



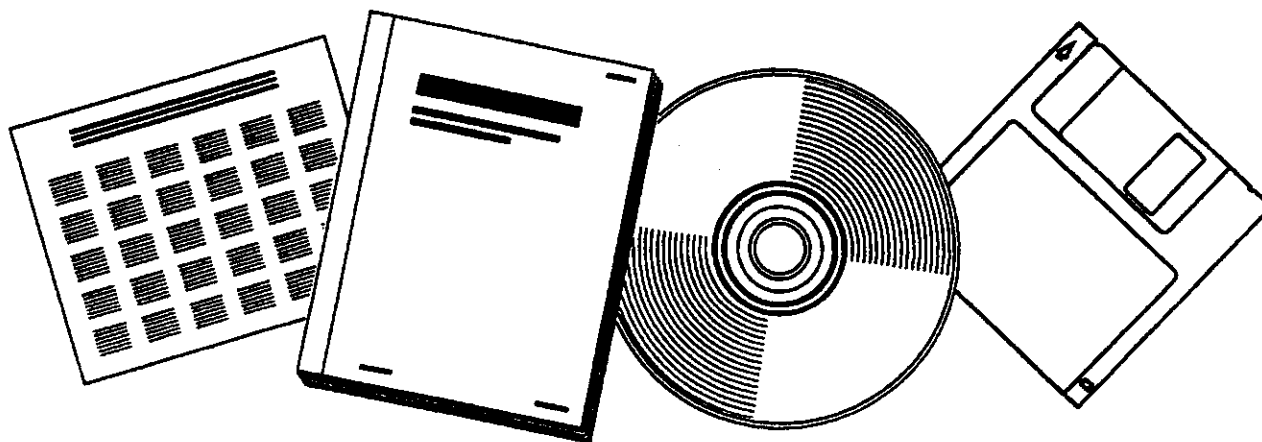
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HYDROGENATION OF CARBON MONOXIDE OVER RUTHENIUM-RHENIUM ON ALUMINA CATALYSTS

AMES LAB., IA

JUL 1982



U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

IS-T--1006

DE83 004975

IS-T-1006

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ruthenium-rhenium on alumina catalysts

by

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M.S. Thesis submitted to Iowa State University

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Date Transmitted: July 1982

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-eng-82

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Printed in the United States of America

Available from
National Technical Information Service
U.S. Department of Commerce
5265 Port Royal Road
Springfield, VA 22161

Hydrogenation of carbon monoxide over
ruthenium-rhenium on alumina catalysts*

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$\text{Ru}/\text{Al}_2\text{O}_3$, $\text{Re}/\text{Al}_2\text{O}_3$ and $\text{Ru-Re}/\text{Al}_2\text{O}_3$ catalysts were synthesized and characterized. A kinetics study was conducted for the methanation reaction on each of these catalysts using a Berty reactor. Operating conditions for kinetic experiments were 200 to 260°C and 35 to 40 ATM. Hydrocarbon products were detected by a gas chromatograph. It was found that the $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Re}/\text{Al}_2\text{O}_3$ gave similar activation energies. The $\text{Ru-Re}/\text{Al}_2\text{O}_3$ catalyst gave a significantly higher activation energy. Kinetic orders with respect to carbon monoxide and hydrogen were determined. Two mechanisms were proposed, one for the $\text{Ru}/\text{Al}_2\text{O}_3$ and $\text{Re}/\text{Al}_2\text{O}_3$ catalysts and one for the $\text{Ru-Re}/\text{Al}_2\text{O}_3$ catalyst, from which the experimentally observed reaction orders could be derived. An Auger electron spectroscopy study was conducted on a 50:50 atom percent ruthenium-rhenium alloy to determine surface segregation. No surface segregation was observed even after heating the alloy for two weeks at 1050°C.

*DOE Report IS-T-1006. This work was performed under contract No. W-7405-Eng-82 with the U.S. Department of Energy.

