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Isoparaffin Synthesis: Hydrogenation of Carbon Monoxide over Cadmium Catalysts

INTRODUCTION

The reaction of hydrogen and carbon monoxide to produce hydrocarbons has been studied for over 75 years (*1*). Because hydrogen/carbon monoxide mixtures can be made from numerous sources of carbon, such as coal, natural gas, or biomass, transportation fuels and petrochemicals can be produced from these abundant natural resources.

The production of straight-chain hydrocarbons by iron, cobalt, nickel, and ruthenium Fischer–Tropsch catalysts has been extensively studied (*2–6, 10*). Under normal synthesis conditions, a broad molecular weight range of products is obtained that requires extensive reprocessing to obtain high yields of transportation fuels (*6*). During the 1930s, a second synthesis of hydrocarbons by hydrogenation of carbon monoxide was discovered (*8, 10*). Products from this process were low molecular weight, aromatic, and branched aliphatic hydrocarbons. This was termed the isosynthesis process, and the catalysts were nonreducible oxides, such as thorium oxide. Isosynthesis catalysts, however, required high reaction temperatures and pressures. Gasoline yields of 90% were obtained at reaction pressures from 350 to 700 atm and temperatures of about 400°C (*8, 9*). Compared with the yields and product distributions from Fischer–Tropsch processing, the higher octane gasoline range hydrocarbons obtained from isosynthesis could offer an attractive alternative if catalysts could be found that would operate at lower pressure.

Because of the high pressures required for the isosynthesis catalysts, comparatively little research has been done in this area since their initial discovery. In this paper we describe a catalyst that operates at medium pressure for producing low molecular weight isoparaffins. The metallic component is cadmium and when combined with acid supports, for example, zeolites or expanded clays, catalyzes the hydrogenation of carbon monoxide to low molecular weight isoparaffins.

EXPERIMENTAL

Catalyst supports were prepared using an alumina sol obtained from American Cyanamid and the appropriate zeolite. For example, 340 g of alumina sol (10.3% aluminum oxide) was mixed thoroughly in a blender with 15.0 g of a rare-earth-exchanged Y zeolite. The alumina was geled by the rapid addition of a 10% ammonium hydroxide solution. The mixture was dried at 120°C and calcined at 540°C for 3 h. Similar catalyst supports were made with ultrastable (US) Y zeolite, mordenite, ZSM-5, and rare-earth-exchanged X zeolites. Supports also were made with a cadmium-exchanged sodium Y zeolite and with an alumina-expanded bentonite clay (*11*).

Cadmium was incorporated by the method of incipient wetness. The pores of the support were filled with an aqueous solution of cadmium nitrate. For example, to 20.0 g of 30% rare earth (RE) Y, zeolite dispersed in an alumina matrix was added 3.00 g of $Cd(NO_3)_2 \cdot 4H_2O$ dissolved in 10 ml of water and mixed well. After standing for 1 h, the catalyst was dried overnight in an

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oven at 120°C and for an additional 3 h in a furnace at 540°C.

Catalysts were crushed to particles passing 12-mesh screens and retained on 20-mesh screens (US standard) and then placed in a reactor and pressurized with a mixture of carbon monoxide and hydrogen. Cadmium catalysts do not require any special activation procedure.

Typically, 5.0 g of catalyst was reacted with syngas in either of two small catalyst testing units—one with a Berty reactor (500 cc) and the other with a fixed-bed, plug-flow tubular reactor (0.5-cm i.d.). With both testing units, gas concentrations and product analysis were determined by two gas chromatographs in series with the reactor. The inlet flow rate for both hydrogen and carbon monoxide were regulated by electronic mass flow controllers. The outlet flow rate was measured by a conventional wet test meter. The outlet gas flow rate, carbon monoxide, and carbon dioxide concentrations were determined first with the reactor at room temperature. After the catalyst was heated to reaction temperature, the outlet gas flow rate, carbon monoxide, and carbon dioxide concentrations were again determined. The carbon monoxide conversion was computed by difference. Generally, the carbon mass balance was 100 ± 5%.

