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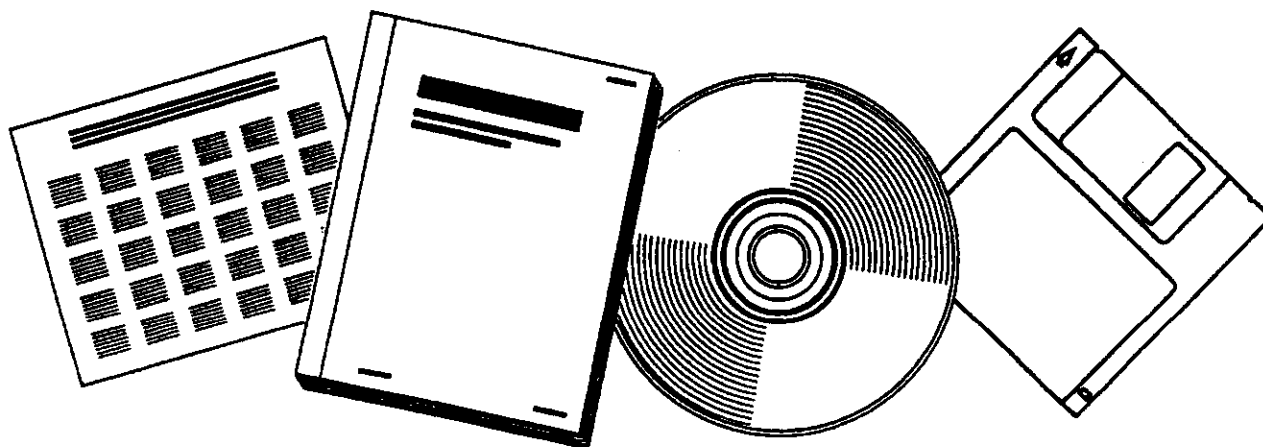
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# CATION PROMOTION EFFECT IN ZEOLITE-SUPPORTED F-T CATALYSTS: FINAL REPORT

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL  
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**CATION PROMOTION EFFECT IN ZEOLITE-SUPPORTED  
F-T CATALYSTS**

**Final Report**

**By**  
**James G. Goodwin, Jr.**  
**Rachid Oukaci**

**August 31, 1986**

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**For**  
**U. S. Department of Energy**  
**Pittsburgh Energy Technology Center**  
**Pittsburgh, Pennsylvania**

**By**  
**University of Pittsburgh**  
**Pittsburgh, Pennsylvania**

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Final Report

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ZEOLITE-SUPPORTED F-T CATALYSTS

DOE Grant No. DE-FG22-83PC60805

by

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August 31, 1986

## OBJECTIVE AND SCOPE OF WORK

Ru is a useful, model catalyst for the study of alkali promotion of F-T synthesis. First, alkali promotion has been found to have a great effect on product selectivity over Ru. Second, Ru does not form any stable carbides, thereby removing this complicating factor. Third, Ru is relatively easy to reduce to the metallic state. Fourth, Ru is the F-T metal easiest to keep inside zeolite crystallites. Fifth, under typical conditions, there is little oxygenated hydrocarbon formation or skeletal isomerization of the hydrocarbons over Ru. Thus, the neutralizing cations in the zeolite support should affect CO hydrogenation over Ru possibly by affecting: CO chemisorption, H<sub>2</sub> chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH<sub>4</sub>, selectivity for olefins, and diffusion in the zeolite.

This research involved a study of the effects of the neutralizing alkali cations on CO hydrogenation (under typical F-T conditions) over zeolite-supported Ru catalysts.

The main objectives of this study were:

1. to develop a better understanding of how neutralizing alkali cations in zeolites can affect F-T product selectivity over a supported metal:

2. to illuminate the effect of these cations on
  - a. chemisorption properties
  - b. the activity and selectivity in CO hydrogenation
  - c. possible secondary reactions
3. To elaborate upon the effect of decreasing ionization potential of the alkali cations on the catalytic properties.

