Catalysis Letters 1 (1988) 159–168

THE HYDROGENATION OF CO OVER MOLYBDENUM/ALUMINA IN THE PRESENCE OF ETHYLENE; COUPLING OF OLEFIN METATHESIS AND CO HYDROGENATION

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Received 5 April 1988

Three reactions, CO hydrogenation, metathesis of C_2H_4 and CO hydrogenation in the presence of C_2H_4, have been investigated on $Mo(+2)/Al_2O_3$ under identical experimental conditions. The products of hydrogenation reactions were methane, ethylene and propylene. The results show that the initial rate of propylene formation for CO hydrogenation in the presence of ethylene is much larger, by a factor of 7, than the sum of the rate of propylene formation for CO hydrogenation and metathesis alone. Furthermore, it was found that ^{13}C labelled propylene was formed in the hydrogenation of ^{13}CO in the presence of ethylene. These results, taken as a whole, suggest that the same intermediate is formed in both CO hydrogenation and metathesis of ethylene, and that these intermediates can be either incorporated into ethylene and higher hydrocarbons by polymerization or incorporated into ethylene to form propylene via olefin metathesis.

1. Introduction

The hydrogenation of carbon monoxide to form a range of hydrocarbons, and in some cases oxygenated hydrocarbons, is perhaps the most extensively studied catalytic reaction. It is catalyzed by virtually all transition metals [1–4]; the product distribution varying, dependent on which transition metal is used as a catalyst. The mechanism, in cases in which exclusively non-oxygen containing hydrocarbons are produced, appears to involve the dissociation of carbon monoxide into adsorbed carbon and oxygen atoms. The oxygen is rapidly titrated from the surface by hydrogen, and the carbon atoms are partially hydrogenated to form so called "carbidic" carbon, which probably consists of adsorbed CH_x species [1,5]. The final product distribution from the catalyst depends on the relative rate at which these species polymerize at the surface versus the rate at which the surface species hydrogenate. A theoretical analysis of the product distribution arising from this model results in the Shultz–Flory equation, i.e. a plot of $\ln(M(p)/p)$ versus p should yield a straight line for the hydrocarbons containing p carbon atoms whose relative yield is $M(P)$. This equation is rather well obeyed in most instances [6,7,9].

In view of this model, attempts have been made, with varying degrees of success, to test it by adding ethylene to the reactants. The argument in this case is that adsorbed ethylene should form a surface species akin to a dimerized CH_x and therefore be incorporated into the growing chain. Radioactive (^{14}C labelled) ethylene was used by Hall and Emmett [8] as an additional reactant along with CO and hydrogen, and formed ^{14}C incorporation into higher hydrocarbons. Since they found a constant molar radioactivity in C_3–C_5 products, they concluded that ethylene could act as a chain growth initiator.

Dwyer and Somorjai [9] found that ethylene acted not only as a chain initiator, but also appeared to participate in chain growth. This conclusion was based on the observation that the total amount of ethylene which was converted to hydrocarbons equalled that of the C_3–C_5 fractions, and also that the chain growth probability was enhanced by the addition of ethylene.

In the following work, we have taken an analogous, but slightly different approach. That is, we have used a catalyst that is active for *both* CO hydrogenation *and* olefin meththesis. It should be mentioned that we include in the term metathesis the homologation reaction that proceeds in parallel with the scrambling of the double bond. In this reaction, for example, ethylene can react to form propylene. The metathesis reaction is proposed to proceed via an initial carbene formation, that, in the case in which ethylene is used as a reactant, implies that ethylene should dissociatively chemisorb at the catalyst surface to deposit CH_2 moieties. This species is clearly closely analogous to the surface carbide intermediate proposed in the CO hydrogenation reaction. If we assume that it is identical, in a reaction mixture containing CO, hydrogen and ethylene, and assuming that the catalyst is active for both CO hydrogenation *and* metathesis, there are two possible sources for surface CH_2 species, namely hydrogenation of CO and dissociation of ethylene. These can be distinguished experimentally by using reactants containing isotopically labelled carbon atoms.

