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PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY: FINAL REPORT FOR PERIOD APRIL 1, 1982-SEPTEMBER 30, 1986

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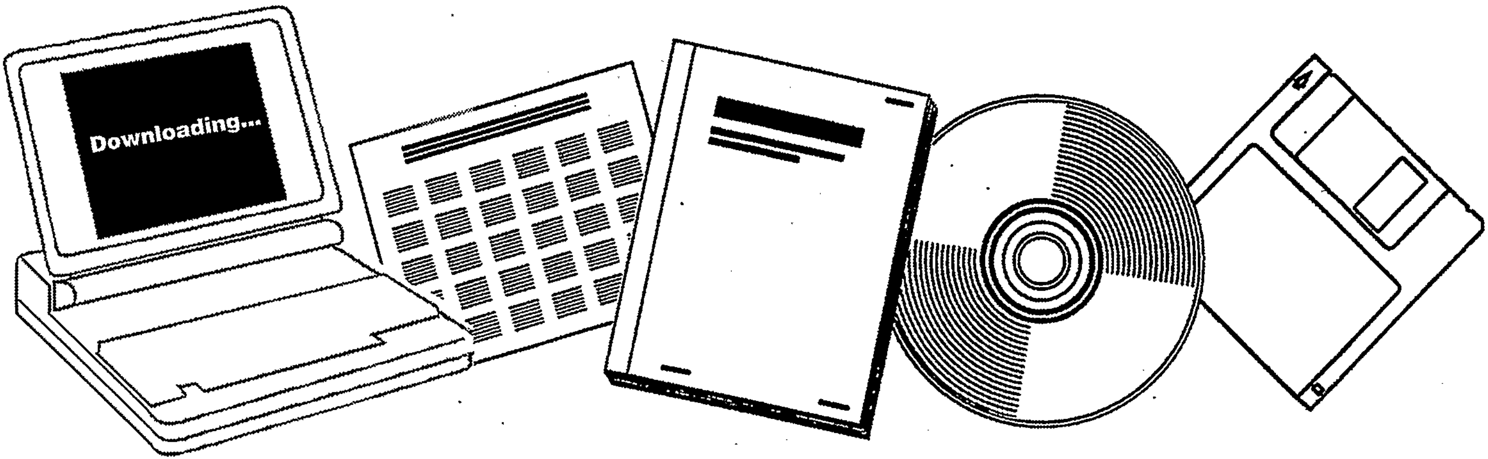

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"PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY"

Final Report

for Period April 1, 1982 - September 30, 1986

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ABSTRACT

The interaction of alkali promoters with supported nickel catalysts and the effects of alkali on CO and CO_2 hydrogenation were studied. Differential reactor studies, temperature-programmed desorption and reaction (TPD, TPR) with mass spectrometric detection, isotope labeling, static chemisorption, and x-ray photoelectron spectroscopy were used. The studies found that the alkali promoters significantly modify the activity and selectivity of supported nickel, and these modifications depend strongly on the support. Nickel catalysts with a range of nickel loadings and a range of potassium loadings were studied on SiO_2, Al_2O_3, TiO_2, and SiO_2-Al_2O_3 supports. Nickel powders were also used to separate the effect of the support. Two reaction sites were identified on Ni/Al_2O_3 catalysts and these sites were found to be significantly influenced by weight loading and promoter concentration. For SiO_2- and Al_2O_3-supported catalysts the K/Ni ratio was shown to not be a valid measure of promoter concentration on the active surface. The effect of alkali was studied as a function of the support, of K/Ni and K/support ratios, and of reduction temperature for Ni/TiO_2 catalysts. On Ni/SiO_2 the effects on the individual reaction steps were also measured and both carbon and carbon hydrogenation were dramatically slowed by potassium. Both CO and CO_2 hydrogenation are found to follow similar mechanisms, and good agreement was obtained between reaction on promoted nickel powders and studies by others on promoted single crystal surfaces.

RESEARCH SCOPE AND OBJECTIVES

The role of alkali promoters in changing catalytic activity and selectivity for CO and CO_2 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), isotope labeling experiments, 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, CO_2, and carbon hydrogenation on a series of supported catalysts. Both differential reactor studies and temperature-programmed reaction experiments were used. The influences of the support, the catalyst loading, the nickel loading, the catalysts preparation, and the reduction temperature were determined. The decomposition of the promoter during preparation was also studied with temperature-programmed decomposition. Some XPS experiments were also carried out. The reaction steps affected by the promoter were studied by separately measuring the rates of carbon and CO hydrogenation, and by studying temperature-programmed desorption of CO and H_2. The following sections describe briefly the results of these studies. The completed papers are included in the Appendices and papers in progress will be forwarded to DOE as they are completed.

