

Olefin Dimerization over Cobalt-Oxide-on-Carbon Catalysts

I. Propylene Dimerization

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Cobalt-oxide-on-carbon catalysts were studied in the propylene dimerization reaction with the aim of obtaining a reasonable yield of *n*-hexenes. Through an investigation of catalyst preparation variables such as activation temperature, metal oxide level, and modifier treatments, a catalyst of greatly increased activity was obtained. These variables exerted a profound effect on product distribution as well as on catalyst activity, and with the preferred catalyst system, a product containing 52% *n*-hexenes was obtained. Optimum conditions for the dimerization reaction were determined in both batch and continuous systems. In the latter, the optimum catalyst composition was capable of producing 100 gal of dimer product per pound of catalyst before regeneration. A mechanism for the dimerization reaction which draws upon recent advances in homogeneous catalysis is proposed.

In 1932 Schuster (1) reported that a cobalt-oxide-on-carbon catalyst was able to dimerize ethylene to mixed *n*-butenes. Following this initial report, several laboratories were active in the study of this catalyst (2, 3, 4). These studies involved primarily ethylene dimerization, although propylene dimerization, ethylene-propylene codimerization (2a,d,e) and ethylene-butadiene codimerization (4) were also reported. In the reported cases of propylene dimerization the conversion was low and the rate of reaction reduced to 0.14 to 0.025 of that of ethylene dimerization.

It was decided to investigate the dimerization of propylene over cobalt-oxide-on-carbon catalyst with special attention being given to specific product characterization and the effect of variables in catalyst preparation and in reaction conditions on the course of the reaction.

EXPERIMENTAL

Pittsburgh Coke and Chemical Co. BPL grade low-ash carbon was used throughout. Cobalt nitrate hexahydrate was Matheson, Coleman, and Bell reagent grade. General

Electric Co. Lamp Grade nitrogen was used throughout. Sinclair Petrochemical polymerization grade (99 + %) propylene was used. Individual hexene and isohexene isomers used were Phillips Petroleum Co. Research grade. Vapor-phase chromatograms were run on an F and M Model 300 instrument using helium carrier gas and a 10-ft 20% dimethylsulfolane-on-Chromasorb column to separate the *n*- and *iso*-hexenes. For complete isomer distribution analyses a Barber-Colman Model 10 instrument with ionization detector, argon carrier gas, and a 450-ft dimethylsulfolane-coated capillary column was used. The cobalt-on-carbon oxidation state analyses were performed using a method developed by Dr. D. E. Willis of the Central Research Analytical Group. Ash, nitrogen, and total cobalt content were determined by standard methods.

Preparation and Activation of Ammoniated 13% Cobalt-Oxide-on-Carbon Catalyst

To 330 g of activated carbon (12 × 30 mesh) was added 300 ml of concentrated ammonium hydroxide. All the liquid was

absorbed. This treated carbon was then dried by heating on a hot plate for 2 hr at 130°C. Only slight ammonia odor was noted on the catalyst after this time. A solution of 200 g of cobalt nitrate hexahydrate in 250 ml of demineralized water was added to the carbon. Almost all the solution was absorbed. The impregnated carbon was heated with occasional stirring on a hot plate at 100–110°C until it appeared dry (about 3 hr). This precatalyst [wt 590 g] was placed in a vacuum oven at 120°C and 100 mm vacuum for 18 hr. The resulting dried precatalyst (395 g) was impregnated with 500 ml of concentrated ammonium hydroxide. After preliminary drying on a hot plate at 105–110°C for 4 hr, the material was dried in a vacuum oven at 120°C and 100 mm vacuum for 25 hr, yield 391 g of finished precatalyst.

A 90-g portion of this precatalyst was placed in a Pyrex activation tube in a furnace. The pressure was reduced to 35 mm and a nitrogen flow of about 90 cc/min over the catalyst was begun. The temperature was raised to 264°C over ¾ hr and kept at 265–275°C for 2 hr. While maintaining a nitrogen atmosphere, the tube was brought to atmospheric pressure, the catalyst transferred hot to small bottles (2–3 g portions) and stored under nitrogen.

The above-described procedure was modified during the studies described in this paper. Carbons other than "BPL" were employed, either or both of the ammonium hydroxide treatments were omitted or replaced by other materials, and the level of cobalt changed by varying the amount of cobalt nitrate used. Other cobalt salts were used in place of the cobalt nitrate and other metal salts were impregnated onto the carbon before, after, with, or instead of the cobalt nitrate. Changes in drying times and temperatures, activation time and temperature, and activation atmosphere were also investigated.

