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FISCHER-TROPSCH SYNTHESIS CATALYZED BY ACTIVATED Fe POWDER GENERATED BY THE REDUCTION OF FeI_2(OR $FeBr_2$) WITH POTASSIUM

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Activated Fe powder prepared by the reduction of FeI_2(or $FeBr_2$) with potassium in THF solvent shows both a preferential formation of C_4 hydrocarbon and a high selectivity of olefin formation in the CO hydrogenation.

Rieke and coworkers have been reporting many applications of activated metal generated by the reduction of metal salts with potassium in an ethereal or hydrocarbon solvent to prepare new organic and organometallic compounds.$^{1-3)}$ In this communication we wish to report a preferential formation of C_4 hydrocarbons and highly selective formation of olefins in CO hydrogenation reaction catalyzed by such activated Fe powder as prepared by the same procedure as Rieke et al.$^{1)}$ except that by-product of alkali metal halide was removed by methanol washing.

Activated iron powders were prepared by the reduction of iron halide(FeI_2 or $FeBr_2$: 0.005 mol) with potassium(0.02 mol) in refluxing THF at a nitrogen atmosphere for 5 h. After the end of reaction remaining potassium was decomposed by a dropwise addition of methanol, the filtered metal powders were washed with 250 ml of methanol to remove KI or KBr. The resulting metal powder was dried at 110 °C under the reduced pressure of 1 mmHg for 2 h.

For the hydrogenation of CO, 100 ml of autoclave containing the activated metal powders was flashed and filled with the mixture of CO and H_2(H_2/CO = 2.0) up to 20 kg/cm^2. Preliminary studies suggested the initial pressure of 20 kg/cm^2 and 260-280 °C as appropriate reaction conditions for Fe powder thus prepared. Duration of reaction is defined as time passed after autoclave temperature reaching the desired one.

The gases produced were transferred from the autoclave to a 2.5 l Pyrex vessel of a gas collecting apparatus equipped with a rotary pump to evacuate its whole system and a Pirani gauge to check the pressure change when small portion of C_2-C_8 hydrocarbons being collected in a small glass tube cooled at liquid nitrogen temperature. Methane, CO, CO_2, and H_2 collected in an air tight syringe were analyzed by gas chromatography both on a 1.5 m activated charcoal column and on a 3 m silica gel column using a thermal conductivity detector. The hydrocarbons of C_2-C_8 collected in the glass tube was analyzed on a 3.0 m Porapak Q column(Shimadzu GC 4BPTF). The oxygenates and hydrocarbons higher than C_8 were recovered by evacuating the inside of the autoclave and then washing the inside twice with normal pentane.

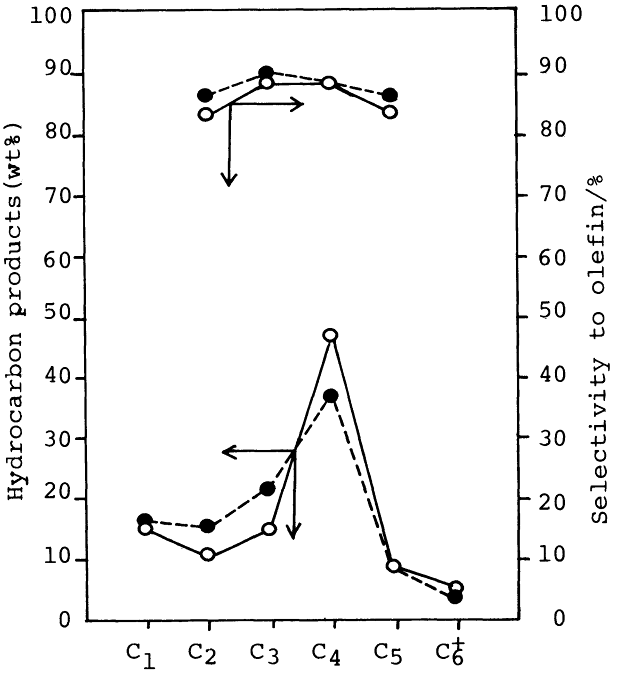

Fig.1. Distribution of hydrocarbon products in F-T synthesis with an activated Fe powder.

—○— : Fe from FeI_2,

--●-- : Fe from $FeBr_2$.

Fe powder obtained by the reduction of FeI_2 and $FeBr_2$ with potassium in refluxing THF was found to be active toward the CO hydrogenation while Fe powder from $FeCl_3$ was found to be less active due to incomplete reduction.

Conversions of CO basis over Fe powder from FeI_2 are 0.4, 7.4, and 11.7% for 0 min at 240, 260, and 280 °C, respectively.

Figure 1 shows the distribution of hydrocarbon products in F-T synthesis(0 min) at 280 °C with an activated Fe powder from FeI_2 and $FeBr_2$(conversion 11.7 and 14.9%). Both Fe powders indicate relatively high selectivity for C_4 hydrocarbon formation, this being remarkable especially with Fe powder from FeI_2. Another features of this catalyst are high selectivity of olefin formation ranging from 83-90%[$C_n^=/(C_n^= + C_n) \times 100$] .

As for the favoured formation of C_4 hydrocarbon, there might be the possibility of trace amount of THF coordinating strongly to Fe powder to contribute to the preferable formation. The blank experiment conducted under the same reaction conditions in the presence of only H_2 over Fe powder gave trace amount(0.1%) of structure-unknown product having an intermediate retention time between C_3 and C_4 fractions on gas chromatograph. This results exclude such possibility as described above.

We confirmed that repeated experiments of CO hydrogenation (0 min at 280 °C) over Fe powder from FeI_2 used for first 15 min CO hydrogenation reaction at 280 °C show no deterioration in its selectivity to olefin(C_2 83%, C_3 90%, C_4 88%, C_5 80%).

Further studies on CO hydrogenation using other metal powders thus prepared and activated metal powder generated in a support by the reduction of corresponding metal halide with potassium are in progress.

References

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