CO Hydrogenation on Alkali-Promoted Nickel

The modification of catalytic activity and selectivity by alkali promoters for CO hydrogenation on nickel was studied for four oxide supports. Steady-state kinetics were measured in a differential reactor (3:1 mixture of H_2:CO) with gas chromatographic detection. Temperature-programmed reaction (TPR) with mass spectrometric detection was carried out in excess hydrogen. In the differential reactor studies a potassium promoter decreased the activity but increased the olefin selectivity when nickel was supported on SiO_2, Al_2O_3, or TiO_2. The extent of activity decrease was a function of the support however, and may be due to different distributions of promoter between the nickel and the supports. For Ni on SiO_2-Al_2O_3, overall activity increased and the selectivity to higher paraffins increased while olefin selectivity was unchanged. An interaction between the promoter and the SiO_2-Al_2O_3 support caused the increase rates of hydrogenation. The TPR results were in good agreement with the differential reactor studies; decreased activities for methane and ethane formation on Ni/SiO_2 and Ni/TiO_2 were due to decreased hydrogenation rates. On Ni/Al_2O_3, the small rate decrease was mainly due to decreased dispersion. TPD results showed that hydrogen was more weakly bound to the promoted Ni/SiO_2 catalyst. For promoted Ni/SiO_2-Al_2O_3, the hydrogenation rates either increased or decreased only slightly in TPR, in agreement with the differential reactor studies.

Effects of Promoter Concentration and Catalyst Preparation

The effect of potassium promoter for CO hydrogenation on supported nickel catalysts was studied in a differential reactor. The influences of the support (SiO_2, SiO_2-Al_2O_3), the promoter concentration (0.05-4% K), the alkali salt (KCl, K_2CO_3, $K_2C_2O_4$, KOH, KNO_3), and the method of preparation (pre- and co-impregnation, and calcination) were studied. The activity and selectivity of promoted catalysts are shown to depend on the support; modifications in catalytic properties are not just due to a K-Ni interaction. On Ni/SiO_2 an exponential decrease in total activity with increased promoter concentration is seen; this decrease is not due to a decrease in percentage nickel exposed (dispersion). A large increase in olefin/paraffin ratios is seen on Ni/SiO_2 as the promoter decreases hydrogenation rates. In contrast, on $Ni/SiO_2-Al_2O_3$, the rate of paraffin formation, including methane, increases and exhibits a maximum with increase promoter concentration. Olefin selectivities decrease and higher paraffin selectivities increase. Much of the potassium salt may react with the silica-alumina support to modify the catalytic properties. The method of preparation has a lesser influence on the catalyst than the potassium concentration. The use of different potassium salts resulted in similar catalytic properties, indicating that for a given support the same potassium compound formed during preparation. A good correlation was found between C_2 and C_3 olefin/paraffin ratios and inverse total activity, showing that olefin selectivities increase as hydrogenation rates decrease.

Multiple Reaction Sites on Ni/Al_2O_3 Catalysts

Temperature-programmed reaction (TPR) with mass spectrometric detection was used to study the details of the hydrogenation of carbon monoxide on two low loading Ni/Al_2O_3 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/Al_2O_3, multiple sites can 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.

These catalysts are shown to differ from high-weight loading nickel/alumina catalysts and are shown to have two distinct pathways for carbon monoxide methanation. These pathways are attributed to two forms of adsorbed CO. The CO site which reacts at low temperature (446 K) appears to be from carbon monoxide adsorbed on nickel atoms that are bonded to other nickel atoms. It has an activation energy for methanation of 51 kJ/mol. The CO site that reacts at high temperature (546 K) has an activation energy of 145 kJ/mol. The high-temperature site, which is sensitive to the pretreatment temperature, results from CO adsorbed on nickel atoms that are interacting strongly with an oxide phase of the catalyst. Interconversion of CO between the two sites occurs and is influenced by hydrogen. Neither of the pathways appears limited by direct hydrogenation of surface carbon; this step is shown to be slightly faster under TPR conditions. The ability of TPR to measure specific reaction rates and to separate reaction pathways that might be obscured in steady-state kinetic measurements is demonstrated.