RESULTS AND DISCUSSION

Low molecular weight isoparaffins can be prepared from syngas at moderate pressures by cadmium catalysts on acidic supports. Catalyst reactivity and product selectivity are sensitive functions of catalyst composition and process conditions. For hydrocarbon synthesis, active catalysts require two components: cadmium oxide and an acidic support. Reactor conditions for the conversion of syngas to isoparaffins are total pressures from 20 to 70 atm or higher, and reaction temperatures from about 300 to 400°C. Hydrocarbon product distributions are only slightly affected by gas rate and hydrogen to carbon monoxide ratios. Hydrocarbon yields increase with increasing gas rate, pressure, and reaction temperature. Water formed as a by-product in the hydrocarbon synthesis reacts with excess carbon monoxide to form carbon dioxide and hydrogen. Carbon dioxide yields decrease with increasing gas rate. The effects of catalyst composition and process conditions are discussed in greater detail in the following sections.

Catalyst Support Composition

Several catalysts were evaluated to determine the effect of the acidic support on hydrocarbon selectivity. Each catalyst, containing 5% CdO on a different acidic support was tested at 400°C and 34 atm using syngas with a hydrogen to carbon monoxide ratio of 2 : 1. The results of tests conducted in the Berty reactor are shown in Table 1. In this table, selectivities for methane by all catalysts is high because of the high-reaction temperature. However, several trends are noticeable. Highly acidic, high aluminum zeolites result in catalysts that give lower methane selectivity and a higher selectivity for C_4 to C_7 isoparaffin products. The catalyst supports in order of decreasing selectivity for C_4 to C_7 isoparaffins are REY, REX, US Y > Al bentonite clay, Cd-Y > H mordenite ⩾ H-ZSM-5. Although not shown in Table 1, catalysts that give the highest selectivities of C_4 to C_7 isoparaffin also give higher yields of hydrocarbon. That is, catalyst activity decreased in the order REY, USY > H mordenite ⩾ H-ZSM-5, for example. The best supports for both high activity and selectivity for isobutane and higher isoparaffins are REY and USY zeolites dispersed in an alumina matrix. For most catalysts, zeolite levels of approximately 30% give good activity and selectivity for isoparaffins.

Among the best catalysts, only minor differences in isoparaffin selectivity were observed. For example, in a tubular plug-flow reactor, REX-supported catalysts, which are similar to REY-supported catalysts, give slightly higher selectivities of isopen-

TABLE 1

The Effect of Zeolite Structure on Hydrocarbon Selectivity[a]

Catalyst:	5% CdO on 30% US zeolite 70% alumina	5% CdO on 30% REY zeolite 70% alumina	5% CdO on 60% ZSM-5 40% alumina	5% CdO on 20% H mordenite 80% alumina	5% CdO on 60% Al bentonite 40% alumina	Cd-exchanged 30% Y zeolite 70% alumina
Feed rate cc gas/h/g cat:	1100	600	2000	1000	2000	1500
Hydrocarbon products, wt%						
Methane	27	24	85	60	28	54
Ethane	6	2	13	7	7	4
Propane	4	19	1	19	11	6
Propene	6	1	—	t[b]	1	2
Isobutane	16	27	t	2	19	12
n-Butane	2	6	—	3	4	2
Isopentane	13	10	t	3	9	7
n-Pentane	1	1	—	t	1	t
Isohexane	9	5	—	1	5	5
n-Hexane	1	t	—	1	1	t
Heavier paraffins	15	5	1	6	14	8

[a] Berty reactor at 34 atm, 400°C, $H_2/CO = 2:1$.

[b] t, trace.

tane and isohexane, while REY-supported catalysts give higher selectivities for isobutane (Table 2). For all cadmium catalysts, the iso/normal ratio for butane is greater than 5, and the iso/normal ratio for pentane is greater than 10.