In the mechanism proposed for olefin metathesis [11–14], ethylene can react with a surface CH_2 to form a metallocycle. This can decompose to yield ethylene leaving a surface carbene, or can alternatively form propylene, both of which can be readily hydrogenated to their saturated analogues. In a reaction mixture containing CO, hydrogen and ethylene, the surface contains a CH_x species either from CO hydrogenation or ethylene dissociation. Polymerization of these species will yield a product distribution which follows a Shultz–Flory formula. Simultaneous metathesis reaction will yield a significant enhancement of C_3 hydrocarbons, relative to that expected from the Shultz–Flory distribution.

The results presented in the following show that there is indeed a significant increase in formation of C_3 hydrocarbons from a reaction between CO, hydrogen and ethylene compared with the individual reactions, implying a common intermediate for both of them. This view is corroborated by the observed C_3 isotope distribution when ^{13}CO is used as a reactant. In view of the proposed mechanism outlined above, this common intermediate is likely to be a CH_2 species.

2. Experimental

Reactions were carried out in an all glass recirculating batch reactor. This type of apparatus has been described previously [16]. The supported catalyst could be enclosed in a furnace for catalyst pretreatment or reaction or immersed in a coolant for reactions carried out below room temperature.

The reactant mixture was recirculated at a rate of 100 cc/min, and the total reactor volume was 275 cc. CO was purified using a Matheson gas purifier and a heated column containing copper turnings. CP grade C_2H_4 and H_2 were purified using a Matheson gas purifier. Reaction products were analyzed by removing a 1 cc aliquot from the reaction mixture via a six-way valve and passing it through a gas chromatography equipped with a flame ionization detector. The column consisted of 3.5 m × 1/8″ poropak N which was capable of separating ethylene from ethane and propylene from propane.

The molybdena/alumina catalysts were prepared by evaporating $Mo(CO)_6$ onto an alumina support which had been calcined at 750 K for 12 hours *in vacuo*. The alumina supported carbonyl was further heated to 570 K for 2 hours, again *in vacuo*. This procedure leads to a catalyst in which the molybdenum has an average oxidation state of about +2 [13,18].

In addition, reactions were carried out using high-purity 13-carbon labelled CO. Following these reactions, the products were trapped in a liquid nitrogen cooled tube, and transferred to a PE RMU-6E magnetic sector mass spectrometer for analysis.

3. Results

(a) CO HYDROGENATION AND OLEFIN METATHESIS

Preliminary experiments were carried out using the above catalyst to ensure that it was active for both CO hydrogenation and olefin metathesis independently. CO hydrogenation was carried out with CO and H_2 partial pressures of 150 and 120 Torr respectively at a catalyst temperature of 573 K. Product accumulation curves are shown in fig. 1, in which the products are methane, ethane and propylene. No ethylene or propane were detected. It should be emphasized that these latter products could be detected and distinguished from ethane and propylene in the gas chromatograph. No higher hydrocarbons or oxygenates were detected. These products are exactly the same as that obtained on an Mo-foil and Mo(100) single crystals [15]. On other transition metal catalysts, such as Co/Al_2O_3, Ni/Al_2O_3, in addition to C_1, C_2 hydrocarbons, higher hydrocarbons and oxygenates are usually produced [4,10].

This product distribution is well described using a Shultz–Flory plot, with a chain growth probability factor, α, equal to 0.26 which is in reasonable agreement with values obtained on other transition metal based catalysts.

