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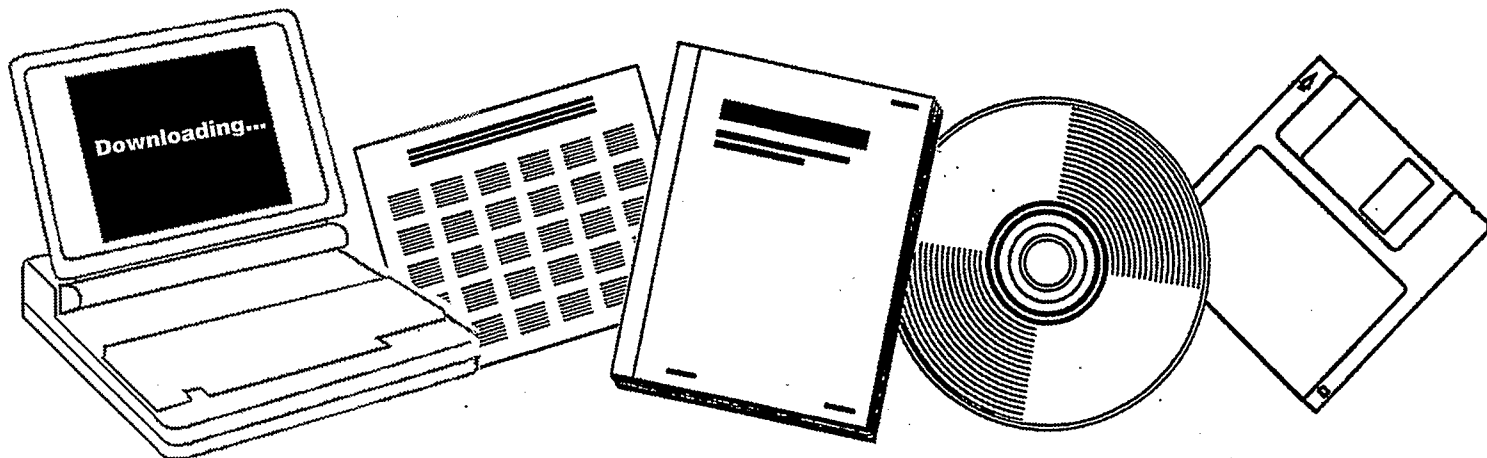
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**PROMOTER MODIFICATIONS OF CATALYTIC
ACTIVITY AND SELECTIVITY. PROGRESS REPORT,
APRIL 1, 1984-OCTOBER 1, 1984**

**COLORADO UNIV. AT BOULDER. DEPT. OF
CHEMICAL ENGINEERING**

08 OCT 1984



U.S. Department of Commerce
National Technical Information Service

DOE/ER/13217--1

DE85 000424

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**"PROMOTER MODIFICATIONS OF CATALYTIC
ACTIVITY AND SELECTIVITY"**

Progress Report

for Period April 1, 1984-October 1, 1984

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October 8, 1984

Prepared for

**The U.S. Department of Energy
Office of Basic Energy Sciences
Division of Chemical Sciences**

Agreement #DE-FG02-84ER13217

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ABSTRACT

Catalytic activity and selectivity for CO and CO₂ hydrogenation on supported nickel catalysts were changed significantly by the addition of alkali promoters; the major factor in determining the change was the oxide support used. On most supports, alkali promoters decrease hydrogenation rates to varying degrees, apparently due to weakened hydrogen bonding. This results in lower methane turnover numbers and large olefin/paraffin ratios for CO hydrogenation. The rate of carbon hydrogenation is also dramatically reduced. For CO₂ hydrogenation, selectivity to CO product increases as overall conversion decreases with promoter concentration. On Ni/SiO₂-Al₂O₃, however, turnover numbers increase for both CO and CO₂ hydrogenation. These changes and studies in which nickel loadings were varied show that the K/Ni ratio is not sufficient to determine the changes due to the promoter. The oxide support and the nickel loading also have major influences, apparently because much of the promoter reacts with the support. The promoter preparation and the promoter salt used have much less effect than the support and the potassium loading.

RESEARCH SCOPE AND OBJECTIVES

The role of alkali promoters in changing catalytic activity and selectivity for CO and CO₂ hydrogenation was studied on supported nickel catalysts. The effects of the support on the promoter's modifications in both adsorption and reaction properties were considered. Steady-state kinetics, temperature-programmed desorption and reaction (TPD, TPR), static chemisorption, temperature-programmed decomposition, and XPS were used. The aim of this research is to understand how alkali metals interact with supported catalysts to change activity and selectivity, and how these interactions depend on the support.