Reduction of Cadmium Oxide to Cadmium Metal

Under some reaction conditions, supported cadmium oxide is reduced to cadmium metal, and some cadmium is lost from the catalyst support and is deposited on the reactor walls. The amount of cadmium lost by reduction of cadmium oxide to cadmium metal is dependent on the acidity of the catalyst support and the cadmium level on the catalyst. For example, little or no cadmium is lost from amorphous, acidic silica–alumina support, while large amounts of cadmium oxide are reduced and volatilized as cadmium metal from weakly acidic materials, such as alumina. The following experiments demonstrate the reduction and loss of cadmium from an alumina-supported cadmium oxide. Equal amounts of a 5% cadmium oxide on alumina catalyst (14/20 mesh) and a cadmium-free 50 wt% ultrastable Y zeolite in an alumina matrix (⅛-in. extrudate) were added to a nonflow autoclave reactor. The reactor was pressurized with one part carbon monoxide and two parts hydrogen, and the reactor was heated to 425°C. The reactor pressure was maintained at 70 atm. After 96 h, the reactor was depressurized, cooled, and the catalysts were removed and separated. The extrudates containing the zeolites, which initially contained no cadmium, were now found to contain 1.8% cadmium. The experiment was repeated with equal amounts cadmium-exchanged Y zeolite in an alu-

TABLE 2

Conversion of Syngas to Hydrocarbons with 5% CdO on 30% Rare-Earth-Exchanged Zeolite/70% Alumina[a]

Catalyst zeolite type:	REY		REX	
Inlet gas composition:				
Hydrogen	64%		65%	
Carbon monoxide	34%		33%	
Carbon dioxide	2%		2%	
Temperature, °C	350	360	350	360
Total CO Conversion, %	27	33	29	34
CO converted to CO_2, %	10	13	12	15
CO converted to product, %	17	20	17	19
Hydrocarbon products, wt%				
Methane, ethane, propane	9	12	6	9
Butanes	43	37	24	27
Pentanes	21	18	38	19
Heavier paraffins	30	30	32	45
Hydrocarbon yield, g/h/g cat	0.072	0.085	0.071	0.082

[a] Tubular reactor; total pressure: 68 atm; Feed rate: 2100 cc/h/g catalyst.

mina matrix (14 to 20 mesh) and a cadmium-free 50 wt% ultrastable Y zeolite in an alumina matrix (⅛-in. extrudate). In this experiment, no cadmium migrated to the ultrastable Y zeolite from the cadmium-exchanged Y zeolite. In both experiments, isoparaffins were formed in high yields.

These experiments demonstrate that cadmium oxide on alumina is easily reduced to volatile cadmium metal by mixtures of hydrogen and carbon monoxide and is lost from the alumina under typical conditions for hydrocarbon synthesis. Cadmium ion-exchanged into a zeolite, however, is not lost under similar conditions. Perhaps, strongly acid supports can retain the volatile cadmium by oxidation of cadmium metal by the acidic support. For many of the zeolite catalysts, it is not necessary to exchange cadmium directly into the zeolite but only that cadmium be associated with an acidic support. In the absence of an acidic support, cadmium oxide, cadmium metal, and other cadmium compounds did not catalyze carbon monoxide reactions.

Cadmium Oxide Loading

The effect of cadmium oxide loading on catalyst performance is shown in Table 3. With catalysts containing 5% cadmium oxide and 20% cadmium oxide, the conversion of carbon monoxide to hydrocarbon products was approximately the same. The catalyst with the higher cadmium oxide loading, however, displayed increased selectivities for methane. A loading of 5% cadmium oxide gave both high activity and good selectivity for C_4 to C_7 isoparaffins.

A catalyst composition of 5% cadmium oxide, supported on a matrix of 30% rare-earth-exchanged Y zeolite dispersed in an aluminum matrix, was used for more extensive experiments to determine the range of reaction conditions for synthesizing isoparaffins from syngas.

Operating Conditions

The effect of operating conditions on catalyst activity and selectivity are given in Table 4.

