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Discussion

Reply to “Discussion on ‘^{13}C-tracer study of the Fischer–Tropsch synthesis: another interpretation’ [B. Shi, B.H. Davis, Catal. Today 58 (2000) 255–261]”

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Abstract

The rebuttal by Maitlis and Turner does not address the basis of our reinterpretation of the data generated by Maitlis and coworkers using ^{13}C-labeled ethene. Maitlis and coworkers considered that the ^{13}C/^{12}C ratio in the surface species decreased with carbon number and we indicated that this was not possible. We reinterpreted their data, using only the ^{13}C-containing components. Because of the agreement between their experimental results and the expectations of a decrease in the ^{13}C content of products of increasing carbon number that was based on their incorrect theoretical interpretation of the isotopic content of surface species, Maitlis and coworkers concluded that ethene initiates chain growth with the formation of a surface bound vinyl intermediate. Our correct interpretation of their experimental data shows that ethene functions to initiate chain growth, and has been advanced previously by several investigators. The ^{13}C-data and other isotopic tracer data, in our view, do not provide direct evidence to favor a surface bound vinyl intermediate over other possible surface species. In their rebuttal, Maitlis and Turner involve new issues, including the view that the addition of ethene alters the α-value for the synthesis, and a few of these issues are addressed. © 2001 Published by Elsevier Science B.V.

1. Introduction

Maitlis and Turner [1] provide a rebuttal to a paper by Shi and Davis [2] who contended that only the ^{13}C-containing products should have been used to reach a correct conclusion for work published by Maitlis and coworkers [3–7]. However, the rebuttal does not address the major items in the alternative interpretation offered by Shi and Davis [2] which were as follows.

(1) Maitlis and coworkers proposed that the decrease in the ^{13}C/mole with increasing carbon number of products was due to a decrease with increasing carbon number of the fraction ^{13}C/^{12}C on the surface. Shi and Davis [2] contended that the ^{13}C/^{12}C fraction of surface species must be independent of the carbon number and that the assumption made by Maitlis of the variability of ^{13}C/^{12}C with the carbon number was not valid. Maitlis and Turner [1] do not address this issue so that we assume they now agree with our assertion that the ^{13}C/^{12}C fraction must be constant for each surface species greater than C$_1$.

(2) Shi and Davis [2] asserted that the correct way to interpret the data for ethene insertion in the various publications by Maitlis and coworkers was to consider only the components containing the ^{13}C-label. When this was done the ^{13}C/mole was constant with increasing carbon number products, as is required when the added ethylene initiates chain growth. There was an exception for C$_4$ which contained slightly more

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^{13}C-label than required for initiation only; we indicated that this was most likely due to a small contribution of dimerization of the added ethene. When only the ^{13}C-labeled components were considered by Shi and Davis, the data of Maitlis and coworkers were in agreement with the earlier work reported in [8].

The rebuttal by Maitlis and Turner [1] addresses the following items that were included in [2]:

(3) Shi and Davis [2] offered an explanation of dilution by unlabeled products formed during the periods when label was not added as the most likely explanation for the decline in ^{13}C/^{12}C content as the carbon number increased. This point is addressed in [1] and we discuss it below.

(4) Shi and Davis [2] indicated that π-bonded adsorbed ethene was equally consistent with the data generated by Maitlis and coworkers as was their assertion that an adsorbed vinyl group was formed.

2. Discussion

Maitlis and Turner [1] state that they collected the products in a liquid nitrogen trap during the entire 30 min during which they add six pulses of $^{13}C_2$ to the syngas. They agree that accumulation of high molecular weight products is likely in a large continuously stirred tank reactor (CSTR) at high pressures but is less likely in a fixed-bed microreactor such as they operate at atmospheric pressure with low conversion. However, they state that accumulation cannot be totally excluded. Maitlis and Turner [1] do not consider that, by collecting the products during the period of adding labeled product and during the period of unlabeled syngas conversion, they must dilute the products formed during the addition of ^{13}C ethene. We continue to assert that the most likely explanation for the decline of ^{13}C/mole with increasing carbon number is that the fraction of hydrocarbon exiting the liquid nitrogen trap with unconverted syngas decreases with the carbon number and that this is responsible for the decrease in ^{13}C/mole with increasing carbon number. The combination of the fixed-bed reactor and the liquid nitrogen trap used by Maitlis and coworkers provides the same opportunity for accumulation of unlabeled product as the CSTR does. The fraction of hydrocarbons condensed in a cold trap should increase with the carbon number even for the experimental procedure described in [1] just as it will in any other reactor. In other words, Maitlis and coworkers must accumulate unlabeled product in the liquid nitrogen trap during the 30 min of operation and the only way that this accumulation would not give the results reported by Maitlis and coworkers is if the vapor pressure of all hydrocarbon products exiting the liquid nitrogen trap was identical for all hydrocarbons that are produced. Until Maitlis and coworkers can provide data to show that the vapor pressures of C_2 through C_7 products in the gas exiting the liquid nitrogen trap are the same, we believe that dilution by unlabeled products that depend upon the carbon number, as vapor pressure clearly does, is the most reasonable explanation for the decrease in ^{13}C/mole with increasing carbon number.