PROJECT ACCOMPLISHMENTS AND TECHNICAL DISCUSSION

The effect of alkali promoters on catalytic activity and selectivity was studied for CO, CO₂, carbon, and C₂H₄ hydrogenation on a series of supported catalysts. Both differential reactor studies (with static chemisorption) and temperature-programmed reaction experiments were used. The influences of the support, the catalyst loading, the nickel loading, the catalyst preparation, and the reduction temperature were determined. The decomposition of the promoter during preparation was also studied with temperature-programmed decomposition. Preliminary XPS experiments were undertaken and because of higher sensitivity in XPS, sodium is being used in present XPS experiments. The reaction steps affected by the promoter were studied separately by measuring rates of carbon, CO, and C₂H₄ hydrogenation. The following sections describe briefly the results of these studies.

Effect of Catalyst Support: CO Hydrogenation

Four supports were used to prepare a series of promoted and unpromoted catalysts. Changes in areal rates of CO hydrogenation upon addition of alkali promoters to supported nickel were measured by temperature-programmed reaction (TPR) and by steady-state kinetics. Good agreement was obtained between the two techniques, indicating that the same reaction process was measured. On Ni/SiO₂ and Ni/TiO₂, addition of 1% potassium decreased methanation activity approximately a factor of 30 and significantly increased selectivity to olefins. On Ni/Al₂O₃ and Ni/SiO₂-Al₂O₃, the activities were essentially unchanged by 1% potassium. On Ni/SiO₂-Al₂O₃, low sodium concentrations increased 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. Alkali promoters change activity and selectivity by altering the nickel sites, and in general, promotion also decreases the number of sites available for methanation.

Effect of Promoter Concentration

The change, with promoter concentration, in activity and selectivity for CO hydrogenation on potassium-promoted catalysts was shown to depend significantly on the oxide support. A series of 20 catalysts was studied in a differential reactor for a 3:1 mixture of H₂ and CO. On Ni/SiO₂, methane and total turnover numbers decreased exponentially with promoter concentration, while olefin turnover numbers increased and olefin/paraffin ratios increased dramatically. On Ni/SiO₂-Al₂O₃, paraffin turnover numbers increased, except at high promoter concentrations. Olefin selectivities decreased and higher paraffin selectivities increased. Thus maximums in methane and total turnover num-

bers were seen. 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 C₃ than for C₂ hydrocarbons. Thus, the support has a bigger influence on the changes induced by the promoter than the promoter concentration does. The preparation method has a much smaller influence on properties of promoted catalysts. Use of different promoter salts has little effect, indicating that the original promoter salt decomposes during catalyst preparation.

Low Weight Loading Ni/Al₂O₃ Catalysts

Temperature-programmed reaction (TPR) was used to study the details of the hydrogenation of carbon monoxide on two low loading Ni/Al₂O₃ catalysts. Since our data indicate that the support significantly affects activity of promoted catalysts, it was important to understand the types of reaction sites present on the unpromoted catalysts. Also, on low loading Ni/Al₂O₃, multiple sites form and the effect that promoters have on these sites may help in determining the location of the promoter on the catalyst. To study the sites present on these catalysts during methanation, heating rate variation, coverage variation, interrupted reaction, and pretreatment temperature variation were used during TPR.

The presence of the two pathways for methanation are due to hydrogenation of CO at two adsorption sites: Site (A), CO adsorbed on nickel atoms that are interacting with other nickel atoms; Site (B), CO adsorbed on nickel atoms interacting with an oxide phase of the Ni/Al₂O₃ catalyst. Temperature-programmed reaction (TPR) detected these sites because of its ability to measure specific rates of reaction. Conversion between these two sites occurs and 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 catalyst 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 some methane is produced at high temperatures from the hydrogenation of polymerized beta-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/Al₂O₃ catalysts.

CO₂ Hydrogenation: Catalyst Support and Promoter Concentration

On Ni/SiO₂ and Ni/SiO₂-Al₂O₃ catalysts, carbon dioxide hydrogenation was studied in a differential reactor as a function of alkali promoter concentration. On unpromoted catalysts, as reported by others, CO₂ hydrogenation has a higher selectivity to methane than CO hydrogenation. On both supports, approximately 95% methane yield was obtained, and the remaining 5% was mostly carbon monoxide. As for CO hydrogenation, addition of promoter caused changes in activity and selectivity. The promoter had different effects, however, on catalysts prepared on the two supports. For a range of promoter concentrations, the methane turnover number increased with promoter concentration on Ni/SiO₂-Al₂O₃ initially and then decreased slightly. The selectivity was relatively constant up to 0.8% K; for 4% K the selectivity to CO increased to 45%. The turnover number for CO formation increased a factor of 20 over that for the unpromoted catalyst.

