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AN OXYGENATED C_1 INTERMEDIATE IN THE FISCHER-TROPSCH SYNTHESIS ON COBALT

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The active surface carbon in the Fischer-Tropsch synthesis over a cobalt catalyst spends most of its time on the surface as an intermediate which is common to both methanol and hydrocarbon products. This intermediate is distinct from CO_{ads} but contains the original C-O bond.

In the CO-H_2 reaction over transition metal catalysts, oxygenated and non-oxygenated hydrocarbon products of various carbon numbers are produced [1–4]. The point at which the CO bond is broken during hydrocarbon formation, the role of oxygenated carbon-containing surface intermediates in the reaction mechanism, and the relationship between the pathways leading to the two sets of products are all unresolved mechanistic issues. This paper contains evidence which shows that at the reported conditions on a supported cobalt catalyst, most of active carbon on the surface during the Fischer-Tropsch synthesis is a common precursor for both the hydrocarbon and methanol products. Furthermore, this intermediate contains the original C-O bond from the CO reactant.

These conclusions were reached by combining the results of a previous isotopic transient study of the higher hydrocarbon synthesis pathway on this catalyst with additional data on the methanol coproduct. In a study of the appearance of ^{13}C in hydrocarbon products after a $^{12}CO–^{13}CO$ switch at reaction steady state it was shown that during the reaction most ($> 95\%$) of the active carbon on a supported cobalt catalyst exists as a C_1 precursor to hydrocarbon chain growth rather than in the form of growing chains [5]. At the conditions of this study minor quantities of methanol and other oxygenated compounds are also produced. Selectivity to methanol and higher alcohols depends on temperature, pressure, and gas composition [6–8]. Oxygenated products are subject to secondary reactions [9,10] which are responsible in part for the selectivity behavior. The simultaneous study of both the hydrocarbon and oxygenated products yields information about the relationship between the two pathways.

The experimental details have been given previously [5]; the reaction conditions and catalytic productivity are summarized in table 1. The catalyst contained

Table 1
Reaction conditions and rates

Temperature, K	475
Pressure, kPa	90
H_2/CO ratio	2
TOF [a]	1.5×10^{-2}
CO conversion	0.04
Production rates (nmol/s g)	
CH_4	56
C_2	11.5
C_3 [b]	16
C_4	14
C_5	12
C_6	9.7
CH_3OH	0.8

[a] CO converted/surface cobalt atom/second.
[b] C_3-C_5 product contained > 80% 1-enes.

23 wt% Co on a SiO_2 support with 2.8% of the cobalt atoms surface exposed. The isotopic transient was measured by GCMS and NMR analysis of portions of the product gas trapped at various times after an abrupt change from ^{12}CO to ^{13}CO in the reactant.

The conclusions of this article rest on the findings in [5] and the following two observations:

1. The pathway to methanol proceeds without dissociation of the original C-O bond from the carbon monoxide.

This is believed to be true in general for catalysts which primarily produce methanol, as there is a general inverse correlation of the ability of a particular metal to dissociate CO with its methanol selectivity [11,12]. Proof of a non-dissociative pathway on a Rh/TiO_2 catalyst was given in a double-label experiment reported by Takeuchi and Katzer [13]. In their experiment no cross-labelled methanol was produced from a mixture of $^{13}C^{16}O$ and $^{12}C^{18}O$. Such a cross-labelling experiment was performed on the cobalt catalyst here by reacting CO

Table 2
Mass spectral data for methanol produced from the hydrogenation of 50% $^{12}C^{16}O$, 44.5% $^{13}C^{16}O$ and 5.5% $^{13}C^{18}O$ [a]

Mass pair	Measured intensity ratio	Expected ratio	
		Non-dissociated	Scrambled
$34^+/35^+$	1.59+0.08	1.56	2.70
$33^+/35^+$	0.91+0.07	0.92	2.08

[a] Measured by GCMS under the reaction conditions in table 1.

