CH$_2$-Species as Important Precursors for Hydrocarbon Formation on Cobalt Catalysts

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CH$_2$-Species were formed on a cobalt catalyst by the Boudouard reaction or by the decomposition of methane; hydrogenation yielded methane as well as α-olefins, while the hydrogenation of carbidic carbon yielded merely methane.

The nature of the precursor species for hydrocarbon formation from CO and H$_2$ has been the subject of speculation by many investigators; it has been shown that the carbon formed on catalysts following the dissociation of CO is an important precursor for methane[1] as well as for higher hydrocarbons.[2] On the other hand, if CH$_2$-species were produced on transition-metal catalysts by decomposing CH$_2$N$_2$ in the presence of hydrogen, hydrocarbons similar to those produced in the Fischer–Tropsch reaction were obtained.[3] Furthermore, recent results by Theopold and Bergman[4] indicated that a bridging CH$_2$-ligand in μ-CH$_2$Co$_2$(CO)$_2$-(η^5-C$_5$H$_5$)$_2$ reacts with ethylene to yield propene. Our interest has focused on the reactivity and/or selectivity of carbonaceous species for the hydrogenation, and we now report results obtained with carbonaceous species prepared on cobalt catalysts by the Boudouard reaction or by decomposing methane.

These carbonaceous species might be composed of CH$_x$, carbidic carbon, and/or free carbon, which will contribute differently to the hydrocarbon-formation processes, and the different species could be successfully distinguished by using ^{13}C and ^{2}H labelled materials. The catalysts, Co/Al$_2$O$_3$ (6.0 wt %) or Co/C (14.7 wt %), were reduced for 1 h at 430 °C in a circulation system of volume *ca.* 275 ml. After the reduction, carbonaceous species were deposited on the catalysts by decomposition of methane or by the Boudouard reaction at 430 °C. The carbon-deposited catalysts were evacuated at 430 °C for about 1 h before the experiments.

As cobalt carbide is unstable at 430 °C,[5] carbidic carbon, if formed, may rapidly decompose to the less reactive free carbon at 430 °C. When these carbon-deposited cobalt catalysts were exposed to H$_2$ or D$_2$, methane was formed rapidly in the initial stage of the reaction. To identify the nature of the reactive species on the carbon-deposited surface,

Table 1. Deuterium distribution in the methane obtained from treatment of carbonaceous species deposited on cobalt catalysts with deuterium at 430 °C.

Run	Catalyst	Reduction of catalyst	Deposition of carbon	Hydrogenation (30 Torr)	Methane (%)				
					CH_4	CH_3D	CH_2D_2	CHD_3	CD_4
1	Co/Al_2O_3	H_2	CH_4	D_2	60	7	24	8	1
2	,,	H_2	CO	D_2	38	15	34	8	5
3	Co/C	H_2	CH_4	D_2	9	10	60	14	7
4	Co/Al_2O_3	H_2	CH_2CO^a	D_2	68	5	26	1	0
5	,,	H_2	$CD_4{}^b$	H_2	8	10	56	4	22
6[c]	Co/C	H_2	CO	D_2	0	1	14	34	51
7	,,	D_2	None	D_2	2	2	8	39	49

[a] Decomposition at 450 °C yielded CO with little CO_2, H_2, and hydrocarbons. [b] Isotopic distribution in the methane used: CH_4, 6; CH_3D, 5; CH_2D_2, 10; CHD_3, 3; CD_4, 76%. [c] Deposition and deuterium treatment were performed at 210 °C.

the carbon-deposited Co/Al_2O_3 was treated with deuterium at 430 °C. Runs 1 and 2 in Table 1 show the deuterium distribution of the methane obtained in the initial 30 s, and it is clear that a disproportionate quantity of CH_2D_2 was formed. Treatment of the carbon-deposited Co/C catalyst with deuterium also yielded a disproportionate amount of CH_2D_2 (run 3), and the relative proportion of CH_2D_2 was greater than that obtained on the Co/Al_2O_3 catalyst. These results suggest the presence of a reactive species such as CH_2 on the carbon-deposited cobalt catalysts. The formation of CH_2D_2 may be caused by the rapid reaction of CH_2-species with D_2 accompanied by slow hydrogen scrambling. In an attempt to confirm this proposed presence of CH_2-species, keten was decomposed on the Co/Al_2O_3 catalyst at 450 °C, followed by treatment with deuterium at 430 °C. The deuterium distribution in the methane obtained (run 4) is similar to that in runs 1 and 2, i.e. CH_4 and CH_2D_2 were prominent.