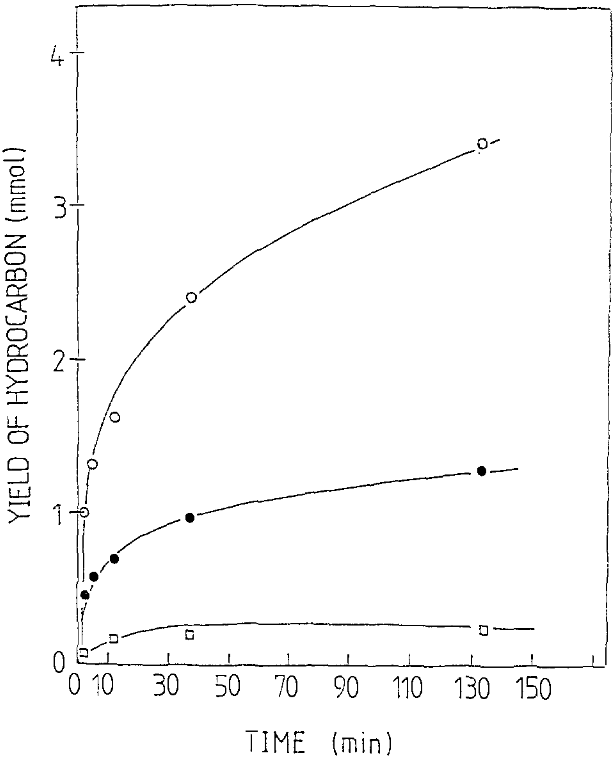

Fig. 1. Plot of concentration of hydrocarbon as a function of time for the hydrogenation of carbon monoxide over 150 mg MoO/Al_2O_3 at 573 K. methane: (o); ethylene: (●); propene: (□).

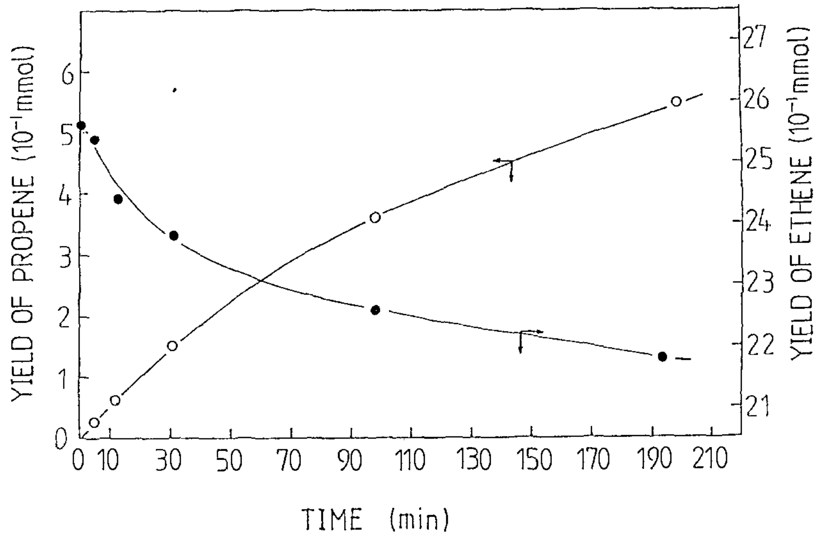

Fig. 2. Plot of concentration of hydrocarbon as a function of time for metathesis of ethylene over 300 mg MoO/Al_2O_3 at 573 K. propene: (o); ethylene: (●).

The Mo(+2)/Al_2O_3 catalyst was also an extremely selective olefin metathesis catalyst. That is, reaction of ethylene over the catalyst produced exclusively propylene. Figure 2 shows the propylene production and ethylene removal curves. The reaction temperature in this case was again 573 K, identical to that for CO hydrogenation, and the initial ethylene pressure was 30 Torr which yielded a propylene formation rate of 1.7×10^{-2} mmoles/min/gram. The rate of propylene formation was 1.7×10^{-1} mmoles/min/gram in the case of CO hydrogenation over an identical catalyst.

(b) REACTION BETWEEN CO + H_2 + C_2H_4

A reaction between CO, H_2 and C_2H_4 was carried out over an identical Mo(+2)/Al_2O_3 catalyst at 573 K using partial pressures of CO, H_2 and C_2H_4 of 150, 120, 30 Torr respectively. These conditions are identical to those of the individual CO hydrogenation and metathesis reactions.

Product accumulation curves are shown in fig. 3 and it is seen that the initial rate of propylene formation is 1.3 mmoles/min/gram, almost 8 times that for CO hydrogenation and certainly far in excess of a simple sum of olefin metathesis and CO hydrogenation. There appears to be a strong synergism between the two reactions. In addition, the rate of methane formation is decreased suggesting an *inhibition* of CO hydrogenation. In fig. 4, product distributions from a CO hydrogenation and a CO + H_2 + C_2H_4 reaction are compared.

