

PROMOTER MODIFICATIONS OF CATALYTIC ACTIVITY AND SELECTIVITY

John L. Falconer
Department of Chemical Engineering
University of Colorado
Boulder, Colorado 80309

Research Scope and Objectives

The influence of alkali promoters on catalytic activity and selectivity for carbon monoxide hydrogenation is being 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. Promoter concentration and chemical state will be measured with X-ray photoelectron spectroscopy. 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.

Description of Research Effort

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 $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$) were used to prepare catalysts by impregnation. Sodium was added by preimpregnation of NaCl and by coimpregnation of NaNO_3 . Potassium was added by pre-, co- and post-impregnation using KCl, $\text{K}_2\text{C}_2\text{O}_4$, K_2CO_3 and KOH. On Ni/ SiO_2 and Ni/ $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$, the concentration of potassium was also varied.

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. Calcination and the method of promoter addition had smaller effects on activity and selectivity.

For most catalysts, methane and paraffin activities decreased with potassium addition. Olefin activity decreased much slower or it increased, so that the selectivity to C_2 to C_4 olefins increased dramatically. The main results of these differential reactor studies are:

- For 1% K on 10% Ni catalysts, the methane activity decreased a factor of 70 for SiO_2 support and a factor of 45 for a TiO_2 support. The methane activity decreased only a factor of 3 on Al_2O_3 and the activity increased slightly for a $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ support.
- Depending on the support, the methane activation energy increased or decreased with promoter addition.
- On Ni/ $\text{SiO}_2\cdot\text{Al}_2\text{O}_3$, methane and paraffin activities go through a maximum with promoter concentration.

- Alkali promoters increased olefin selectivity and the olefin to paraffin ratio significantly. The ratio of olefin to paraffin formation increased a factor of 200 on Ni/SiO₂ for C₂ and 100 for C₃.
- The support did not change the olefin selectivity much, but the promoter did. The promoter effect is in addition to the support effect. Thus on promoted Ni/TiO₂, more than 50% of the product were olefins.
- All methods of promoter addition on Ni/SiO₂ resulted in decreased CO hydrogenation rates, but differences were seen between the methods. Calcination appeared to cause an increase in olefin selectivity; over 54% olefins were seen on a calcined Ni/SiO₂ catalyst. Increased potassium loading increased olefin selectivity but decreased overall activity.

Temperature-programmed reaction for CO hydrogenation showed that the decreased methane activities were not due to site blocking or to decreased dispersion; the specific rates of reaction decreased. Agreement between TPR and differential reactor studies was very good. On Ni/SiO₂·Al₂O₃ the specific rate of methanation increased while on the other catalysts the rate decreased.

Detailed TPR and TPD studies, including coverage variation, were carried out on Ni/TiO₂ catalysts with and without potassium promoter. Both the rates of methane and ethane formation were significantly decreased by promoter addition. A larger fraction of unreacted CO was also seen after promoter addition. This change in activity was apparently due to a dramatic change in the CO desorption spectra. The fraction of adsorbed CO that disproportionated to CO₂ was much smaller, and the more strongly-bound CO was almost completely eliminated on the promoted catalyst. Hydrogen was also more weakly bound on the promoted Ni/TiO₂ and Ni/SiO₂ catalysts.

Carbon was deposited by CO disproportionation at 573 K and the rate of carbon hydrogenation was studied by temperature-programmed reaction. On Ni/SiO₂ both sodium and potassium decreased the rate of carbon hydrogenation, apparently due to the decreased hydrogen bonding.

Future Research

To determine the dependence of promoters on the supports, TPD experiments for H₂ and CO on Ni/SiO₂·Al₂O₃ and Ni/SiO₂ will be carried out in detail. On Ni/SiO₂·Al₂O₃, potassium increased the rate of hydrogenation at low concentrations, while on Ni/SiO₂ and Ni/TiO₂, the rate decreased. The effect of promoter concentration and preparation method will be studied with TPD, TPR and by carbon hydrogenation. X-ray photoelectron spectroscopy (XPS) will also be used to attempt to distinguish differences in the chemical state of the promoters on different supports and to relate changes in TPD and TPR to those in XPS. Because higher concentrations of promoters and calcination of nickel catalysts both increase olefin selectivity, these conditions will be used in an attempt to obtain higher olefin selectivities. The selectivities will then be studied in 2:1 and 1:1 H₂:CO ratios, at low and high conversions. TPR, TPD and differential reactor studies will also be carried out for promoted Ru and Fe on several supports.