Temperature. Isoparaffin synthesis with a 5% cadmium oxide on 30% REY zeolite in an alumina matrix was investigated over a temperature range from 315 to 400°C. Hydrocarbon yields increase with increasing temperature, although methane, C_2, and C_3 selectivity also increased with increasing temperature. The temperature where hy-

TABLE 3

The Effect of CdO Content on Catalyst Reactivity and Selectivity[a]

Catalyst cadmium level:	5% CdO		20% CdO		
Catalyst support:	30% REY/70% alumina		30% REY/70% alumina		
Feed rate, cc gas/h/g cat:	1350	1200	1400	1400	1400
Temperature, °C:	315	340	315	340	370
Total CO conversion, %	33	43	17	27	34
CO converted to CO_2, %	16	25	6	14	20
CO converted to product, %	17	14	11	13	14
Hydrocarbon products, wt%					
Methane, ethane, propane	2	6	11	20	42
Butanes	31	38	33	33	21
Pentanes	14	10	19	19	13
Heavier paraffins	53	44	37	28	24
Hydrocarbon yield, g/h/g cat	0.049	0.036	0.033	0.039	0.042

[a] Tubular reactor; total pressure: 34 atm, inlet gas composition: hydrogen 64%, carbon monoxide 34%, carbon dioxide 2%.

TABLE 4

The Effect of Operating Conditions on Catalyst Reactivity and Selectivity[a]

Pressure, atm:	10	20	34	34	34	34	68	68	68	68
Temperature, °C:	360	360	340	360	360	360	360	360	315	400
Inlet: Feed rate, cc/h/g cat:	1435	1420	1470	1470	2855	1415	2815	1410	1423	1423
CO, %	28.83	29.40	29.31	29.31	28.29	43.96	29.53	29.29	29.47	29.47
CO_2, %	5.14	5.20	5.06	5.06	5.04	7.79	5.28	5.20	5.25	5.25
Outlet: Gas rate, cc/h/g cat:	1416	1369	1355	1340	2680	1304	2510	1140	1305	1152
CO, %	29.42	28.81	27.25	25.85	27.00	40.14	25.28	22.84	28.40	21.60
CO_2, %	4.92	5.98	6.95	7.53	5.88	11.06	7.51	12.37	7.58	10.97
CO conversion, %	1.0	5.5	14.3	19.6	10.4	15.9	23.7	37.0	11.6	40.7
Selectivity, %										
Carbon dioxide	nd	34.8	32.1	31.4	16.3	34.5	20.3	44.4	49.7	30.3
Methane, ethane, propane	nd	17.2	11.4	13.9	18.4	13.0	12.8	12.2	8.2	20.2
Butanes	nd	25.7	31.2	31.6	34.1	29.5	30.5	26.5	21.5	29.8
Pentanes	nd	12.9	14.5	13.7	16.0	13.2	20.4	10.7	11.5	12.0
Hexanes and heavier	nd	9.4	10.8	9.4	14.4	9.8	16.0	6.2	9.1	7.7
Hydrocarbon selectivity, % CO_2-free basis)										
Methane	23.0	7.9	4.4	6.2	6.7	5.2	5.1	7.1	4.5	11.4
Ethylene	6.8	4.5	4.3	3.8	4.0	4.5	3.1	2.9	4.4	3.6
Ethane	1.5	2.5	0.9	1.4	1.7	2.1	1.2	2.6	1.4	1.2
Propylene	18.0	6.0	2.3	2.2	4.6	2.2	1.7	0.8	1.5	1.2
Propane	3.4	5.5	4.9	6.5	4.9	5.9	4.7	8.5	4.1	11.5
Isobutane	15.0	37.4	43.8	43.4	33.4	42.4	35.7	43.6	40.4	37.5
n-Butane	—	2.0	2.3	2.9	2.2	2.7	2.5	4.1	2.3	5.2
Isopentane	13.2	19.3	19.8	18.7	20.0	19.8	19.3	18.2	21.9	15.9
n-Pentane	0.5	0.5	1.4	1.1	1.0	0.4	0.9	1.0	0.8	1.3
Isohexane	14.8	11.4	10.9	10.0	10.6	10.0	11.2	6.8	12.0	8.3
n-Hexane	—	0.1	0.8	0.6	0.6	0.2	0.2	0.1	0.1	0.1
Heavier hydrocarbons	3.7	2.9	4.2	3.2	5.3	4.5	14.4	4.3	6.6	2.8
Hydrocarbon yield, g/h/g cat	—	0.009	0.026	0.036	0.044	0.040	0.098	0.053	0.015	0.074
Carbon dioxide yield, g/h/g cat	—	0.016	0.039	0.052	0.027	0.067	0.078	0.133	0.048	0.102

