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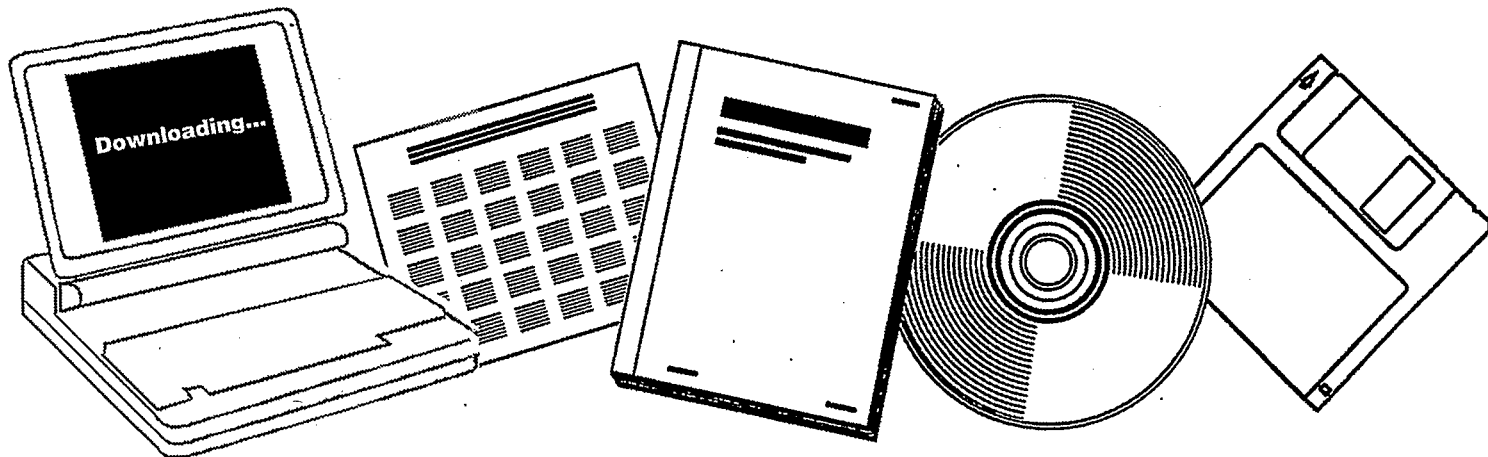
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**CATION PROMOTION EFFECTS IN
ZEOLITE-SUPPORTED F-T CATALYSTS. ELEVENTH
QUARTERLY REPORT, MARCH-MAY 1986**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

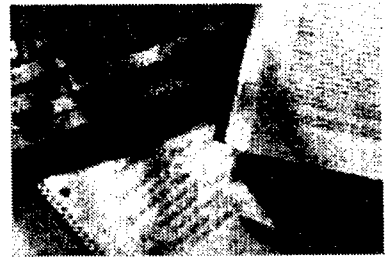
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CATION PROMOTION EFFECTS IN
ZEOLITE-SUPPORTED F-T CATALYSTS

11th Quarterly Report
March 1986 - May 1986

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TABLE OF CONTENTS

I.	OBJECTIVE AND SCOPE OF WORK.....	1
II.	SUMMARY OF PROGRESS.....	2
III.	DETAILED DESCRIPTION OF TECHNICAL PROGRESS.....	3
	1 - Catalysts Preparation and Characterization.....	3
	2 - Reaction Studies.....	3
IV.	FORECAST OF WORK.....	7
	REFERENCES.....	7
	TABLES.....	8

I. OBJECTIVE AND SCOPE OF WORK

An investigation into zeolite-supported F-T catalysts begun under Grant #DE-FG22-81PC40774 (Office of Fossil Energy, D.O.E.) has produced results which suggest that alkali cations, remaining in a zeolite and serving to neutralize the structure, act to promote higher hydrocarbon formation. It appears that the F-T metal must be highly dispersed throughout the zeolite in the vicinity of these cations for this promotion effect to take place. This effect is also highly dependent upon alkali cation concentration.