(c) REACTION WITH ^{13}CO + H_2 + C_2H_4

Identical CO + H_2 + C_2H_4 reactions (ie. $P(CO) = 120$ Torr, $P(H_2) = 140$

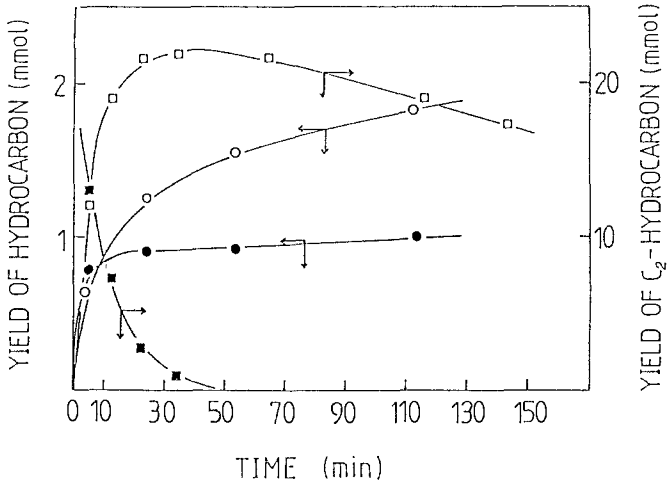

Fig. 3. Plot of concentration of hydrocarbon as a function of time for the hydrogenation of carbon monoxide in presence of ethylene over 150 mg MoO/Al_2O_3 at 573 K. methane: (○); propene: (●); ethane: (□); ethylene: (■).

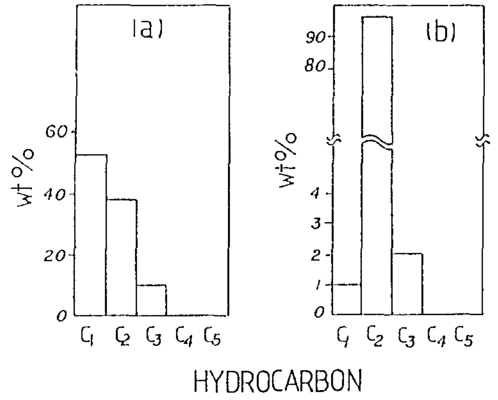

Fig. 4. Histogram of product distributions from, (a) CO hydrogenation, and (b) $CO+H_2+C_2H_4$ reaction.

Table 1
Histogram of the product distribution for the hydrogenation of ^{13}CO in presence of ethylene

Mass	Molecular formula	Mol %
42	$CH_2{=}CH{-}CH_3$	50
43	$^{13}CH_2{=}CH{-}CH_3$	6
44	$^{13}CH_2{=}^{13}CH{-}CH_3$	0
44	$CH_3{-}CH_2{-}CH_3$	25
45	$^{13}CH_2{=}^{13}CH{-}^{13}CH_3$	7
45	$^{13}CH_3{-}CH_2{-}CH_3$	0
46	$^{13}CH_3{-}^{13}CH_2{-}CH_3$ or $^{13}CH_3{-}CH_2{-}^{13}CH_3$	7
47	$^{13}CH_3{-}^{13}CH_2{-}^{13}CH_3$	5

Torr, $P(C_2H_4) = 20$ Torr, $T = 573$ K) were carried out using isotopically labelled ^{13}CO. The mass spectrum in the region of C_3 and C_2 hydrocarbons was deconvoluted using the known fragmentation patterns of propylene, propane and C_2 hydrocarbons obtained using identical conditions. Relative proportions of different C_3 hydrocarbon products are shown in table 1. Analysis of the C_2 hydrocarbons shows that approximately 60% of the product consists of ethane, and that ~ 27% of the product incorporates a single ^{13}C and about 6% two ^{13}C atoms.

4. Discussion

The data presented in figs. 1 and 2 clearly indicate that the $Mo(+2)/Al_2O_3$ catalyst is both an active CO hydrogenation and olefin metathesis catalyst. The rate of propylene formation in the case of CO hydrogenation is 1.7×10^{-1} mmoles/min/gram and in the case of olefin metathesis 1.7×10^{-2} mmoles/min/gram.

The question at issue is whether the proposed intermediates in CO hydrogenation and olefin metathesis, namely a surface "carbide" and a surface CH_2 species respectively, are chemically interchangeable. In other words, is it possible for a CH_2 species formed from CO and hydrogen to further react with ethylene to form a metallocycle and thence propylene [11,14].