In run 5, carbon was deposited from CD_4 at 430 °C; hydrogenation with H_2 gave CD_4 and CD_2H_2. This result and those from runs 1—4 suggest that CH_2- or CD_2-species formed on the cobalt catalysts by the decomposition of CH_4 or CD_4 are quite reactive with hydrogen. However, the details of the mechanism of the formation of CH_4 or CD_4 in these experiments on the Co/Al_2O_3 catalyst are ambiguous at present. In all the experiments the carbonaceous species formed on the cobalt catalysts at 430 °C are mainly in the form of the less reactive free carbon; CH_2-species comprise only a small portion of the deposited carbon.

The products of the hydrogenation of the carbon-deposited Co/C catalyst were found to contain ethylene and propene as well as methane, whereas the hydrogenation of Co/C on which no carbonaceous species had been deposited yielded only methane and no ethylene or propene; i.e. the gasification of solid carbon under the same experimental conditions gave only methane. To study the intermediate species for formation of methane as well as of higher hydrocarbons, carbidic carbon was treated with deuterium. By performing the Boudouard reaction with D_2 at 210 °C, carbidic carbon can be prepared on the cobalt catalyst, which is more reactive with D_2 than the free carbon. The methane obtained from treatment of the carbidic carbon at 210 °C showed a rather random deuterium distribution as shown in run 6;

i.e., a disproportionate amount of CH_2D_2 was not formed as it was in runs 1, 2, and 3. Of more interest is the fact that the methane obtained from treatment with deuterium of the solid carbon support for the Co catalyst (run 7) at 430 °C has a very similar deuterium distribution to that obtained from treatment of the carbidic carbon catalyst at 210 °C (run 5).

This suggests that the hydrogenation of the solid carbon to methane may occur via carbidic carbon formed on the cobalt surface. The contribution of the carbidic carbon in the formation of higher hydrocarbons such as C_2H_4 and C_3H_6 was confirmed by depositing ^{13}C from $^{13}CH_4$ on a Co/C catalyst. The methane and ethylene obtained in the first 10 min at 430 °C were analysed by mass spectroscopy. A substantially different ^{13}C content was observed: 31% in the methane compared with 83% in the ethylene (Table 2). This shows that the precursor species for methane from solid carbon do not undergo scrambling with the precursor species for ethylene. Provided that the hydrogenation of solid carbon as well as of free carbon proceeds via formation of carbidic carbon, the CH_2-species is an important precursor for methane as well as for olefins, whereas the carbidic carbon yields only methane (Scheme 1). Formation of propene in the hydrogenation of the carbon-deposited cobalt catalyst suggests a homologation-type reaction between CH_2-species
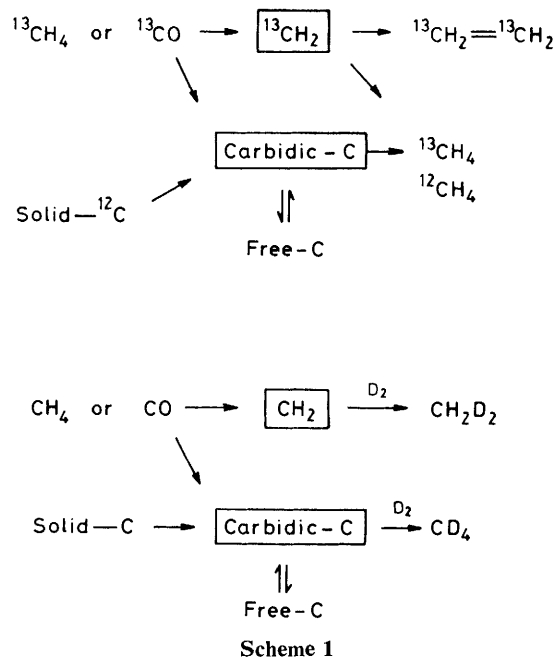
Table 2. Isotopic distribution in the methane and ethylene obtained in the hydrogenation of a ^{13}C-deposited Co/C catalyst at 430 °C with 65 Torr of H_2.

Methane (%)		Ethylene (%)		
$^{12}CH_4$	$^{13}CH_4$	$^{12}C_2H_4$	$^{12}CH_2={}^{13}CH_2$	$^{13}C_2H_4$
69	31	1	32	67

Scheme 1

and C_2H_4 as occurs on W-metal,[6] Mo- and W-complexes,[7] Ti-complexes,[8] and Pt-complexes.[9]

We have recently found that the reaction of $^{12}C_2H_4$ with a ^{13}C-deposited cobalt catalyst yielded propene containing one ^{13}C-atom, which supports the metallacyclobutane mechanism proposed for the homologation reaction.[6]

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