CO and CO_2 Hydrogenation on Ni/Al_2O_3: Effects of Nickel Loading

The effects of weight loading on the adsorption and reaction properties of Ni/Al_2O_3 catalysts were studied for CO and CO_2 hydrogenation by temperature-programmed reaction (TPR). The role of the support, which interacts sufficiently strongly with nickel ions during preparation so that reduction to the metal is more difficult, is to create two distinct reaction sites for methanation, i.e. nickel crystallites and less reactive nickel atoms surrounded by oxygens of the alumina lattice. Both sites are present at Ni loadings from 1.8-15%, but the fraction of the less reactive sites is much larger at lower Ni loadings. Methane from both sites is seen in TPR of CO adsorbed at 298 K and of CO_2 adsorbed at 473 K. Thus, methanation of CO and of CO_2 (following activated adsorption) proceed by the same mechanism on each type of site on Ni/Al_2O_3. Methane from the more reactive nickel crystallites is not seen in TPR of CO_2 adsorbed at 298 K because CO_2 adsorption is activated on nickel and because of competition with H_2 for these sites.

CO_2 Hydrogenation: Catalyst Support and Promoter Concentration

The kinetics of carbon dioxide hydrogenation were investigated on potassium-promoted Ni/SiO_2, Ni/SiO_2-Al_2O_3, and unsupported nickel catalysts for a range of potassium loadings. On unpromoted catalysts, as reported by others, CO_2 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. Potassium does not increase higher hydrocarbon or olefin selectivity, but it changes the CH_4/CO product distribution. Also, potassium does not change the CO_2 methanation mechanism; the mechanism seems to be quite similar to that for CO hydrogenation. The changes in activity and selectivity with potassium loading depend significantly on the support, however. Addition of potassium (as a carbonate salt) to unsupported nickel powder causes the same changes in kinetic properties as seen when potassium was evaporated onto single crystal nickel; in both cases potassium at low coverages is a true promoter for methanation. That is, potassium increases the methanation rate. It appears that the same potassium species may be present during reaction for both cases. On Ni/SiO_2-Al_2O_3 and Ni/SiO_2 catalysts, potassium has opposite effects; it increases hydrogenation rates on Ni/SiO_2-Al_2O_3 and decreases them on Ni/SiO_2. Modification of the support properties of SiO_2-Al_2O_3, by reaction with acid sites, may be responsible for the differences. On all three types of surfaces studied, the amount of hydrogen adsorption increases with the addition of potassium, and thus static H_2 chemisorption may not be a good measure of nickel surface area.

Chrysocolla as a Methanation Catalyst Support

The kinetic properties of nickel supported on chrysocolla (CHR) and nickel-copper mixtures supported on silica and alumina were measured by steady-state kinetics (CO hydrogenation), temperature-programmed desorption (CO, H_2), and temperature-programmed reaction (CO and C hydrogenation). Leached chrysocolla, a silica-like material containing 7.1% copper, is shown to be an effective catalyst support; Ni/CHR has similar methanation activity and adsorption properties (H_2, CO) to Ni/SiO_2. The Ni/CHR catalyst has a much higher selectivity to methane formation, however, and a lower activation energy. The copper in the CHR support does not appear to affect the catalyst properties and thus apparently does not interact with the nickel. Copper in Cu-Ni catalysts decreases the turnover number for methanation, the amount of hydrogen adsorption, the strength of H_2 binding to the surface, and the rate of CO disproportionation. Copper also increases higher hydrocarbon selectivity at higher temperature, but the temperature at which this occurs depends significantly on the support. The rate of carbon hydrogenation, however, is relatively independent of support or the presence of copper. Good agreement was obtained between CO hydrogenation kinetics measured by steady-state reaction and by temperature-programmed reaction.

Reaction Steps on Ni/SiO_2 Catalysts

The individual steps in CO hydrogenation to methane were studied on Ni/SiO_2 catalysts with three weight loadings of potassium. By using temperature-programmed desorption and reaction (TPD, TPR), the individual steps in the reaction were studied. Both CO and carbon hydrogenation rates were dramatically decreased by the addition of potassium. These decreases in hydrogenation rates were not due to site blocking; the specific rate of reaction was significantly decreased. The large decrease in carbon hydrogenation rate, which is more significant than the decrease in CO hydrogenation rate, explains the decreased methane yield and the higher olefin/paraffin ratios seen in steady-state measurements. Hydrogen TPD shows that this decrease may be due to decreased bonding of hydrogen to the promoted catalysts, which also increases the overall hydrocarbon yield. Promoters both decrease the bonding strength of hydrogen and cause adsorption to become activated.

Potassium Promoters on Ni/Al_2O_3 Catalysts

The nickel weight loading was varied for a series of 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 were used to help determine where the promoter is located.

Four unpromoted catalysts with loading ranging from 1 to 19% were prepared and four promoted 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.

