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PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY. FINAL REPORT, APRIL 1, 1982-MARCH 31, 1984

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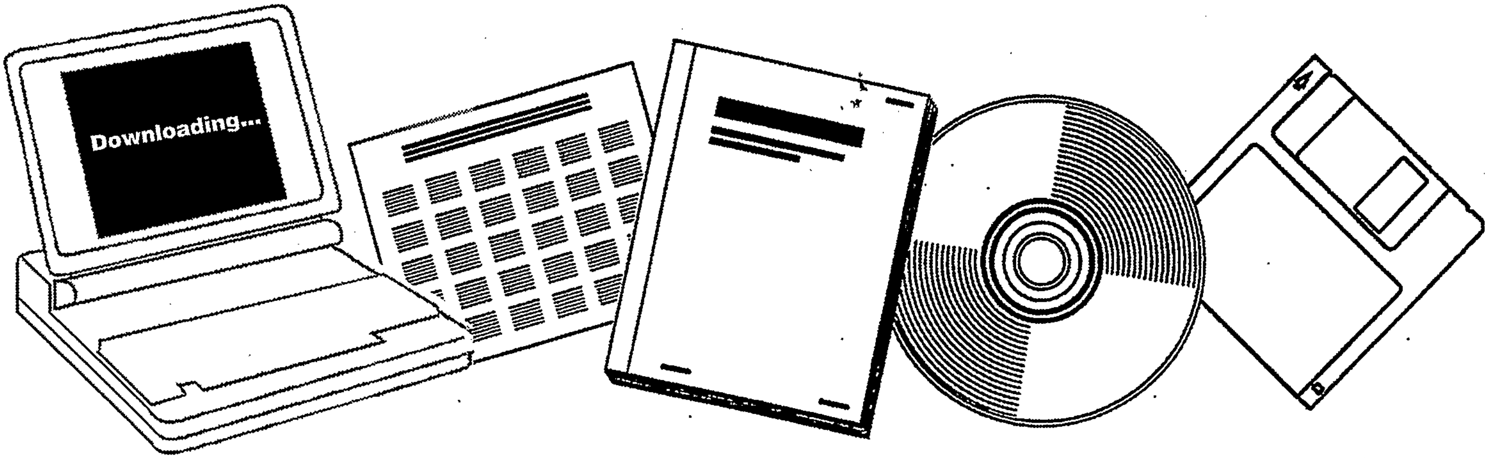

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"PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY"

Final Report

for Period April 1, 1982-March 31, 1984

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NOTICE

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Preprints of Papers

1) CO Methanation on Low-Weight Loading Ni/ Al_2O_3 Catalysts
2) Alkali Promoters on Supported Nickel: Role of Support, Preparation and Alkali Concentration
3) CO Hydrogenation on Alkali-Promoted Nickel Catalysts

Preprints Removed.

ABSTRACT

The effect of alkali promoters on the activity and selectivity for CO hydrogenation was studied on supported nickel catalysts. Temperature-programmed desorption and reaction, and steady-state reaction were used. The support was shown to have a strong influence on the *changes* induced by the alkali promoter. On Ni/SiO_2 and Ni/TiO_2, hydrogenation rates were significantly reduced, apparently due to weakened hydrogen bonding. This resulted in a significant increase in the olefin selectivity. On Ni/$SiO_2 \cdot Al_2O_3$, the hydrogenation rates were increased, and a maximum was observed in the rates of methane and higher paraffin formation. Little change in the Ni/Al_2O_3 catalysts was seen, except for a decrease in surface area. Temperature-programmed reaction and steady-state kinetics show good agreement for the series of catalysts. On Ni/Al_2O_3, the presence of multiple reaction sites was observed and studied in detail; a model was developed.

The effect of potassium concentration on Ni/SiO_2 was large and the activity decreased rapidly even at the low concentrations. Preparation method and alkali salt used were shown to have small effects on the changes in activity and selectivity. The strong effect of the support was attributed to an interaction of the support with the promoter.

RESEARCH SCOPE AND OBJECTIVES

The influence of alkali promoters on catalytic activity and selectivity for carbon monoxide hydrogenation was studied on supported metal catalysts. The interaction of the promoter and the oxide support, and the effect of promoter concentration and preparation method are of interest. Temperature-programmed desorption (TPD) and reaction (TPR) are used with mass spectrometric detection to determine how promoters affect binding energies, individual reaction steps, reaction mechanism and specific activity. Selectivity and activity are measured in a differential reactor with gas chromatographic analysis. The aim of this research is to understand how a catalytically-inert alkali metal modifies CO hydrogenation and to determine if the changes in activity and selectivity due to the promoter are affected by the support.

PROJECT ACCOMPLISHMENTS AND TECHNICAL DISCUSSION

Temperature-programmed desorption (TPD) and reaction (TPR) and differential reactor studies were used to study CO hydrogenation on supported nickel catalysts. Four supports (SiO_2, Al_2O_3, TiO_2 and $SiO_2 \cdot Al_2O_3$) were used to prepare catalysts by impregnation. The changes in the activity and selectivity were studied in a differential reactor for a 3:1 H_2:CO mixture at atmospheric pressure. Alkali promoters were found to have a very large effect on both the activity and selectivity to higher hydrocarbons. However, the support significantly influenced these *changes* in kinetic properties. Some of the catalysts were also characterized by Auger spectroscopy and x-ray photoelectron spectroscopy to verify the presence of alkali.

