Water-Gas Shift Kinetics over Iron Oxide Catalysts at Membrane Reactor Conditions

Annual Progress Report

Reporting Period Start Date: 6/30/00
Reporting Period End Date: 6/29/01

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August 10, 2001

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Abstract

This report covers the second year of a project investigating water-gas shift catalysts for use in membrane reactors. It has been established that a simple iron high temperature shift catalyst becomes ineffective in a membrane reactor because the reaction rate is severely inhibited by the build-up of the product CO_2. During the past year, an improved microkinetic model for water-gas shift over iron oxide was developed. Its principal advantage over prior models is that it displays the correct asymptotic behavior at all temperatures and pressures as the composition approaches equilibrium. This model has been used to explore whether it might be possible to improve the performance of iron high temperature shift catalysts under conditions of high CO_2 partial pressure. The model predicts that weakening the surface oxygen bond strength by less than 5% should lead to higher catalytic activity as well as resistance to rate inhibition at higher CO_2 partial pressures. Two promoted iron high temperature shift catalysts were studied. Ceria and copper were each studied as promoters since there were indications in the literature that they might weaken the surface oxygen bond strength. Ceria was found to be ineffective as a promoter, but preliminary results with copper promoted FeCr high temperature shift catalyst show it to be much more resistant to rate inhibition by high levels of CO_2. Finally, the performance of sulfided $CoMo/Al_2O_3$ catalysts under conditions of high CO_2 partial pressure was simulated using an available microkinetic model for water-gas shift over this catalyst. The model suggests that this catalyst might be quite effective in a medium temperature water-gas shift membrane reactor, provided that the membrane was resistant to the H_2S that is required in the feed.

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Introduction

The objective of this project is to identify water-gas shift (WGS) catalysts that are well suited to use in a membrane reactor. Water-gas shift, equation (1), is a well-studied and highly optimized commercial process that is practiced using conventional packed bed reactors. The engineering challenge in WGS derives from its reversibility and exothermicity. Elevated reaction temperatures are desirable because they correspond to higher rates and smaller volumes of catalyst, but reduced temperatures are required to reach greater equilibrium conversions. Current WGS practice, for example in ammonia synthesis plants, uses excess steam in the WGS feed. This has two beneficial effects upon conversion. It increases the equilibrium conversion due to the excess reactant and it also decreases the adiabatic temperature rise, again leading to increased equilibrium conversion. Addition of excess steam alone is not usually sufficient, however, and consequently the reaction is run in a series of catalyst beds with cooling between them. Iron-chromium oxide catalysts are normally used in the first, higher-temperature stages, and copper-zinc oxide catalysts are normally used in the later, lower-temperature stages.

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad\qquad (1)$$

It has been suggested that a membrane reactor might represent an alternative approach to efficient WGS following coal gasification. The gasification of coal produces a mixture of gases that includes H_2O, CO, CO_2 and H_2. These gases are generated at moderately high temperatures. If the coal is being gasified for the purpose of making transportation fuels that can substitute for gasoline, then following coal gasification the product gas will be fed to a Fischer-Tropsch process. Before doing so, WGS will likely be necessary to adjust the CO/H_2 ratio because the ratio exiting the gasifier will not normally be suitable for direct use in Fischer-Tropsch processing. The CO/H_2 ratio required for hydrocarbon synthesis varies between 1:1 and 1:3 depending on the desired hydrocarbon product. Alternatively, if the coal is being gasified for the purpose of making H_2 fuel, perhaps with sequestration of the co-produced CO_2, then WGS will likely be used to convert as much as is practical of the CO into CO_2.

The excess steam, the multiple staged catalysts beds and the associated inter-stage cooling are neither needed nor desired if a membrane reactor is employed as schematically indicated in Figure 1. Instead, the reaction would proceed to high levels of conversion because one reactant (H_2 in the case shown in Figure 1) was selectively removed from the reaction zone of the reactor. As a consequence, the overall CO conversion in the reactor would be limited only by the outlet partial pressure of the H_2 that had permeated through the membrane. That is, the reaction could proceed to the point where the partial pressure (or more correctly the fugacity) of H_2 was equal on the two sides of the membrane and the reaction side was simultaneously at WGS reaction equilibrium. Importantly, it would not be necessary to cool the gasifier product gas prior to shift, it would not be necessary to add excess steam, and it would not be necessary to operate the WGS in stages with cooling between them.
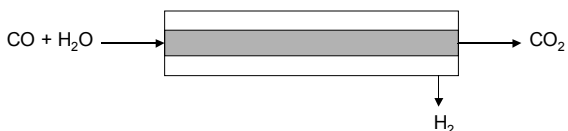

Figure 1. A membrane reactor for water-gas shift. The reactants at high pressure are fed to the catalyst side (gray), and hydrogen permeates selectively through the membrane to the low-pressure recovery side.

This project is focused upon an issue associated with the use of membrane reactors that is not always taken into consideration. Since WGS is such a well-studied process, it is often assumed that the catalysts used in present commercial processes will be equally effective when used in a membrane reactor like that shown in Figure 1. In fact, current high temperature WGS catalysts are quite effective when excess steam is present. However, CO_2 is known to inhibit the reaction and lower the reaction rate over high temperature WGS catalysts. In a membrane reactor there will not be any excess steam, and the concentration of CO_2 will build to very high levels since the other product is being removed through the membrane. Hence, while current high temperature catalysts are quite effective and sufficiently active when used in traditional WGS processes, they may not be suitable for use in membrane reactor processes.