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ABSTRACT

$\text{Ru/Al}_2\text{O}_3$, $\text{Re/Al}_2\text{O}_3$ and $\text{Ru-Re/Al}_2\text{O}_3$ catalysts were synthesized and characterized. A kinetics study was conducted for the methanation reaction on each of these catalysts using a Berty reactor. Operating conditions for kinetic experiments were 200 to 260°C and 35 to 40 ATM. Hydrocarbon products were detected by a gas chromatograph. It was found that the $\text{Ru/Al}_2\text{O}_3$ and $\text{Re/Al}_2\text{O}_3$ gave similar activation energies. The $\text{Ru-Re/Al}_2\text{O}_3$ catalyst gave a significantly higher activation energy. Kinetic orders with respect to carbon monoxide and hydrogen were determined. Two mechanisms were proposed, one for the $\text{Ru/Al}_2\text{O}_3$ and $\text{Re/Al}_2\text{O}_3$ catalysts and one for the $\text{Ru-Re/Al}_2\text{O}_3$ catalyst, from which the experimentally observed reaction orders could be derived. An Auger electron spectroscopy study was conducted on a 50:50 atom percent ruthenium-rhenium alloy to determine surface segregation. No surface segregation was observed even after heating the alloy for two weeks at 1050°C.

INTRODUCTION

In recent years, the increasing demand for petroleum and the difficulty in finding supplies of oil has led to renewed interest in the production of fuels from a mixture of carbon monoxide and hydrogen. This mixture when heated and passed over a metal or metal oxide will produce hydrocarbons consisting of methane, paraffins, olefins and/or oxygenated compounds. This mixture of carbon monoxide and hydrogen can be obtained from coal, oil shale and tar sands by gasification with steam or oxygen (Fig. 1). Upon removal of methane and sulfur, this is a suitable feed for the synthesis of hydrocarbons. This synthesis is called the Fischer-Tropsch synthesis reaction.

The reaction was first reported by Sabatier et al. in 1902. They produced methane from a mixture of carbon monoxide and hydrogen at atmospheric pressure with supported nickel and cobalt catalysts (1,2). This is properly termed methanation which is a special case of the Fischer-Tropsch reaction in which only methane is produced.

From 1922 to 1928, Franz Fischer and Hans Tropsch studied the hydrogenation of carbon monoxide at atmospheric pressure. They made the following primary fundamental observations of this process:

- 1) Iron, cobalt and nickel are active catalysts for the reaction. Cobalt tends to produce higher hydrocarbons and nickel tends to produce methane.
- 2) Oxides such as ZnO and Cr_2O_3 have increased catalytic activity and are more resistant to sintering than metals.

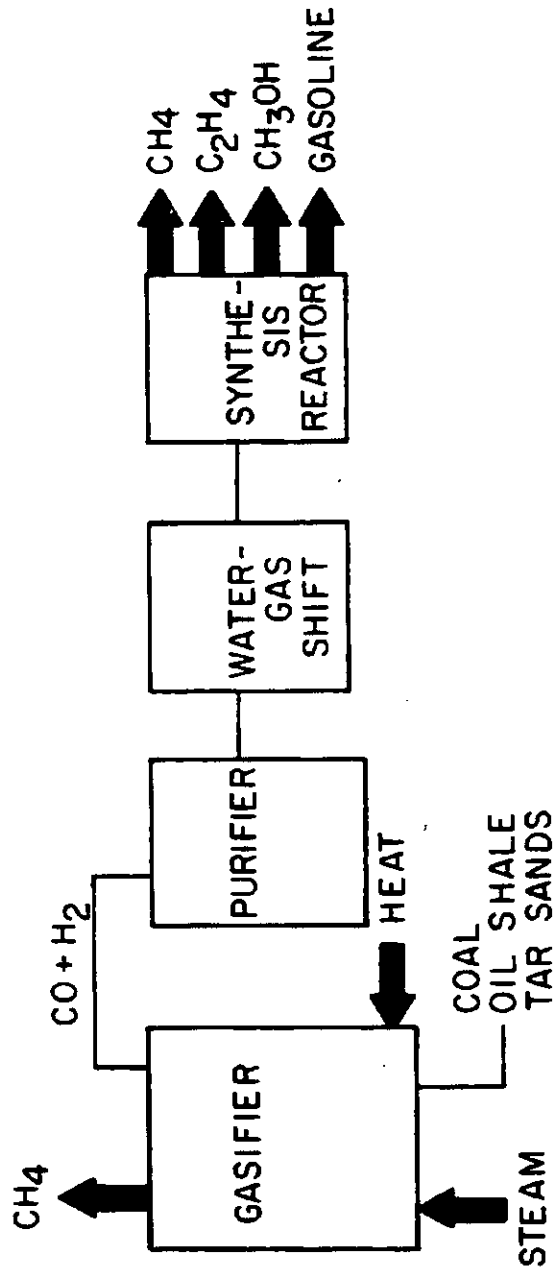
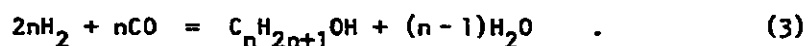
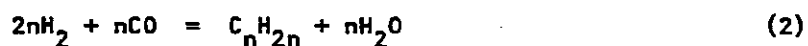
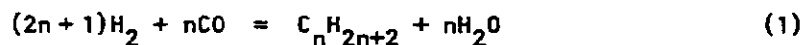


