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# METHYLENE SPECIES AS PIVOTAL PRECURSORS FOR HYDROCARBON FORMATION REACTIONS ON COBALT CATALYSTS

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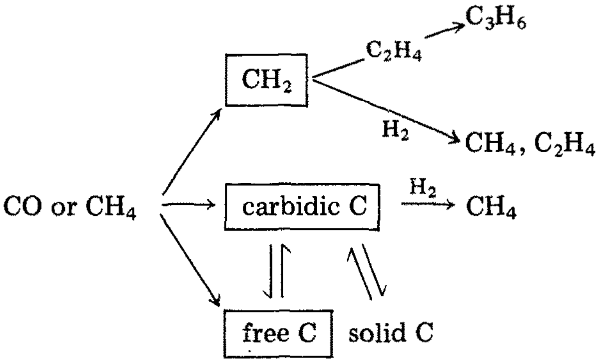
## Summary

The presence of $CH_2$ species on a carbon-deposited cobalt catalyst has been demonstrated by the disproportionate formation of $CH_2D_2$ in the reaction with $D_2$. Hydrogenation of a $^{13}C$-deposited Co/C catalyst at 430 °C yielded methane and a trace amount of ethylene, and it was found that the $^{13}C$ content was substantially different in methane (31%) from that in ethylene (83%). If ethylene was brought into contact with the $^{13}C$-deposited Co/C catalyst at 180 °C, ($^{13}C_1$)-propene was predominantly formed via a homologation reaction. These results may be summarized as follows:



It is known that the reactions of the $CH_2$ species on Co catalysts are quite similar to those of the $\mu^2$-$CH_2$ ligand in dinuclear complexes.

## Introduction

Since the first discovery of a terminal methylene complex, ($\eta$-Cp)$_2$-Ta($CH_3$)$CH_2$, by Schrock *et al.* [1] and of a bridging methylene complex, ($\eta$-Cp)$_2$(CO)$_4$Mn$_2$($\mu$-$CH_2$), by Herrmann *et al.* [2] in 1975, many transition

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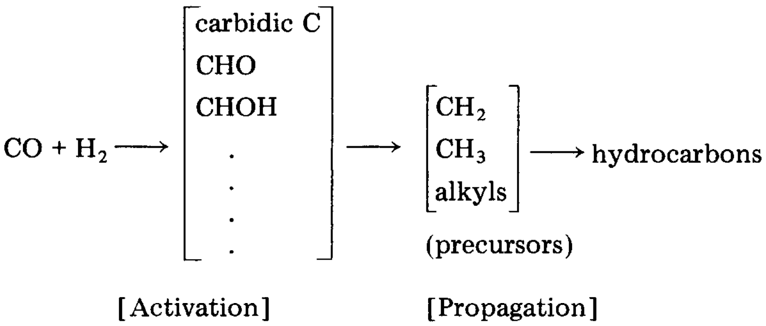
metal alkylidene complexes have been prepared. The characteristic reactivity of these alkylidene ligands is particularly interesting with respect to olefin metathesis, homologation and the Fischer–Tropsch synthesis. Further, if $CH_2$ species are formed on the transition metal catalysts by the decomposition of $CH_2N_2$, hydrocarbons similar to those afforded by the Fischer–Tropsch reaction are formed in the presence of hydrogen [3].

The selective synthesis of desired olefins from CO and $H_2$ could be the final goal of hydrocarbon synthesis reactions. Provided that methylene and alkyl species are the precursors for the hydrocarbon formation reaction, the hydrocarbon synthesis reaction from CO and $H_2$ may be characterized by the activation of the reactant molecules and propagation via precursor species as described below.



$$CO + H_2 \longrightarrow \underset{\text{[Activation]}}{\begin{bmatrix} \text{carbidic C} \\ CHO \\ CHOH \\ \cdot \\ \cdot \\ \cdot \\ \cdot \end{bmatrix}} \longrightarrow \underset{\substack{\text{(precursors)} \\ \text{[Propagation]}}}{\begin{bmatrix} CH_2 \\ CH_3 \\ \text{alkyls} \end{bmatrix}} \longrightarrow \text{hydrocarbons}$$

If the reaction proceeds according to this mechanism, the synthesis of hydrocarbons may be controlled by propagation processes involving alkyls and methylene as precursors; some evidence which may support this speculative reaction mechanism are presented in this paper.