During the first year of this project a reactor system was constructed and the kinetics of WGS over an iron oxide catalyst were studied with emphasis upon conditions that would prevail in a membrane reactor. In particular, two situations were examined. In the first, it was assumed that a membrane could selectively remove CO_2 from the reaction zone. This would mean that the H_2 partial pressure would steadily increase, and it would become very high near the outlet of the reactor. It was experimentally shown that once the H_2 partial pressure built up to a critical value, the catalyst would be reduced to metallic iron. At this point, the WGS activity would decline, and in addition, Fischer-Tropsch chemistry would start to take place. This would render the membrane reactor ineffective. The other situation studied during the first year assumed that H_2 was selectively removed by the membrane, leaving the CO_2 partial pressure to build within the reaction zone. It was experimentally observed that the rate of reaction decreased markedly as the CO_2 partial pressure built. Extrapolation of the results at characteristic conditions suggested that by the time 90% CO conversion was attained, the reaction rate would have decreased by over three orders of magnitude. A mechanistic, microkinetic model for the kinetics of WGS over iron oxide catalysts was also developed during the first year of the project.

This report covers activity and results obtained during the second year of the project. During the present reporting period, the focus shifted from assessing existing catalysts to seeking improved catalysts. More specifically, this report describes results in four areas of investigation. The first section describes how the microkinetic model was further refined and then the second section tells how it was used to design improved, "virtual" WGS catalysts that are predicted to perform much better in membrane reactors than do existing catalysts. The third section describes experimental research attempting to make real catalysts that correspond to the "virtual" catalysts. In particular, these sections describe studies on the effects of either Ce or Cu as a promoter of iron oxide WGS catalysts. The fourth section describes a modeling study that assessed the suitability of sulfided $CoMo/Al_2O_3$ catalysts for WGS in a membrane reactor.

Executive Summary

   This is the second year of this project. In brief, the problem with iron oxide high temperature water-gas shift catalysts is that their activity is severely inhibited at high CO_2 partial pressures. If a membrane reactor is developed and used to drive water-gas shift to high conversions, it will likely function by selectively removing H_2 through the membrane. This will cause the CO_2 partial pressure to build even faster than it does in a conventional reactor. The objective of this project is to identify catalysts that will perform better under such conditions. The research during this reporting period can be grouped into four areas of investigation: development of an improved microkinetic model for high temperature water-gas shift over iron oxide catalysts, use of the microkinetic model to explore reformulation of a "virtual" catalyst that displays superior resistance to rate inhibition by CO_2, testing of two real promoted catalysts that were hoped to exhibit the behavior of the superior "virtual" catalyst, and simulation of the performance of sulfided $CoMo/Al_2O_3$ catalysts for water-gas shift under high CO_2 conditions.

   The rate expressions for each mechanistic step in a microkinetic model include two kinetic parameters and two thermodynamic parameters. The kinetic parameters (forward pre-exponential factor and activation energy) are unknown and are found by fitting the model to experimental data. The thermodynamic parameters for the reaction steps, in turn, are related to the thermodynamic properties of the species that participate. For gas phase species, these are usually known, but for surface species, they are often found by fitting at the same time as the kinetic parameters are estimated. In the past, it has been common to evaluate the thermodynamic properties of the gas phase species at an average reference temperature. As a consequence of this practice, the rate predicted by the microkinetic model will only display the correct asymptotic behavior as the composition approaches equilibrium if the temperature equals the reference temperature. At all other temperatures, the asymptotic behavior will not be correct.

   In this program, the microkinetic model is being used as a predictive tool, both for catalyst design and for simulation of membrane reactor performance. Furthermore, the limitations of iron oxide catalysts become most apparent as the composition approaches equilibrium. Therefore, the first task during this year involved reformulation of the microkinetic model so that it now incorporates the temperature dependence of the thermodynamic properties of the gas phase species. By doing so, the model now displays the proper asymptotic behavior at all temperatures upon approaching equilibrium. This modification had only a slight effect upon the quality of the fit to the experimental data, but it will make the model much more reliable when used as a predictive design tool.

   The second task for this reporting period made use of the refined microkinetic model to explore how the catalyst might be improved. Specifically, individual kinetic parameters or thermodynamic parameters in the model could be perturbed, and then the effects upon catalyst performance could be explored by simulation of the reaction. In short, the model predicts that lowering the surface oxygen bond strength by less than 5% should lead to a catalyst that is more active than the base iron oxide catalyst, and at the same time, this catalyst should be much less severely inhibited by CO_2. Of course, this prediction will only prove true if the microkinetic model is an accurate description of the reaction process.

   The third task during this reporting period was to identify a way to modify the iron oxide catalysts so that the surface oxygen bond strength might be lower than in an unmodified catalyst. Examination of the recent literature revealed two catalyst promoters that might have the desired

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effect. These promoters are Ce and Cu, and for both promoters, the evidence that they might weaken the surface oxygen bonds is the same. When iron oxide high temperature shift catalysts are promoted with either Ce or Cu, the peak in the temperature programmed reduction profile shifts to lower temperature. One interpretation of this observation is that the catalysts are more easily reduced (and by extension, that the surface oxygen bonds are weaker). However, there are other possible interpretations of the observed behavior that do not involve surface bond weakening.

Promoted catalysts were prepared and tested, with emphasis upon testing at conditions of high CO_2 partial pressure. Ce-promoted iron oxide and Ce-promoted FeCr oxide were both studied, and in both cases, the promoter had no effect upon performance. The promoted catalysts were still severely inhibited by CO_2. However, a Cu-promoted FeCr oxide catalyst was found to be much less susceptible to inhibition by CO_2. This is a very promising lead that will be followed during the coming year. At the least, it will be necessary to replicate the result, determine the effect of varying the amount of Cu, examine whether the kinetics have changed in other ways, and more fully characterize the physical and chemical properties of the catalyst.