The current research involves a study of the promotion effects of the neutralizing alkali cations on CO hydrogenation (under typical F-T conditions) over zeolite-supported Ru catalysts. Ru is a useful, model catalyst for the study of such promotion of this 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, H₂ chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH₄, selectivity for olefins, and diffusion in the zeolite. Each of these items will be investigated for the catalysts proposed to be studied.

The main objectives of this study are:

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. CO disproportionation
 - c. the mechanism of CO hydrogenation
 - d. the deactivation characteristics
3. to elaborate upon the effect of decreasing ionization potential of the alkali cations on the catalytic properties
 4. To investigate the effects of Rb and Cs promotion, studied only superficially in the past.

In order to accomplish these objectives, several series of catalysts have been prepared. These catalysts are mainly zeolite-supported Ru prepared using NaX, NaY, KL, X and Y zeolites containing a range of alkali cations (Cs^+ , Rb^+ , K^+ , Na^+ and Li^+), and a series of dealuminated NaY zeolites. Preparation and characterization of these samples by means of gas volumetry and atomic absorption have been described in a previous quarterly report. Further investigations of surface and catalytic properties are under way.

This investigation should provide a more fundamental understanding of the involvement of alkali cations in determining the catalytic properties of zeolite-supported metals for CO hydrogenation.

II. SUMMARY OF PROGRESS

The effect of Si/Al ratio on the possible secondary reactions during CO hydrogenation were investigated with different zeolites, RuNaX, RuNaY, RuKY, RuKL, and RuNa-mordenite. These catalysts were prepared by ion-exchange and characterized by the same procedures described in previous reports.

NaX, NaY, KL, and Na-mordenite were used as catalysts in butene reactions in order to eliminate the effect of Ru on the transformation of olefins. These reactions were carried out under similar conditions as those of CO hydrogenation for the series of ion-exchanged zeolite-supported Ru catalysts.

In order to understand the olefin reactions over the acid sites in the ion-exchanged Ru zeolites, H mordenite was chosen for study because it has the highest Si/Al ratio, hence the strongest acid sites. Deactivation of H-mordenite was studied in detail for the propylene and butene reactions.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

1 - Catalyst Preparation and Characterization

The zeolites, NaX, NaY, KL, and Na-mordenite were from Strem Chemicals. Ru-loaded zeolites were prepared by ion-exchange using $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (Strem Chemicals). The preparation procedure used for these catalysts was described in previous reports. H_2 and CO chemisorption were used for the characterization of the catalysts.

The results of H_2 and CO chemisorption for RuNaX, RuNaY, RuKL, and RuNa-mordenite are listed in Table 1. The metal particle size and dispersion of catalysts were calculated from the H_2 chemisorption results. The CO/H ratio obtained for RuKL and RuNa-mordenite showed a significant suppression of hydrogen chemisorption. This is in agreement with the results reported by Wang et al. (1)

2 - Reaction Studies

Experimental

(A) CO Hydrogenation

CO hydrogenation was carried out in a tubular micro-reactor with a 1:1 mixture of H_2 and CO flowing at 2.4 l/hr. The conditions of reaction were atmospheric pressure and temperatures of 483-573 K. The reaction products were analyzed by gas chromatography after five minutes of reaction. This five minute reaction period was followed by a 40 minute hydrogen treatment of the catalyst in order to obtain reproducible results in successive runs.

(B) Olefin Reactions

Butene reactions were carried out in the same reaction system used in CO hydrogenation. The reactant mixture was 100 ml/min of 1% butene in hydrogen at atmospheric pressure. The temperature was fixed at 523 K. The amount of catalyst used was 0.1 g.

Products from the reactor were also analyzed by gas chromatography after five minutes of reaction. The GC column used was able to fully separate the C₄- fraction into its components.

(C) Deactivation of H-Mordenite

In order to determine the deactivation characteristics of the strong acid sites, butene and propylene reactions were carried out over H-mordenite. The same reaction conditions as described above for butene reactions were used except for the reaction time which was of course varied.