On Ni/SiO₂, the turnover number for CH₄ formation decreased

rapidly with promoter concentration, though not as fast as when CO hydrogenation was carried out on the same series of catalysts. This decrease in methane turnover number was accompanied by an increase in CO formation so that the decrease in overall CO₂ conversion was small except at high promoter concentrations. The selectivity changed rapidly between 0% K and 0.8% K from 95% methane to 5% methane.

Even at the higher promoter concentrations, little ethane was produced on either catalyst and essentially no propane or higher hydrocarbons. In contrast, promoters caused large increases in olefin formation for CO hydrogenation.

Suppression of Hydrogenation Rates

On Ni/SiO₂ catalysts with and without promoters, carbon, CO, and C₂H₄ hydrogenation were studied by TPR and pulse reaction to determine the effect of promoters on various hydrogenation steps. Carbon monoxide was hydrogenated in a differential reactor on the same catalysts. These studies show that the major effect of potassium on Ni/SiO₂ catalysts is to decrease hydrogenation rates of carbon and CO. A large decrease in carbon hydrogenation rate was seen; this is apparently responsible for the decreased methanation rates. The decreased hydrogenation rate also results in an increased olefin/paraffin ratio. Hydrogen TPD shows that this decrease is due to decreased hydrogen bonding on the promoted catalysts, which also increases the higher hydrocarbon yield. Promoters both decrease the bonding strength of hydrogen and cause adsorption to become activated. The surface area available for hydrogen adsorption is also decreased, as the areal rates decreased.

Ni/Al₂O₃ Catalysts

The nickel weight loading was varied for a series of Ni/Al₂O₃ catalysts to study the interaction of the promoter with the support. Nickel/alumina catalysts display two distinct methane peaks which we have attributed to CO adsorbed on nickel crystallites and CO adsorbed on nickel that is in close contact with alumina or nickel oxide. The amount of each type of CO depends on the Ni loading. The changes in these two peaks with promoter addition are being used to determine where the promoter is located.

Four unpromoted catalysts with loading ranging from 1 to 19% were prepared and four promoter catalysts were also prepared from these samples. Temperature-programmed reaction of adsorbed CO, temperature-programmed desorption of hydrogen and carbon monoxide, steady-state rates and selectivities, and percent reduction were measured on these eight catalysts.

On 10% Ni/Al₂O₃, for example, the addition of K decreased the rate of reaction for the CO located near the support, but did not affect the methane peak due to CO on nickel crystallites. On the 1% catalyst, potassium resulted in a new methane peak at low temperature. Steady-state kinetics were consistent with the TPR results; the activity increased on the promoted 1% catalyst, but decreased on the other promoted catalysts. The K/Ni ratio increased as the nickel loading decreased, yet the fractional decreases in overall hydrogenation activity on the promoted catalysts were the same, except for the 1% catalyst, for which the activity actually increased. In contrast, when the nickel loading was maintained constant on Ni/Al₂O₃ catalysts, but the K/Ni ratio was increased, the activity decreased. These studies show that the K/Ni ratio is not sufficient to characterize the

promoter effect on a given support. They indicate also that much of the interaction of the promoter is with the support.

Ni/TiO₂ Catalysts

Desorption (TPD) and reaction (TPR) of H₂ and CO were studied on 10% Ni/TiO₂ catalysts with and without alkali promoters.

Nickel/titania has a high selectivity to higher hydrocarbons and the selectivity is further increased by the addition of alkali promoters. During TPR methane and ethane formed in narrow peaks; ethane formed at a slightly lower temperature than methane and the ethane yield was only 5% of the methane yield. The product peak temperatures during TPR did not change with initial coverage, indicating first-order processes, though desorption rate isotherm analysis indicates second order processes.

Potassium caused a significant decrease in the rate of CO hydrogenation in TPR, as seen in steady-state experiments. The percentage of CO that reacted to ethane increased, while the amount of unreacted CO increased from 19 to 29%. Addition of potassium weakened hydrogen bonding to the surface and decreased hydrogen adsorption. As on Ni/SiO₂, this decreased bonding resulted in decreased hydrogenation rates on Ni/TiO₂.

Carbon monoxide bonding was dramatically changed on promoted Ni/TiO₂. When 1% K was added, the strongly-bound and the weakly-bound CO were almost eliminated. The remaining CO desorbed between 500-600 K, and the desorption kinetics appear to change from second order to first order with promoter addition. The promoted catalyst deactivated more rapidly with repeated desorptions, suggesting that CO desorption products remain on the surface. The amount of CO₂, from CO disproportionation, however, was drastically reduced and it formed at a lower

temperature on the promoted Ni/TiO₂. Thus, it appears that CO disproportionation is not increased with promoter addition.

