QUARTERLY TECHNICAL PROGRESS REPORT

Submitted to U.S Department of Energy

GRANT TITLE: Investigation of Syngas Interaction in alcohol Synthesis Catalysts

GRANT NO: DE-FG22-93MT93010 (XU: 235-860)

STARTING DATE: 09-01-93

ENDING DATE: 08-31-97

PROJECT DIRECTOR: MURTY A. AKUNDI
PHYSICS/ENGINEERING DEPARTMENT

INSTITUTION: Xavier University of Louisiana
New Orleans, La 70125

*U.S. / DOE Patent Clearance is not required prior to the publication of this document
Quarterly Technical progress Report
(Period October 1 to December 31)

This report presents the work done on "Investigation of Syngas Interaction in Alcohol Synthesis Catalysts" during the last quarter. FTIR absorption studies on Cu/Co/Cr catalysts using CO as a probe molecule are presented in this report.

Introduction:

The aim of this study is to investigate the nature of infrared adsorption of CO on copper-cobalt-chromia catalysts. The chemisorption of CO on metal particles can be associative/dissociative depending upon the nature of the metal, the type of exposed faces and adsorption temperature.

Several investigators [1-3], classified cobalt as a border line element which under particular conditions can dissociate CO. For instance the (0001) face of CO is known to be inactive for CO dissociation at room temperature, while the stepped (1012) face is active at very moderate temperatures [4-5] with formation of surface carbide. Of the dissociated species carbon could form a surface carbide and simultaneously the oxygen could form a surface oxide. With a view to examine the metal surface interaction with CO, FTIR absorption studies of Cu/Co/Cr composites were undertaken.

Experimental Studies:

The FTIR experimental arrangement for CO adsorption studies was described in the earlier report [6]. All the samples were prepared by co-precipitation of nitrates in 7 - 8 pH sodium hydroxide solution at 80°C. The precipitate is washed several times, air dried overnight at 80°C and calcined at 350°C for 18 hrs. The calcined sample is loaded in to the sample cup of the Diffuse Reflectance Accessory (DRA). The sample is then reduced in a flowing stream of hydrogen for 18 hrs. Hydrogen was outgassed while reducing the temperature to 25°C. Before admitting CO, a spectrum was generated to serve as a background for eliminating the CO2 and water bands along with any vibrational lines due to the pure sample. CO was admitted at this temperature and allowed to flow continuously through the sample at about 20 cc/min. While continuously flowing carbon monoxide temperature was increased stepwise to 250°C and spectra were taken at each step. At 250°C CO was outgassed and the temperature was decreased in the reverse order to obtain the desorbed spectra CO. Total of six samples (0.5< Cu/Co< 5.0) covering the range from hydrocarbons to mixed alcohols to methanols were studied in this investigation. All the spectra obtained were recorded with 500 scan accumulation at a resolution 4 cm⁻¹.

Results and Discussion:

Figures 1-4 represent the FTIR spectra of Cu/Co/Cr catalysts. Average vibrational frequencies of all samples are listed in Table 1.

In all the samples investigated we observed mainly (A) three strong bands in the region 1600-850 cm⁻¹, and (B) weak bands in the region 2000 - 1800 cm⁻¹ region.
The bands in the A region have been attributed to carbonyl and carbidic formations on the metal surface by earlier investigators (7-10). The bands in the region B may due to physisorption process and CO may be weakly bonded to the surface metal atoms. In the following paragraphs are presented the effect of temperature, desorption, and metal ratio on the vibrational frequencies.

**Effect of Temperature:**

Temperature seems to have no significant effect on the vibrational frequencies. However, with increasing temperature the carbonyl bands seem to become stronger in all metal ratios studied. This indicates that chemisorption or chemical reactions between metal and sample are promoted as temperature increases giving rise to formation of carbonyls/carbonates/carbides.

![Temperature effect](image1)

**Effect of Desorption:**

The weak bands observed in the region B attributed to physisorption are not noticeable upon desorption of CO at 250°C (Fig 2), while the bands formed due to chemical interaction seems to be persistent and appear to become sharp. This seems to indicate that only those CO molecules which have chemically interacted with the metal composite formed metal carbonyls, metal carbides or carbonates and are persistent even after CO desorption.

