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FISCHER-TROPSCH SYNTHESIS–A C_2 INITIATOR FOR HYDROCARBON CHAIN GROWTH ON RUTHENIUM

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We wish to report that higher hydrocarbon formation in the Fischer-Tropsch synthesis on a ruthenium catalyst involves a relatively long-lived C_2 intermediate and that the chains grow by terminal addition. These findings result from the application of an isotopic transient experiment in which we follow the incorporation of ^{13}C into the various carbon positions of the hydrocarbon chains after a rapid switch from ^{12}CO to ^{13}CO in the reactant gas. Such experiments wherein an isotopic perturbation is applied and followed while the overall reaction remains at steady state are powerful non-invasive probes of complex reaction mechanisms. Recently they have been applied to catalytic systems including the hydrogenation of carbon monoxide [1–6]. We have previously reported the results of such an experiment on both promoted iron and supported cobalt catalysts [6]. In these cases we observed a single isotope displacement rate at all positions in the C_2–C_6 products. This result showed that reactive surface carbon spends almost all of its residence time on the catalyst surface as a C_1 precursor and a very small fraction ($< 3\%$) as growing hydrocarbon chains. This in turn requires a small inventory of growing chains on the catalyst surface at steady state ($< 3\%$ of the active carbon coverage).

For the experiments on supported ruthenium, we modified our published experimental procedure slightly [6,7]. In these experiments a pulse of ^{13}CO-H_2 was administered by syringe injection immediately after the isotopic switch. This served to rapidly displace the large amount of reversibly adsorbed CO from the calalyst and provide a clean isotope switch in the adsorbed CO [8]. Strictly speaking, this disturbed the steady state by introducing a short period of increased reactant flow rate but did not perturb the H_2 and CO partial pressures. Table 1 lists the productivity of the Ru catalyst [9] and the operating conditions which were chosen to give low conversions and high selectively to 1-olefins.

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Table 1
Operating conditions and catalytic activities

Temperature	455 K
Pressure	100 kPa
H_2/CO ratio	1.0
Hydrocarbon production rates, nmol s^{-1} (g catalyst)$^{-1}$	
CH_4	7.6
C_2's	2.6
C_3's	4.1
C_4's	3.8
C_5's	3.1
C_6's	2.7
Butene/Butane	7
1-Butene/C_4's	0.8

Figure 1 shows the amount of ^{13}C at each position in the C_2–C_5 hydrocarbons produced between 4 and 24 seconds after the switch from ^{12}CO to ^{13}CO [10]. The results show two distinct isotope displacement rates. The last two positions in these short chains show a common rate of replacement which is slower than that for the remaining positions. This reflects a surface residence time for these

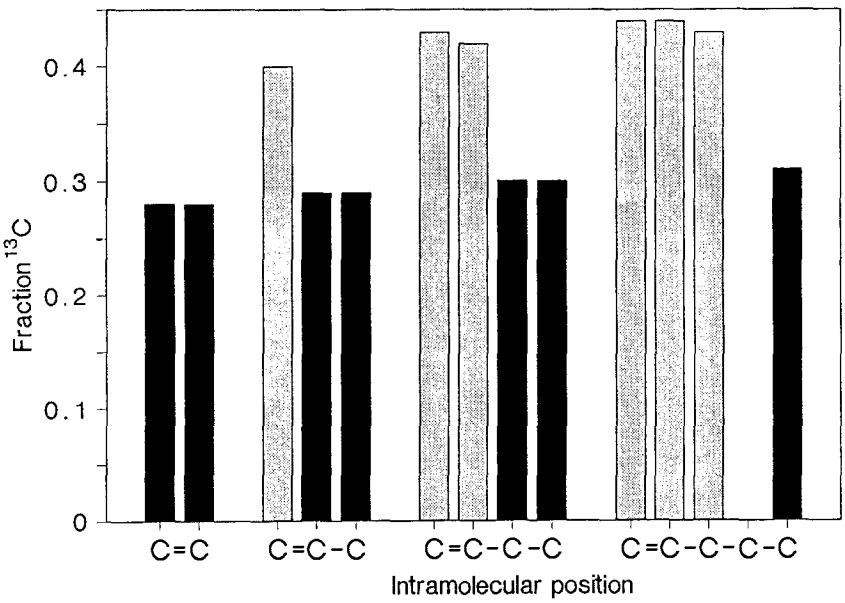

Fig. 1. Distribution of ^{13}C content among the positions in the ethylene, propylene, 1-butene, and 1-pentene in hydrocarbon products trapped between 4 and 24 seconds after a switch from ^{12}CO to ^{13}CO. Conditions are given in table 1. The NRM resonances for the 4-position in pentene could not be resolved from interfering minor components.