Temperature-Programmed Decomposition

Post-impregnation catalysts were prepared using ¹³C-labeled potassium carbonate in order to study the rate of decomposition of the potassium salt during the reduction stage of catalyst preparation. Mass spectrometric detection observed methane, carbon monoxide and carbon dioxide products during programmed heating. Heating was carried out to 1300 K, even though catalyst reduction is normally only up to 773 K. The higher temperature allowed decomposition that did not occur during typical reduction to also be studied.

On the supports without nickel, a large difference was observed in the rate and the amount of carbonate decomposition. Similarly, the extents of decomposition were quite different for potassium carbonate on supported nickel catalysts. For example, the amount of carbonate decomposition was much larger for Ni/SiO₂ than for Ni/SiO₂-Al₂O₃. Part of this appears to be due to decomposition near room temperature for the silica-alumina, and the decomposition temperature on the silica catalyst is sufficiently high that much of the carbonate apparently does not decompose during typical catalyst preparation procedures. Analysis of these results have been complicated by the presence, at high temperatures, of methane that apparently forms from carbon or carbon dioxide on the support. The results to date indicate that the amount of potassium on the transition metal depends on the support, but additional experiments are still needed.

Catalyst Preparation

Catalyst preparation had a small influence on the activity and

selectivity relative to the effect of support and promoter concentration. Similar results were obtained for pre- and co-impregnation and for calcined catalysts. The use of carbonate, oxalate, chloride and nitrate salts gave similar activities. On Ni/SiO₂, the methanation activity decreased less for the same promoter loading on post-impregnation catalysts, but the olefin selectivity also increased less. The support still strongly influences the change in activity. The methane turnover number dropped more rapidly on post-impregnated Ni/SiO₂ catalysts than on post-impregnated Ni/Al₂O₃.

Ni/TiO₂: Effect of Reduction Temperature

Both TPR and steady-state kinetics were used to study promoted and unpromoted catalysts as a function of reduction from 573 K to 848 K. For Ni/TiO₂, the amount of methane formed in TPR dropped rapidly with increased reduction temperature, while the peak temperature remains essentially unchanged. While the ethane peak also decreased, its peak temperature decreased. Similar results were seen on the promoted catalyst, but the changes occurred at different reduction temperatures. In steady-state experiments, a large change in selectivity occurred between 573 and 773 K for the promoted catalyst and between 773 and 848 K for the unpromoted catalyst. The changes correlate with the changes seen in TPR.

CONCLUSIONS

The effect of alkali promoters on the catalytic properties of a series of supported nickel catalysts was studied for the CO and CO₂ hydrogenation reactions. Steady-state kinetics, temperature-programmed desorption and reaction, and temperature-programmed decomposition were used. These studies have shown that the catalyst support is the major factor affecting the changes induced by the promoter. In addition, these studies have found that

- Alkali promoter decrease turnover numbers for CO hydrogenation on Ni/SiO₂, Ni/Al₂O₃ and Ni/TiO₂; the amount of decrease strongly depends on the support.
- Alkali increases turnover number for Ni/SiO₂-Al₂O₃
- Olefin selectivity can be increased several orders of magnitude by alkali; the olefin:paraffin ratio correlates with inverse activity.
- TPR and steady-state kinetics yield good agreement on specific activities.
- On Ni/Al₂O₃, two distinct CO sites that react to CH₄ at different rates were detected.
- The support determines the effect of alkali on CO₂ hydrogenation; alkali increases selectivity for CO formation.
- A major role of alkali on Ni/SiO₂ and Ni/TiO₂ is to suppress hydrogenation rates by weakening hydrogen bonding.
- On Ni/TiO₂, CO bonding and CO disproportionation is dramatically changed by promoter addition.
- The K/Ni ratio is shown, for Ni/Al₂O₃, to not be a good indicator of the activity and selectivity. Interaction with the support means that the Ni loading is also an important

variable.

- Potassium carbonate decomposes at different rates on different supports; at typical reduction temperatures, the amount of decomposition depends on the support.
- Catalyst salt and preparation method have small effects on activity; only post-impregnation is different; the activity decreases less and olefin selectivity increases less.
- Promoters change the reduction temperatures required for transitions in selectivity and activity for CO hydrogenation on Ni/TiO₂.

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- 4) K. G. Wilson, K. Keirein, P. D. Gochis, and J. L. Falconer, " TPR and TPD Studies on Promoted Ni/TiO₂ Catalyst".
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