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Studies of the Fischer-Tropsch Process on Uranium Catalysts

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In the study of the catalytic reaction of uranium powder, phenylacetylene and dimethylacetylenedicarboxylate were converted to polymers via *linear-oligomerization and cyclo-oligomerization reactions [6]. Our results indicate a new synthetic pathway of the carbon-carbon bond formation through the participation of f-orbital elements. In this report, reactions of methylenediiodide, diazomethane and ketene were studied. The products of these reactions,* i.e., *C_1 and C_4 alkanes and alkenes, suggested that the bond could be formed by the insertion of methylene radicals. An interesting phenomenon, where the carbon number of products increased with the duration of reaction period, was found.*

The role of the uranium element in the Fischer-Tropsch process was studied. Hydrogen and carbon monoxide were catalyzed to methane (60–70%), CH_3OH (20–25%), C_2H_5OH and $CH_3OCH_2OCH_3$ at one atmosphere pressure and 250 °C. The Fischer-Tropsch process could proceed through uranium alkoxide intermediates. This oxide-formation mechanism was tested by the pyrolysis of uranium alkoxides.

Introduction

The search for new practical energy sources and organic raw materials, because of the uncertainty and cost of crude oil imports, has renewed interest in the production of fuels and chemicals from hydrogen-deficient compounds. Hydrocarbon and oxygenated compounds can be catalytically formed from synthetic gas ($CO + H_2$). The production of chemical feedstocks or motor fuels from any combustible carbon-containing source, including coal, biomass, or garbage, would be an attractive alternative to politically-unstable supplies of petroleum. In addition, the Fischer-Tropsch synthesis has an advantage over direct hydrogenation reactions, where environmentally harmful by-products are produced.

Although the Fischer-Tropsch synthesis has been studied for more than 50 years and at least 14 mechanisms have been proposed for the reaction [1–3], no understanding of the mechanism exists that is sufficient to predict products under various conditions, or to unify the observations in a detailed way. For the past work, the syntheses concentrated mainly on transition metals as catalyst. Few studies have been reported where actinide elements were used as a catalyst.

We have successfully developed a new catalyst, which has higher catalytic power than the uranium powder from the decomposition of uranium hydride [4, 5]. The catalyst can polymerize acetylenes, conjugated dienes and allylhalides. Using the same catalyst, 1,3-butadiene and isopropene were selectively converted to the 1,4-cispolymer. The linear-oligomerization of acetylene and cyclo-oligomerization of phenylacetylene and dimethylacetylenedicarboxylate have also been demonstrated [6]. Carbon–carbon bonds could be formed through the participation of the f-orbital element. Studies of the catalytic reactions with methyleneiodide, diazomethane and ketene, which produced methylene radicals easily at high temperatures, were attractive where carbon–carbon bonds could be formed instead of the π bond substrate. Further studies of related Fischer-Tropsch process are reported in this work.

Experimental

Apparatus and Materials

All operations were carried out under dry nitrogen atmosphere or in evacuated systems. Infrared spectra of gas samples were produced on a Perkin-Elmer Model 397 IR spectrometer. Gas chromatography/mass spectrometry (GC/MS) were performed on a Hewlett-Packard GC/mass spectrometer. Gas chromatographic analysis of gaseous products was performed on a Gow-Mac 750 FID detector or a Hewlett-Packard FID detector with helium as the carrier gas. Porapak Type 2 2mm ID × 4′ column was used for the GC/mass analyses. The solids were characterized by a Diano-8100 AD Model with a Cu target tube and a Ni filter.

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All solvents and liquid substrates were distilled from drying agents prior to use. The solids and gases (Mathson) were used as supplied. Diazomethane and ketene were prepared via standard methods [7, 8]. The catalyst, uranium powder, was prepared as described elesewhere [4]. The catalyst was used as reactant, or the catalyst was dispersed on a fixed bed, continuous flow, electrically-heated cylindrical reactor.

Reactions of Methylenediiodide, Diazomethane and Ketenes

Excess of methylenediiodide (10 ml) was refluxed with 2 g of uranium powder for 2 hrs. The gaseous products condensed in the vacuum system for analysis. A 68% yield was found. The gaseous products were identified by gas chromatography and the analysis results are shown in Table I. After extracting the reaction residues with hot xylene, the filtrate was found not to contain polymethylene or polyethylene. The solid was analyzed as a mixture of uranium metal and uranium iodide.

Diazomethane and ketene were allowed to react or circulate through a fixed 3″ X 3″ catalyst bed. All gaseous products were analyzed by gas chromatography, and are listed in Table I. An isolated system was used to calculate the reaction yield and to analyze the gaseous products shown in Table II during the reaction. Both reactions of diazomethane (32 mmol) and ketene (32 mmol) with 2 g of uranium powder were nearly quantitative. The consumption of diazomethane and ketene was proved by infrared spectra and gas chromatography.