Results and Discussion

(A) CO hydrogenation

Table 2 compares the turnover frequencies (TOF) and the hydrocarbon product distributions obtained at 523 K on Ru/zeolites with different Si/Al ratios, i.e. RuNaX, RuKL and RuNa-mordenite. For the sake of comparison, the results obtained for RuNaY and RuKY and reported in previous quarterly reports are included. Although RuKY has the same Si/Al ratio as RuNaY, it is included in Table 2 since it allows a better comparison with RuKL. The C₃[≡]/C₃[≠] ratios and the isobutane content of the C₄- fraction is also given in Table 2. From these results it can be seen that while the TOF remains practically constant at 523 K, suggesting no effect of the acidity on the intrinsic properties of

the metal, the C_3^-/C_3^+ ratio decreases with Si/Al ratio, while the selectivities for CH_4 and isobutane increase significantly with Si/Al ratio.

Since all the zeolite-supported catalysts studied here are expected to have had the same number of acidic sites (they all had similar metal loadings) the variation in selectivities may be correlated with variation in acid strength. Indeed it is well known that the strength of the acid sites present in the zeolite increases with Si/Al ratio, especially for Si/Al < 6 (2).

In contrast to the results obtained when the nature of the neutralizing cation was varied, the product selectivity (Table 2) shifted towards lower molecular weight hydrocarbons, especially methane, with increasing Si/Al ratio.

The activity of the catalysts for secondary olefin hydrogenation represented by the C_3^-/C_3^+ ratio, and the isobutane selectivity follow the same trend as the methane selectivity. These results suggest an enhancement of the various secondary reactions such as oligomerization, cracking, hydrogen transfer, etc., which are known to be favored with the more acidic catalysts (3).

However, the selectivity for isobutane obtained with RuNa-mordenite was not significantly higher than that obtained with RuNaY. This may be explained by the fast deactivation of the strongest acid sites in RuNa-Mordenite, as illustrated in the following section by the deactivation characteristics of H-mordenite.

(B) Butene Reaction on Zeolites without Ru

The metal Ru can also contribute to the secondary hydrogenation and isomerization of primary products. In order to eliminate the effect of the metal on secondary reactions, butene transformation was carried out on zeolites without Ru. The product selectivities are listed in Table 3. The

isomerization of butene on zeolites can involve double bond shift, cis-trans isomerization, and skeletal isomerization (4). Since these alkali zeolites have only few acid sites, mainly the hydroxyls terminating the zeolite crystals, only double bond shift and cis-trans isomerization were observed. There was no oligomerization or skeletal isomerization of olefins for which stronger acid sites are required. Furthermore, contrary to Topchieva et al. (5) suggestion that the cations may exhibit significant activity for the hydrogenation of olefins when treated with hydrogen at high temperature, no hydrogenation activity was observed with all the zeolites. The only products obtained from 1-butene reactions were cis- and trans-2-butenes.

(C) Deactivation Study of H-mordenite

The purpose of this deactivation study was to show how the acid sites change with reaction time. Table 4 shows how the formation rate of each product from butene reaction varies with reaction time. The formation rate of isobutane decreased rapidly with reaction time. The yield of isoparaffins from the transformation of olefins on acid catalysts can be taken as a measure of the oligomerization, disproportionation, hydrogen transfer and cracking activity of these catalysts. The results, thus, suggest that the strong acid sites in H-mordenite, active for the oligomerization of olefins, deactivate rapidly. After less than four minutes of reaction, the reaction path shifted from the oligomerization-disproportionation reactions to double bond shift and cis-trans isomerization which can occur on very weak acid sites.

This phenomenon was also observed for the reaction of propylene (Table 5). The formation rate of isobutane decreased significantly as reaction time increased. The formation rate of all products decreased as reaction time increased to 17 minutes. Therefore, all the acid sites deactivate with reaction time with the strong acid sites deactivating the fastest.

IV. FORECAST OF WORK

During the next quarter, the main focus will be on the analysis and integration of all the results, and writing of the final report.