Figure 1. Schematic for the conversion of hydrogen deficient materials to useful chemicals and fuels

- 3) Small doses of alkali favor the formation of larger hydrocarbon molecules.
- 4) Copper-iron mixtures are more active than iron alone.
- 5) Sulfur poisons the catalysts.

These extensive studies, largely conducted at atmospheric pressure in the temperature range 250-400°C, gave this process the Fischer-Tropsch name (3-5).

In 1938, Pichler (6) found that a ruthenium catalyst at 140°C and 150 atmospheres would produce paraffins of much higher molecular weights (up to 400,000 g/mole) than previously obtained. His catalyst was also very stable over long periods of time. General reactions for this process, leading to paraffins, olefins and alcohols, are:



If we let $n = 1$ in Eq. (1), we have the methanation reaction



which is the reaction under study in this investigation.

The possibility of producing gasoline according to Eq. (1) from the reagents CO and H₂ (readily formed from the reaction of steam with coal) spurred much research on the Fischer-Tropsch synthesis prior to 1940, and the process was extensively used by Germany to produce fuel for

military operations during World War II. Following World War II, low petroleum prices attending the development of the Middle East oil fields led to a reduction of interest in the process; recent steep increases in petroleum prices have led to renewed interest in the Fischer-Tropsch synthesis and it is at present the principal source of gasoline in South Africa.

REVIEW OF LITERATURE

The purpose of this investigation is to expand on the already numerous investigations of hydrogenation of carbon monoxide over bi- or multi-metallic supported group VIII metals. Although the Fischer-Tropsch process has been extensively investigated, methane and gasoline made by present versions of it are at least twice as expensive as present market prices of these products. The mechanism of the Fischer-Tropsch (including methanation) reaction is yet to be established. Excellent reviews of these processes exist (7-10). Table 1 is a summary of some metals and their uses.

The production of methane from carbon monoxide and hydrogen is thermodynamically favorable. There are a few reactions which can occur under the same conditions as the Fischer-Tropsch and methanation reactions. The water-gas shift reaction (see Fig. 1),



which is normally used to vary the carbon monoxide to hydrogen ratio in feed streams, can also change the carbon monoxide to hydrogen ratio during reaction. Two reactions which produce adsorbed carbon atoms are



which are the Boudouard reaction (6) and coke deposition (7). These reactions can deactivate catalysts but are reversible by high tempera-

Table 1. Catalysts used in the Fischer-Tropsch reaction

Metal	Use
Nickel	Used for methanation.
Cobalt	Can be promoted with ThO_2/MgO and supported on Kieselguhr. Used for making higher hydrocarbons at atmospheric pressure and paraffins at medium pressure.
Iron	Most important medium pressure catalyst in use today.
Ruthenium	Unique for production of high molecular weight hydrocarbons.
Metal Oxides	Used in production of oxygenated products.

ture reduction. The metal carbide reaction (8) is considered



to be irreversible and gives permanent deactivation of the catalyst.