The final task during the current reporting period involved using an existing microkinetic model for sulfided $CoMo/Al_2O_3$ water-gas shift catalysts to simulate their performance at higher CO_2 partial pressures. The results are promising; CO_2 has little effect upon the rate of reaction, there being only an 8% drop in rate as the CO_2/CO ratio increases from 0 to 4. This catalyst requires a sulfur source in the feed to maintain the catalyst in an active state. This might not be a problem for a coal conversion process as many coals contain sulfur. There are literature reports of dense metal membranes that are stable and functional in the presence of small amounts of sulfur. Additional study would be needed to determine the necessary sulfur level and also to study whether the source of sulfur is important. In the experiments used to derive the microkinetic model, H_2S was always the sulfur source. Study is also necessary to determine how high the temperature can go with this catalyst before its catalytic properties begin to degrade at an unacceptable rate.

The project has made good progress during this year. The focus going into the final year of the project is upon more thorough characterization of the promoted iron oxide catalysts, Cu promoted catalysts in particular.

Experimental

The design and operation of the reactor system used to study WGS kinetics in this project was presented in detail in the technical report for the first year. Briefly, CO (Cryogenic Supply, CP grade), CO_2 (Cryogenic, Bone Dry Grade), H_2 (Cryogenic, Pre-purified Grade) and Ar (Cryogenic, High Purity Grade) are metered using mass flow controllers. Steam is generated by feeding liquid water to a packed bed of heated 100 mesh glass beads using a syringe pump; the mixed process gases flow through this bed and pick up the evaporated water. The reactor is a tubular packed bed, typically containing 0.5 g of catalyst. The reactor is positioned within a split tube furnace (Lindberg type 54231). The thermocouple built into the furnace is used to control the temperature via an Omega CN9000A temperature controller, while the catalyst bed rests upon glass wool, centered within the furnace. Bed temperature is measured with separate thermocouples above and below the bed. There are provisions for sampling with a gc before and after the reactor. A gc column packed with 80-100 mesh Porapak QS (Alltech) is used to separate the gases, which are detected using a thermal conductivity detector. The gc output is recorded using a PC and analyzed using the program PeakSimpleII.

Several different catalysts were used experimentally. Unpromoted iron oxide came from two sources. The first, Fe-A, was purified grade iron oxide powder obtained from Fisher Scientific. The other, Fe-B, was precipitated from an aqueous mixture of ferrous and ferric ammonium sulfates using ammonium hydroxide. Cerium promoted iron oxide was prepared by mixing cerium nitrate and the iron oxide powder in ethanol and then evaporating the solvent. A doubly promoted (Ce and Cr) catalyst was prepared by precipitation from an acidified aqueous solution of ferrous sulfate, ferric sulfate, chromium sulfate and cerium sulfate using ammonium hydroxide. A Cr promoted catalyst was prepared by precipitation from an aqueous solution of ferric and chromium sulfate. Finally, a Cu promoted catalyst was prepared by mixing the FeCr catalyst and copper nitrate in ethanol and evaporating the solvent. The compositions of the catalysts are reported in Table 1.

Table 1. Composition of promoted iron oxide WGS catalysts

Catalyst	Ce:Fe	Cu:Fe	Cr:Fe
Fe-A	-	-	-
Fe-B	-	-	-
Ce-A	0.17	-	-
Ce-B	0.03	-	-
CeCr	0.05	-	0.01
CuCr	-	0.05	0.1

Kinetic data were collected at steady state. The inlet and outlet compositions were measured using the gas chromatograph. At least three sets of inlet and outlet analyses were used to ensure the system had indeed reached steady state. The inlet composition was determined from the full gas chromatographic analysis of the inlet gas stream. The CO conversion, x_{CO}, was calculated using equation (2) and the inlet and outlet ratios of CO_2 to CO, as measured gas chromatographically.

$$x_{CO} = \frac{\left(\dfrac{CO_2}{CO}\right)_{out} - \left(\dfrac{CO_2}{CO}\right)_{in}}{1 + \left(\dfrac{CO_2}{CO}\right)_{out}} \tag{2}$$

A mechanistic microkinetic model for the kinetics of WGS over a commercial Fe-Cr catalyst was developed during the first year of the project. According to simple transition state theory the rate of an elementary surface reaction step can be described using an expression of the form given in equation (3) where r denotes the net rate per unit area, ρ_{sites} is the density of active sites per unit area of catalyst, A is the kinetic pre-exponential factor, E is the activation energy, R is the gas constant, T is the absolute temperature, σ_f is a geometric factor for the forward reaction, σ_r is a geometric factor for the reverse reaction, P is a partial pressure, θ is a fractional surface coverage, v is a stoichiometric coefficient (always positive), ΔS is the entropy change upon reaction, and ΔH is the enthalpy change upon reaction, and where the subscript j denotes the mechanistic reaction step, i_{gr} denotes a gas phase reactant, i_{sr} denotes a surface phase reactant, i_{gp} denotes a gas phase product and i_{sp} denotes a surface phase product. The entropy change upon reaction and the enthalpy change upon reaction are found from the standard entropies, S^0, and enthalpies of formation, ΔH_f^0, of the species as given in equations (4) and (5).