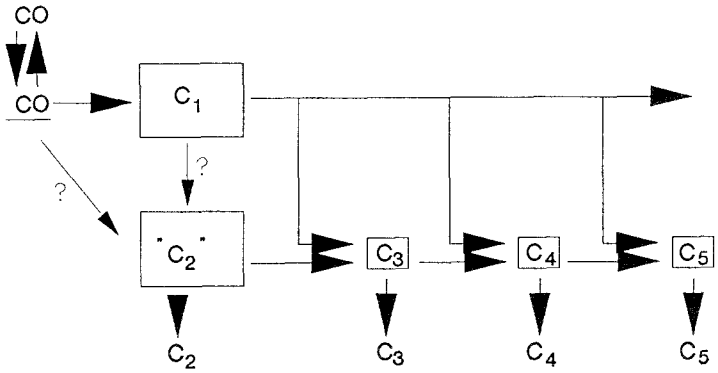

Fig. 2. Generalized compartmental diagram of the carbon reaction pathway on ruthenium. The relative sizes of the compartments indicate the relative population (and residence time) of the intermediate or group of intermediates represented.

"initiator" carbon atoms which is approximately 50% longer than that for the others. These results contrast with those previously obtained an iron and cobalt [6] where a single replacement rate was observed. If, as is commonly assumed, the chain growth process is not rapidly reversible, the results allow us to draw several conclusions about the mechanism of chain growth under these conditions. These conclusions, which are listed below, are summarized in the simple compartmental diagram of the surface reaction pathway shown in fig. 2. In this diagram, the relative size of each compartment is a qualitative indication of the surface residence time (and surface concentration) of the intermediate or intermediates represented by that compartment.

1. *There is a relatively slow step in chain growth associated with the C_2 stage.* A number of mechanistic origins of this "C_2 initiator" are consistent with the data. It could reflect an unreactive C_2 intermediate which is either in the main pathway of chain growth or constitutes a diversion from the main reaction pathway and thus forms a "backwater" reservoir. Vinylidene and ethylidene are plausible candidates for such a long lived C_2 intermediate given recent reports of their surface stability [11,12]. Readsorption of ethylene to form this unreactive intermediate could also give these results [13–16] although similar participation of higher olefins would be likely in this case and no evidence of such participation is seen in the isotopic data. An alternate explanation is that a distinct long lived C_1 intermediate is involved in the initiation step. However, more complete examination of the isotope distribution (by ^{13}C NMR) shows that the "initiator" carbon atoms spend an appreciable fraction of their time on the surface as C_2 fragments [17].
2. *Chain growth beyond the C_2 stage is rapid* compared to the rate of reaction of the non-initiator carbons. This produces the isotropic distribution in the growth positions (e.g. positions 1–3 in pentene) which is similar to the results obtained on cobalt and iron. Modelling calculations show that the growth

steps from C_3 to C_5 must occur in less than 1 second apiece at these conditions. Such rapid growth rates also require that less that 0.5% of the exposed metal surface atoms are occupied by growing chains longer than C_2 [5,6].

3. *Chain growth occurs by terminal addition to what eventually becomes the olefinic end of the hydrocarbon molecule.* The C_2 "initiator" serves as a marker to demonstrate this for the growth step from C_2 to C_3. Succeeding steps are expected to proceed in an analogous manner. While in agreement with many proposed chain growth schemes including alkyl migration onto surface CH_x groups [18,20] as well as CO insertion [21], it contradicts growth by CH_2 insertion into vinylidene [22]. Such a mechanism would leave the two carbon atoms in the "initiator" at opposite ends of the molecule.
4. *The "slow" C_2 units are not used to a significant degree in subsequent chain building.* Such an occurrence would dilute the ^{13}C content in the added carbon atoms in C_{4+} products relative to the C_3 products. Such a dilution is not seen in the data.

Previous isotope replacement studies on ruthenium [2,4,5] showed no evidence of a slow C_2 intermediate. The rapid chain growth seen here is in general agreement with these previous results [2,4,5] but disagrees with the lifetimes and coverages obtained by Dautzenberg et al. [23]. A more complete discussion, including the modelling calculations will be published separately.

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[7] Briefly, the rate of incorporation of ^{13}C into the hydrocarbon products is followed by GCMS analysis of aliquots of product gas trapped at various times after the CO isotopic switch. GC/MS analysis rather than simple mass spectroscopy was necessary because of the extensive fragmentation of olefins even at rather low electron energies. The positional distribution of ^{13}C is determined by proton NMR analysis of the product collected during a portion of the isotope transient. Splitting of the proton resonance shows the presence of ^{13}C at a given position. The transient experiment was repeated 12 times to accumulate sufficient transiently labelled product for NMR examination. This product was GC separated into carbon number fractions before distillation into NMR tubes containing 1,1,2 trifluoro-2,2,1 trichloroethane solvent.
[8] The amount of displaceable CO on this catalyst corresponded to approximately 1 per ruthenium atom in the catalyst sample.
[9] The catalyst was prepared by mixing an acetone slurry of calcined y-alumina (Alon-C) was mixed with aqueous $Ru(NO_3)_3$. After drying in O_2 for 7 hr at 150 °C and reduction in 10% hydrogen at 450 °C, the catalyst contained 4.5 wt% ruthenium metal.
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