Over the past 70 years, the Fischer-Tropsch reaction has received more attention than the methanation reaction. Three reasons for studying the methanation reaction are:

- 1) to form a high BTU methane rich fuel with low carbon monoxide content.
- 2) to eliminate carbon monoxide present in small amounts in hydrogen rich gases by conversion to methane.
- 3) to avoid methane formation during a Fischer-Tropsch synthesis.

Early research was concerned primarily with reason three. Later work was concerned with reason two. Interest was to purify natural gas of carbon monoxide impurities so that it would meet Federal standards for pipelines (0.1 ppm maximum). Recently, with the growing shortage of oil and natural gas, the production of methane from alternate fuel sources is looking more feasible.

Thermodynamics of the methanation reaction are summarized in Table 2. The reaction is thermodynamically more favorable (ΔG° is more negative) the lower the temperature but lower temperatures reduce the kinetic rate. Thus, experimenters must compromise by choosing some intermediate temperature, typically in the 300°C to 500°C range, where reaction rate and equilibrium position are both reasonably satisfactory. Once a reaction temperature has been selected, one must take precautions to prevent the highly exothermic reaction from overheating and sintering the catalyst.

Table 2. Methanation thermodynamics (11).
All reactants and products have
gaseous standard states

T(K)	ΔG° (kcal/mole)	ΔH° (kcal/mole)
300	-33.9	-49.3
400	-28.6	-50.4
500	-23.0	-51.3
600	-17.3	-52.1
700	-11.4	-53.2
800	- 5.5	-52.7
900	0.5	-53.6
1000	6.5	-53.9

Results from earlier methanation studies show great diversity. This variation is due to differences in reaction parameters, catalyst support, and methods of pretreatment. Usually, the data are fit to a rate law of the form:

$$r_{\text{CH}_4} = K P_{\text{CO}}^x P_{\text{H}_2}^y \quad (9)$$

with y between 0.5 and 1.5 and x between 0 and -1.0. Interaction from products is weak; commonly the rate is independent of product partial pressures (i.e., is zero order in them). The general belief is that the catalyst surface (during reaction) is covered with strongly adsorbed carbon monoxide. The weakly bound hydrogen competes for the remaining sites.

Vannice was the first to determine the specific activities of all group VIII metals, except osmium, for the methanation reaction (12). He conducted his experiments at atmospheric pressure and 205°C to 285°C. He also used alumina supports. The activities of these metals are as follows:



The specific activities varied two orders of magnitude from ruthenium to iridium. This compares to Sinfelt's work on hydrogenation of ethane where the specific activities varied eight orders of magnitude from the least reactive metal to the most reactive metal. This work by Vannice (12) started a new way of reporting methanation kinetics. The data collected before 1975 did not include any measurement of the

surface areas of the catalysts. Information gained was useful, but comparison of data was impossible because rates are dependent on the number of metal surface sites. Vannice introduced specific activity (molecules of methane per site per second) which is independent of the catalyst total surface area. Data since 1975 are generally reported in the form of specific activities making comparisons much more informative.

All metal elements that will catalyze the Fischer-Tropsch or methanation reaction have been investigated. So far no catalyst will make these reactions work with economic feasibility. One trend recently has been toward the synthesis of mixed metal catalysts for these reactions.

When two metals are mixed on a support, there are three possible situations (13);

- 1) Both metals are inactive for the reaction, but the mixture is active.
- 2) Both metals are active, but the mixture has higher or lower activity.
- 3) One of the metals is inactive, but the other is active for the reaction.

When one combines two metals on the surface of a support, it is wise to consider how these two metals will interact. For example, will they form two separate phases composed of the separate metal particles or will they form alloys or intermetallic compounds? Another consideration is the surface composition. This is almost always different from the bulk composition. For situation three above, one might find a molecule which adsorbs to both metals, and another molecule which adsorbs to only one metal. Then one would be able to determine the

number of respective sites on the catalyst surface. There are instrumental techniques to determine the surface composition (Auger, ESCA), but results from these techniques must be carefully interpreted since they generally reflect compositions of several atomic layers, besides the surface layer.