Preparation of Low-Ash Carbon

To 200 g of "BPL" carbon was added 450 g of 48% aqueous hydrofluoric acid. The mixture was let stand at 25°C with occasional stirring for 2 hr. The excess liquid

was decanted and the procedure repeated three more times. The carbon was then washed with water until the water after washing had a pH of 4. The carbon was dried in a vacuum oven (100 mm) at 130°C for 48 hr yielding 177 g of low-ash carbon. Analysis: Ash before leaching, 5.57%; ash after leaching, 0.38%. Additional hydrofluoric acid treatments would afford carbon of even lower ash content. The resulting carbons were used in the procedure above for preparation of catalysts.

Propylene Dimerization over Ammoniated Cobalt Oxide on Carbon

I. At 85°C. A mixture consisting of 2.4 g of doubly ammoniated cobalt-oxide-on-carbon catalyst and 10 ml of heptane was placed in a 300-ml autoclave in a nitrogen atmosphere. The autoclave was sealed, cooled to about -70°C, and charged with 110 g of propylene. The autoclave was placed in a rocker and heated at 85°C for 5 hr. After cooling to 25°C, the unreacted propylene was vented (30.0 g, 27.3%) and the catalyst and liquid product recovered, yielding 76.3 g, (69.4%, 31.8 g product/g catalyst) of dimer product.

II. At 25°C. The above procedure was repeated using a charge of 115 g of propylene, 2.8 g of catalyst, and 10 ml of heptane and was run at 25°C for 5 hr. All the propylene was consumed (none vented) and 114.8 g of dimer product (99.8%, 41.0 g product/g catalyst) was obtained.

III. Process modification. The procedures described above were modified during the studies described in this paper. The above optimum procedures were those used for evaluation of catalyst modifications, but changes in reaction time, temperature, solvent, and effect of additives on the reaction were also evaluated. The process was also used in 3-liter reactors by scaling up all quantities by a factor of 10 and eliminating the heptane solvent.

IV. In tubular fixed-bed reactor. The ammoniated cobalt-oxide-on-carbon catalyst (9 g) is placed in a tubular reactor in a nitrogen atmosphere and pressured with nitrogen to 450 psig. Liquid propylene at 450-psig pressure which has been passed

through a molecular sieve drying system is admitted. The temperature of the reactor is controlled by a thermostated water jacket. After passing through a filter, the propylene-propylene dimer stream is returned to atmospheric pressure and the dimer product separated from propylene in a 25°C trap fitted with a Raschig ring-filled condenser held at -30°C. Vented propylene is measured in a gas meter. Some results with this reactor are presented in Table 4.

Olefin Isomerization Studies

I. Sealed systems. Cobalt-oxide-on-carbon catalyst activated at high temperatures (450-550°C) and specific olefin isomers (*cis*- and *trans*-4-methylpentene-2 or *cis*- and *trans*-hexene-2) are sealed in a rocking autoclave under nitrogen (olefin:catalyst ratios vary from 7:1 to 12:1) and heated at the specified temperatures for 5 hr. After cooling to 25°C the autoclave is opened and the isomer mixture analyzed by gas chromatography. Results are listed in Tables 5 and 6.

of charge) was recovered in a Dry Ice-acetone-cooled trap. Results of gas chromatographic analyses of the isomer mixtures are given in Tables 5 and 6.

Determination of Cobalt Oxidation States in Cobalt-Oxide-on-Carbon Catalysts

In a procedure developed by Dr. D. E. Willis of the Central Research Department Analytical Section, cobalt metal on the catalyst is extracted by gaseous chlorine in anhydrous methyl alcohol and cobalt(II) oxide by acetic acid. The residual cobalt is reported as cobalt(III) oxide. The cobalt extracted by the various procedures is titrated in warm acetate buffer solution with EDTA using Xylenol Orange indicator.

RESULTS AND DISCUSSION

It was found that propylene could be dimerized with 95% selectivity to a mixture of 50-55% *n*-hexenes and 45-50% branched-chain hexenes with a cobalt-oxide-on-carbon catalyst. These results were

TABLE I
DISTRIBUTION OF HEXENE PRODUCTS FROM PROPYLENE DIMERIZATION OVER COBALT OXIDE ON CARBON

<i>n</i> -Hexenes		Methylpentenes		Dimethylbutenes	
Hexene-1	1.5%	4-Methylpentene-1	4.5%	2,3-dimethylbutene-1	0.5%
<i>trans</i> -Hexene-2	29.5%	<i>trans</i> -4-Methylpentene-2	21.9%	2,3-dimethylbutene-2	0%
<i>cis</i> -Hexene-2	17.5%	<i>cis</i> -4-Methylpentene-2	17.3%		
<i>trans</i> -Hexene-3	2.7%	2-Methylpentene-1	3.8%		
<i>cis</i> -Hexene-3	0.6%	2-Methylpentene-2	0.3%		
Total <i>n</i> -hexenes	51.7%	Total methylpentenes	47.8%	Total dimethylbutenes	0.5%