$$r_j = \rho_{sites} A_j \exp\left(\frac{-E_j}{RT}\right)\left[\sigma_{f-j}\left(\prod_{i_{gr}} P_{i_{gr}}^{v_{i_{gr}}}\right)\left(\prod_{i_{sr}} \theta_{i_{sr}}^{v_{i_{sr}}}\right) - \frac{\sigma_{r-j}\left(\prod_{i_{gp}} P_{i_{gp}}^{v_{i_{gp}}}\right)\left(\prod_{i_{sp}} \theta_{i_{sp}}^{v_{i_{sp}}}\right)}{\exp\left(\frac{\Delta S_j(T)}{R}\right)\exp\left(\frac{-\Delta H_j(T)}{RT}\right)}\right] \tag{3}$$

$$\Delta S_j(T) = \sum_{i_{gp}} v_{i_{gp}} S_{i_{gp}}^0(T) + \sum_{i_{sp}} v_{i_{sp}} S_{i_{sp}}^0(T_{ref}) - \sum_{i_{gr}} v_{i_{gr}} S_{i_{gr}}^0(T) - \sum_{i_{sr}} v_{i_{sr}} S_{i_{sr}}^0(T_{ref}) \tag{4}$$

$$\Delta H_j(T) = \sum_{i_{gp}} v_{i_{gp}} \Delta H_{f-i_{gp}}^0(T) + \sum_{i_{sp}} v_{i_{sp}} \Delta H_{f-i_{sp}}^0(T_{ref}) - \sum_{i_{gr}} v_{i_{gr}} \Delta H_{f-i_{gr}}^0(T) - \sum_{i_{sr}} v_{i_{sr}} \Delta H_{f-i_{sr}}^0(T_{ref}) \tag{5}$$

When the mechanistic models were fit to the data during the first year of the project, all four terms on the right hand sides of equations (4) and (5) were evaluated at a reference temperature, T_{ref}. This temperature was chosen to be the average temperature of the kinetic data. The ultimate consequence of this choice is that for an equilibrium composition the microkinetic model will correctly predict a net rate of zero only at the reference temperature. At any other temperature, the microkinetic model would predict a non-zero rate even though the composition corresponds to equilibrium. As can be seen in equations (4) and (5), this deficiency has now been eliminated by using the temperature dependent thermodynamic properties of the gas phase species. Even though the surface thermodynamic properties are still evaluated at the reference temperature, the microkinetic model will nevertheless correctly predict a rate of zero for the equilibrium composition at any temperature. In this study, the temperature dependent

thermodynamic properties of the gas phase species were found using formulae found in the NIST Chemistry web book (http://webbook.nist.gov/chemistry/).

In equations (3) ρ_{sites}, R, σ_f, σ_r, and the v values are known constants. The temperature and the partial pressures are experimentally set or determined variables while the surface coverages are unknown, but experimentally determined variables. The temperature dependent standard entropies and enthalpies of formation of the gas phase species are experimentally set (through the temperature) variables. This leaves as unknown and undetermined, the values of A and E for each reaction and the values of $S^0\left(T_{ref}\right)$ and $\Delta H_f^0\left(T_{ref}\right)$ for each surface species. In principle, all of these quantities could be found by fitting of the mechanistic microkinetic model to the experimental data. In this project, however, the pre-exponential factors, A, for each of the reactions were estimated using transition state theory and then held fixed at the resulting estimated values. Similarly, the standard entropies of the surface species at the reference temperature were estimated by finding the entropy of the species as if it existed in the gas phase (from standard thermochemical tables) and then subtracting its translational entropy (assuming ideal gas behavior). As with the pre-exponential factors, the standard entropies of the surface species were held fixed at these estimated values.

This leaves the activation energies, E, and the heats of formation of the surface species at the reference temperature as undetermined parameters. A better intuitive "feel" for the latter parameters results if the standard heat of formation of the surface species is taken to equal the heat of formation of the species as if it existed in the gas phase (a constant that can be found in standard thermochemical tables) less the "bond strength" between the species and the surface. In this way, the undetermined parameters are the activation energies and the surface bond strengths of the surface species. These parameters were used to fit the microkinetic model to the experimental data. A plug-flow reactor design equation was written for each species using equation (3) for the rate of each mechanistic reaction. A set of mixed algebraic and ordinary differential equations results. Initial guesses for the activation energies and surface bond strengths were fed into a parameter estimation routine that iteratively solved the set of equations, determined the least squares error for the available data, and generated improved guesses for the parameters until the least squares error was minimized. Athena Visual Workbench [1] was used for this purpose.

Results and Discussion

<u>Improvement of the Mechanistic Microkinetic Model</u>

Equations (6) through (13) present the mechanistic microkinetic model that was fit to the data during the first year of the project. This model was re-fit to experimental data for WGS over a commercial Fe-Cr catalyst as described in the experimental section. Figure 2 presents a rectifying plot comparing the model's predictions to experimental observation, and Table 2 presents the parameters that were found to give the best fit of the model to the data. The use of temperature dependent thermodynamic properties for the gas phase species did improve the quality of the fit slightly. The main reason for making the change was not to improve the fit, but so that the resulting model might be more reliable when extrapolated to conditions near equilibrium, as might happen when modeling the performance of a membrane reactor and comparing it to the performance of a conventional packed bed reactor.
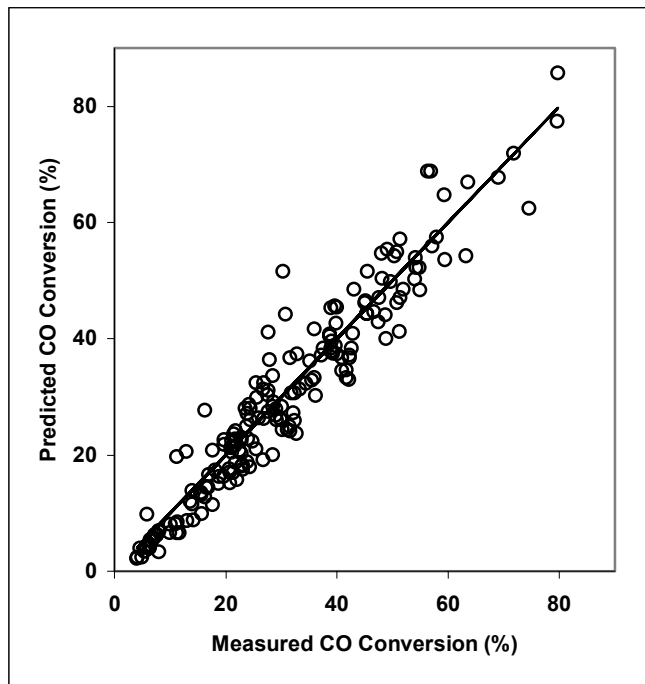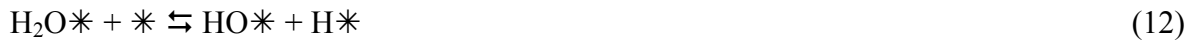
$$CO + 2\,O* \leftrightarrows CO_3*_2 \tag{6}$$