## Experimental

The reaction was carried out in a closed circulation system either 260 ml or 275 ml in volume. Co/$\gamma$-$Al_2O_3$ (Co: 6.0 wt.%) and Co/C (Co: 14.7 wt.%) were prepared by impregnating $\gamma$-$Al_2O_3$ or granular pure carbon (10 - 30 mesh, for chemical analysis) with cobalt nitrate solution. The catalysts were dried in air at 90 °C, evacuated at 450 °C for 3 h and reduced. Carbonaceous species were deposited on the catalysts by decomposing $CH_4$ or $C_2H_6$, or by the Boudouard reaction, and $^{13}C$ deposits were obtained by the decomposition of $^{13}CH_4$ ($^{13}C$: 90%) or $^{13}CO$ ($^{13}C$: 88%) obtained from MSD Japan.

The deposition of carbonaceous species on a cobalt catalyst at 200 °C produces mainly carbidic carbon. Free carbon is mainly formed by the decomposition of $CH_4$ or by the Boudouard reaction at 430 °C, since carbidic carbon on cobalt catalysts is unstable at temperatures higher than *ca.* 230 °C [4]. Carbidic carbon is far more reactive towards hydrogen than free carbon deposits. The reactive carbidic carbon can be removed from the catalyst surface by either reaction with hydrogen or thermal decomposition. In this work, the carbidic carbon was removed by decomposition at 430 °C, thus enabling the demonstration of the particular reactions of the $CH_2$ species which are formed concomitantly on the catalyst during the deposition of carbonaceous species.

## Results and discussion

The treatment of the Co/C catalyst at 430 °C yielded only methane, which was formed by the hydrogenation of the carbon support. In contrast, when carbonaceous species were deposited on the catalyst through the decomposition of methane or via the Boudouard reaction at 430 °C, trace amounts of ethylene and propene as well as of methane were produced by treatment with $H_2$ at 430 °C. These facts indicate that the carbonaceous species deposited on the cobalt catalyst involve precursor species which are pivotal for ethylene and propene formation reactions, while solid carbon merely gives methane.

The carbonaceous species may be composed of $CH_x$, carbidic carbon and/or free carbon in general, and these species may contribute differently to the hydrocarbon formation processes. It is known that cobalt carbide is unstable at temperatures higher than 230 °C [4], so that carbidic carbon (if formed on the cobalt catalyst) may decompose rapidly to free carbon and cobalt at 430 °C. Accordingly, the carbon-deposited cobalt catalysts prepared at 430 °C probably have little carbidic carbon on the catalyst.

Since carbidic carbon is active for the reaction with $H_2$ but free carbon is entirely inactive, it is unlikely that free carbon formed on the catalyst could participate in olefin formation processes. The question therefore arises as to what is the precursor for olefin formation.

### *Evidence for $CH_2$ species*

The carbonaceous species prepared by the Boudouard reaction or by decomposition of $CH_4$ on Co/C or Co/$Al_2O_3$ catalysts at 430 °C may be composed of less reactive free carbon and small amounts of $CH_x$ species. On exposure of this carbon-deposited catalyst to hydrogen, however, methane was rapidly evolved during the initial stages of the treatment. To identify the reactive species which can remain on carbon-deposited cobalt catalysts up to 430 °C, the catalysts were treated with deuterium at a pressure of *ca.* 30 mmHg and the methane formed during the initial 30 s of reaction was subjected to mass spectroscopic analysis. The data listed as run 1 in Table 1 relate to the Co/C catalyst, where the carbon was deposited by decomposing $CH_4$ at 430 °C and evacuating for *ca.* in 1 h before reaction with $D_2$. It is clear that a disproportionate amount of $CH_2D_2$ (60%) was formed during the initial stages of deuteration of the carbon-deposited Co/C catalyst. A similar disproportionate formation of $CH_2D_2$ was observed on the Co/$Al_2O_3$ catalyst as shown in Table 2. Deuteration of the carbon-deposited Co/$Al_2O_3$ catalysts