II. Tubular flow system. A 10-g portion of ammoniated cobalt oxide on carbon was activated at 500°C for 4 hr as described above. The furnace temperature was then lowered to 300°C and the pressure raised to atmospheric, maintaining nitrogen flow at 90 cc/min. A 10-ml (6.8 g) portion of olefin was added dropwise over 30 min to the nitrogen stream passing over the catalyst. Nitrogen flow was maintained for 10 min after the olefin addition was complete. Liquid product amounting to 5.4 g (80.6%

independent of conditions of reaction and catalyst preparation. However, the product distribution within the *n*-hexene and isohexene products and the amount of conversion of propylene to dimer were greatly dependent upon the mode of catalyst preparation and the reaction conditions. A typical product distribution for the cobalt-oxide-on-carbon catalyst of greatest activity is given in Table I. Within this dimer product, deviation from olefin isomer equilibrium values is the rule rather than the exception.

Catalyst Preparation

Cobalt oxide on carbon appears to be unique in its ability to dimerize propylene to high levels of *n*-hexenes. While cobalt oxide on many other supports (silica-alumina, silica-magnesia, alumina, etc.) was active for propylene polymerization, the dimer product obtained was one typical of an acid-catalyzed process (<10% *n*-hexenes). All types of activated carbons tried (bone, wood, coconut, pecan shell, and coke charcoal) gave the same product distribution but in greatly varying conversion. In general, coke charcoal seemed to be the most highly active support for the cobalt oxide and was used in all further studies.

Previously, it had been reported (3d) that increased catalyst activity was obtained when the carbon was leached with nitric acid prior to impregnation with the cobalt salt. In the present work, it has been found that an equivalent increase in activity is obtained by impregnation of the carbon support with concentrated ammonium hydroxide. When a catalyst is treated with ammonium hydroxide both before and after cobalt impregnation, a fourfold increase in activity (expressed as g of product per g catalyst) in batch dimerization is noted. An even greater increase in activity is found when this catalyst is used in a continuous reactor system. Other impregnation systems (amines, ammonium salts, bases, sulfides, etc.) either poisoned the catalyst or afforded no improvement over untreated cobalt oxide on carbon. Several of these treatments did change the product *n*-hexene:isohexene ratio, however. These effects will be the subject of a subsequent paper.

It was found that the ash content (Al_2O_3 , SiO_2 , etc.) of the carbon was important in determining the level of cobalt oxide necessary for maximum activity. When a very low ash carbon (0.1% ash) was employed, 15% cobalt oxide was needed for maximum activity, but when a carbon containing 6-7% ash was used, only 7% to 8% cobalt oxide was needed for maximum activity. In both cases the product

mixture of hexenes was identical, thereby indicating that the reaction is due to cobalt and is not promoted by some trace element present in the carbon. In addition, part of the requirement for cobalt oxide could be replaced by another metal oxide (for example, nickel, chromium, or iron oxides) provided that the other metal oxide was impregnated on the carbon prior to the cobalt oxide. Two conclusions are possible from this information. Either part of the cobalt is disposed on dimerization-inactive sites and only after these sites are filled does a significant amount of cobalt go to dimerization-active sites, or ensembles of cobalt atoms are necessary for the active site and are not present until 13% total oxide (cobalt plus ash) content is reached.

A variety of cobalt salts were evaluated as impregnants. None approached the nitrate in effectiveness and only those which could decompose to cobalt oxide were active. None of the metal oxides which were evaluated as promoters for the reaction were effective and, in fact, many caused a lowering of dimerization activity when they were co-impregnated with the cobalt salt onto carbon. No other metals supported on carbon were found which were active for propylene dimerization.

Catalyst Activation

It was found that the process of catalyst activation was critical in the determination of the type of catalytic activity and of the product distribution. In previous studies (1-4), the cobalt-oxide-on-carbon catalyst activation had been effected by reduction in hydrogen at 300-450°C or by heating in nitrogen at 400-500°C. In our studies it was found that dimerization activity could be imparted to the catalyst by activation in nitrogen at temperatures as low as 200°C and that the highest dimerization activity was reached with activation temperatures of about 275°C. When activation temperatures were raised above 325°C, the product distribution began to change as a second catalytic function, isomerization, was imparted to the catalyst. This isomerization activity reached a maximum with a catalyst activation temperature of 450°C. This

TABLE 2
ISOMERIZATION ACTIVITY OF CoO/C AS A FUNCTION OF ACTIVATION TEMPERATURE

Activation temperature (°C)	200	240	275	300	365	400	450	500	550	600	650	700 ^a
% 2MP2 in product	0	0	0	2	10.7	15.0	26.5	21.2	18.1	11.3	13.2	0
2MP2 as % of total isohexenes	0	0	0	4.2	22.2	31.3	55.2	44.2	37.7	24.6	27.5	0

^a No dimerization was observed at this temperature.

isomerization activity is noted by the appearance of 2-methylpentene-2 (2MP2) in the propylene dimer product along with increased amounts of hexene-3 (see Tables 2 and 3). The introduction of isomerization activity does not, however, change the ratio of *n*-hexene to methylpentene.

reaction and not due solely to an isomerization reaction.