In order to accomplish these objectives, several series of catalysts were been prepared. these catalysts were mainly zeolite-supported Ru prepared using NaX, NaY, KL, Na mordenite and Y zeolites containing a range of alkali cations ( $\text{Cs}^+$ ,  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$  and  $\text{Li}^+$ ).

The results of this investigation described in detail in this report, provide a more fundamental understanding of the involvement of alkali cations in determining the catalytic properties of zeolite-supported metals for CO hydrogenation.

## ABSTRACT

The present work was undertaken to investigate systematically the influence of Group IA neutralizing cations on CO hydrogenation over zeolite-supported ruthenium catalysts. These catalysts were prepared from  $\text{NH}_4\text{Y}$ ,  $\text{LiY}$ ,  $\text{NaY}$ ,  $\text{KY}$ ,  $\text{RbY}$ ,  $\text{CsY}$ ,  $\text{NaX}$ ,  $\text{KL}$ , and Na-mordenite zeolites by ion-exchange with ruthenium hexammine chloride.

The nature of the group IA cations was found to have little effect on chemisorptive properties and on the activity and chain growth probability in CO hydrogenation on Ru. However, it was established that secondary acid-catalyzed reactions of the primary olefinic products from CO hydrogenation can play a major role in shaping product selectivity.

Using model reactions such as olefin transformations on the zeolites without the metal, it was established that the strength of the acid sites is a strong function of the nature of the neutralizing alkali cations remaining in the zeolite. Acid site strength was found to decrease with molecular weight of the alkali cation used.

This study established the bifunctional nature of the zeolite-supported F-T catalysts and its importance in CO hydrogenation. The results suggest that the catalyst selectivity can be controlled by varying the strength of the

zeolite acid sites, the most important active centers for secondary reactions of the primary olefinic F-T products. Depending on the concentration and the strength of the acid sites, a function of the Si/Al ratio and the nature of the residual neutralizing cations, various competitive reaction paths can be observed for the transformation of olefinic compounds. These include isomerization, oligomerization, cracking, hydrogen transfer, etc.



## 1.0 INTRODUCTION

The need to convert coal or natural gas, both more abundant than the natural reserves of liquid hydrocarbons, into more suitable energy carriers, especially for automotive purposes, have led in the last decade to an upsurge of interest in new hydrocarbon synthesis routes, alternative to the classical petrochemical processes. The catalyzed conversion of synthesis gas, a mixture of carbon monoxide and hydrogen, which can be obtained either by coal gasification or by steam reforming of natural gas, has, therefore, attracted enormous attention since it offers the possibility of achieving these new synthesis routes. This process has a long history which started in the early part of this century with its first development by Fischer and Tropsch. (1-2)\*

Depending on the catalyst and the reaction conditions, in particular, pressure, temperature and  $H_2/CO$  ratio, it is possible to produce numerous fuels and chemicals by the catalytic conversion of synthesis gas. However, only in the case of methane and methanol can a selectivity of 100% be achieved. In general, CO hydrogenation over conventional

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\*Parenthetical reference placed superior to the line of text refer to the bibliography.

Fischer-Tropsch (F-T) catalysts leads to the formation of a wide spectrum of products ranging from methane to heavy oils and waxes as well as various oxygenated products.<sup>(3)</sup> Extensive refining and further processing of the CO hydrogenation product stream are, therefore, required in order to obtain suitable automotive fuels or chemical feedstocks. None of these processes seems at the moment to be economically feasible. Hence, catalyst selectivity may be considered a very important problem in the F-T synthesis.

In recent years, several studies undertaken in this field were aimed at developing highly selective catalysts for the conversion of syngas into liquid fuels and chemical feedstocks.<sup>(4-5)</sup> Several approaches have been attempted to circumvent the Anderson-Schulz-Flory (ASF) polymerization probabilities which characterize most systems in CO hydrogenation.<sup>(6)</sup> A number of studies<sup>(7-11)</sup> have provided evidence that the adsorption and catalytic properties of the F-T catalyst depend markedly on the nature of the material on which it is supported, especially in well dispersed systems.