Experimental

A steady-state flow system for measurement of differential reactor kinetics was designed, constructed and tested. A sand bath heater was used for reactor temperature control, and a gas chromatograph with TC and FID detectors was purchased, put into operation and calibrated. Data obtained with this system for unpromoted catalysts agreed with values reported in the literature.

A number of catalysts was prepared with different supports (SiO_2, Al_2O_3, TiO_2, $SiO_2 \cdot Al_2O_3$), ranges of promoter concentration, both sodium and potassium promoters, different preparation methods (pre-, co- and post-impregnation, calcination) and with different promoter salts (KCl, $K_2C_2O_4$, K_2CO_3, KOH). Aqueous impregnation to incipient wetness was used in these studies, and all nickel and alkali weight loadings were measured by atomic absorption.

Parts were purchased for an x-ray photoelectron spectrometer (XPS); this Leybold-Hereaus system was put into operation and calibrated, and an hydrogen flow system was added to allow catalyst reduction before analysis by XPS. Preliminary XPS experiments are underway.

The detailed results of this project are described in the reprints at the end of this report. These results will be briefly summarized here.

Support, Promoter Concentration, and Preparation Effects

The activity and selectivity for CO hydrogenation on potassium-promoted catalysts is shown to depend on the oxide support. On Ni/SiO_2, due to a weak interaction between the support and the promoter, most of the promoter is on the nickel and the total activity decreases rapidly with promoter concentration. Olefin activities increase and olefin/paraffin ratios increase dramatically, as observed on single crystal nickel. Potassium on nickel apparently decreases hydrogenation rates.

On Ni/$SiO_2 \cdot Al_2O_3$, paraffin activities increase except at high promoter concentrations. Olefin selectivities decrease and higher paraffin selectivities increase. Thus maximums in methane activity and total activity are seen. Apparently the silica-alumina support interacts more strongly with potassium, and thus most of the potassium is on the support. A reaction between the support and promoter causes a weak metal-support interaction which increases hydrogenation rates. Only at higher promoter concentrations, when more of the promoter is on the nickel, do the hydrogenation rates decrease, and the olefin/paraffin ratios increase.

The following variables show a decreasing effect on activity and selectivity for promoter addition:

support > promoter concentration > preparation method > promoter salt.

Post-impregnation of the promoter yields a higher activity but a lower olefin selectivity; calcination increases the relative olefin yield at higher temperatures. Use of different salts has little effect, indicating that the original promoter salt decomposes during catalyst preparation. A good correlation was seen between the olefin/paraffin ratio and the inverse overall activity for most catalysts. The olefin/paraffin ratio was 10 times larger for C_3 than for C_2 hydrocarbons.

TPR and Steady-State Kinetics

Changes in areal rates of CO hydrogenation upon addition of alkali promoters to supported nickel were measured by temperature-programmed reaction (TPR) and steady-state kinetics. Good agreement was obtained between the two techniques, indicating that the same reaction process was measured. On Ni/SiO_2 and Ni/TiO_2, addition of 1% potassium decreases methanation activity approximately a factor of 30 and significantly increases selectivity to olefins. Potassium decreases hydrogenation rates on Ni/SiO_2 by weakening hydrogen bonding. On Ni/Al_2O_3 and $Ni/SiO_2{\cdot}Al_2O_3$, the activities are essentially unchanged by 1% potassium. On $Ni/SiO_2{\cdot}Al_2O_3$, low sodium concentrations increase methanation activity slightly. The dependence of activity changes on the support may be because the alkali distribution between the nickel and the support depends on the support. On Ni/Al_2O_3 and $Ni/SiO_2 \cdot Al_2O_3$, a strong promoter-support interaction keeps more of the promoter on the support. The reaction of the promoter with the support then modifies the nickel properties through a metal-support interaction. Alkali promoters change activity and selectivity by altering the nickel sites, and in general, promotion also decreases the number of sites available for methanation.

Low Loading Ni/Al_2O_3 Catalysts

The presence of two pathways for methanation has been observed on low weight-loading Ni/Al_2O_3 catalysts. These two pathways are due to hydrogenation of CO at two adsorption sites: (A) CO adsorbed on nickel atoms that are interacting with other nickel atoms; (B) CO adsorbed on nickel atoms interacting with an oxide phase of the Ni/Al_2O_3 catalyst. Temperature-programmed reaction (TPR) detected these sites because of its ability to measure specific rates of reaction. Conversion between these two sites occurs but is influenced by surface hydrogen. The alumina support increases the difficulty of reducing nickel and creates B sites on the partially-reduced catalysts and on the catalysts where nickel atoms interact intimately with the oxide support.