$$CO_3*_2 \leftrightarrows CO_3* + * \tag{7}$$

$$CO_3* \leftrightarrows CO_2 + * \tag{8}$$

$$H_2O + * \leftrightarrows H_2O* \tag{9}$$

$$H_2O* + O* \leftrightarrows 2\,HO* \tag{10}$$

$$2\,HO* \leftrightarrows 2\,O* + H_2 \tag{11}$$

$$H_2O* + * \leftrightarrows HO* + H* \tag{12}$$

$$2\,H* \leftrightarrows H_2 + 2* \tag{13}$$

Figure 2. Rectifying plot of microkinetic model predictions *vs.* experimental conversions.

It should be noted that reaction steps (12) and (13) were added to the model only for mathematical completeness. Under normal operating conditions, steps (6) through (11) are all that are necessary to describe the performance of the catalyst. However, if one were to start with a surface that was 100% vacant and pass a feed of only CO and H_2O, steps (6) through (11) would provide no way for the reaction to take place. Clearly, steam could adsorb according to step (9), but it could not dissociate according to step (10) because there would be no surface oxygen. Similarly, the CO could not even adsorb. If no CO_2 was present in the feed, surface oxygen could never be generated, and the reaction could never get started. Equations (12) and (13) simply add a route for initially generating surface oxygen from steam over a completely vacant surface. These steps thus might be important in a transient start-up experiment, but for steady-state kinetics, they are neither important nor significant. The data set used in fitting did not include such experiments, so the values of the activation energies for reactions (12) and (13) were set very high and the bond strength for $H*$ was set very low. In subsequent fitting, the quality of the fit was not sensitive to the values of these parameters, and so, they were not reliably estimated.

The quality of the fit of the microkinetic model using this new procedure was only marginally better than the fit when all the thermodynamic properties in equation (4) were estimated at a reference temperature. This reflects two facts: first, the older method was not too seriously in error, and second, most of the kinetic data used for fitting were not at conversions near equilibrium. If measurements were made at conversions approaching the equilibrium conversion, there is little doubt that the new procedure would lead to a better fit. Also, when the

Species or Reaction	Bond Strength or Activation Energy (kJ/mol)
$O*$	606.5
CO_3*_2	767.4
CO_3*	619.5
H_2O*	60.5
$HO*$	355.7
$H*$	0.1
$CO + 2\,O* \leftrightarrows CO_3*_2$	5.5
$CO_3*_2 \leftrightarrows CO_3* + *$	11.2
$CO_3* \leftrightarrows CO_2 + *$	0.0
$H_2O + * \leftrightarrows H_2O*$	12.5
$H_2O* + O* \leftrightarrows 2\,HO*$	54.4
$2\,HO* \leftrightarrows 2\,O* + H_2$	10.2
$H_2O* + * \leftrightarrows HO* + H*$	320.3
$2\,H* \leftrightarrows H_2 + 2*$	403.8

Table 2. Estimated microkinetic model parameters

microkinetic model is used to make predictions (as in the next section), it is better to have a rate expression that will display the correct asymptotic behavior as equilibrium is approached at all temperatures. The parameters estimated from the fitting procedure are reasonable, with one exception. The model predicts an endothermic adsorption of H_2 (all other adsorption steps are predicted to be exothermic). It would be expected that the adsorption of H_2 would be exothermic; the contrary result suggests that some refinement of the model is still needed. The experimental data almost exclusively involved very low hydrogen partial pressures, and this may have contributed to the result.

Design of a "Virtual" Iron Oxide Water-Gas Shift Catalyst

During the first year of the project, it was experimentally demonstrated that the rate of WGS decreased severely as the CO_2 partial pressure increased. It can be seen in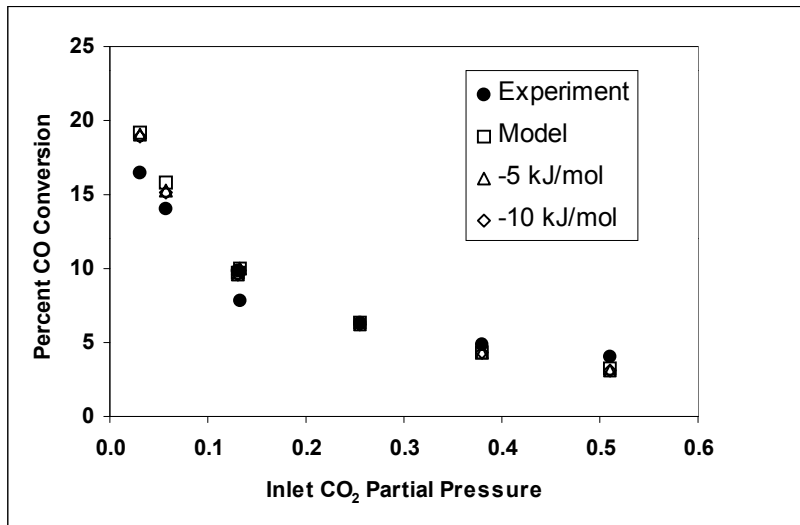 Figure 3 that the microkinetic model captured this behavior. The figure shows the experimentally measured CO conversion in a series of experiments where the CO_2 inlet partial pressure was varied. It also shows the prediction of the microkinetic model, and it can be seen that the agreement is very good. This suggested that the microkinetic model might be used to design a new "virtual" catalyst for WGS. That is, various parameters in the microkinetic model (activation energies and/or bond strengths) could be altered, and then the model could be used to see whether the change lessened the degree of rate inhibition by CO_2.