It was found that catalyst activity was also a function of activation time. In Figs. 1 and 2, the interdependence of activation time and temperature are shown. The results can be explained by assuming the

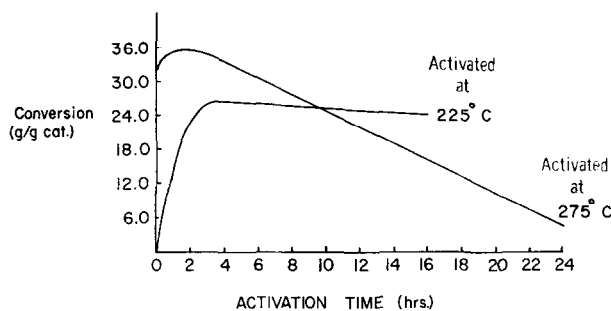


FIG. 1. Effect of activation time and temperature on propylene dimerization.

The 2-methylpentene-2 is formed at the expense of the other methylpentenes and the hexene-3 at the expense of hexene-2 (see Table 3). The 2-methylpentene-1 is found in constant amounts with all cobalt-oxide-on-carbon catalysts used, even when no 2-methylpentene-2 is present. This must therefore, be a primary product of the

mobile formation and decomposition of the active site. That is, activation for short times at lower (<250°C) temperatures is insufficient for total active site formation. Once this active site is formed, it is thermally sensitive and is destroyed by heating at moderate temperatures (275–350°C) for long periods of time or at higher temperatures for increasingly shorter times. In these studies, it is possible to determine the optimum activation time and temperature necessary to obtain catalysts of highest activity.

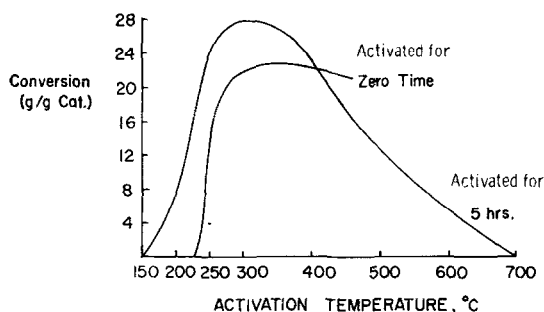


FIG. 2. Effect of activation time and temperature on propylene dimerization.

Nitrogen was the preferred atmosphere in which to conduct the catalyst activation, although several others (helium, propane, carbon dioxide) were nearly as effective. Use of carbon monoxide or hydrogen atmospheres in the catalyst activation gave a catalyst of reduced activity, and, in the case of hydrogen, one of increased isomer-

TABLE 3
EFFECT OF CATALYST ACTIVATION TEMPERATURE ON PROPYLENE DIMER PRODUCT DISTRIBUTION

Component (%)	4MP-1	c-4MP-2	t-4MP-2	2MP-1	2MP-2	2,3-DMB-1	Total
CoO/C							
Activated at 275°C	4.5	17.3	21.9	3.8	0.3	0.5	48.3
at 375°C	2.3	6.7	29.6	3.4	6.0	0.7	48.7
Component	H-1	c-H-2	t-H-2	c-H-3	t-H-3	Total	
CoO/C							
Activated at 275°C	1.5	17.4	29.5	0.6	2.7	51.7	
at 375°C	1.3	10.3	27.4	2.0	10.3	51.3	

ization activity. All catalysts were oxygen-sensitive and, to prevent loss of activity had to be protected from air at all times after activation.

Dimerization Reaction

The striking effect of the double ammoniation of cobalt-oxide-on-carbon catalyst on dimerization activity may be seen in Fig. 3. A batch autoclave propylene

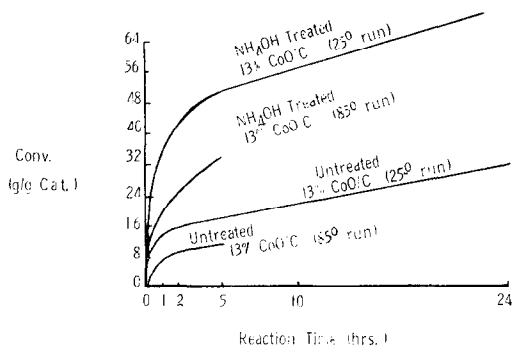


Fig. 3. Co/C catalyst activity for propylene dimerization; effect of NH_4OH treatment.

dimerization using doubly ammoniated cobalt oxide on carbon reaches levels of conversion in 1 to 2 hr that are not attained in 24 hr using an untreated catalyst. A significant increase in productivity is also noted when the reaction temperature is lowered from 85° to 25°C . Studies in which reaction temperatures as high as 200°C were used showed no change in activity from the 85°C reaction. One is led to postulate a thermal degradation of the catalyst-active site from both this data and the observation above that increasing activation time causes decreased catalyst activity.