In the work by Maitlis and coworkers, it has never been clear to us what is being analyzed. In [1], it is stated that, “The trap is isolated, allowed to warm to room temperature and the contents analyzed by GC–MS.” It appears to us that in order for this to be adequate, all products must be in the gas phase or, if two phases are present, each phase is analyzed and a correct mass balance is applied. Because of our uncertainties about the analysis, we restricted our interpretation of the data obtained for labeled-ethylene although presumably the same phenomenon applies for the other labeled compounds used by the Maitlis group.

Maitlis and Turner [1] now indicate that α decreases from α_1 to α_2 when ethene is added to the syngas and indicate that an exact computation is beyond the scope of their discussion. Thus, we do not discuss this except to point out that our Eq. (1) (in [2])

$$\frac{L_{n-1}}{L_{n-1}+P_{n-1}}=\frac{L_n}{L_n+P_n}=\frac{L_{n+1}}{L_{n+1}+P_{n+1}}=C \quad (1)$$

must be true during the addition of ^{13}C-labeled ethene under steady-state conditions and that the ^{13}C/mole in the products is constant for all carbon numbers, a result that was not obtained by Maitlis and coworkers. If there are different α’s during the conversion of syngas and during the addition of labeled ethene, then the deviation from our equation must be due to unlabeled product accumulation during the conversion of unlabeled syngas that produces α_1. However, even when two α’s are involved, a calculation based only on ^{13}C-containing compounds, as we did in [2], will still be correct.

Maitlis and Turner [1] also invoke a second termination step that involves coupling reactions. Thus, the addition of ethene increases the amount of butene. We agree that some coupling occurs and that this is responsible for the ^{13}C/mole for the C_4 products being higher than would occur if ethene served only to initiate chain growth, as shown by Shi and Davis (in Figs. 2 and 3 of [2]). In our view, any coupling occurs outside the normal Fischer–Tropsch synthesis pathway. The concentration of surface species $[C_1, C_2, \ldots, C_n, \ldots]$ must be determined by α which in turn is determined by the relative rates for propagation and termination; when this is not the case we are dealing with a mechanism that does not follow normal Anderson–Schulz–Flory distribution and a single α does not apply. If we consider the termination pathway which involves coupling of ethene, this must occur with equal probability for all surface species belonging to the FTS mechanism; i.e. all $[C_1, C_2, \ldots, C_n, \ldots]$ species will couple with ethene in proportion to their surface concentration, determined by α, and that the products produced by this coupling must therefore have the same α as the other FTS reaction pathway which involves termination by desorption.

Shi and Davis [2] provided an alternative interpretation of the data obtained by Maitlis and coworkers for the addition of ^{13}C-labeled ethene to syngas. The one used by Maitlis and coworkers that involved surface species in which the ^{13}C/mole decreased with increasing carbon number is incorrect. Using the incorrect interpretation of the data led Maitlis and coworkers to the conclusion that the ^{13}C-data show that ethene initiates chain growth. Shi and Davis, using a correct calculation procedure, reached the conclusion that ethene initiates chain growth. Maitlis and coworkers' data are therefore consistent with the conclusion that has been reached by numerous workers since the pioneering work in the early 1950s of Emmett and his coworkers and by Rogozinski and his coworkers. There is, in our opinion, no direct evidence in any of the data using stable or radioactive tracers provide direct evidence to support the adsorption of ethene as a vinyl or a π-bonded ethene. While most of the early work was at atmospheric pressure, our work at higher pressure agrees with the earlier studies [8]. In our reinterpretation of the ^{13}C-data, we agree that ethene initiates chain growth; however, we disagreed with the approach Maitlis and coworkers interpreted their data to reach this conclusion. There is ample evidence in inorganic chemistry for either structure bonding to a metal. However, iron carbide is also a catalyst for FTS and ethene initiates chain growth with this catalyst [9]. If a vinyl group is the initiating structure for chain growth, then metal carbide as well a metal catalysts must be able to readily form the vinyl group.

References

[1] P.M. Maitlis, M.L. Turner, Catal. Today, this issue.
[2] B. Shi, B.H. Davis, Catal. Today 58 (2000) 255.
[3] M.L. Turner, H.C. Long, A. Shenton, P.K. Byers, P.M. Maitlis, Chem. Eur. J. 1 (1995) 549.
[4] H.C. Long, M.L. Turner, P. Formasiero, J. Kašper, M. Graziani, P.M. Maitlis, J. Catal. 167 (1997) 172.
[5] M.L. Turner, P.K. Byers, H.C. Long, P.M. Maitlis, J. Am. Chem. Soc. 115 (1993) 4417.
[6] P.M. Maitlis, H.C. Long, R. Quyoum, M.L. Turner, Z.-Q. Wang, J. Chem. Soc., Chem. Commun. 1 (1996).
[7] P.M. Maitlis, R. Quyoum, H.C. Long, M.L. Turner, Appl. Catal. A: Gen. 168 (1999) 363.
[8] A. Raje, B.H. Davis, in: J.J. Spivey (Ed.), Catalysis, Vol. 12, The Royal Society Chemistry, Cambridge, 1996, pp. 52–131.
[9] L.M. Tau, H.A. Dabbagh, Energy & Fuels 4 (1990) 94.