TABLE 1

Deuterium distribution in methane obtained from the treatment of carbon-deposited Co/C catalyst with $D_2$

| Run No. | Co/C catalyst | | Deuterium distribution (%) | | | | |
|---|---|---|---|---|---|---|---|
| | Deposited from (temp.) | Treated with (temp.) | $CH_4$ | $CH_3D$ | $CH_2D_2$ | $CHD_3$ | $CD_4$ |
| 1 | $CH_4$ (430 °C) | $D_2$ (430 °C) | 9 | 10 | 60 | 14 | 7 |
| 2 | CO (210 °C) | $D_2$ (210 °C) | 0 | 1 | 14 | 34 | 51 |
| 3 | none | $D_2$ (430 °C) | 2 | 2 | 8 | 39 | 49 |

TABLE 2

Deuterium distribution in methane obtained from the treatment of carbon-deposited $Co/Al_2O_3$ with $D_2$ or $H_2$

| Run No. | $Co/Al_2O_3$ catalyst | | Deuterium distribution (%) | | | | |
|---|---|---|---|---|---|---|---|
| | Deposited from (temp.) | Treated with (temp.) | $CH_4$ | $CH_3D$ | $CH_2D_2$ | $CHD_3$ | $CD_4$ |
| 1 | $CH_4$ (430 °C) | $D_2$ (430 °C) | 60 | 7 | 24 | 8 | 1 |
| 2 | $CD_4$[a] (430 °C) | $H_2$ (430 °C) | 8 | 10 | 56 | 4 | 22 |
| 3 | CO (430 °C) | $D_2$ (430 °C) | 38 | 15 | 34 | 8 | 5 |

[a] Isotope distribution in the methane used: $CH_4$, 6%; $CH_3D$, 5%; $CH_2D_2$, 10%; $CHD_3$, 3%; $CD_4$, 76%.

prepared either by the decomposition of $CH_4$ at 430 °C (run 1) or by the Boudouard reaction at 430 °C (run 3) yielded a disproportionate amount of $CH_2D_2$ [5]. It is noteworthy that an unexpectedly large amount of $CH_4$ was also formed at the same time during deuteration of the carbon-deposited $Co/Al_2O_3$ catalysts in runs 1 and 3 of Table 2.

As the deuteration was performed with excess $D_2$, the yields of $CH_4$ and $CH_2D_2$ listed in Tables 1 and 2 certainly deviate from a statistical distribution. A further check on this curious formation of $CH_4$ during deuteration of the carbon-deposited $Co/Al_2O_3$ catalyst was performed by using $CD_4$ instead of $CH_4$ at 430 °C and was followed by reaction with $H_2$. In this case, the yields of $CD_4$ and $CH_2D_2$ were prominent, as shown by the data for run 2 in Table 2.

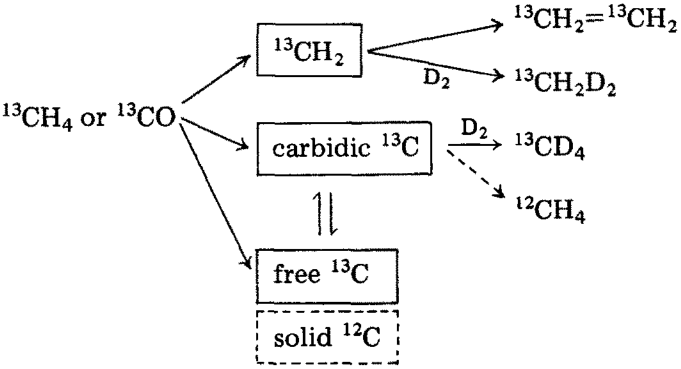
Such disproportionate formation of $CH_4$ or $CD_4$ was only characteristic of the $Co/Al_2O_3$ catalyst; deuteration of the carbon-deposited Co/C catalyst merely afforded a disproportionate amount of $CH_2D_2$ as shown in Table 1 (run 1). The mechanism of this curious $CH_4$ or $CD_4$ formation on the $Co/Al_2O_3$ catalyst remains to be established at present, but it may be safely said that the reactive species remaining on the carbon-deposited cobalt catalysts at 430 °C involve methylene ($CH_2$) species. These species formed on carbon-deposited cobalt catalysts are quite reactive with hydrogen and give $CH_2D_2$ on reaction with $D_2$, but free carbon which is the main component of the deposition of carbon at 430 °C is far less reactive.