containing $^{12}C^{16}O$, $^{13}C^{16}O$ and $^{13}C^{18}O$. The appearance of $^{12}CH_3{}^{18}OH$ from such a mixture is a measure of the amount of CO bond breaking. Table 2 compares measured mass spectral intensity ratios with those expected from both a non-dissociative pathway and one which scrambles the isotopes [14]. These data indicate that on this cobalt catalyst, all the intermediates in the methanol synthesis pathway contain the original C-O bond. No CO scrambling was detected during the experiments ($< 0.1\%$ $^{12}C^{18}O$ at the reactor outlet).

2. The surface residence times of the carbon precursors of methanol and hydrocarbon products are very similar

Figure 1 compares the isotopic transient of the carbon in methanol with that of the hydrocarbon products. The detailed behavior of the isotopic replacement in the hydrocarbons in discussed in [5]. Figure 1 reproduces the decay of ^{12}C content in the butene product at the conditions of this experiment. As previously reported, this transient is common to all carbon atoms at all positions in the C_2-C_6 hydrocarbon products and reflects the fact that carbon surface residence times and concentrations are dominated by a C_1 precursor to chain growth. Also included in figure 1 are NMR data for the ^{12}C decay in the methanol product. This limited data set shows that the isotopic contents of the two products track each other quite closely, although there is an indication of a slight lag in the ^{12}C

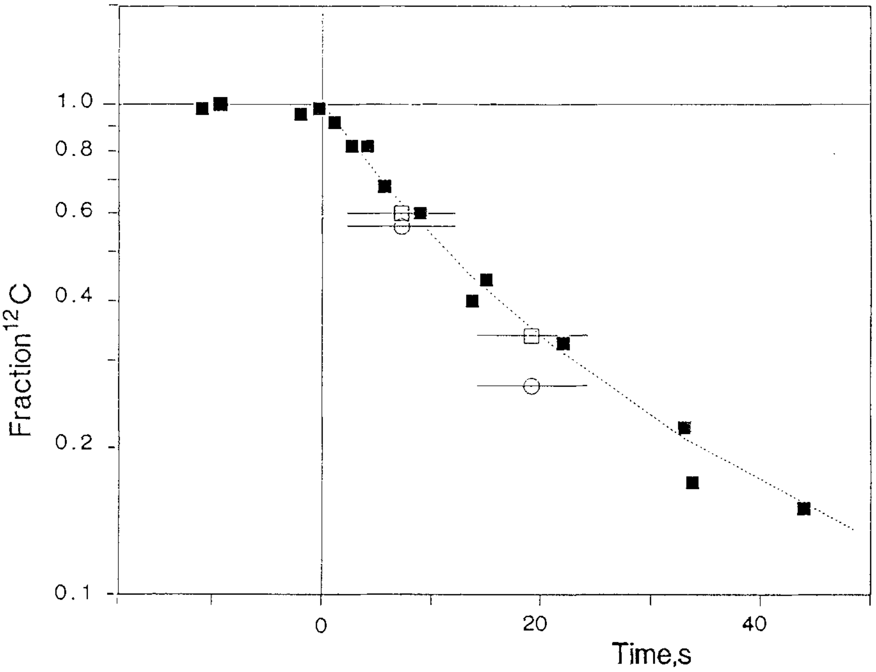

Fig. 1. Disappearance of ^{12}C in CO-H_2 reaction products after an abrupt switch from ^{12}CO to ^{13}CO in the reactants: [] = C_4 hydrocarbons by GCMS, -[]- = C_3-C_6 hydrocarbons by NMR (all internal positions), -O- = CH_3OH by NMR. Reaction conditions are given in table 1.

