Time-Resolved XANES Investigation of CuO/ZnO in the Oxidative Methanol Reforming Reaction

T. L. Reitz,[1] P. L. Lee,[2] K. F. Czaplewski,[1] J. C. Lang,[2] K. E. Popp,[1] H. H. Kung[1]
[1] *Department of Chemical Engineering, Northwestern University, Evanston, IL, U.S.A.*
[2] *Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.*

Introduction

The autothermal reforming of methanol, also known as oxidative methanol reforming (OMR), has been investigated as a means to supply H_2 for automotive fuel cell systems. In this process, methanol and steam are supplied together with air to the reactor system. The ratio of the three reactants is such that the overall reaction is thermal-neutral or only modestly exothermic. Although it produces less hydrogen per mole of methanol compared with steam reforming, OMR does not require a supply of external heat. As a result, the reactor systems are significantly less complicated, which is more suitable for mobile applications. Currently the catalyst used for this process is an industrial $CuO/ZnO/A_{l2}O_3$. The objective of this study was to use time-resolved XANES to investigate, in situ, the $CuO/ZnO/A_{l2}O_3$ during the oxidative methanol reforming reaction.

Methods and Materials

In situ time-resolved XANES measurements of the copper K absorption edge were obtained by employing the energy dispersive monochromator of beamline 1-BM at the Advanced Photon Source at Argonne National Laboratory. The reaction flow and analytical systems are described elsewhere.[1] Data were regressed using the factor analysis technique developed by Malinowski.[2]

Results and Discussion

After regression of the copper K edge data for a given experiment by factor analysis, the relative concentrations of the principal components (Cu^0, Cu^{+1}, and Cu^{+2}) were obtained. An example of these data and the concurrent H_2 evolution in the gas phase are plotted in Fig. 1 as a function of time from the start of the temperature ramp at 180°C to 240°C for an oxygen partial pressure of 6.9 kPa. Examination of Fig. 1, displayed more closely by the insert, shows that during this experiment, Cu^+ is formed as a transient phase with an observable bulk concentration up to 7 minutes after the start of the autothermal process. The maximum concentration of Cu^+ is 76.1% and occurs at about 4.6 min. The data suggest that the reduction of Cu^{+2} proceeds in a stepwise manner, initially producing Cu^+ before the formation of metal (Eq. 1):

$$Cu^{+2} \rightarrow Cu^+ \rightarrow Cu^0 \rightarrow \qquad (1)$$

Using data such as these, the industrial $CuO/ZnO/Al_2O_3$ catalyst was found to perform more than one function in the oxidative methanol reforming reaction. For small oxygen conversions, oxidation is predominant over the Cu^{+2} phase with only minimal selectivity to H_2. As oxygen conversion nears completion, the copper is rapidly reduced to metal. It is then, over a reduced catalyst, that reforming activity is observed with principal selectivity to H2. The *in situ* XANES measurements showed clearly that Cu^0 is needed for steam reforming.

Increasing oxygen partial pressure resulted in more rapid reduction of the catalyst because of more severe local heating of the catalyst by the faster combustion of methanol and depletion of oxygen. For all of the samples, the reduction of Cu^{+2} to Cu^0 proceeds via Cu^+, which has not been associated with either oxidation or reforming activity.

Many of the issues surrounding long-term performance of an operational $CuO/ZnO/Al_2O_3$ catalyst remain unresolved. However, much is now known about the initial performance of the catalyst as well as its activation process. Such information should be useful in developing strategies that allow a more fundamental approach to eliminate the remaining obstacles to implementation of these systems for automotive use.

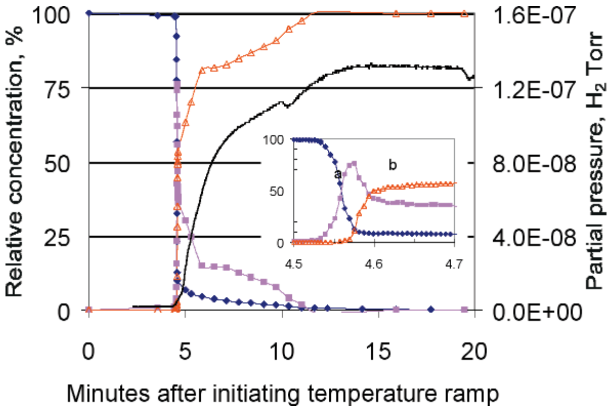

FIG. 1. Changes in the relative concentrations of different copper oxidation states in a $CuO/ZnO/Al_2O_3$ catalyst during reaction with a feed containing P_{O2} = 6.9kPa, ramp rate = 2°C/min. Insert shows magnified area from 4.5 to 4.7 minutes after initiation of the temperature ramp, (♦) Cu^{+2}, (Ç) Cu^{+1}, (Δ) Cu^0.

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References

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