In the standard batch autoclave studies, heptane was added as a solvent and diluent

to ease handling problems, especially when low conversions to products were obtained. The effect of specific product isomers and of other solvents on the catalyst was determined by replacing the heptane with the compound under study. Relative conversions (heptane = 1.00) were 4-methylpentene-1, 1.18; *cis*-4-methylpentene-2, 0.53; *trans*-4-methylpentene-2, 0.52; hexene-1, 1.08; hexene-2, 0.98; 3-methylbutene-1, 0.02; toluene, 0.98. It may be seen that only those compounds possessing the easily removable tertiary allylic hydrogen were inhibitory in the dimerization reaction. In the present system, 39% of the dimer product is inhibitory towards the catalyst. The fact that, when 4-methylpentene-1 is used as a solvent, no inhibition is noted is an excellent argument for the lack of isomerization activity of the catalyst. This further substantiates the assumption that the observed products are the primary products of the reaction.

A number of compounds were evaluated as additives in the propylene feed. Several sulfur compounds at low levels (<30 ppm) appeared to promote the reaction slightly, but when used at higher levels were inhibitory. Chloroform, water, and furfural were slightly inhibitory at low levels (20–30 ppm) while piperylene was extremely inhibitory even at 15 ppm. Only helium and nitrogen atmospheres in the batch autoclave allowed good conversion. Hydrogen, carbon monoxide, carbon dioxide, and air all reduced dimerization activity.

Studies were also made with a tubular fixed-bed reactor. In these continuous flow studies the effect of the ammonium hydroxide treatment upon the catalyst was even more striking than in the case of the

TABLE 4
CONTINUOUS REACTOR DIMERIZATION OF PROPYLENE OVER CoO/C

Catalyst type	Av. space vel. ^a (gC ₃ /hr)	Total C ₃ fed ^a (kg)	Total dimer (kg)	Overall conversion (%)	Average productivity (g/g cat/hr)	Total production (g/g cat)	Reaction	
							Time (hr)	Temp. range (°C)
Untreated	23.2	1.21	0.038	3.1	0.72	4.3	6	30–70
NH_4OH treated	17.6	35.18	5.46	15.5	2.73	606.5	222	36–62

^a C₃ indicates propylene.

batch reactor studies (Table 4). In this long, flow-type dimerization reaction an appreciable weight increase in the catalyst due to polymer formation is noted. Extraction of the spent catalyst with suitable solvents afforded some of this polymer for characterization. The molecular weight was found to be 2000–3000 and the melting point 148°C. Further studies on this polymer and other factors affecting catalyst deactivation will be reported in a subsequent paper.

Catalyst Isomerization Activity

A further investigation of the isomerizing power of high-temperature-activated ammonium-hydroxide-treated cobalt-oxide-on-carbon catalysts was made. Using pure *cis*- and *trans*-4-methylpentene-2 and a catalyst

as isomerization activity was present. No diolefin product was found in the product, but it would be expected that the diolefin would be absorbed by the catalyst since other diolefins are poisons for cobalt oxide on carbon and since the catalyst recovered from the 300°C isomerization run was completely inactive for propylene dimerization. Very similar results were obtained using mixed *n*-hexenes both in sealed systems at 150°C and in the tubular flow system at 300°C (Table 6). Verification of the hydrogen transfer activity of this catalyst was obtained by using cyclohexene as the olefin feed at 300°C in the tubular flow system. In this case benzene (61.1%) and cyclohexane (38.9%) were the only liquid products found.

TABLE 5
ISOMERIZATION OF 4-METHYLPENTENE-2 OVER CoO/C ACTIVATED AT 500°C

Component: Conditions	4-Methyl- 1-pentene	<i>cis</i> -4-Methyl- 2-pentene	<i>trans</i> -4-Methyl- 2-pentene	2-Methyl- 1-pentene	2-Methyl- 2-pentene	2-Methyl- pentane
Starting material	—	43.4	56.6	—	—	—
5 hr 25°C	3.4	32.6	58.7	0.2	5.1	—
5 hr 85°C	7.0	30.6	57.1	0.8	4.5	—
5 hr 200°C	7.1	8.8	40.9	10.7	32.5	—
300°C at 760 mm	5.0	4.7	19.7	20.3	35.9	14.4

activated at 500°C, the isomerization was studied in sealed systems at 25°, 85°, and 200°C and in a fixed bed tubular flow system at 300°C and 1 atm pressure with nitrogen diluent. In this last case contact time was estimated to be less than 30 sec.