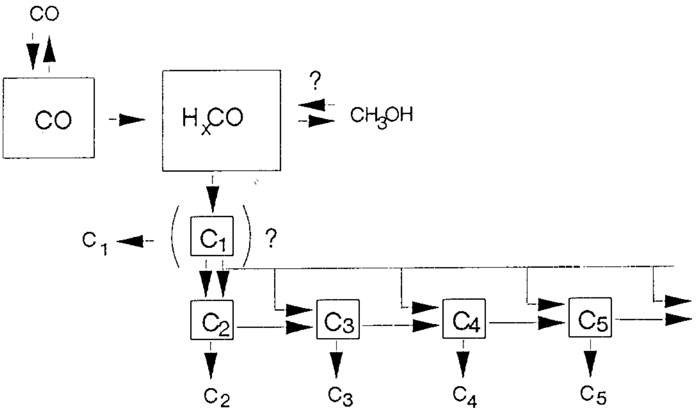

Fig. 2. Compartmental diagram of proposed reaction pathway for CO hydrogenation on cobalt. Each compartment represents an intermediate (or group of intermediates in partial equilibrium). The relative sizes of the compartments qualitatively represent the relative lifetimes of the intermediates.

decay in the hydrocarbon products relative to methanol. The match in surface lifetimes for the carbon in both products leads to the supposition that both products arise from a common intermediate (or intermediates). The match in residence time is only a necessary and not a sufficient condition for this conclusion. However other mechanistic interpretations require a coincidental match in surface residence times for two parallel product channels.

A scheme such as the simple compartmental flow diagram shown in fig. 2 illustrates the conclusions here. The common intermediate pool is labelled H_xCO to distinguish it from the majority state of adsorbed CO (CO_a) and speculate on the possibility that it contains hydrogenated species ($x = 0$–4). Adsorbed CO is displayed by gas phase CO from this cobalt catalyst [5] and others [15,16] in less than one second at these conditions. The large relative size of the H_xCO compartment reflects that fact that the common intermediate comprises most ($> 95\%$) of the active carbon inventory on the surface during the reaction. The possibility of methanol readsorption is indicated by reverse arrows in fig. 2.

Several observations support the notion that the intermediate is adsorbed on the metal surface rather than on the support. Although they arrived at different conclusions regarding chain growth rates, Biloen and co-workers observed similar overall carbon residence times to ours in isotopic transient studies over a precipitated (unsupported) cobalt catalyst which produced a similar hydrocarbon distribution [17]. Furthermore, the temperature dependence of the carbon residence time on this catalyst closely follows that of the overall reaction rate on many catalysts [5].

Oxygenated intermediates have been proposed in Fischer-Tropsch synthesis since the work of Elvins and Nash [6]. In some proposed mechanisms CO is hydrogenated before it dissociates to an active C_1 intermediate [18–20]. In others hydrocarbon chain growth involves an oxygenated monomer [1,9] including CO_a [21,22]. Infrared and surface science studies have shown the plausibility of various oxygenated intermediates. This study shows that an oxygenated intermediate is likely involved in the steady state reaction pathway on this Co catalyst and that its reaction is the slow step in the formation of both methanol and the hydrocarbons.

It is not possible to distinguish further among the proposed mechanisms from these data alone. The pathways connecting the common intermediate to the products can involve any number of subsequent steps if the lifetimes of these subsequent intermediates are a small fraction of the overall surface residence time. Because of the possibility of intervening species with short lifetimes, many of the previously proposed schemes of higher hydrocarbon formation are consistent with the data. Thus the actual hydrocarbon chain building monomer can be chemically different from H_xCO and may not be oxygenated itself (a speculation indicated in fig. 2 by the tentative inclusion of C_m). The slightly longer residence time of the hydrocarbon carbons is consistent with a separate intermediate although another carbon reservoir could be responsible for the added residence time [5,23]. We find that there is at least one oxygen-containing intermediate in the pathway after COa, a conclusion seemingly at odds with CO dissociation as the first mechanistic step as proposed in Fischer's carbide theory [24]. However, since we have not shown that the intermediate is hydrogenated, it could be a strongly bound, non-displaceable CO such as the type recently seen on transition metal surfaces [25] and still conform with the carbide theory. The identification of this intermediate and its exact role in the mechanism awaits the *combination* of kinetic and spectroscopic investigations [26].