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Table 1: Catalysts Characteristics

Catalyst	Ru Loading (wt %)	$\frac{\text{Si}}{\text{Al}}$ ratio	$\text{H}_2(\text{irr.})(\text{a})$ (μ mol/g.cat.)	D ^(b) (%)	d_p ^(b) (Å)	CO/H ^(c)
RuNaX	3.0	1.23	80	54	16	-
RuNaY	3.8	2.41	126	67	12	3.7
RuKL	3.2	3.00	53	36	24	5.0
RuNaM	3.2	4.52	39	26	32	4.3

(a) Irreversible H_2 chemisorption.

(b) Dispersion (D) and particle size (d_p) from H_2 chemisorption measurements.

(c) From CO and H_2 chemisorption measurements.

Table 2: TOF, $C_3^=/C_3^-$ and Hydrocarbon Distributions from CO Hydrogenation at 523 K over Ru/Zeolites with various Si/Al ratio

Catalyst	TOF(a) ($s^{-1} \times 10^3$)	$C_3^=/C_3^-$	i-C ₄ (%)(b)	Selectivity (wt%)					
				C ₁	C ₂	C ₃	C ₄	C ₅	C ₆ ⁺
RuNaX	5.8	13.6	0	17.3	11.7	24.8	19.4	15.1	11.6
RuNaY	6.8	4.2	20.2	32.7	14.0	21.5	17.0	10.9	4.0
RuKY	7.8	6.4	1.8	30.7	13.7	23.5	15.8	11.0	5.2
RuKL	8.4	3.8	12.3	49.5	12.3	17.8	11.7	6.1	2.6
RuNaM ^(c)	8.0	0.5	24.0	56.0	16.6	12.3	9.9	2.0	3.2

(a) From H₂ chemisorption results.

(b) Isobutane in C₄-fraction.

(c) M = Mordenite.

Table 3 Product Selectivities From 1-butene reactions*

Catalyst	Conversion (%)	$\frac{\text{Trans-2-Butene}}{\text{1-Butene}}$	$\frac{\text{Cis-2-Butene}}{\text{Trans-2- Butene}}$
NaX	25.0	0.22	0.74
NaY	8.5	0.06	0.60
KL	14.7	0.11	0.64
NaM	11.2	0.11	0.64

* Reaction mixture: 1% Butene in H₂
 Flowrate: 100 ml/min
 Temperature: 523 K

Table 4 Product Formation Rates from Butene Reaction on H-mordenite

Products	1*	2*	4*	6*
	Rates (mol/hr. g. cat. 10E3)			
methane	0.03	0.03	0.03	0.03
ethane + ethene	0.02	0.02	0.02	0.01
propane	0.44	0.56	0.35	0.40
propylene	0.21	0.56	0.71	0.87
isobutane	6.35	5.30	0.97	0.65
butane	0.47	0.59	0.54	1.70
trans-2-butene	0.06	0.61	4.47	9.47
cis-2-butene	0.04	0.39	2.94	6.21
total C-5	1.40	2.48	1.14	1.00
total C-6	0.08	0.11	0.08	0.07

Reaction mixture: 1% Butene in H₂
 Flowrate: 100 ml/min
 Temperature: 523 K
 * accumulated reaction time (min)

Table 5 Products Formation Rates from the Reaction of Propylene on H-mordenite

Products	1*	4*	17*
	Rates (mol/hr. g. cat. 10E3)		
ethane + ethene	0.08	0.09	0.08
propane	1.08	1.37	0.48
iso-butane	5.86	1.44	0.01
butane	0.54	0.46	0.04
1-butene	0.06	0.46	0.04
trans-2-butene	0.02	0.38	0.05
cis-2-butene	0.01	0.24	0.02
total C-5	1.00	1.17	0.04
total C-6	0.40	0.10	0.00

Reaction mixture: He: H₂: C₃ = 60: 39: 1

Flowrate: 100 ml/min

Temperature: 523 K

* accumulated reaction time (min)

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