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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS. SECOND QUARTERLY REPORT, DECEMBER 1983-FEBRUARY 1984

PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
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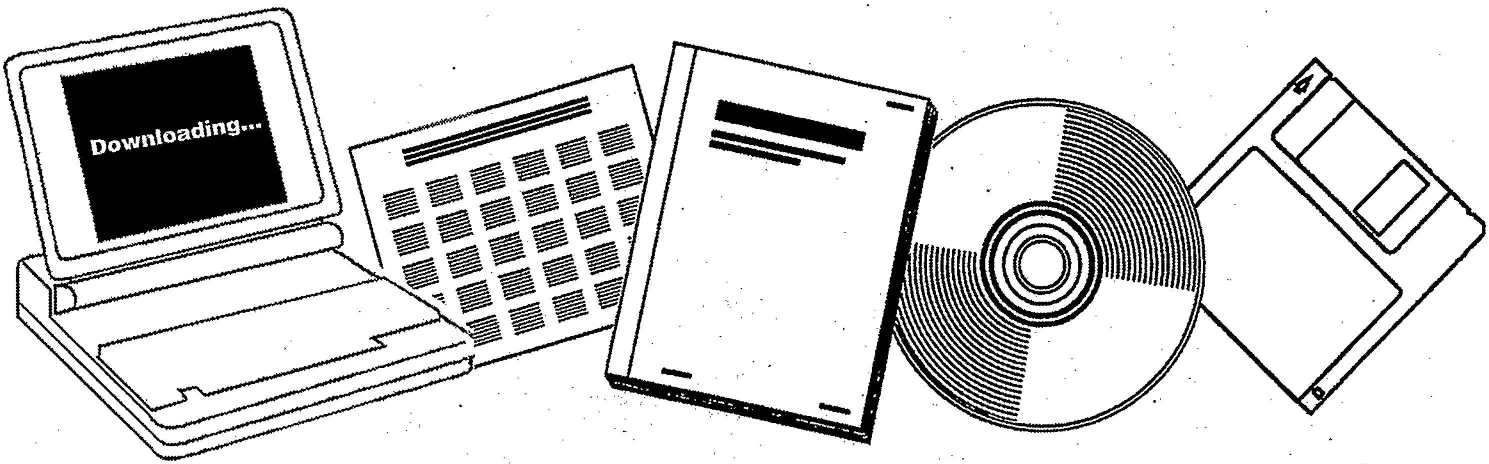

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CATION PROMOTION EFFECTS IN ZEOLITE-SUPPORTED F-T CATALYSTS

2nd Quarterly Report
December 1983 - February 1984

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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 isometrization 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_2 chemisorption, carbon deposition, catalytic activity, chain growth probability, selectivity for CH_4, 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 on 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 and studied by gas volumetry and atomic absorption. Further investigations will be done by temperature programmed desorption, IR spectroscopy, catalytic reaction and thermogravimetry. These catalysts are mainly zeolite-supported Ru prepared using NaX, NaY, NH_4Y, KL, X and Y zeolites containing a range of alkali cations (Cs^+, Rb^+, K^+, Li^+), and a series of dealuminated NaY zeolites. For comparison purposes a few catalysts supported on silica and alumina have also been prepared.

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

During this quarter, December 1, 1983, to February 29, 1984, work has been continued in all tasks of the project. More than thirty catalysts have been prepared. All of them have been analyzed by means of atomic absorption. Substantial progress in characterization of these catalysts by means of H_2 chemisorption has been made. A paper dealing with particle size dependence of reversible H_2 chemisorption on supported ruthernium has already been written and submitted for publication. Further investigation of the adsorptive properties of some representative samples are being made by the frequency response technique.

Construction of a high pressure reaction system has just been completed. For the time being, preliminary tests of the apparatus, especially the analytic system (calibration of G.C. detectors), are in progress. Catalytic runs of CO hydrogenation will begin very shortly.

III. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

III-1. CATALYST PREPARATION

During this quarter catalyst preparation has continued. Various series of Ru catlysts have been prepared mostly by ion-exchange of hexammine ruthenium (III) chloride. This method has been described in detail in the first quarterly report. Catalysts prepared may be divided into five series.

3%RuMY ($M=Na^+$, Li^+, K^+, Rb^+, Cs^+): Starting with a commercial NaY zeolite supplied by Strem, a first ion-exchange step enables us to prepare Y zeolite containing other alkali cations than Na^+ (1). Ru is then introduced by ion-exchange of $Ru(NH_3)_6Cl_3$ in a diluted hydrochloric acid solution. These catalysts are intended to study the effect of alkali cations as promotors and the influence of electrostatic field on the properties of Ru, particularly in CO hydrogenation.

3%RuZ (Z=NaY, NaX, HY, KL): These samples have been prepared in the same manner. The supports have been used as received. They serve to study the dependence of adsorptive and catalytic properties of Ru upon the nature of the zeolite.

1% Ru/dealum.NaY: Controlled dealumination of NaY has been conducted using the H_2EDTA extraction method reported by Kerr (2). Three samples with approximately 20, 40, and 60% of Al^{3+} removed have been prepared. X-ray diffraction analysis shows that they still maintain high crystallinity. Due to the lowered exchange ability of these dealuminated zeolites, the metal loading has been limited to 1 wt%.

0.15%RuZ (Z=HY, NaY, KY, LiY, NaX, KL, HY): These catalysts have been prepared by ion-exchange in order to study cyclopropane hydrogenolysis. Indeed, results for this reaction carried out on Pt/SiO_2 and PtNaY (3) and on Ru/SiO_2 and RuNaY (4, 5) have indicated that cyclopropane hydrogenolysis is very sensitive to the zeolite electrostatic field effect. However, it seems that RuNaY catalysts are too active to achieve accurate differential conditions. That is the reason why Ru loading has been limited to 0.15%. Furthermore, these catalysts should have different electrostatic field strengths. Hence, hydrogenolysis of cyclopropane should provide valuable information about this effect.

Ru/SiO_2, Ru/Al_2O_3: This set of catalysts contain four samples which have been prepared by incipient wetness in order to compare Ru/Z behavior with more conventional ones.

$Ru/SiO_2[1]$, $Ru/Al_2O_3[1]$: These catalysts have been prepared by ion-exchange of $Ru(NH_3)_6Cl_3$ using the same procedure as used for the zeolite-supported samples.

$RuSiO_2$ [2]: Even though the quantity of Ru used was supposed to produce $Ru/SiO_2[1]$ with 3 wt% Ru, the final catalyst did not contain more than 0.25 wt% Ru. this is undoubtedly due to the fact that the pH was too low to allow ionization of the SiO_2 surface which is a prerequisite to ion-exchange with silica. On the other hand Ru(III) ammines are unstable at high pH. An alternative, reported by Gay (6), is to use Ru(II) complexes instead of Ru(III) ones. The following procedure has been used for the preparation of $Ru/SiO_2[2]$ containing 2.5 wt% Ru. A calculated amount of $RuCl_3 . 1.5H_2O$ is dissolved in 6 ml of H_2O per gram of SiO_2 used and added to the SiO_2 (Strem) under vigorous stirring. Hydrazine hydrate, 0.8 ml per gram of silica, is then added slowly in order to generate in situ Ru(II) ammine species (7). The mixture is allowed to stand overnight under continuous shaking. Then the catalyst is washed with cold 1M ammonia, dried at 100°C for three hours and reduced at 350°C for two hours.

$Ru/Al_2O_3[2]$: This catalyst has been prepared using Dalla Betta's method (8). γ-Al_2O_3 (Strem) is first washed by 15% NH_4OH for 5 mn, then ion-exchanged with $Ru(NH_3)_6Cl_3$ during 18 hours. The catalysts are then washed and dried.