It seemed most reasonable that the inhibiting effect of CO_2 was due to strong adsorption of CO_2 on the catalyst surface. This would block sites that might otherwise catalyze the reaction, and thereby cause the observed inhibition. Following along this line of reasoning, simulations were performed wherein the CO_3* surface bond strength was decreased by 5 kJ mol^{-1} and then by 10 kJ mol^{-1} from its microkinetically estimated value of 619.5 kJ mol^{-1}. Figure 3 shows the results of these simulations, and it can be seen that decreasing the surface bond strength of the unidentate carbonate intermediate had essentially no effect upon the observed inhibition. At first, this observation was surprising, however an examination of the surface coverages predicted by

Figure 3. Effect of CO_3* bond strength upon WGS inhibition by CO_2.

the microkinetic model showed that the predominant surface species was $O*$, not an adsorbed form of CO_2.

Therefore, a series of microkinetic simulations was performed wherein the surface oxygen bond strength was varied. The results are shown in Figure 4, which also reproduces the experimental observations and the base model from Figure 3. The surface oxygen bond strength was reduced by 5, 10, 15, and 25 kJ mol^{-1} from its microkinetically-estimated value of 606.5 kJ mol^{-1}. Figure 4 shows that there are two effects of reducing the surface oxygen bond strength. First, the catalyst activity increases, as evidenced by the higher overall CO conversions. The conversion at the lowest inlet CO_2 partial pressure more than doubled from ca. 20% to ca. 45% as the surface oxygen bond strength was decreased. It also appears that the effect of decreasing the surface oxygen bond strength reaches an asymptote; there is very little difference between a 15 kJ mol^{-1} bond strength reduction and a 25 kJ mol^{-1} reduction.

The second effect of decreasing the surface oxygen bond strength predicted by the model is more important for the present project. It can be seen in Figure 4 that the magnitude of the inhibition by CO_2 is less when the surface oxygen bond strength is lower. Specifically, in the base case, the CO conversion decreases by 76% as the CO_2 partial pressure is increased; in the case of the virtual catalyst whose surface oxygen bond strength was decreased by 25 kJ mol^{-1}, the CO conversion only dropped by 12.6% as the CO_2 partial pressure increased. The microkinetic model predicts that even with the 25 kJ mol^{-1} decrease in the surface oxygen bond strength, greater than 99% of the surface remains covered by $O*$.

Thus, an improved "virtual" WGS catalyst was successfully designed. This catalyst offers a higher catalytic
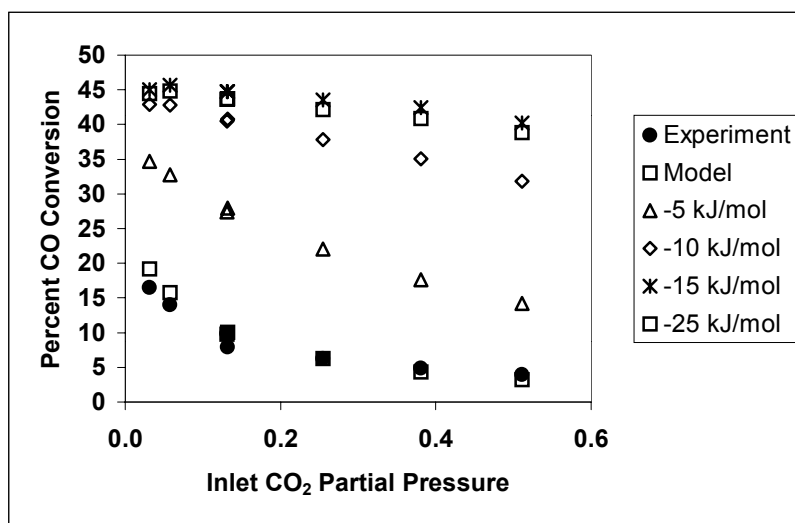

Figure 4. Effect of $O*$ bond strength upon WGS inhibition by CO_2.

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activity and much improved resistance to inhibition by CO_2. The crucial questions then become whether it is possible to synthesize the corresponding real catalyst, and whether that real catalyst will, in fact, perform as the model predicts. The latter question depends upon the accuracy of the mechanistic microkinetic model. It is always true in mechanistic kinetic modeling, that no matter how well a given model describes the data, the possibility remains that a different mechanistic model might fit the data equally well, or even better. The WGS literature evidences such a situation in that there are formate-based models for WGS that are claimed to better explain the mechanism of WGS. One could spend time developing a microkinetic model involving formate intermediates and then devise experimental tests to discriminate between the redox model presently being used and the formate model. However, this would bring the project no closer to its objectives.

Instead, the prediction that lowering the surface oxygen bond strength will improve catalyst performance can be used as a test of the validity of the microkinetic model. If a catalyst is synthesized with a lower surface oxygen bond strength, it can be tested in WGS. If its performance is superior to the base iron oxide catalyst, this will increase confidence in the microkinetic model; if its performance is not superior to the base iron oxide catalyst, that will indicate that the microkinetic model needs to be improved or replaced. Thus, the challenge becomes synthesis of a real catalyst with properties corresponding to the "virtual" catalyst.