Zeolites are one class of supports which offers enormous potential in the search for means by which the product selectivity of F-T catalysts may be controlled. Due to their equivalent high surface areas, high metal dispersion can be maintained on such supports.<sup>(12-15)</sup> Owing to the incorporation of the metal particles in a

geometrically-restricted environment, zeolite-supported catalysts may exhibit shape selectivity,<sup>(16-18)</sup> thus restricting the normal chain growth process which characterizes F-T catalysts. In addition, the ion-exchange capability of zeolites can be used to tailor their properties, such as acidity, thus anticipating the importance of secondary reactions such as isomerization, usually acid catalyzed, which can also strongly influence the product distribution.<sup>(8,14-15,19)</sup>

Metal-zeolite interactions may also play a role in the selectivity control during F-T synthesis on zeolite-supported metal catalysts. In the case of zeolite-supported ruthenium catalysts a number of studies<sup>(20-21)</sup> have shown that the adsorption stoichiometries and states of H<sub>2</sub> and CO on ruthenium, dispersed in zeolites of different Si/Al ratios, can be significantly affected by the type of zeolite in which the metal is entrapped. The observed changes in adsorption as well as in the activity and selectivity of these catalysts for CO hydrogenation have been attributed mostly to modifications of the electronic structure of the metal particles as a result of metal-support interactions.<sup>(14-15,20-23)</sup> However, the trends for these support effects still remain somewhat inconsistent and ambiguous. Indeed, at least as far as the activity of these catalysts is concerned, Jacobs et al.<sup>(22)</sup> found that the

less acidic zeolites acted as promoters for CO hydrogenation. However, others have demonstrated just the opposite effect of support acidity<sup>(23)</sup> or have found no effect at all.<sup>(8)</sup>

A recent study<sup>(15)</sup> of the effect of the type of zeolite supports on the catalytic properties of Ru in F-T synthesis seemed to indicate that the neutralizing alkali cations in the zeolite may be able to promote hydrocarbon formation. Furthermore, the effect on selectivity of alkali promoters in conventional F-T catalysts<sup>(24-25)</sup> suggests that metal interactions with the alkali cations remaining in the zeolite may have an important influence on selectivity. The role of these cations in adsorption and catalysis by zeolite-supported metals has not received much attention to date.

The present work was undertaken to investigate systematically the influence of Group IA neutralizing cations and Si/Al ratio on CO hydrogenation over ion-exchanged zeolite-supported ruthenium catalysts. An attempt is made to assess the importance of metal-support interactions which may be involved during CO hydrogenation on these catalysts. Both electronic effects, where partial electron transfer from metal to support or inversely, and bifunctional effects, where sites on the support and on the metal particles can act somewhat independently on the reactants and intermediates, are considered throughout this

investigation. Ruthenium is used in this study since it is considered to be one of the most active metals which catalyze carbon monoxide hydrogenation. (26-27) Its characteristics for F-T synthesis have been studied since the late 1930's. (28) In addition, it can be kept in a highly dispersed state inside the zeolite crystallites, hence, in intimate contact with the alkali cations present in the zeolites. (13-17) Furthermore, under typical F-T conditions, it produces little or no oxygenated hydrocarbons or branched hydrocarbons which can be, if present, a complicating factor in the interpretation of the reaction results.