On the other hand, carbidic carbon which is prepared by decomposing $CH_4$ or by the Boudouard reaction on the cobalt catalysts at 210 °C is more reactive with hydrogen than free carbon, and the reaction of carbidic carbon with $D_2$ at 210 °C gave a somewhat random distribution of deuterium atoms in the methane as shown by the results of run 2 of Table 1, where the carbidic carbon was prepared via the Boudouard reaction.

Random distribution of deuterium in the methane from carbidic carbon contrasts with the disproportionate amount of $CH_2D_2$ formation from the carbon-deposited catalysts prepared at 430 °C. It is also interesting that the deuteration of the solid carbon support by the cobalt catalyst at 430 °C yielded methane with a random deuterium distribution as shown by run 3 in Table 1. In view of these two facts, it would be interesting to see whether carbidic carbon can also contribute to the formation of olefins such as ethylene and propene.

To study this problem, a $^{13}C$-deposited Co/C catalyst was prepared by decomposing $^{13}CH_4$ ($^{13}C$: 90%) at 430 °C. The methane and ethylene obtained during the first 10 min of hydrogenation with 65 mmHg of $H_2$ were analyzed by mass spectrometry. It was found that the $^{13}C$ content was substantially different in ethylene (83%) from that in methane (31%) as shown in Table 3. The $^{13}C$ content indicates that ethylene is formed entirely by the dimerization of $^{13}CH_2$ species and that these species do not undergo any scrambling with the precursors for $^{12}CH_4$ arising from the solid carbon support.

On the basis of these results, the characteristic reactivity of deposited carbonaceous species such as $CH_2$ species, carbidic carbon and free carbon, as well as of the solid carbon support, may be described by the following scheme:



### *Homologation reactions involving $CH_2$ species*

As demonstrated above, $CH_2$ species are pivotal precursors for ethylene formation on cobalt catalysts. This suggests that the propagation reaction of

TABLE 3

Distribution of $^{13}C$ in the methane and ethylene obtained from the treatment of a $^{13}C$-deposited Co/C catalyst with 5 mmHg of $H_2$ at 430 °C

| Co/C catalyst | | $^{13}C$ distribution (%) | | | | |
|---|---|---|---|---|---|---|
| Deposited from (temp.) | Treated with (temp.) | Methane | | Ethylene | | |
| | | $^{12}CH_4$ | $^{13}CH_4$ | $^{12}C_2H_4$ | $^{12}CH_2{=}^{13}CH_2$ | $^{13}C_2H_4$ |
| $CH_4$ (430 °C) | $H_2$ (430 °C) | 69 | 31 | 1 | 32 | 67 |

TABLE 4

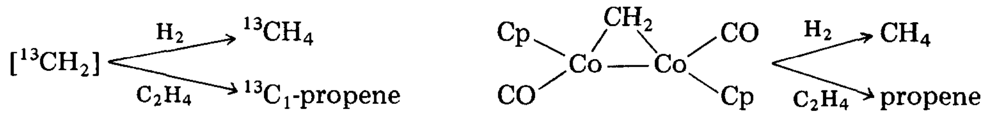
Distribution of $^{13}C$ in the propene and n-butane obtained from the treatment of a $^{13}C$-deposited Co/C catalyst with ethylene at 180 °C.