Fortunately, the recent literature suggests two iron oxide promoters that might cause a reduction in the oxygen bond strength of the catalyst. For both Ce-promoted [2] and Cu-promoted [3] iron oxide catalysts it has been reported that the maximum in the temperature programmed reduction profile shifts to lower temperatures when iron oxide is promoted. This may be an indication of a weakening of the surface oxygen bond strength, but it could also have other causes. For example, if a separate CeO or CuO phase coexists with the iron oxide, the lowering of the temperature could be due to reduction of this new phase. It could also be related to differences in the bed properties or other experimental parameters. Still, these two catalyst systems represent a reasonable first attempt to synthesize a real catalyst with properties like the improved "virtual" catalyst.

Experimental Assessment of Ce and Cu as Promoters

Hu et al. [2] reported that Ce-promotion improved an FeCr WGS catalyst. Among the results presented was a temperature-programmed reduction profile where the maximum reduction rate shifted to lower temperature with the promoted catalyst. The modeling work already described suggests that if this temperature shift is indicative of a weaker oxygen bond strength, then the Ce-promoted FeCr catalyst should be less susceptible to inhibition by CO_2. Therefore, catalyst was synthesized following the procedure described by those authors, and it was tested in a series of experiments where the inlet CO_2 concentration was varied at fixed CO and H_2O inlet concentrations. Additionally, two other catalysts were prepared with Ce promoter, but without the Cr.

Figure 5 shows the results for the two Cr-free catalysts and compares them to an unpromoted iron oxide catalyst. There is no measurable difference in the susceptibility to inhibition by CO_2 for these catalysts. The behavior of the CeCrFe catalyst, though not shown, was also the same. This result was disappointing, as the Ce promotion had no effect. Characterization of this catalyst is on going. It is suspected that the shift in the temperature-programmed reduction curves reported for Ce-promoted catalysts may be caused by the onset of
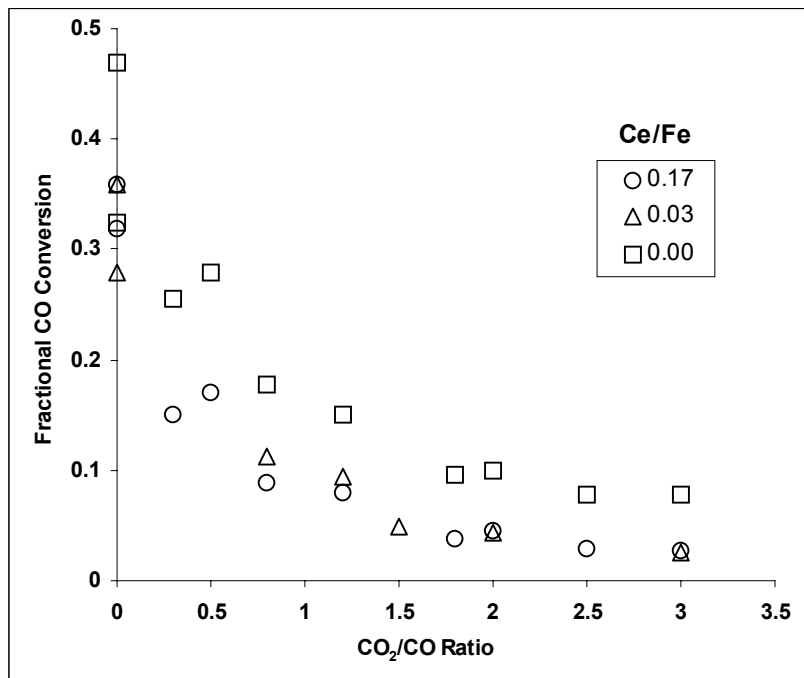
Figure 5. Comparison of CO_2 inhibition over Ce promoted and unpromoted catalyst.

CeO_2 reduction and thus may have no significance to the iron-oxygen surface bond strength. It will be important to test this interpretation during the next year of the project.

Kappen et al. [3] reported the same kind of change in the temperature programmed reduction profile when an FeCr WGS catalyst was promoted with Cu. They noted that this could be an effect of differences in heating rate, preparation, or an effect of the presence of the copper promoter atoms. As with Ce, a catalyst was prepared for testing the effect of Cu promotion upon the inhibition by CO_2. This work has just begun, but the results shown in Figure 6 suggest that copper is effective in lessening the susceptibility to inhibition by CO_2. Thorough characterization of this catalyst is planned for the next year of the project. Plans call for studying the effect of Cu loading, detailed physical characterization, and microkinetic modeling. Simulation of membrane reactor performance will also be conducted.
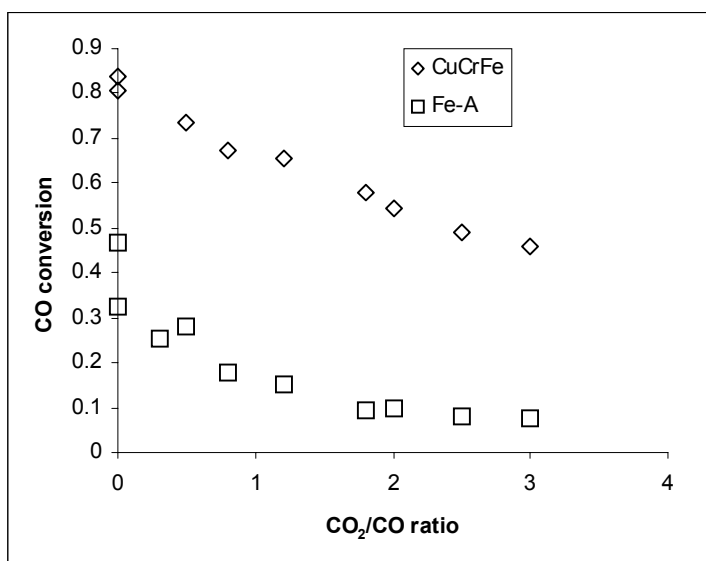

Figure 6. Comparison of CO_2 inhibition over Cu promoted and unpromoted catalyst.

