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(12) Patent:

(54) CATALYSTS FOR ELEVATED PRESSURE-MODERATE TEMPERATURE REACTIONS OF CARBON MONOXIDE

(54) CATALYSEURS POUR REACTIONS A HAUTE PRESSION ET TEMPERATURE MOYENNE D'OXYDE DE CARBONE

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This invention relates to novel cobalt catalysts for effecting the reaction of unsturated compounds with carbon monoxide at elevated pressure and moderate temperatures. The novel catalysts of this invention are particularly useful in the reaction of olefinic compounds with carbon monoxide and hydrogen to produce carbonylic compounds.

Supported cobalt catalysts wherein cobalt is supported on surface-active materials, such as Filter Cel and kieselguhr; have heretofore been employed in the reaction of unsaturated compounds with carbon monoxide at elevated pressure and moderate temperatures. The conversion of olefins, carbon monoxide and hydrogen to carbonylic compounds, a conversion which henceforth will be called the carbonylation reaction, has ordinarily been effected with a Fischer-Tropsch cobalt catalyst comprising 32 per cent cobalt, 64 per cent Filter Cel, 3 per cent magnesia and 1 per cent thoria, hereafter a supported catalyst of this composition will be designated a standard cobalt catalyst. Since supported catalysts were the most active cobalt catalysts for the hydrogenation of carbon monoxide and hydrogen to form synthetic fuel, supported cobalt catalysts such as the standard cobalt catalyst heretofore have been used almost exclusively for the carbonylation reaction. The use of supported cobalt catalysts in the carbonylation reaction was accompanied by a serious drawback, namely, the rapid decline in activity shown by such catalysts. As a consequence of the short catalyst life of supported cobalt catalysts, frequent regenerations were required. This invention discloses novel unsupported promoted cobalt

catalysts which not only are substantially more active initially in the carbonylation reaction than supported cobalt catalysts but also possess a longer catalyst life. This invention represents a significant advance in elevated  
5 pressure - moderate temperature reaction of unsaturated compounds with carbon monoxide; better yields and fewer regenerations are both substantial factors in establishing the commercial feasibility of this process.

In accordance with this invention, the reaction  
10 of carbon monoxide with unsaturated compounds at high pressures and moderate temperatures is effected in the presence of an unsupported cobalt catalyst promoted with one or more of the following metal oxides, namely, alumina, magnesia, chromia, beryllia, titania and calcium oxide.

15 The novel carbonylation catalysts of this invention comprise 50 to 95 per cent cobalt and 5 to 50 per cent of one of the aforementioned metal oxide promoters. The promoted cobalt catalyst of this invention may contain in addition 1 to 15 per cent activators, such as ferric oxide, nickel oxide,  
20 thoria or boria. A further requirement of the unsupported promoted cobalt catalysts of this invention is that they contain a low alkali content; the alkali content should be less than 0.4 per cent alkali metal oxide.

The novel catalysts of this invention preserve  
25 an effective mol ratio of cobalt metal to cobalt oxide in the catalyst during the elevated pressure - moderate temperature reaction of unsaturated compounds with carbon monoxide and hydrogen. We have discovered that a ratio of cobalt metal to cobalt oxide between 0.05 and 20 is a

prerequisite for a high level of activity in cobalt  
carbonylation catalyst. Apparently the rapid loss in  
activity shown by supported cobalt catalysts is often  
attributable to reduction of cobalt oxide to cobalt metal  
5 during the carbonylation reaction with the result that  
supported catalysts soon lose the prerequisite effective  
ratio of cobalt metal to cobalt oxide. The novel catalysts  
of this invention maintain a high level of activity for  
prolonged periods of time. The long catalyst life of the  
10 unsupported promoted catalysts of this invention is  
apparently associated with the fact that the presence of a  
promoter of the prescribed type inhibits reduction of  
cobalt metal to cobalt oxide so that an effective ratio of  
cobalt metal to cobalt oxide is preserved for a substantial  
15 period during the carbonylation reaction. The foregoing  
theoretical considerations on the mechanism of the  
catalysts of this invention are offered by way of explana-  
tion and not by way of limitation. Whatever be the explana-  
tion of the increased catalyst activity and longer catalyst  
20 life of the novel catalysts of this invention, the appli-  
cants have made a substantial contribution to the catalysis  
of the carbonylation reaction.