[a] Tubular reactor; catalyst: 5% CdO on 30% REY/alumina.

drocarbon synthesis gives high yields of C_4 to C_7 isoparaffins and minimizes C_1 to C_3 yields is near 360°C.

Pressure. At reaction pressures of 10 atm, only traces of hydrocarbon and carbon dioxide products are obtained. Above 20 atm, however, yields of isoparaffins and carbon dioxide products increase with increasing reaction pressure. Hydrocarbon distributions were only slightly affected by reaction pressure (Table 4).

Gas rate. Gas rates (total carbon monoxide and hydrogen) of 1400 and 2800 cc/h/g catalyst were examined for their effect on isoparaffin synthesis. The higher gas rate increased hydrocarbon yield. A larger increase in hydrocarbon yield with high gas rate was observed at 68 atm, while a modest increase in hydrocarbon yield was obtained at 34 atm. At reaction pressures of 34 and 68, atm, the carbon dioxide yield was approximately inversely proportional to the gas flow rate. High gas flow rates were the most effective way of limiting carbon dioxide formation.

Gas composition. The gas composition has a minor effect on catalyst activity or product hydrocarbon selectivity. With a hydrogen to carbon monoxide ratio of 1 : 1, the hydrocarbon yields were approximately

10% higher than with a 2 : 1 hydrogen to carbon monoxide ratio. Sulfur was found to be a severe poison for cadmium syngas catalysts. Addition of H_2S to the feed resulted in the irreversible formation of CdS which was catalytically inactive.

In summary, isoparaffins were produced at reaction pressures above 20 atm, temperatures from 315 to 400°C with gas rates of 1400 and 2800 cc/h/g catalyst, and with hydrogen to carbon monoxide ratios from 2 : 1 to 1 : 1. Yields of isoparaffins ranged from traces of products at 10 atm up to 0.1 g/h/g catalyst at higher reaction pressures and gas rates. High gas rates reduce the carbon dioxide formed during the synthesis reactions. For this catalyst, no aromatic or oxygenated products were obtained at any of the process conditions. At these reaction conditions, cadmium catalysts are stable. Tests show no significant loss in activity or changes in product selectivities over a period of 30 days.

Reaction Intermediates

For most cadmium syngas catalysts, C_1 to C_7 paraffins, along with low concentrations of olefins, were the only observed products. In addition, most of the C_4 to C_7 hydrocarbons were isoparaffins. As shown in Table 4, with 5% cadmium on 30% REY zeolite in an alumina matrix, no oxygenated products were observed over a wide range of reaction conditions.

For two catalysts, however, dimethyl ether and methanol were reaction products under some reaction conditions. Table 5 shows that for 5% cadmium oxide on 30% US Y zeolite in an alumina matrix at 315°C, dimethyl ether is the only product. At higher temperatures, 370°C, dimethyl ether and methanol yields decrease while isobutane and isopentane appear as reaction products. Table 5 also shows the products of the reaction of hydrogen and carbon monoxide over cadmium oxide on alumina.