Computational Evaluation of sulfided $CoMo/Al_2O_3$ Catalysts

A microkinetic model for water-gas shift over sulfided Mo/Al_2O_3 and sulfided $CoMo/Al_2O_3$ was developed a few years ago [4,5]. Since the mechanism of the reaction on these catalysts is believed to be very different from that on iron oxide catalysts, it seemed quite possible that the rate would not be inhibited by CO_2. This was tested by simulation using the available microkinetic model for sulfided $CoMo/Al_2O_3$. Figure 7 shows the result of a series of simulations of a conventional reactor operating at 14.6 atm. and 548 K with a feed that contains varying
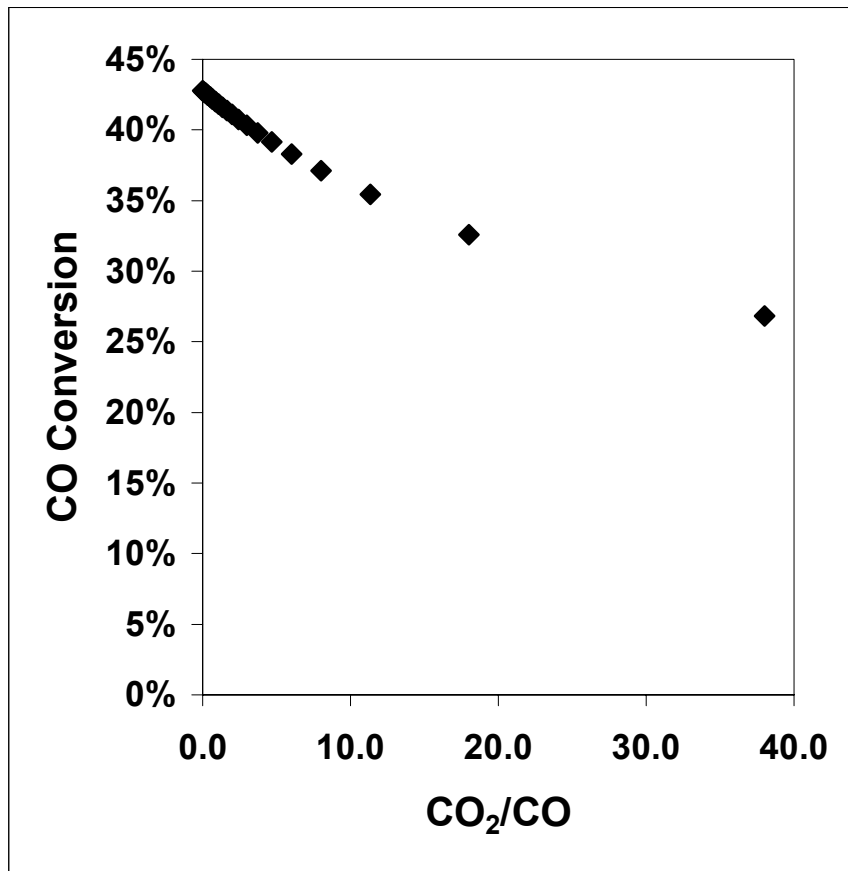
Figure 7. Predicted CO conversion over sulfided CoMo/Al$_2$O$_3$ as inlet CO$_2$ is varied.

amounts of CO$_2$. There is very little inhibition of the rate as CO$_2$ is added to the feed; the conversion drops only 8% upon changing from a CO$_2$/CO ratio of 0 to a ratio of 4. This is a promising lead that should be followed up.

There are also a few caveats that should be mentioned. First, these catalysts must have a sulfur source in order to maintain their activity. It appears that there are dense membrane materials that may function in the presence of low levels of H$_2$S. For example, at this year's contractors' meeting, Way reported on one such material that is being studied in another project from the University Coal Research Program. The catalyst should be studied experimentally to determine what sulfur sources can be used (all studies to date used H$_2$S) and what their critical concentrations are. For coal conversion processes, there will likely be a source of sulfur in the original coal, so the need for sulfur might not pose a significant problem. The performance of these catalysts should also be examined at higher temperatures to determine the range of operability.

Plans

The project is entering its final year of support. During the coming year, it is planned to focus primarily upon the promoted iron oxide catalysts for WGS. The effect of promoter concentration will be studied, microkinetic models will be formulated and compared to the base catalyst, and the catalysts will be characterized by a variety of physical, chemical, and spectroscopic methods in an attempt to develop a clear understanding of structure and function. Both Ce promoted and Cu promoted catalysts will be examined, but the emphasis will be on the latter since they appear to be most promising.

Conclusion

This year has been very productive. Two materials have been identified that offer superior performance under membrane reactor conditions. The Cu-promoted FeCr catalyst appears to be the best material to date for high temperature operation in a membrane reactor with selective

removal of H_2. Sulfided $CoMo/Al_2O_3$ catalysts appear to offer advantages for operation at lower temperatures and in the presence of sulfur. These leads are very encouraging and provide a good basis for continued research.

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Submitted Presentation based upon this Project

"Water-Gas Shift over Promoted Iron Oxide," AIChE Annual Meeting, Reno, NV, November 2001. Co-author: Z. Mang.