III-2. DECOMPOSITION AND REDUCTION

The typical procedure to decompose and reduce the catalysts is the following. The Ru samples are decomposed under pure helium flowing at 60

cm^3/min while the temperature is raised from ambient to 420°C at 0.5°C/mn and held at 420°C for two hours with hydrogen flowing at the same rate. Helium (Air Products, UHP) is purified by passing through a heated copper trap to remove oxygen traces and then through a molecular sieve trap to remove water. Hydrogen is passed through an Engelhardt Deoxo purifier followed by molecular sieve trap before contacting the catalysts.

III-3. ATOMIC ABSORPTION

Analysis of Ru has been performed using a Perkin-Elmer Model 380 atomic absorption spectrometer. Depending on the concentration of ruthenium in the catalyst, 25 to 100 mg are accurately weighed into a teflon beaker and dissolved using Fa[illegible]'s method (9) with slight modifications. Concentrated H_2SO_4 (2 ml) and an e[illegible] HI (49%) are added. The mixture is then allowed to stand overnight c[illegible]plate maintained approximately at 100°C. Thereafter, the contents [illegible]nsferred to a 50 ml volumetric flask and brought to volume with an aqu[illegible]tion containing 10% HCl and 2000 mg/L of aluminum ions.

Calibration curves are obta[illegible]g controlled dilutions of a standard 1000 mg/L Ru solution. All addit[illegible] HCl, H_2SO_4, $Al(NO_3)_3$ $9H_2O$) are taken into account when producing the calibration curves.

III-4. HYDROGEN CHEMISORPTION

Hydrogen adsorption measurements are being performed in a typical gas volumic apparatus. The system consists of a high vacuum manifold, an adsorbate gas manifold, a gas handling and storage system, pressure measuring instruments and a detachable glass pyrex cell. A dynamic vacuum of 10^{-6} torr is currently obtained. A liquid nitrogen trap is employed between the adsortpion apparatus and the pumping section.

For adsorption measurements, approximately 0.5g of pre-reduced catalyst is placed in the pyrex cell and evacuated. Then, the sample undergoes a second reduction under static hydrogen while heating up to 420°C with a heating rate of 2°C/min. and held at that temperature during two hours. Thereafter the cell is evacuated for two hours and cooled to room temperature.

Air Products UPC-grade hydrogen and helium are passed through a liquid nitrogen trap before being admitted to their respective reservoirs. Helium is used for dead-volume determination.

The hydrogen adsorption measurements are made at 25°C and isotherms of total H_2 adsorption on the fresh catalyst are determined from 50 to 400 torr. For the first point of the isotherm, the catalysts are allowed to equilibrate overnight. Further points are determined using an equilibration time of about one hour. The catalyst is then evacuated for two min at the same temperature and a second isotherm is obtained in the same manner.

Since H_2 chemisorption has been shown to give the best results for characterization of highly dispersed Ru catalysts (10), these results are used to calculate Ru surface areas assuming a stoichiometry of $H_{irr}/Ru_s=1$ and an average Ru area of 8.17 $Å^2$ (11). The average Ru crystallite size, $\overline{d}$, is determined using the relationship $d=5/S\rho$, where ρ is the density of the metal, and S the surface area of Ru per gram of Ru. The dispersion, which is the relative amount of metal lying on surface is given by $D=(Ru_s/Ru_T)$ x 100%.