The reaction of unsaturated compounds such as ole-  
fins with carbon monoxide and hydrogen is ordinarily effected  
25 at pressures above 150 pounds per square inch, and prefer-  
ably between 300 and 5000 pounds per square inch. Reaction  
of liquid olefins with carbon monoxide and hydrogen in a  
slurry system is ordinarily effected at pressures between  
about 1500 and 3000 pounds per square inch. Reaction of

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gaseous olefins, such as ethylene and propylene are often effected at lower pressures between 300 and 1500 pounds per square inch.

Moderate temperatures are prescribed for the carbonylation reaction because temperatures below 400°F. are necessary in order to assure that the primary reaction is the addition of carbon monoxide and hydrogen to olefins rather than the production of liquid hydrocarbons by reaction of carbon monoxide and hydrogen in a Fischer-Tropsch reaction. Preferred temperatures fall within the range of 100 to 300°F.

The promoted catalysts of this invention are applicable to the conversion of low molecular weight olefins such as ethylene, and propylene into carbonyl products as well as to the more conventional slurry-type operation ordinarily employed for converting higher molecular weight olefins into carbonyl products. The superiority of the novel promoted catalysts will be demonstrated hereafter in the conversion of ethylene into diethylketone and in the batch slurry conversion of di-isobutylene into a C<sub>9</sub> aldehyde.

The unsupported promoted catalysts of this invention contain at least 50 weight per cent cobalt; advantageously the cobalt content falls within the range of 70 to 95 per cent of the total catalyst. The term, the cobalt content, as used in this application assumes complete reduction of cobalt oxide to cobalt metal, even though a substantial portion of the cobalt is in the form of oxide. In preparing the catalysts of this invention, the ingredients are added on the assumption that complete

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reduction of cobalt salts to cobalt occurs.

Promoters employable in the novel catalyst of this invention are alumina, chromia, magnesia, beryllia, titania and calcium oxide and mixtures thereof. All of the afore-  
5 mentioned metal oxides inhibit the reduction of cobalt oxide to metallic cobalt during the reaction of an unsaturated compound with carbon monoxide and hydrogen. As a consequence, the presence of the promoter of the afore-  
described type provides a carbonylation catalyst which  
10 retains a high degree of catalytic activity for a substantial period. The novel catalysts may contain 5 to 50 per cent promoter but promoter contents between 5 to 25 per cent are advantageously employed. Alumina is the preferred promoter.

15 The promoted catalysts of this invention are sensitive to alkali and the presence of more than 0.4 weight per cent alkali metal oxide seriously decreases the catalytic activity of the catalyst. Preferably the alkali content of the catalysts of this invention is below 0.2 per  
20 cent; excellent catalysts contain of the order of 0.1 per cent alkali metal oxide. It is recommended that they be washed until the alkali content is below the level prescribed above. Ordinarily, the alkali content can be reduced to about a 0.1 per cent level by approximately four washings  
25 with equal volumes of water. However, six washings are recommended in order to insure the preparation of a catalyst with an alkali content less than the prescribed amount. Instead of multiple washings to assure a low alkali content catalyst, ammonium hydroxide or carbonate  
30 may be used to precipitate the catalyst from the solution

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of soluble salts. The ammonium salts decompose to gaseous by-products during the drying and reduction of the catalyst.

Conventional procedures are employed for the preparation of the novel unsupported promoted catalysts of this invention. Detailed procedures will be presented hereafter, but in general cobalt in the form of a soluble salt, such as cobalt nitrate and a soluble salt of the metal or metals whose oxides comprise the promoters are dissolved in water in the desired proportions and are precipitated therefrom by the addition of an alkaline solution such as 10 per cent sodium hydroxide. After filtration, the precipitate is washed a plurality of times until the catalyst contains less than 0.4 weight per cent alkali metal oxide. Thereafter the catalyst is dried and pelleted to the desired size. The catalyst is then reduced at a temperature between 450 and 750<sup>o</sup>F.; 24 hours is a convenient period of reduction although shorter duration reductions may be employed. It is also possible to calcine the pelleted catalyst prior to reduction.

The superiority of the novel catalysts of this invention from the viewpoint of longer catalyst life and increased catalyst activity are demonstrated in Figures 1 and 2 wherein there are compared the yields obtained with a standard cobalt catalyst and with the novel catalysts of this invention.

In Figure 1 the superiority of the novel catalysts of this invention is shown for a gas phase conversion of ethylene, carbon monoxide and hydrogen into a product comprising mainly diethylketone. The yields of liquid product

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on the basis of grams per cubic meter of 2/1/1 ethylene, CO, hydrogen mixture charged are plotted against time. In Figure 2, there is demonstrated the superiority of the catalysts of this invention for a batch slurry conversion of di-isobutylene into a C<sub>9</sub> aldehyde. In Figure 2 the amount of conversion expressed as pressure drop in pounds per square inch gauge is plotted against time.