![CO @150°C](image2)

**Metal Ratio:**

For Cu/Co ≤ 1, the FTIR spectra (Fig 4) show strong carbonyl formations and no appreciable changes were observed in the positions of the physisorbed bands. For Cu/Co =
1.5, carbonyl bands appears to become weak showing several minor peaks perhaps due to large number of multiple carbonyl structures. At Cu/Co metal ratio of 2.0 no detectable carbonyl formations are seen. As the ratio increases (Cu/Co ≤ 4.5) we find again very weak multiple carbonyl structures reemerging.

These observations might indicate that for Cu/Co ≤ 1, the surface cobalt atoms promote carbonyl formations. In the intermediate range 1 ≤ Cu/Co ≤ 3.0, carbonyl formations seems to be inhibited. Further increase of copper content (Cu/Co ≥ 3.0), seems to promote cobalt reduction and it appears that weak carbonyl structures reemerge.

Table 1 A: Adsorbed frequencies

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1772(wb)</td>
<td>1980(w)</td>
<td>1927(vw)</td>
<td>1937(w)</td>
<td>1941(vw)</td>
<td>1756(vw)</td>
</tr>
<tr>
<td>1673(s)</td>
<td>1661(m)</td>
<td>1673(vw)</td>
<td>1688(vw)</td>
<td>1646(w)</td>
<td>1705(vw)</td>
</tr>
<tr>
<td>1537(s)</td>
<td>1544(m)</td>
<td>1581(w)</td>
<td>1602(vw)</td>
<td>1593(wb)</td>
<td></td>
</tr>
<tr>
<td>1434(m)</td>
<td>1450(sb)</td>
<td>1513(wb)</td>
<td>1522(vw)</td>
<td>1539(vw)</td>
<td>1527(vw)</td>
</tr>
<tr>
<td>1367(m)</td>
<td>1378(s)</td>
<td>1364(w)</td>
<td>1380(vw)</td>
<td>1383(w)</td>
<td>1372(vw)</td>
</tr>
<tr>
<td>1328(m)</td>
<td>1332(s)</td>
<td>1289(w)</td>
<td></td>
<td>1261(w)</td>
<td></td>
</tr>
<tr>
<td>1170(w)</td>
<td>1061(w)</td>
<td>1006(w)</td>
<td></td>
<td>1017(wb)</td>
<td>1098(vw)</td>
</tr>
<tr>
<td>871(s)</td>
<td>848(w)</td>
<td>855(w)</td>
<td></td>
<td>858(w)</td>
<td></td>
</tr>
<tr>
<td>713(s)</td>
<td>762(w)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

s = sharp, m = medium, w = weak, vw = very weak, sb = sharp and broad
mb = medium broad, wb= weak and broad, n = noisy
Table 1B: Desorbed frequencies

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1556(s)</td>
<td>1598(s)</td>
<td>1598(m)</td>
<td>1595</td>
<td>1591(s)</td>
<td>1692(n)</td>
<td></td>
</tr>
<tr>
<td>1446(s)</td>
<td>1546(s)</td>
<td>1360(n)</td>
<td>1359</td>
<td>1503(n)</td>
<td>1544(mb)</td>
<td></td>
</tr>
<tr>
<td>1344(s)</td>
<td>1352(s)</td>
<td>1309(b)</td>
<td>1332</td>
<td>1268(w)</td>
<td>1371(n)</td>
<td></td>
</tr>
<tr>
<td>1058(s)</td>
<td>1047(s)</td>
<td>1011(m)</td>
<td>1145</td>
<td>1147(w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>879(s)</td>
<td>845(s)</td>
<td>857(s)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Future Plans:**

The present studies provided some interesting data. We plan to repeat these experiments to reproduce the results and confirm our findings. More indepth analysis and identification of observed frequencies will be made. Further, we plan to investigate the CO adsorption on Fe/Cu/Zn catalysts.

**Student Training:**

One of the objectives of this project is to provide training for minority undergraduate students at a school with predominant minority enrollment. Out of the students involved in the project, one is engineering major and three are physics majors. Students mastered the techniques of preparing the catalysts, operation of the vacuum system and FTIR Spectrometer. Currently students are being trained to analyze and interpret the infrared data. Some students who are working on this project for the last two years are able to train new students in the preparation of catalysts and the operation mechanism of the FTIR spectrometer. Two students have presented papers at the Louisiana Academy of Sciences (February, 1997). The abstracts of these presentations are enclosed.

**References:**


Amsterdam, 1982) p. 427, and references there in.