Reaction of Carbon Monoxide with Hydrogen

The hydrogen gas was physisorbed on fresh uranium powder at room temperature. Carbon monoxide gas was adsorbed on the catalyst at 250 °C; the amount of adsorption can be expressed as CO/U = 0.2

0.6 atm gas mixture with (1:2) molar ratio of carbon monoxide to hydrogen was introduced to react with 0.5 g of uranium in an isolated system. The reaction temperature was raised to 250 °C and the reaction kept for 12 h. Liquid products were observed at the glass wall. The gas products were analyzed with GC/mass spectrometry, and the results are listed in Table III. Since carbon monoxide was not detected by GC and IR, the reaction was nearly quantitative. The solid was proved to be uranium oxide, by the X-ray method.

TABLE I. Hydrocarbon Products Weight Distribution over Uranium Metals.

	CH_2I_2	CH_2N_2	CH_2CO
Gaseous products (relative intensity)	CH_4 (35) C_2H_4 (45) C_2H_6 (6) C_3H_8 (5) C_4H_{10} (2)	C_2H_4 (1) C_3H_8 (3) C_4H_{10} (5)	C_2H_4 (10) C_3H_8 (10) C_4H_8 (2) C_4H_{10} (1)
Reaction condition (yield)	Reflux for 2 hrs (68%)	Reaction in fixed bed at room temperature (>90°%)	Reaction in fixed bed at room temperature (>90°%)

Pyrolysis of Uranium Alkoxides

0.5 g of uranium compounds, $U(OCH_3)_5$, $U(OC_2H_5)_5$ and $U(OCH_3)_6$ from the previous method [9], was introduced to a modified break-sealed tube. The pyrolysis tube was wrapped with heating tapes and kept at 300 °C for 2 hours. After the break seal was broken the gaseous products were immediately removed to the GC/mass spectrometer by a Luer-Lock syringe; the analysis results are shown in Table III. The solid was shown by X-ray analysis to contain no uranium dioxide.

Results and Discussion

Reactions of Methylenediiodide, Diazomethane and Ketene

Pettit *et al.* have reported that the reaction of diazomethane and methylenediiodide with or without hydrogen over various transition metals produced hydrocarbons [11]. The results of experiments were introduced to support the original proposal of the Fischer-Tropsch process, made in 1926, that the formation of hydrocarbons produced upon reaction

TABLE II. Gaseous Products of CH_2N_2 over Uranium Metals in Different Time Periods.

Reaction time	8 hrs	12 hrs	48 hrs
Products			
Gaseous products (relative intensity)	CH_4 (3) C_2H_4 (2) C_3H_8 (2)	CH_4 (<1) C_2H_4 (6) C_3H_8 (8)	CH_4 (<1) C_2H_4 (1) C_3H_8 (3) C_4H_{10} (5)

TABLE III. Gaseous Products of Fischer-Tropsch Process and Pyrolysis from Hexamethoxyluranium.

Fischer-Tropsch	Pyrolysis from $U(OCH_3)_6$
CH_4 (60–70)	CH_4 (<2)
C_2 (trace)	CH_3OH (trace)
CH_3OH (20–25)	C_2H_5OH (90)
C_2H_5OH (5–8)	$CH_3OCH_2OCH_3$ (8)
$CH_3OCH_2OCH_3$ (10)	

of CO and H_2 on certain transition metal surfaces proceeded *via* 'polymerization of methylene groups' on the metal surface. In our study, the reaction of methylenediiodide, diazomethane and ketene over uranium catalyst was motivated by this radical in polymerization mechanism. In other words, these reactions were studied to extend the Fischer-Tropsch process to actinide elements.

The gaseous products from these reactions were analyzed with gas chromatography and the analysis results are shown in Table I. An experiment has also been done to prove that polymethylene did not exist in the products from reaction of methylenediiodide. From the catalytic view-point, in the case of methylenediiodide and diazomethane, the uranium catalyst is unexpectedly more powerful than a transition metal catalyst.

Kinetic data were also observed, and the gaseous products in different reaction periods were analyzed and listed in Table II. It is hard to explain why the carbon numbers of hydrocarbons increase with the duration of the reaction. The relative intensities in paratheses were reported after averaging over three sets of data, and the products were dependent on the size, shape and packing of the metal powder.

Reaction of Carbon Monoxide with Hydrogen

Hydrogen gases were physisorbed on uranium powder surface at room temperature. This phenomenon was different from that of the uranium powder from decomposition of uranium hydride, where hydrogen gases were physisorbed at 240 °C. Carbon monoxide gas was adsorbed on the surface at 250 °C; the amount of adsorption corresponded to the molar ratio CO/U = 0.2. The excited molecules thus resulted from simultaneous chemisorption of both carbon monoxide and hydrogen at the catalyst surface, reacting at 250 °C and under around one atmosphere pressure, to obtain the products shown in Table III, with quantitative yield of two categories, hydrocarbons and oxygenated species. After pumping to dryness, the residue was characterized as uranium dioxide with an X-ray powder diffractometer. Carbon monoxide and water were undetectable. Methane was the main product, whereas the oxygenated species were the minor product. One of the oxygenated species, dimethoxylmethane, is interesting because the compound indicates that CH_2 intermediate fragments exist. The methylene biradical coupled with methoxyl moiety to yield the product, and this will be discussed later.