In a separate series of experiments, K_2CO_3 was postimpregated to 4 different concentrations on 10% Ni/Al_3O_3. Steady-state and TPR was also carried out in these studies. The methane peak due to Ni atoms that interact with other nickel atoms (peak A) decreased in rate but increased in amplitude as the CH_4 due to peak B (nickel atoms interacting with oxide) decreased in amplitude. Dramatic changes were observed in CO desorption and disproportionation, while the hydrogen TPD was relatively unchanged. Potassium did not significantly block nickel sites since the amount of H_2 chemisorption did not decrease.

On the 1% Ni catalyst, potassium resulted in the formation of methane peak at low temperature; on the unpromoted catalyst only the high-temperature peak was present. 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/Al_2O_3 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 that much of the interaction of the promoter is with the support. These results are still being analyzed.

Potassium Promoters on Ni/TiO_2 Catalysts

Desorption (TPD) and reaction (TPR) of H_2 and CO were studied on 10% Ni/TiO_2 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.

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/SiO_2, this decreased bonding resulted in decreased hydrogenation rates on Ni/TiO_2.

Carbon monoxide bonding was dramatically changed on promoted Ni/TiO_2. 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.

$C^{18}O$ Desorption from Ni/TiO_2

The use of $C^{18}O$ with temperature-programmed desorption (TPD) was used to study in detail the desorption and disproportionation of carbon monoxide on Ni/TiO_2, $Ni/K/TiO_2$, Ni powder, and Ni/K powder. The use of ^{18}O labeling allows the reaction steps to be better separated and most of the high temperature carbon monoxide was unlabeled from all the catalysts. Exchange with the TiO_2 support was also significant and the amount of exchange was measured with pulse experiments. The TiO_2 was reduced below 400 K by adsorbed CO to form CO_2. The CO_2 that formed during TPD from Ni/TiO_2 exchanged with the TiO_2. These results are still being analyzed.

Ni/TiO_2: 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/TiO_2, the amount of methane formed in TPR dropped rapidly with increased reduction temperature, while the peak temperature remains essentially unchanged. While the amount of ethane that formed decreased, its peak temperature also 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 673 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.

Temperature-Programmed Decomposition

Post-impregnated catalysts were prepared using ^{13}C-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 allows detection of 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 to be studied 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/SiO_2 than for $Ni/SiO_2-Al_2O_3$. 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 may depend on the support.

Catalytic Activity of Promoted Ni Powders

Because of the strong influence of the support on the activity and selectivity, several powders were used for CO and CO_2 hydrogenation. Static chemisorption was also used. The unpromoted powders showed behavior similar to single crystal studies. An unexplained step-function increase in rate with temperature was observed, however, and this was reversible and repeated for a number of samples. The promoted powders behaved like Ni/SiO_2 and like single crystal nickel. The reduction temperature had a large influence on activity for promoted powder catalysts.

Changes in the K/Ni and K/SiO_2 Ratios

Because the K/Ni ratio in a supported catalyst does not appear to be a good measure of catalytic properties, two series of catalysts were prepared on a SiO_2

support. One series had 14% Ni and the other had 0.74% Ni. Potassium was then postimpregnated to obtain the desired K/Ni ratio of approximately 0.1 on the 14% Ni/SiO_2 catalyst. Two loadings of potassium were added to the 0.74% Ni/SiO_2 catalyst in order to obtain the same K/Ni ratio and the same K/SiO_2 ratio as on the 14% Ni/SiO_2. These catalysts were also washed after impregnation to see if removal of small amounts of K would be uniform.

These catalysts were then characterized by H_2 and CO chemisorption, and by CO and by CO_2 hydrogenation. The CO and CO_2 hydrogenation show very good agreement for all the catalysts; this again confirms the similar mechanism of the two reactions. For most of the catalysts, hydrogen chemisorption did not decrease or it increased with potassium addition. That is, there is no indication from the H_2 chemisorption that any Ni sites are blocked. In contrast, the CO chemisorption was significantly decreased by potassium addition.

Washing caused only slight changes in the K loading (as measured by atomic absorption) but large changes in the activity. That is, it appears that K was preferentially removed from the nickel, and perhaps redistributed onto the support. The K/Ni ratio is found to be a very poor indicator of activity, but the activity, for both nickel loadings, correlated with the K/SiO_2 ratio. That is, much of the K is on the SiO_2.