Earlier work (12) on highly dispersed NaY-supported Ru(d=0.9-1.6nm) has shown that the reversible fraction of hydrogen chemisorption is a function of average particle diameter and it was suggested that this hydrogen is accomodated on lower-energy sites. This means that reversible hydrogen chemisorption may be used as a probe for studying those specific sites. In order to gain more accurate information about this aspect, particular attention has been paid to determining the reversibly chemisorbed hydrogen fraction under strictly the same conditions using supported Ru catalysts with a wide range of particle sizes (d=0.9-12.5 nm). It has been found that this fraction increases from 7 to 30% of the total chemisorption as the average Ru particle size increases from 0.9 nm to 1.6 nm and then decreases to zero as the average Ru particle size increases from 1.6 nm to 2.5 nm. These findings enable us to state that loosely held hydrogen is accommodated on multiatomic sites ("ensembles") of the same kind as the so-called B_5-sites described by Van Hardeveld and Hartog (13). A paper dealing with this work has been submitted for publication.

III-5. EQUIPMENT DESIGN AND FABRICATION

Permanent gas handling lines enabling us to supply simultaneously four systems with various gases under pressure has been constructed and leak tested. Before use, all gases pass through suitable high pressure purifiers.

A microreactor system has also been constructed for performing high pressure Fischer-Tropsch synthesis from syngas. This reaction system will allow us to carry out F.T, synthesis in the range pressure 1-20 atm. It consists of a flow system, a microreactor and gas chromatograph for product analysis.

In order to achieve differential conditions for F-T. synthesis, the syngas mixture (H_2+CO) will be diluted with helium. The gas streams of H_2, CO and He will first pass through different purifiers to remove traces of H_2O and O_2. The flow rates of the individual streams and thus the composition of the gas stream downstream will be controlled by mass flow controllers (BROOKS

5850). The pressure will be measured by a pressure transducer and maintained by the back-flash pressure regulator. After the gas mixture passes through the catalytic reactor, the outlet stream composition will be analyzed by a gas chromatograph (VARIAN 3700) equipped with a flame ionization detector.

This system has now been completely constructed. Preliminary tests, such as leak checking, calibration of the detectors and optimization of G.C. analysis conditions, are being conducted. Hydrogenation of CO studies will begin early in the next quarter.

Another similar system is being constructed in order to carry out light hydrocarbon (ethane, propane, cyclopropane) hydrogenolysis at atmospheric pressure.

IV. FORCAST OF WORK

In the next quarter the following tasks are planned.

-A thorough study of CO hydrogenation. We will focus on the catalytic properties depending upon the nature of zeolite and that of alkali cations.

-Completion of the atmospheric pressure reaction system..

-Beginning of cyclopropane hydrogenolysis studies in connection with an investigation of the so-called electrostatic field effect.

-Continuation of characterization studies by means of H_2 and CO adsorption.

REFERENCES

1. Goodwin, J. G., Jr., and Sayari, A., First Quarterly Report, U. S. Dept. of Energy, Grant No. DE-FG22-83PC60805.

2. Kerr, G. T., J. Phys. Chem. 72, 2594 (1968).

3. Naccache, C., Kaufherr, N., Dufaux, M., and Imelik, B., in "Molecular Sieves II", J. R. Kartzer, Ed., ACS, Washington, D. C., 1977.

4. Galvagno, S., Schwank, J., and Parravano, G., J. Catal. 61, 223 (1980).

5. Sajkowski, D. J., Schwank, J., and Goodwin, J. G., Jr., to be published.

6. Gay, I. D., J. Catal. 80, 231 (1983).

7. Allen, A. D., Harley, F. B., Harris, R. O., Reinsalu, V. P., and Senoff, C. V., Inorg. Synth. 12, 3 (1970).

8. Dalla Betta, R. A., J. Phys. Chem. 79, 2519 (1975).

9. Fabec, J. L., Atomic Spec. 4, 46 (1983).

10. Goodwin, J. G., Jr., J. Catal. 68, 227 (1981).

11. Dalla Betta, R. A., J. Catal 34, 57 (1974).

12. Yang, C. H., and Goodwin, J. G., Jr., J. Catal. 78, 182 (1982).

13. Van Hardeveld, R., and Hartog, F., Surface Sci. 15, 189 (1969).

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