| Co/C catalyst | | $^{13}C$ distribution (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Deposited from (temp.) | Treated with (temp.) | $CH_4$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | n-$C_4H_{10}$ | i-$C_4H_{10}$ |
| $^{13}CH_4$ (430 °C) | $C_2H_4$ (180 °C) | 3.2 | — | 57.8 | 1.8 | 0.7 | 36.1 | 0.5 |
| | | | | | $[^{13}C_0]/[^{13}C_1]/[^{13}C_2]$ | | $[^{13}C_0]/[^{13}C_1]$ | |
| | | | | | 14.3:84.5:0.3 | | 96.4:3.6 | |

ethylene to higher oelfins is a further interesting problem. To confirm reaction of the $CH_2$ species with ethylene, a $^{13}C$-deposited Co/C catalyst, having been prepared by decomposing $^{13}CH_4$ at 430 °C, was treated with ethylene at 180 °C. Treatment with ethylene produced propene as well as n-butane and isobutane, as shown in Table 4. The relative amounts of n-butane to propene depended on the batches of catalysts employed and on the pretreatment conditions. The formation of n-butane suggests that propene may be formed either by homologation of ethylene or through the decomposition of n-butene which may be formed by the dimerization of ethylene, since the decomposition of 2-butene can occur on this catalyst at 180 °C.

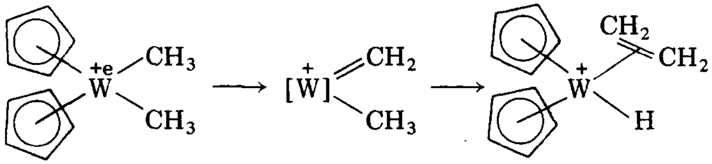
The precursors for propene and n-butane can be identified from the distribution of $^{13}C$ atoms in these materials. As shown in Table 4, the propene contained precisely one $^{13}C$ atom per molecule while the n-butane contained almost no $^{13}C$ atoms at all. Accordingly, it may be concluded that the propene is formed by reaction of the $^{13}CH_2$ species with ethylene over the carbon-deposited Co/C catalyst, while the n-butane is formed by dimerization of ethylene with subsequent hydrogenation. Carbidic carbon is active for reaction with $H_2$, but it is not clear whether carbidic carbon can contribute to the homologation reaction.

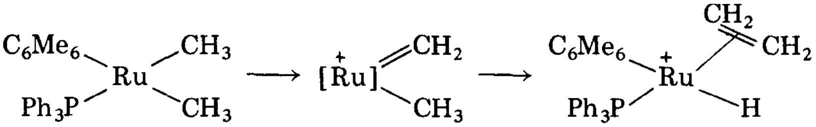
Recently, spectroscopic evidence for the formation of bridging $CH_2$ species on a Ru (001) surface has been obtained through the use of EELS [6]. It is noteworthy that the reaction characteristics of $CH_2$ species formed on the cobalt catalyst are quite similar to the reactions of the $\mu^2$-$CH_2$ ligand in dinuclear complexes [7 - 9] as depicted in the following scheme:



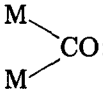
The reactions of carbene ligands are compared on occasions to those of carbonyl ligands, but the reactivity characteristics of these two ligands are quite different.

As far as we are aware, no substantial evidence to support differing reactivity for terminal and bridging carbonyls has been reported, although the reactivities of terminal carbene and bridging carbene ligands are entirely different. It has been suggested that the insertion or migration of an alkyl ligand onto a terminal carbene ligand is favoured when the central metal atom is electrophilic as in the following insertion reactions [10]:



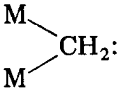


On the basis of these facts, it may be concluded that a pivotal precursor for the homologation reaction could be the bridging $CH_2$ species while the terminal $CH_2$ species is a feasible precursor for olefin metathesis, *i.e.*

M=CO, 

: no appreciable differences in reactivity;

M=$CH_2$: active precursor for olefin metathesis;



: active precursor for olefin homologation.

If this is the case, the carbidic carbon could contribute to the homologation reaction provided that it can change to the bridging $CH_2$ species. In other words, the catalytic synthesis of higher hydrocarbons by direct hydrogenation of solid carbon could be established if the catalyst had the ability to convert the carbidic carbon to the bridging $CH_2$ species.

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