Neither of the pathways has the hydrogenation of dispersed surface carbon as a rate-limiting step, though there is some methane produced at high temperatures from the hydrogenation of polymerized β-carbon formed during interrupted TPR. The hydrogenation of CO(A) had an activation energy of 51 kJ/mol; the hydrogenation of CO(B) had an activation energy of 145 kJ/mol. Both pathways for the hydrogenation of CO should be present in steady-state kinetic studies on low-weight-loading Ni/Al_2O_3 catalysts.

Promoted Ni/ TiO_2 Catalysts

The hydrogenation of CO on 10% Ni/ TiO_2 was studied in detail using TPR and TPD since Ni/ TiO_2 has a high selectivity to higher hydrocarbons and the selectivity is further increased by the addition of alkali promoters. The initial coverage was varied by interrupted desorption and reaction. For TPR, after CO adsorption to saturation coverage, the catalyst was heated in hydrogen to a specified temperature, cooled to room temperature and then heated at 1 K/s to 723 K in a normal TPR.

Methane and ethane were formed in narrow peaks and two distinct methane peaks were seen. Ethane formed at a slightly lower temperature than methane; the ethane yield was only 3% of the methane yield. The methane, ethane and propane peak temperatures did not change with initial coverage, indicating first-order processes.

Adding potassium to Ni/ TiO_2 caused a significant decrease in the rate of TPR reaction, as seen in steady-state experiment. Temperature-programmed reaction also observed a large increase in methane and ethane peak temperatures, as well as an increase in the temperature of unreacted CO. The percentage of CO that reacted to ethane also increased with the addition of potassium.

On Ni/ TiO_2, hydrogen desorbed from the unpromoted catalyst over a wide temperature range, and addition of potassium weakened the hydrogen bonding to the surface. Hydrogen adsorption also appeared to be activated.

These changes in hydrogen bonding appear to be reflected in the TPR and steady-state experiments. Since promoters weaken hydrogen bonding on Ni/ TiO_2 and Ni/ SiO_2, the rates of CO and C hydrogenation decrease in TPR. Similarly, the rates of hydrogenation of CO to methane and higher paraffins also decrease. Thus, more olefins are observed on the promoted catalysts.

Carbon monoxide bonding was also significantly changed on promoted Ni/TiO_2. When 1% K was added to Ni/TiO_2, the strongly-bound and the weakly bound CO are almost eliminated. The remaining CO is in the 500-600 K range.

Temperature-programmed desorption of CO also yields CO_2 due to disproportionation. On unpromoted Ni/TiO_2, the CO_2 is observed over a relatively narrow temperature range. After addition of promoter, the amount of CO_2 is decreased drastically and the CO_2 also forms at a lower temperature.

CONCLUSIONS

An extensive study of the effects of supports, preparation and concentration on the addition of alkali promoters was carried out for supported nickel catalysts. Activities and selectivities for a series of catalysts were measured in a differential reactor with gc detection. Specific activities, active site concentrations and the presence of multiple sites were measured by temperature-programmed reaction (TPR) with mass spectrometric detection. Carbon monoxide and hydrogen bonding were measured by temperature-programmed desorption.

A strong dependence of alkali promoters on supports was observed and the interaction between support and promoters was used to explain the differences. On Ni/SiO_2, alkali promoters were shown to decrease hydrogenation rates; on Ni/$SiO_2 \cdot Al_2O_3$, hydrogenation rates were increased by alkali promoters. Good agreement was obtained for methanation rates with TPR and steady-state kinetics. The decreased hydrogenation rates were related to decreased hydrogen bonding. Accompanying decreased hydrogenation rates was increased olefin selectivity. On Ni/SiO_2, olefin selectivity increased three orders of magnitude. An excellent correlation was found between olefin/paraffin ratios and inverse activities.

The effects of preparation and alkali salt were shown to be much smaller than the effect of support on the promoter. The concentration of potassium was varied over two orders of magnitude on Ni/ SiO_2 and the rate dropped rapidly. On Ni/ $SiO_2 \cdot Al_2O_3$, the rates of methane and higher paraffins increased.

The strong interaction of nickel with Al_2O_3 supports was studied in detail and the presence of multiple sites, some of which are due to interaction with oxide, was found. The effect of alkali promoters on desorption and reaction was also studied in detail on Ni/ TiO_2 catalysts.

Publications

1) K. B. Kester and J. L. Falconer, "CO Methanation on Low-Weight Loading Ni/ Sl_2O_3: Multiple Reaction Sites," accepted for publication in *J. Catalysis* (attached).

2) G. Y. Chai and J. L. Falconer, "Alkali Promoters on Supported Nickel: Role of Support, Preparation and Alkali Concentration," submitted to *J. Catalysis* (attached).

3) J. L. Falconer, K. M. Bailey, and P. D. Gochis, "CO Hydrogenation on Alkali-Promoted Nickel Catalysts," submitted to *J. Colloid Interface Science* (attached).

4) K. Wilson, P..D. Gochis, and J. L. Falconer, "Alkali Promoters on Ni/ TiO_2 Catalysts: TPR and TPD Studies," in preparation (to be forwarded to DOE).