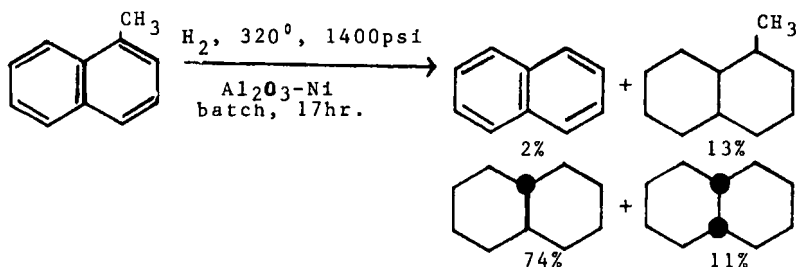
CONCLUSIONS

Metal oxide particles with surfaces containing bound
carboxylates have been prepared by reacting metal oxides
(or metals) with a deficiency of carboxylic acids. The
outer amorphous layer renders these metal oxides soluble
in hydrocarbon solvents. Aggregation equilibria were dis-
covered and aggregation is promoted by polar solvents.
These particles serve as catalysts in "homogeneous
reactions" where catalysis actually takes place at the
solution-particle interface. The unique feature here
is that a liquid-solid interface is the site of catalysis,

yet the solid is "solublized" in the liquid to give a
fluid-phase reaction which has many features of homogeneous
catalysis.   This represents a new type of interfacial
catalysis.

Several advantages may result from the application of this
concept. First, these particles will be compatible with the
use of hydrocarbon solvents.   In exothermic reactions, the sol-
vent may be used to carry heat away from the particles' surfaces
and "hot-spots" should not become a problem. Reactions that are
promoted by the solvent can now be carried out, if that solvent
is also matched with the particles' carboxylic acid distribution
to insure solubility. These particles will resist agglomeration,
precipitation, and the clogging of equipment which can occur if
suspended metal oxides were employed instead. By the use of cent-
rifugation gradient separations, in good solvents, narrow particle
size distributions can be isolated. These might be used to prepare
supported (heterogeneous) metal oxide catalysts with defined metal
oxide particle sizes.

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