Catalyst Analysis

In an attempt to learn more about the cobalt-oxide-on-carbon catalyst and its active dimerization sites, nitrogen and cobalt analyses were obtained. Impregnation of the untreated carbon with cobalt nitrate fol-

TABLE 6
ISOMERIZATION OF *n*-HEXENES OVER CoO/C ACTIVATED AT 500°C

Components: Conditions	Hexene-1	Hexene-2		Hexene-3		<i>n</i> -Hexane
		<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	
Starting material—A	4.7	36.6	←—41.2—→		17.5	—
300° at 760 mm	8.8	20.4	←—31.7—→		22.5	16.7
Starting material—B	1.1	72.0	21.4	0.4	5.1	—
12 hr, 150°C	6.3	24.2	46.2	5.9	17.4	—

The results are given in Table 5. Even at 25°C a significant amount of isomerization was found. In the 300°C vapor-phase run, a large amount of 2-methylpentane was found, indicating that at these temperatures, hydrogen transfer activity as well

lowed by a normal (275°C) activation caused no increase in nitrogen level over that of the activated support alone (0.55%). However, impregnation of the carbon with ammonium hydroxide followed by activation caused an increase in nitrogen

TABLE 7
 COBALT ANALYSES ON CoO/C CATALYSTS

Catalyst type	Activation	Cobalt (as Co ^o in %)			
		Co ^o	Co(II)	Co(III)	
CoO/Untreated carbon	2 hr at 275°C	6.32	3.80	0.08	
CoO/Double NH ₄ OH-treated carbon	2 hr at 275°C	2.37	7.98	0.19	
CoO/Double NH ₄ OH-treated carbon Spent catalyst from fixed bed reactor; corrected for polymer present	2 hr at 275°C	1.58	7.70	1.27	
CoO/Double NH ₄ OH-treated carbon Activated in 1:1 N ₂ :H ₂	2 hr at 275°C	3.98	5.80	0.01	
CoO/Acid-leached, NH ₄ OH-treated carbon	A:	2 hr at 230°C	3.84	6.57	0.38
	B:	2 hr at 550°C	5.40	5.54	0.26

content to 0.72%. The final, activated, double ammonium-hydroxide-treated cobalt-oxide-on-carbon catalyst had a nitrogen content of 1.12% when fresh. After the completion of a fixed bed tubular reactor run, the nitrogen level of the spent cobalt-oxide-on-carbon catalyst had dropped to 0.80% (0.63% before correction for polymer present). A method was developed for the determination of cobalt metal, cobaltous oxide, and cobaltic oxide on the carbon support. Some results of this method are listed in Table 7.

From the above tabulated data, the following points can be made:

1. The untreated cobalt-oxide-on-carbon catalysts have completely different balances of oxidation state than do the ammonium-hydroxide-treated ones. It appears that the NH₄OH treatment stabilizes the cobalt(II) valence state in the presence of the essentially reductive environment of carbon.

2. Increasing activation temperature causes increasing amounts of cobalt metal to be formed. This finding confirms the observation of increasing amounts of catalyst ferromagnetism with increasing activation temperature.

3. Activation in a reducing atmosphere causes formation of increasing amounts of cobalt metal relative to cobalt oxide but much of the cobalt present is still in the divalent state.

4. There is a significant change in ratio of oxidation states from fresh to spent

catalyst. The amount of cobalt(II) changes but little, but there is a considerable decrease in cobalt metal and increase in cobalt(III) content.

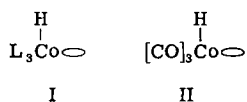
Mechanism of the Reaction

Any reasonable mechanism proposed for the propylene dimerization reaction over cobalt oxide on carbon must account for and explain the following:

1. The source and configuration of the active sites.
2. The primary product distribution; including the presence of 2-methylpentene-1 and absence of 2-methylpentene-2; the presence of 2,3-dimethylbutene-1 and absence of 2,3-dimethylbutene-2; and the relatively low amounts of hexene-1 and 4-methylpentene-1 in the primary reaction product.
3. The poisoning effect of dienes.
4. The inhibition of the reaction by 4-methylpentene-2.
5. The reversible inhibition of the reaction by carbon monoxide.
6. The temperature effects encountered; increasing rate of reaction with decreasing temperature.
7. The route to the high polymer.

The mechanism proposed below accounts for all the observations made on the system thus far and is related in a number of ways to well-known reactions in homogeneous catalysis and metal complex chemistry. The

active site is designated as a cobalt hydride which has at least one free coordination site available for π -olefin complexing (I). The other ligand positions, which are at least in part associated with the support surface, are simply indicated by "L" and are not described further at this time. This designation is very similar to that of the active catalyst (II) proposed for the homogeneous hydroformylation of olefins by cobalt hydrocarbyl (5).