CONCLUSIONS

The effects of alkali promoters on the catalytic properties of a series of supported nickel catalysts was studied for the CO and CO_2 hydrogenation reactions. Steady-state differential kinetics, temperature-programmed desorption and reaction, and temperature-programmed decomposition were used. Isotopic labeling provided additional information in these transient reaction experiments, and static chemisorption was used to measure surface area for H_2 and CO adsorption. Preliminary XPS experiments were also completed. These studies have shown that the catalyst support is the major factor affecting the changes induced by the promoter. Alkali promoters significantly modify catalytic activity and selectivity. In addition, these studies have found that:

- Alkali promoters decrease turnover numbers for CO and CO_2 hydrogenation on Ni/SiO_2, Ni/Al_2O_3 and Ni/TiO_2; the amount of decrease strongly depends on the support.
- Alkali increases turnover number for CO and CO_2 hydrogenation on Ni/SiO_2-Al_2O_3 catalysts.
- Olefin selectivity can be increased several orders of magnitude by alkali; the olefin:paraffin ratio correlates well with inverse activity.
- TPR and steady-state kinetics yield good agreement in specific activities.
- On Ni/Al_2O_3, two distinct CO sites that react to CH_4 at different rates were detected, and the reasons for these two sites were presented.
- The support modifies the effect of alkali on CO_2 hydrogenation; it increases selectivity for CO formation.
- A major role of alkali on Ni/SiO_2 and Ni/TiO_2 is to suppress hydrogenation rates by weakening hydrogen bonding.
- On Ni/TiO_2, CO bonding and CO disproportionation are dramatically changed by promoter addition.
- The K/Ni ratio is shown, for Ni/Al_2O_3 and Ni/SiO_2, to not be a good indicator of the activity and selectivity. Interaction with the Al_2O_3 support means that the Ni loading is also an important variable. Detailed studies of promoted Ni/Al_2O_3 were carried out. On Ni/SiO_2, much of the K is on the support and the activity correlates with K/SiO_2 ratio.
- Catalyst salt and preparation method have small effects on activity.
- Promoters change the reduction temperatures required for transitions in selectivity and activity for CO hydrogenation on Ni/TiO_2.
- Isotope studies are a significant advantage for separating reaction steps for CO desorption and disproportionation, and the steps for promoted and unpromoted Ni/SiO_2, Ni/TiO_2, and Ni powder were elucidated.
- The mechanisms for CO and CO_2 hydrogenation are shown to be quite similar under a range of conditions.
- A new support was observed to selectively form methane without significant higher hydrocarbon formation.

PUBLICATIONS

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2. G.Y Chai and J.L. Falconer, "Alkali Promoters on Supported Nickel: Effect of Support, Preparation and Alkali Concentration," J. Catalysis 93, 152 (1985).

3. J.L. Falconer, K.M. Bailey and P.D. Gochis, "CO Hydrogenation on Alkali-Promoted Nickel Catalysts," Catalysis of Organic Reactions, Vol. 22, 135, Marcel Dekker, Inc., New York (1985).

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5. T.K. Campbell and J.L. Falconer, "Carbon Dioxide Hydrogenation on Potassium-Promoted Nickel Catalysts," submitted to J. Catalysis.

6. Q.C. Shi, J.L. Falconer and T.C. Chen, "Chrysocolla as a Methanation Catalysts Support," submitted to Applied Catalysis.

PAPERS IN PREPARATION

7. K.M. Bailey, T.K. Campbell and J.L. Falconer, "Potassium Promoter in Ni/Al_2O_3 Catalysts: TPR and Kinetic Studies".

8. K.M. Bailey, G.Y. Chai and J.L. Falconer, "Potassium-Promoted Ni/Al_2O_3 Catalysts: Changes in Distribution of Sites".

9. K.G. Wilson and J.L. Falconer, "Desorption and Disproportionation of $C^{18}O$ on Ni/TiO_2 and $Ni/K/TiO_2$".

10. K.G. Wilson and J.L. Falconer, "Effect of Pretreatment Temperatures on $Ni/K/TiO_2$ Catalysts".

11. K.M. Bailey, P.D. Gochis and J.L. Falconer, "Effect of Potassium on Reaction Steps on Ni/SiO_2 Catalysts".

12. J.D. Lang and J.L. Falconer, "Promoter Location on Ni/SiO_2 Catalysts".

13. K.M. Bailey, Q.C. Shi and J.L. Falconer, "$C^{18}O$ Desorption from Ni/SiO_2 Catalysts".

14. Q.C. Shi, K.M. Bailey and J.L. Falconer, "Potassium Influence on CO Desorption and Dissociation".

15. K. Wilson and J.L. Falconer, "Normalized Curve Analysis of TPD Curves: Effects of Noise, Coverage Errors and Axial Dispersion".

STUDENTS AND VISITORS WORKING ON RESEARCH

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Keith M. Bailey	M.S., 1983 Ph.D., 1987 (expected)
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