TABLE 5

Dimethyl Ether and Methanol as Reaction Intermediates[a]

Catalyst:	5% CdO on 30% US zeolite 70% alumina			5% CdO on (no zeolite) 100% alumina		
Feed rate, cc gas/h/g cat:	1400	1400	1400	3000	1500	3000
Temperature, °C:	315	340	370	325	340	370
Total CO conversion, %	15	20	24	29	32	41
CO converted to CO_2, %	5	10	14	11	14	18
CO converted to product, %	10	10	10	18	18	23
Products, wt %						
Methane	0	10	32	9	29	41
Ethane	—	—	—	—	—	—
Propane	—	—	—	—	—	—
Propene	—	—	—	—	—	—
Isobutane	—	6	21	—	—	—
n-Butane	—	—	—	—	—	—
Isopentane	—	—	13	—	—	—
n-Pentane	—	—	—	—	—	—
Isohexane	—	—	—	—	—	—
n-Hexane	—	—	—	—	—	—
Heavier paraffins	—	—	—	—	—	—
Methanol	0	7	6	17	11	10
Dimethyl ether	100	78	28	74	60	24

[a] Tubular reactor at 34 atm; hydrogen: carbon monoxide 2 : 1.

With the less acidic alumina catalyst, methanol and dimethyl ether are again observed at low reaction temperatures. Unlike the CdO/zeolite catalysts, methane is the only hydrocarbon product at high reaction temperatures. No C_2 or higher molecular weight products were found with CdO/alumina catalysts at any reaction temperature.

The formation of dimethyl ether at low reaction temperatures suggests that CdO first converts carbon monoxide and hydrogen to methanol which rapidly forms dimethyl ether. Isoparaffins result from the secondary acid catalyzed reactions of methanol. Additionally, cadmium oxide may function to prevent the rapid deactivation of the zeolite acid sites by the build-up of carbonaceous deposits from the methanol to hydrocarbon reaction. In the absence of cadmium oxide, the same zeolites which have been used in combination with cadmium for isoparaffin synthesis from carbon monoxide and hydrogen, also react with methanol to form isoparaffins (*12, 13*). For example, REY zeolite catalyzes the conversion of methanol to isoparaffins at 375°C and atmospheric pressure. These results indicate that isoparaffins obtained over from cadmium syngas catalysts are produced by the acid-catalyzed reaction of methanol, similar to the methanol to gasoline reaction of ZSM-5 (*13*).

CONCLUSIONS

Cadmium oxide catalysts on acidic supports are highly reactive for the conversions of hydrogen and carbon monoxide to saturated, low molecular weight isoparaffins. Catalyst activity and selectivity are sensitive functions of catalyst composition and process conditions. For isoparaffin formation, active catalysts require two components. First, active catalysts contain approximately 5% cadmium oxide, which converts carbon monoxide to reactive intermediates, possibly methanol and dimethyl ether. Second, to stabilize the cadmium ion in a catalytically active state, an acidic support is required: for example, a zeolite, an expanded clay, or even amorphous silica–alumina. Although the product distribution is highly dependent on the type of acid component, the hydrocarbon products are characterized by a distribution of C_1 to C_7 paraffins. In addition, most of the C_4 to C_7 hydrocarbons are isoparaffins. Olefins in the products are low, generally under 10%. Under optimum conditions, methane yields are low, and isobutane and isopentane are the predominant products. No aromatic hydrocarbons or oxygenates, other than methanol and dimethyl ether, were detected. The preferred catalysts for producing isoparaffins from syngas are cadmium oxide supported on faujasite or aluminum-expanded clays. Cadmium oxide supported on shape-selective zeolites, such as ZSM-5, which gives gasoline range hydrocarbons form methanol, gives methane form syngas.

The acid-supported cadmium oxide catalysts give products similar to those of the thorium isosynthesis catalyst developed in Germany during the 1940s. The mechanism of the isosynthesis catalyst was believed to involve the formation and dehydration of alcohols—primarily methanol and isobutanol (*8, 9*). Like the thorium oxide isosynthesis catalysts, methanol is the likely reaction intermediate for the cadmium catalyst. Over cadmium catalysts, however, isoparaffins are formed as a result of the secondary acid-catalyzed reactions of methanol by the acidic support, for example, zeolite. Thus the mechanism for the synthesis of isoparaffins from cadmium may be similar to the ZSM-5-catalyzed methanol to gasoline reactions, rather than the dehydration of higher molecular weight alcohols postulated for the isosynthesis catalysts.

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