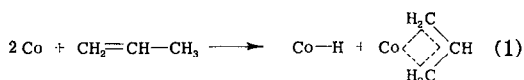


This cobalt hydride bond could be formed in several ways:

1. By reaction of the cobalt with residual hydrogen or hydrogen sources on the carbon surface.

2. By reaction with ammonia on the surface or in complexes after the ammonium hydroxide treatments.

3. By hydrogen abstraction from propylene to form the cobalt hydride and a cobalt π -allylic complex [Eq. (1)].



At this time the second route to the hydride site seems to be the most likely. If residual hydrogen or hydrogen sources (other than ammonia) were the cause of activity, then ammonia treatment would not be expected to exhibit so drastic an effect on productivity. If propylene were the source of hydrogen for the cobalt hydride, catalyst activation time should not exert an effect on catalyst activity. However, it has been shown that increasing activation time (at 275°C) does cause a decrease in catalyst activity (Fig. 1). The ammonium hydroxide treatments may also cause the formation of cobalt-ammonia complexes which on activation could lose ammonia to afford the free orbital for olefin complexing.

In order to emphasize the analogous

nature of the propylene dimerization reaction and the olefin hydroformylation reaction the two mechanisms are presented in parallel below:

In the case of the propylene dimerization reaction the two insertion steps can lead to mixtures of products [Eqs. (3a) and (5a)]. In the first insertion, that of propylene across the cobalt hydride, there is apparently only a very small preference for the *n*-propylcobalt product (III) over the isopropylcobalt (IV). On the other hand, in the second insertion, that of propylene into the propylcobalt, the apparent preference for formation of a secondary cobalt alkyl over a primary cobalt alkyl is about 13:1 for insertion into the *n*-propyl cobalt and about 87:1 for insertion into the isopropylcobalt. The routes to the other dimer isomers are summarized in Eqs. (8) and (9).

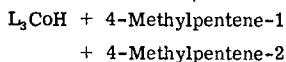
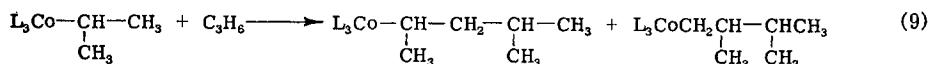
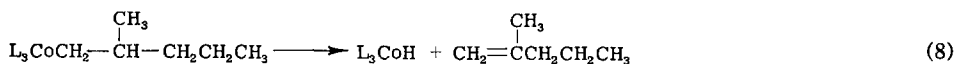
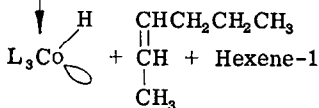
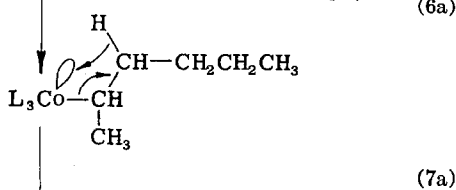
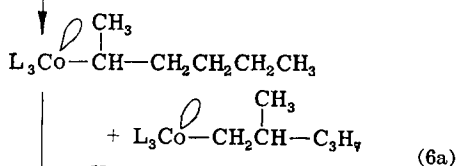
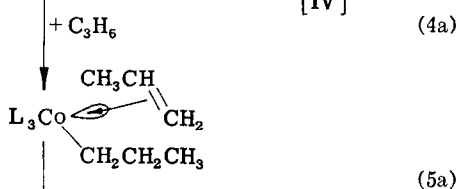
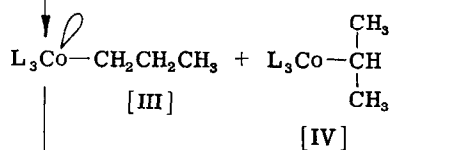
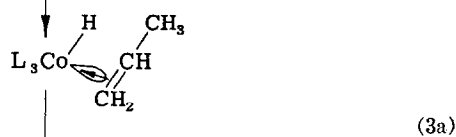
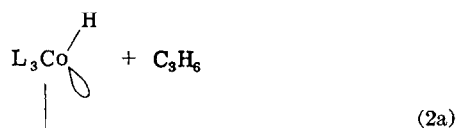
The preference for internal rather than terminal olefins (i.e., hexene-2 over hexene-1 and 4-methylpentene-2 over 4-methylpentene-1) can be explained if one assumes that in the hydrogen transfer reaction [Eq. (7a) above] the carbon from which the hydrogen is being transferred assumes a partially positive character.

Therefore, that system which would give a secondary carbonium ion would be favored. In addition, this *cis* type of elimination would explain the predominance of *trans* olefin isomers found [Eq. (10) and (11)] since the configuration leading to *trans* olefins would have considerably less steric strain.