In Figure 1, Curves I, II, III, IV, and VI indicate the results obtained with the novel catalysts of this invention in the catalytic conversion of ethylene, carbon monoxide and hydrogen into principally diethylketone. Curve V indicates the activity of a supported cobalt catalyst in the same conversion under similar reaction conditions. As is indicated in the legend under Figure 1, Curves I, II, and III indicate the results obtained in diethylketone reaction employing cobalt-alumina catalysts of varying compositions: a catalyst comprising 90 parts cobalt and 10 parts alumina gave the results indicated by Curve I; Curves II and III were indicative of the results obtained with an 80 cobalt - 20 alumina catalyst and a 60 part cobalt - 40 part alumina catalyst, respectively. Curve IV was obtained with a catalyst comprising 90 weight per cent cobalt and 10 weight per cent chromia. Curve VI indicates the activity of a catalyst comprising 80 per cent cobalt, 10 per cent alumina and 10 per cent ferric oxide. Curve V illustrates the activity of a supported standard cobalt catalyst comprising 32 parts cobalt, 64 parts Filter Cel, 3 parts magnesia and 1 part thoria.



All of the runs shown in Figure 1 were made at similar reaction conditions. These conditions may be briefly summarized as follows:- Ethylene, carbon monoxide and hydrogen in a mol ratio of 2/1/1 were introduced at a space velocity of about 100 volumes of reactant mixture per volume of catalyst per hour into a reaction zone containing the catalyst which had been reduced at 660°F. prior to being placed in the reaction zone in the form of a fixed bed of dense particles of approximately 10 to 20 mesh; the reaction zone was maintained at a pressure of 300 pounds per square inch and at a temperature of 150°F. by indirect heat exchange.

The superiority of the unsupported promoted catalysts of this invention over supported cobalt catalysts as exemplified by the standard Fischer-Tropsch catalyst is readily apparent from an inspection of Figure 1. Not only is the initial activity substantially greater but the life of the novel promoted catalysts of this invention is outstandingly superior. For example, after 84 hours on stream, 700 grams of liquid product per cubic meter of charge was still being obtained with an 80 Co - 20 Al<sub>2</sub>O<sub>3</sub> catalyst as is illustrated in Curve II, whereas after a similar time on stream only 100 grams of liquid product per cubic meter of charge gas was obtained with a standard cobalt catalyst as illustrated in Curve V.

In Figure 2, the superiority of the catalysts of this invention over supported cobalt catalysts is demonstrated for the batch slurry reaction of di-isobutylene with carbon monoxide and hydrogen to produce a C<sub>9</sub> aldehyde. The

efficiency of the catalysts is illustrated by the pressure drop in pounds per square inch gauge realized with a standard cobalt catalyst and with a novel catalyst of this invention under similar operating conditions. Curves VII and VIII show the pressure drop obtained in units of time with a standard cobalt catalyst comprising 32 parts cobalt, 64 parts Filter Cel, 3 parts magnesia and 1 part thoria. Curves IX and X indicate the activity of a novel catalyst of this invention containing 90 weight per cent cobalt and 10 weight per cent alumina.

The runs in Figure 2 were all made under similar operating conditions which are briefly summarized as follows:- Di-isobutylene and a mixture of 1/1 CO-H<sub>2</sub> were charged to a pressure vessel maintained at a temperature of 300°F. The reaction vessel was maintained at a pressure of 1500 to 2500 pounds per square inch gauge throughout the reaction by intermittent repressuring with 1/1 Co-H<sub>2</sub> mixture.

Figure 2 establishes the superiority of the novel catalysts of this invention for the carbonylation of liquid olefins by slurry operation. After only approximately four hours on stream the novel catalysts of this invention effected as much carbonylation as measured by the pressure drop, as was effected by a standard cobalt catalyst after approximately twenty hours on stream. The superiority of catalysts of this invention is of such magnitude that substantial economies in commercial adaptation of the carbonylation process are realized by employing the catalyst of this invention.