If the two intermediates were chemically not at all interchangeable, it would be expected that the product distribution would merely be the sum of the reaction products from the individual reactions, presumably scaled by a factor dependent on the relative areas of the catalyst being used for each reaction. However, since the rate of propylene formation is approximately 7 times larger than the combined rate of propylene from CO hydrogenation and metathesis in the individual reactions there is clearly a synergism between both reactions and a reaction intermediate from one can be used by the other. Since the rate of methane formation is *decreased* in the $CO + H_2 + C_2H_4$ reaction while the rate of propylene formation is increased, (see fig. 3), this implies that the surface carbides formed by CO hydrogenation can react to form a metallocycle and thence form propylene, implying that at least a portion of the "carbidic" carbon formed by CO hydrogenation is a CH_2 species. These observations, in addition, provide corroborative evidence that olefin metathesis *does* proceed via a carbene intermediate.

Further evidence for coupling between the two reactions is provided by the C_3 hydrocarbon product distribution. If CO hydrogenation and olefin metathesis proceeded independently, exclusively $^{13}C_3H_6$ would be formed from CO hydrogenation, while $^{12}C_3H_6$ would be formed from olefin metathesis. While these isotope distributions are indeed observed, a significant proportion of the C_3 hydrocarbons incorporate either one or two ^{13}C atoms corroborating the notion that the two reactions are coupled. However, the majority of the C_3 products (75%) incorporate *no* ^{13}C. This could be taken as evidence that majority of the surface is active for olefin metathesis alone, and only a minor portion active for the coupled reaction. This view is at variance with the overall rate enhancement in conjunction with the observed ^{13}C incorporation into the C_3 hydrocarbons.

If it is assumed that the overall rate of C_3 hydrocarbon formation is enhanced because the surface CH_2 species are more rapidly formed by CO hydrogenation than by carbon-carbon double bond scission, the ratio of these rates should be about 7 (by approximately the factor by which the rate of propylene formation is increased). This conjecture is in line with recent data that carbenes deposited onto the surface using CH_2I_2 considerably enhance metathesis activity [17]. If the homologation reaction to form C_3 hydrocarbons were the only fate of the surface CH_2 species, the C_3 hydrocarbons should incorporate a significantly larger portion of ^{13}C than indicated in table 1.

However, olefin metathesis and homologation proceed in parallel; a surface $^{13}CH_2$ reacts with $^{12}C_2H_4$ to form a surface C_3 species, which can decompose leaving $^{12}CH_2$, and incorporating a ^{13}C into the ethylene. That is, a surface

$^{13}CH_2$, once formed can be rapidly exchanged for a $^{12}CH_2$ from gas phase ethylene, diminishing the $^{13}CH_2$ which originated from ^{13}CO and hence incorporating fewer ^{13}C atoms in the propylene. Confirmation that this reaction is proceeding is furnished by the C_2 hydrocarbon distribution which indicates that 27% of the ethylene is $^{13}C^{12}CH_4$ and 6% is $^{13}C_2H_4$.

Finally, it should be noted that in the case of CO hydrogenation and olefin metathesis above, propylene was formed with high selectivity in both cases. In the $CO + H_2 + C_2H_4$ reaction, a portion of the C_3 hydrocarbon consists of propane. A possible source of this product is via hydrogenation of some reaction intermediate.

5. Conclusions

We have reacted a mixture of $CO + H_2 + C_2H_4$ over a supported $Mo(+2)/Al_2O_3$ catalyst which is active for both CO hydrogenation and olefin metathesis. Both the final product distribution and an analysis of the ^{13}C distribution in C_3 hydrocarbons from a reaction with isotopically labelled CO indicate a synergism between the two reactions. These results strongly imply that the reactions have a common intermediate which is likely to be a surface CH_2 species. This has been proposed as an intermediate in olefin metathesis (as a carbene) and in CO hydrogenation (as carbidic carbon).

Acknowledgements

We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, and an Atlantic Richfield Foundation Grant of the Research Corporation and the University of Wisconsin-Milwaukee Graduate School for their support. We also acknowledge the valuable assistance of F. Laib during the course of this work.

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