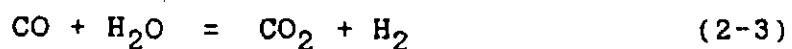
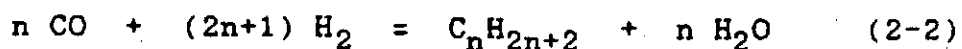
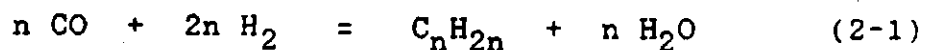
## 2.0 BACKGROUND

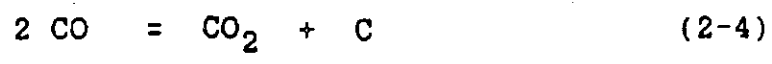
### 2.1 CO Hydrogenation

Since its development by Fischer and Tropsch, (1-2) the CO hydrogenation process has been the object of numerous investigations which have been reviewed by several authors. (28-36) Much of the research work was aimed at elucidating the mechanism of the F-T synthesis. Several reviews dealing specifically with the various proposed mechanisms of CO hydrogenation can be found in the literature. (36-41) Since the aim of this study is mainly to establish the ways in which zeolite supports of F-T metals may influence the catalytic properties of these, no attempt will be made here to describe these mechanisms.

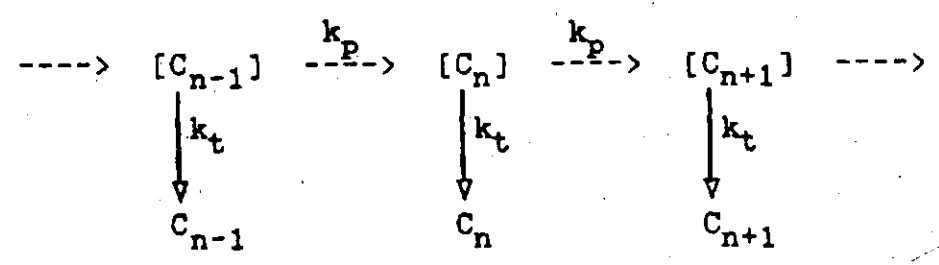
#### 2.1.1 Nature of the Selectivity Problem in F-T Synthesis

In spite of the complexity of the F-T synthesis which involves a great number of competing reactions, the overall stoichiometry of these reactions can be described by the following equations:





Two side reactions, the water-gas shift reaction (2-3) and the Boudouard reaction (2-4) are included since they may play an important role in overall selectivity and deactivation of the catalyst. The distribution of the products that can be obtained from these reactions is obviously sensitive to such parameters as the catalyst metal, its state of dispersion, the reaction conditions, and the nature of promoter added to the metal. The synthesis of hydrocarbons from CO and H<sub>2</sub> is generally viewed as a polymerization process which was first described by Anderson in 1950<sup>(42)</sup> and which can be illustrated by the following scheme:



Essentially, starting from an initial C<sub>1</sub> monomer derived from CO, this involves a gradual buildup in molecular size to produce higher hydrocarbons. A propagation step with rate constant k<sub>p</sub> competes with a termination step with rate constant k<sub>t</sub> leading to product formation. Under steady

state conditions, the probability of either step occurring is independent of the chain length of the oligomer attached to the surface. Whatever the nature of the building blocks, the  $C_1$  monomer, which in itself constitutes the object of numerous investigations and considerable controversy, the polymerization process remains the same. The products follow a Schulz-Flory<sup>(43-44)</sup> distribution of molecular weights commonly found in oligomerization and polymerization processes and which can be described mathematically by the following equation:

$$W_n = n a^{n-1} (1-a)^2 \quad (2-5)$$

where  $W_n$  represents the weight fraction of oligomer  $C_n$ ,  $n$  the carbon number, and  $a$  the probability of chain growth. From this equation the maximum weight fraction of a hydrocarbon product  $C_n$ , where  $n > 2$ , can be predicted as illustrated in Figure 2.1.<sup>(5)</sup> The chain growth probability,  $a$ , is a constant which depends on both the nature of the catalyst and the reaction conditions, i.e., temperature, pressure,  $H_2/CO$  ratio, space velocity.<sup>(34)</sup> However, utilization of the latter variables to control the selectivity of F-T synthesis has produced only limited shifts in the broad product distribution which remains within the selectivity constraints predicted by ASF polymerization probabilities.<sup>(33)</sup>