The preparation of the novel catalysts of this invention is illustrated by the detailed preparations of the 90-10 Co - Al<sub>2</sub>O<sub>3</sub> catalyst whose activity is illustrated in Curve I of Figure 1. 1730 grams of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 283  
5 grams of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in 5 liters of water to which 5100 cc of 10 per cent sodium hydroxide was added slowly with agitation until the system was fairly pink to phenolphthalein. The precipitate thereby obtained was filtered and the filtrate was found to give no precipitate  
10 with NaH<sub>2</sub>PO<sub>4</sub>. After washing four times with 5 liters of water at each wash, the precipitate was dried on a steam bath. Thereafter the precipitate was sieved to 14 mesh, pelleted in a 1/2" die and broken up into 10 to 20 mesh pellets. As indicated heretofore, the catalysts were all  
15 reduced at 660°F. prior to use.

The foregoing examples are merely illustrative of the novel catalysts of this invention. Cobalt may be promoted with magnesia, beryllia, titania and calcium oxide as well as alumina and chromia. Activators, such as nickel  
20 oxide, thoria and boria can be employed in place of ferric oxide. Moreover, the novel catalysts of this invention are applicable to all carbonylation reactions involving the reaction to olefins, carbon monoxide and hydrogen to form  
carbonyl compounds and to all elevated pressure and moderate  
25 temperature reactions of unsaturated compounds, such as nitriles and dienes, with carbon monoxide either in the presence or absence of hydrogen.

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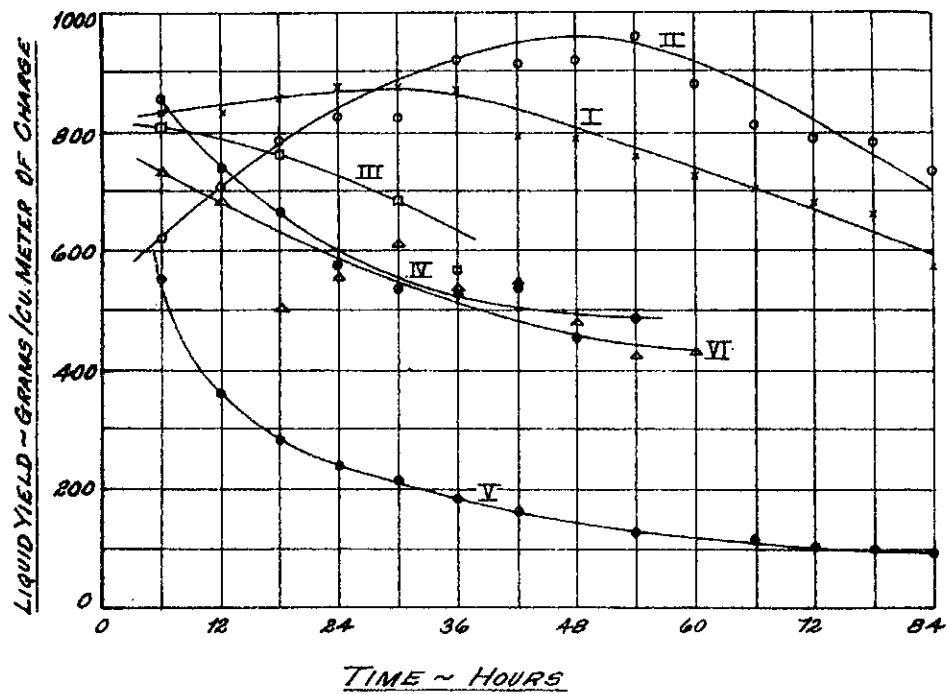
Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in  
5 the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed as follows:

1. Catalysts for the reaction of unsaturated compounds with carbon monoxide and hydrogen at elevated pressures and moderate temperatures comprising 50 to 95 per cent cobalt, 5 to 50 per cent promoter selected from the group consisting of alumina, magnesia, chromia, titania, beryllia, calcium oxide and mixtures thereof, 1 to 15 per cent activator selected from the group consisting of ferric oxide, nickel oxide, thoria, boria, and mixtures and containing less than 0.4 weight per cent alkali content.
2. Catalysts for the reaction of olefins with carbon monoxide and hydrogen to form carbonyl products at elevated pressures and moderate temperatures comprising 50 to 95 per cent cobalt and 5 to 50 per cent promoter selected from the group consisting of alumina, magnesia, chromia, titania, beryllia, calcium oxide and mixtures thereof.
3. A catalyst of the composition specified in Claim 2 in which the cobalt content is between 70 and 95 per cent and the promoter content is between 5 and 25 per cent.
4. Catalysts for the reaction of olefins with carbon monoxide and hydrogen to form carbonyl products at an elevated pressure of 100 to 5000 pounds per square inch and temperature of 100 to 400°F. which comprise 50 to 95 per cent cobalt, 5 to 50 per cent promoter selected from the group consisting of alumina, magnesia, chromia, titania, beryllia, calcium and mixtures thereof, and containing less than 0.4 weight per cent alkali content.