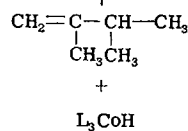
High-polymer formation could occur by propylene polymerization in a radical manner due to traces of oxygen in the system which could react with the cobalt hydride active site to form a cobalt hydroperoxide. This could then cleave heterolytically to form a cobalt oxide and hydroxyl radical which could initiate propylene polymerization [Eq. (12)].

Poisoning by dienes could occur by either (or both) of two ways. The diene might form a diolefin π complex with two ligand sites or, more likely, one of the olefin groups would undergo the insertion reaction to form a cobalt alkenyl which could then

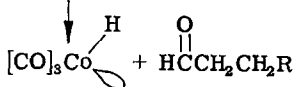
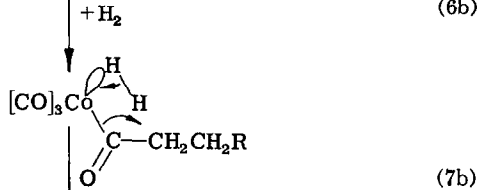
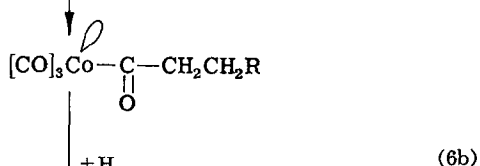
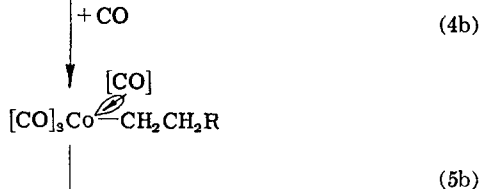
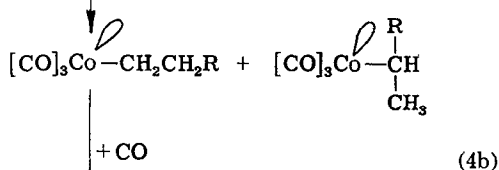
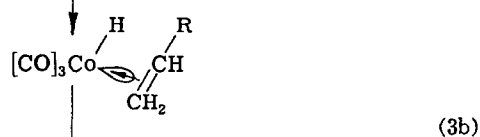
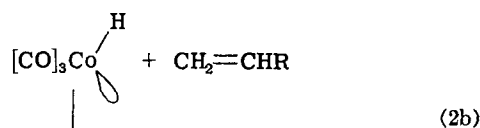
A: PROPYLENE DIMERIZATION

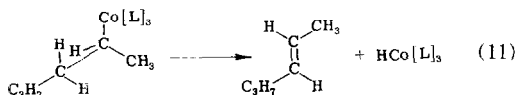
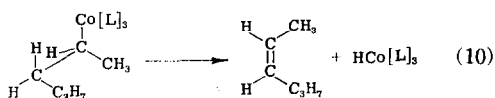


[87:1]



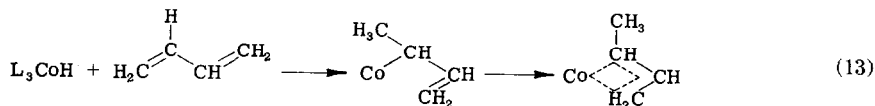
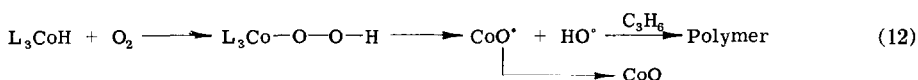
B: OLEFIN HYDROFORMYLATION



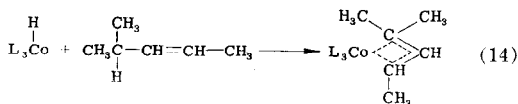


rearrange to form a cobalt π -allyl complex [Eq. (13)] (6).

Inhibition of the catalyst by 4-methylpentene-2 could occur by hydrogen abstrac-



tion of the tertiary allylic hydrogen (the most labile hydrogen in any of the isomers) and subsequent π -allyl complex formation [Eq. (14)]. In both this case and that of diene poisoning, it should be noted that the formation of the π -allylic complex ties up two coordination sites on the cobalt, thereby effectively removing its catalytic potential.



It has been found that adsorption of carbon monoxide inhibits the dimerization reaction but that reactivation of the poisoned catalyst affords complete recovery of activity (in contrast to diene poisoning). Here, carbon monoxide probably complexes reversibly with the open coordination site on the catalyst and can be removed by thermal regeneration. (It is well known that cobalt carbonyls decompose with loss of carbon monoxide on heating.)

The unexpected finding that apparent catalyst activity is higher at lower reaction

temperatures can be accounted for by assuming that the initial π -olefin complex is less stable at the higher temperature and also that the rates of the competing side reactions (catalyst poisoning) increase more rapidly when temperature is raised than does the dimerization reaction itself.

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