Next I would like to report on some mixed metal catalysis work from various sources for the hydrogenation of carbon monoxide reaction.

Vannice et al. studied this reaction over a ruthenium-iron mixture supported on silica (14). Their analyses included chemisorption of hydrogen and carbon monoxide, x-ray diffraction and Mössbauer spectroscopy. Catalysts investigated contained the following atom percents of ruthenium: 100, 96.5, 84.7, 64.8, 35.6 and 0.0. For these ratios and their reduction conditions, 450°C, ruthenium and iron form a continuous series of solid solutions (15). This means that there will be no thermodynamic barriers preventing these two metals from forming an actual alloy on the surface of the support. It was found that ruthenium-iron ratios from 0.5 to 2 inhibited methanation more than the overall carbon monoxide hydrogenation activity. Also noted was a decrease in the apparent activation energy for formation of methane. These ratios led to an enhanced production of olefins. No evidence for the production of oxygenated compounds was found.

This same system (powdered ruthenium and iron) has also been investigated by Ott et al. (16). They kept the ruthenium bulk composition greater than 25%, where ruthenium and iron form a continuous series of solutions. They sought to define the surface composition with x-ray

photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS). They conclude that the surface of the catalysts became enriched with iron.

Another study by Oblad et al. investigated the kinetics of hydrogenation of carbon monoxide over a cobalt-copper on alumina catalyst. This catalyst was prepared by a co-precipitation technique. From Hansen (17), these metals are only slightly soluble in each other at reduction temperatures. I would expect after reduction of the catalysts there would exist on the surface of the supports separate islands of cobalt and of copper.

They observed that the mixed metal catalysts compared to the cobalt catalyst gave

- 1) an increase in metal surface area,
- 2) a higher selectivity for C_2 to C_4 products, and
- 3) a decrease in CH_4 and CH_3OH production.

Araki and Ponc investigated the influence of alloying copper and nickel on the hydrogenation of carbon monoxide reaction (18). These authors, using an ultra-high vacuum system, prepared alloy films of copper and nickel. They successively deposited these metals at $\sim 200^\circ C$ at a pressure of 10^{-10} to 10^{-9} Torr. This was followed by annealing at $350^\circ C$ where these metals are miscible (17).

Reaction conditions were 0.58 Torr total pressure, a hydrogen to carbon monoxide ratio of 5, and a temperature of $250^\circ C$. They noted a rapid drop in methanation activity with addition of copper to nickel. From this, one might conclude that nickel is an active catalyst for

methanation and that copper is not. This is so. This rapid drop in the production of methane is attributed a reduction in the size and number of the nickel clusters. They presume that such clusters composed of several active sites are necessary for this reaction to occur on nickel.

Another system that has been investigated is the hydrogenation of carbon monoxide over manganese-cobalt on alumina catalysts. It is known that addition of manganese to cobalt will modify selectivity and activity, given that these catalysts are prepared by standard techniques (from salts of these compounds, followed by reduction in hydrogen) (19). Vanhove et al. impregnated alumina ($250 \text{ m}^2/\text{g}$) with solutions of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$ to make 1% weighting for cobalt with total metal content not to exceed 2.5% (20). These clusters were then decomposed to give the active catalysts. They found that a manganese to cobalt ratio of one was the most active for the hydrogenation of carbon monoxide. The manganese appears to give a catalyst with a longer lifetime as compared to the cobalt catalyst. They explain that this stability comes from formation of a well-dispersed alloy on the support surface. From Hansen, these two metals are quite miscible in each other (17).

An investigation of intermetallic (one component is an actinide or rare earth and the other is a 3d transition metal) catalysts for the hydrogenation of carbon monoxide has appeared in the literature. Neutron diffraction studies of hydrogenated rare earth intermetallics show that atomic hydrogen is present in the lattice. This suggests that this combination of compounds might make effective catalysts for the