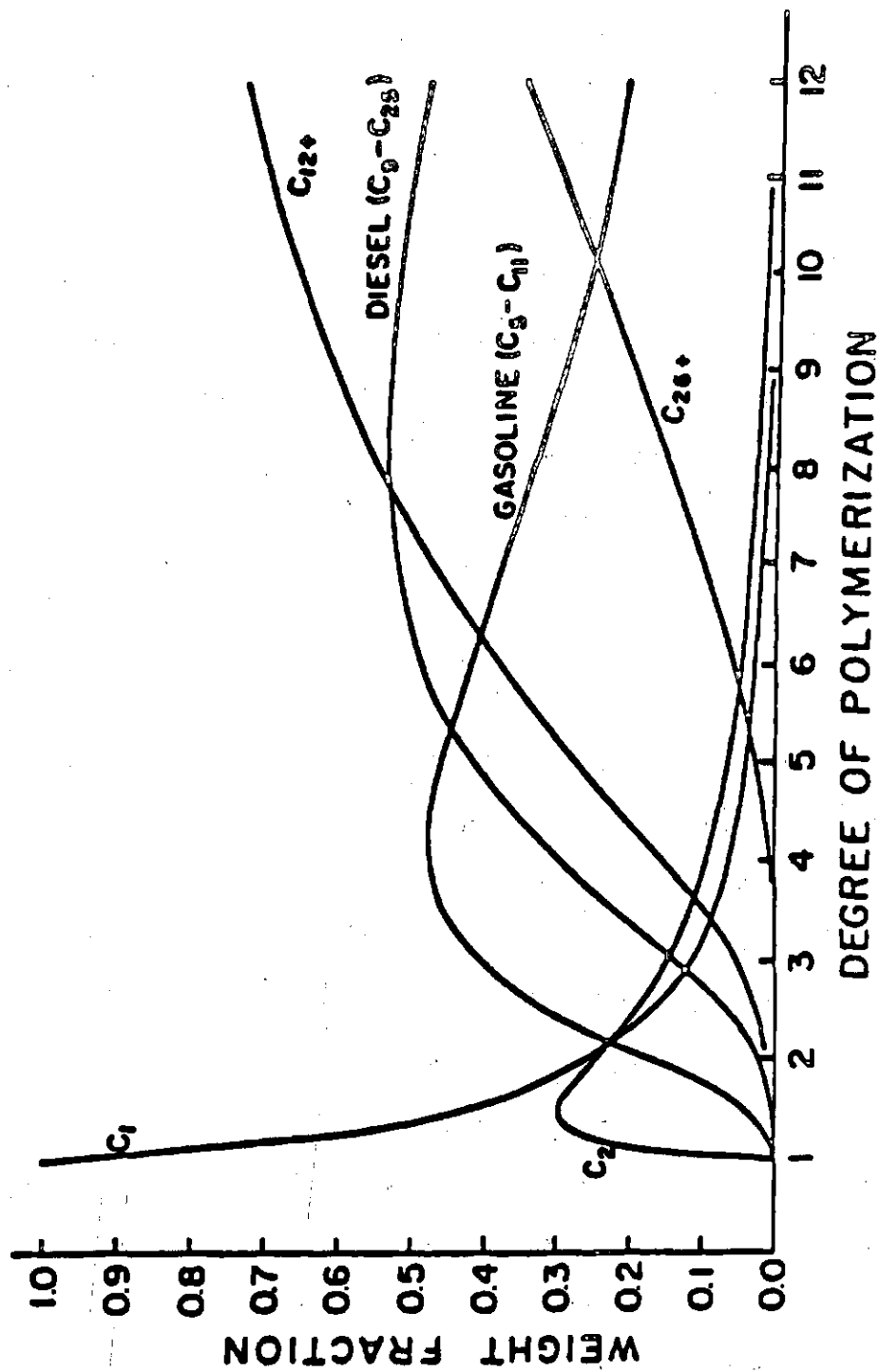


Figure 2.1 Selectivity Limitations on F-T Synthesis as Determined by the ASF Distribution Function (5)