5. A catalyst of the composition specified in Claim 4 in which the alkali content is of the order of 0.1 per cent.
6. A catalyst of the composition specified in Claim 4 in which the catalyst comprises about 80 per cent cobalt to about 20 per cent alumina and about 0.1 per cent alkali metal oxide.
7. A catalyst of the composition specified in Claim 4 containing 90% cobalt, 10% chromia, and about 0.1 weight per cent alkali metal oxide.
8. A catalyst for the reaction of olefins with carbon monoxide and hydrogen to form carbonyl products at an elevated pressure of 100 to 5000 pounds per square inch and a temperature of 100 to 400°F. which comprises about 50 to 95 per cent cobalt, about 5 to 50 per cent promoter selected from the group consisting of alumina, magnesia, chromia, titania, beryllia, calcium oxide and mixtures thereof, and about 1 to 15 per cent activator selected from the group consisting of ferric oxide, nickel oxide, thoria, boria and mixtures thereof.
9. A catalyst of the composition specified in Claim 8 containing 80 per cent cobalt, 10 per cent alumina and 10 per cent iron oxide and less than 0.4 weight per cent alkali metal oxide.

Fig. 1.



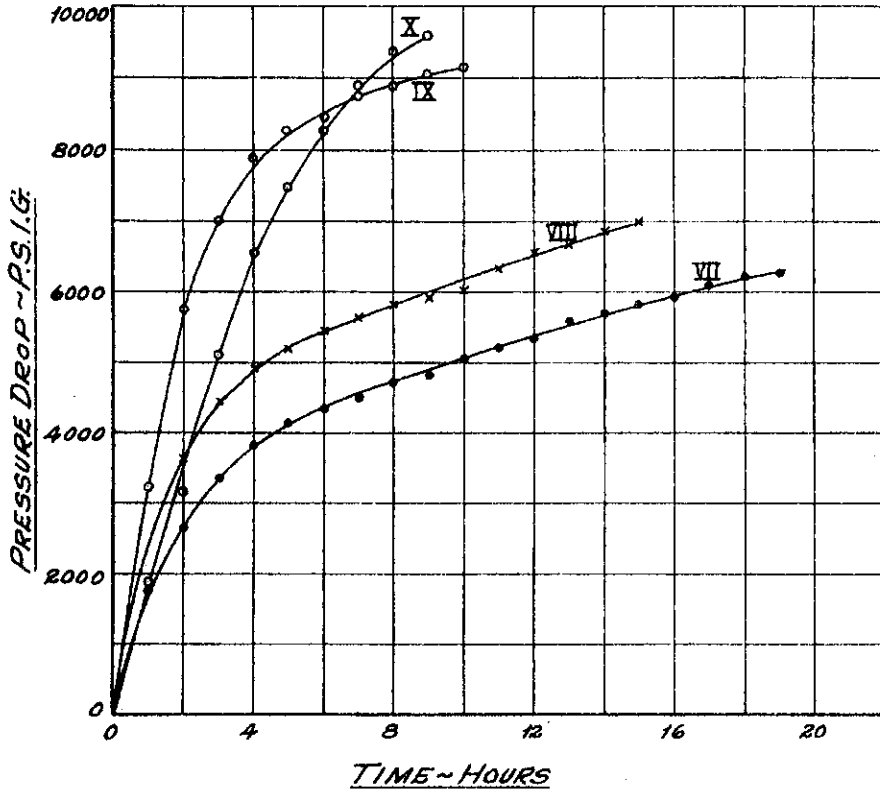
- I - 90 Co - 10 Al<sub>2</sub>O<sub>3</sub>
- II - 80 Co - 20 Al<sub>2</sub>O<sub>3</sub>
- III - 60 Co - 40 Al<sub>2</sub>O<sub>3</sub>
- IV - 90 Co - 10 Cr<sub>2</sub>O<sub>3</sub>
- V - 32 Co - 64 FILTER CEL - 3 MgO - 1 ThO<sub>2</sub>
- VI - 80 Co - 10 Al<sub>2</sub>O<sub>3</sub> - 10 Fe<sub>2</sub>O<sub>3</sub>

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Fig. 2.



VII, VIII - 32 Co - 64 FILTER CEL - 3 MgO - 1 ThO<sub>2</sub>  
IX, X - 90 Co - 10 Al<sub>2</sub>O<sub>3</sub>

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