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References

[1] R.B. Anderson, *The Fischer-Tropsch Synthesis* (Academic Press, New York, 1984).
[2] M. Smutek and S. Cerny, Int. Rev. Phys. Chem. 3 (1983) 263.
[3] P. Biloen and W.M.H. Sachtler, Adv. Cat. 30 (1983) 165.
[4] M.A. Vannice, Catal. Rev.-Sci. Eng. 14 (1976) 153.
[5] C.A. Mims and L.E. McCandlish, J. Phys. Chem. 91 (1987) 929.
[6] O.C. Elvins and A.W. Nash, Nature, Lond. 118 (1926) 154.
[7] H. Pichler, Adv. Catal. 4 (1952) 271; Erdol. u. Kohle-Erdgas-Petrochem-Brennstoff-Chem. 26 (1973) 625.
[8] H. Koch, H. Pichler and H. Kolbel., Brennstoff-Chem. 16 (1935) 382.

[9] W.K. Hall, R.J. Kokes and P.H. Emmett, J. Am. Chem. Soc. 82 (1960) 1027.

[10] J.T. Kummer and P.H. Emmett, J. Am. Chem. Soc. 75 (1953) 5177;
W.K. Hall, R.J. Kokes and P.H. Emmett, J. Am. Chem. Soc. 79 (1957) 2983, 2989.

[11] J. Rabo, A.B. Risch and M.L. Poutsma, J. Catal. 53 (1978) 295.

[12] V. Ponec and W.A. van Barneveld, Ind. Eng. Chem. Prod. Res. Dev. 18 (1979) 268.

[13] A. Takeuchi and J.R. Katzer, J. Phys. Chem. 85 (1981) 937.

[14] The mass spectra were obtained by GCMS. The electron energy in the ionizer was 40 eV which produced the following fragmentation pattern for CH_3OH: $CH_3OH^+ = 1.0$, $CH_3O^+ = 1.67$, $CH_2O^+ = 0.20$, $CHO^+ = 1.13$.

[15] P. Biloen, J.N. Helle, F.G.A. van den Berg and W.M.H. Sachtler, J. Catal. 81 (1983) 450.

[16] Y. Kobori, H. Yamasaki, S. Naito, T. Onishi and K. Tamaru, J. Chem. Soc., Faraday Trans. 1, 78 (1982) 78, 1473;
H. Yamasaki, Y. Kobori, S. Naito, T. Onishi and K. Tamaru, J. Chem. Soc., Faraday Trans. 1, 77 (1981) 2913.

[17] X. Zhang and P. Biloen, J. Catal. 98 (1986) 468.

[18] Ya. T. Eidus, Izv. Akad. Nauk. SSSR, otd. khim. nauk. (1943) 65.

[19] S. Hamai, Bull. Chem. Soc. Japan 16 (1941) 213.

[20] M.A. Vannice, J. Catal. 37 (1975) 462.

[21] G. Henrici-Olive and S. Olive, Angew. Chem. Int. Ed. Engl. 15 (1976) 136.

[22] I. Wender, S. Friedman, W.A. Steinber and R.B. Anderson, Chem. Ind. (London) (1958) 1694.

[23] Y. Soong, K. Krishna and P. Biloen, J. Catal. 97 (1986) 330.

[24] F. Fischer and H. Tropsch, Brennstoff Chemie 7 (1926) 97.

[25] D.W. Moon et al., J. Am. Chem. Soc. 107 (1985) 4363; Surf. Sci. 180 (1987) L123;
N.D. Shinn and T.E. Madey, J. Chem. Phys. 83 (1985) 5928.

[26] P. Biloen, J. Mol. Cat. 21 (1983) 17.