Recently Spaienza proposed an oxide mechanism for F-T syntheses [12], suggesting that chemisorbed carbon monoxide on metal surfaces reacts with hydrogen to yield an oxygen- rather than a carbon-coordinated species. In other words, the physisorbed hydrogen reacts with undissociated carbon monoxide, possibly through M–O=C, M=O=CH_2, M–OCH_3 intermediates. In actinide chemistry, no carbonyl compounds of f-orbital metal have yet been found, apart from existence in a 4 K argon matrix detected by infrared spectroscopy. According to studies of Marks *et al.* on carbonylation of bis(pentamethylcyclopentadienyl) actinide alkys, oxygen-metal bonding was observed instead of the actinide to carbon sigma bonds [13]. The background study supports that the oxygen does have strong affinity to the uranium. In order to understand the possible mechanism of F-T synthesis, uranium compounds $U(OR)_5$ and $U(OR)_6$ were pyrolyzed to obtain the products shown in Table III and IV. Among the listed products, ethanol, methanol, dimethoxylmethane and methane from the latter compound, $U(OR)_6$, agree with the products from F-T synthesis, only the relative intensities of pyrolyzed products being different. However, the hydrocarbon products obtained from the former, $U(OR)_5$, did not contain alcohols that were supposed to exist, at least in trace amounts: probably the oxygenated species were left in the viscous residue.

TABLE IV. Gaseous Products of Pyrolysis from Pentaalkoxyluranium Compounds.

Retention time[a]	From $U(OCH_3)_5$	From $U(OC_2H_5)_5$
0.29	CH_4 (85)	CH_4 (95)
1.45	C_2H_4 (trace)	C_2H_4 (trace)
2.09	C_2H_6 (2)	C_2H_6 (1)
3.17	?	X
5.41	C_3H_6 (trace)	C_3H_6 (trace)
5.70	? (4)	? (trace)
6.15	? (trace)	X
6.29	? (trace)	X
6.38	? (trace)	X
7.58	E (6)	X
7.99	2-methylpropane (1)	2-methylpropane (2)
8.47	n-C_4H_{10} (trace)	n-C_4H_{10} (trace)
9.69	? (trace)	? (trace)
10.25	? (trace)	X
10.41	X	Isopentane (trace)
10.69	X	2-pentene (trace)
12.24	X	2-methylpentane (trace)

[a]Initial temperature: 50 °C. Final temperature: 230 °C. Stay time: 2 min. Inj. temp. 200 °C. Rate: 16 °C/min. FID temp. 250 °C.

The highest oxidation number of uranium is 6. When the hexavalent compound is pyrolyzed, the lone pair electrons will shift to the interval between uranium and oxygen. The oxygen-carbon bond will break, and then the double bond between oxygen and uranium is formed. Simultaneously the methoxyl group in the opposite position must be removed, so the methoxyl radical and methyl radical collide either with the uranium compounds and/or with each other to produce ethanol, *etc.* On the other hand, pentavalent compounds were pyrolyzed to produce alkyl radical only. The alkyl radical collides with the alkyl group in the uranium compound to cause a chain reaction to yield the hydrocarbon, *e.g.* abstraction of hydrogen to form methane. The gaseous products from pyrolyzed $U(OCH_3)_5$ and $U(OC_2H_5)_5$ are almost the same, except for the extra product (E) in $U(OC_2H_5)_5$.

Following the previous discussion on the pyrolysis of pentavalent and hexavalent uranium compounds, uranium tetramethoxide was excluded, because it was difficult to purify. The results, the major product being hydrocarbons for the pentavalent compound and alcohol for the hexavalent compound, are compared to the F-T synthesis. The oxide mechanism is a reasonable explanation. The intermediates of the oxygen-coordinated compound are through $U(OC)_n$, perhaps a mixture of 4, 5 and 6, because the coordinated number can be up to 6 for carbon monoxide. The $U(OCH_3)_n$ from hydrogenation of $U{-}(OC)_n$ intermediates is then decomposed to yield the products.

Conclusions

(1) The radical intermediate could cause the polymerization and carbon-carbon bond formation on the uranium surface, although the bond between carbon and uranium is thermally unstable.

(2) The uranium catalyst can be used in the Fischer-Tropsch process, but the strong bonds of uranium oxide could not be made catalytic.

(3) The pyrolysis of uranium methoxides is introduced to explain the role of the oxide mechanism in Fischer-Tropsch syntheses.

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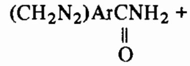
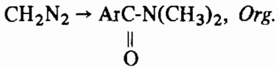
7 H. E. Baumgarten, Diazomethane 
$(CH_2N_2)Ar\underset{\underset{O}{\|}}{C}NH_2 +$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