Quarterly Technical Progress Report

**Quarterly Report
April 1 - June 30, 1997**

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QUARTERLY TECHNICAL PROGRESS REPORT

Submitted to U.S Department of Energy

GRANT TITLE: Investigation of Syngas Interaction in Alcohol
Synthesis Catalysts

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Project Director

Date

Quarterly Technical progress Report
(Period April 1 to June 30)

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:

A comprehensive FTIR investigation on the catalysts was undertaken to unfold the picture of the gas - metal interactions. Our magnetization studies have provided valuable information on the changes in the magnetic character of the ferromagnetic metal due to CO adsorption. The FTIR results showing the effect of the adsorbate-adsorbent interactions on the stretching frequencies of the CO vibrational modes are presented in this report.

Experimental:

A detailed description of the experimental arrangement of the FTIR spectrometer with the diffuse reflectance accessory was given in an earlier report (1). A series of 10 calcined samples with $0.5 < \text{Cu/Co} < 5$ were loaded in the sample cup of the environmental chamber of the FTIR spectrometer and were reduced in-situ before exposing to carbon monoxide. Carbon monoxide was admitted at room temperature, and while flowing CO, temperature was increased gradually in steps of 50°C and FTIR spectra were recorded at each temperature up to 250°C .

Results:

The FTIR results are presented in Tables 1- 2. and graphically represented in Figs. 1.- 4. We did not find any significant differences in the spectra taken at different temperatures. This suggests that gas-metal interactions occur even at room temperature. Except for the single band in the region $820 - 900\text{ cm}^{-1}$, all the observed bands seem to arise from four distinct metal carbonate structures. as suggested by A. A. Davydov (2).

Suggested Structures :

The disproportionation of carbon monoxide molecule produces CO_2 ads according to Boudouard reaction

The CO_2 produced is believed to be stabilized in the matrix in the form of a) non coordinated carbonates (structure II), b) mono-dentate carbonates (structure III), and c) Bi-dentate carbonates (structures IVa, and b) because of the reaction

The non coordinated carbonates generate bands in the regions: $1420-1450\text{ cm}^{-1}$ ($\nu_{as}CO_3^{2-}$) and $1020-1090\text{ cm}^{-1}$ ($\nu_sCO_3^{2-}$), monodentate carbonate structures produce bands in the region $1470-1530\text{ cm}^{-1}$ ($\nu_{as}COO^-$), $1370-1300\text{ cm}^{-1}$ (ν_sCOO^-), and $1040-1080\text{ cm}^{-1}$ ($\nu C-O$), and bidentate carbonate structures produce bands in the region $1530-1620\text{ cm}^{-1}$ ($\nu C=O$), $1250-1270\text{ cm}^{-1}$ ($\nu_{as}COO$), and $1020-1030\text{ cm}^{-1}$ (ν_sCOO) for

Vibrational frequencies of Cu-Co-Cr
Figure 1

Comparison of Adsorbed Frequencies

Figure 3

Comparison of Desorbed Frequencies

Figure 4

IVa type and $1620-1670\text{ cm}^{-1}(\nu_{\text{s}}\text{C=O})$, $1220-1270\text{ cm}^{-1}(\nu_{\text{as}}\text{COO})$, $980-1020\text{ cm}^{-1}(\nu_{\text{s}}\text{COO})$ for IVB type. Table 1 shows the stretching frequencies of CO bands as Cu/Co metal ratio increases from 0.5 to 5.0. Since the $860 \pm 40\text{ cm}^{-1}$ band consistently appears for all metal ratios we believe this is due CO adsorption on Cr_2O_3 . The bands due to structures II, III and IVb seem to be independent of the changes in the Cu/Co intermetallic ratio. The ground state electronic configuration of CO is (3)

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$$

Broden et.al., (4) consider that the 5σ orbital of CO is essentially non-bonding with respect to the carbon and oxygen and therefore donation from the 5σ orbital to the metal should not affect greatly the C-O bond strength /stretching frequency. As such in these structures, the gas metal interaction could be through the overlap of 5σ CO orbital and d orbitals of the metal. Our magnetization data support this view that charge transfer occur from CO to Co, as evidenced by the drop in the magnetic moment of Co. The behavior of structure IVa is unique and closely parallels the magnetization results which show an increase in magnetic moment for the alcohol selective catalysts. The frequency increases from 1544 cm^{-1} for $\text{Cu/Co} \leq 1$ to 1604 cm^{-1} for $\text{Cu/Co} = 4$ and drops for Cu/Co ratios > 4 . An increase in magnetic moment is possible when the metal loses electron to the adsorbate. CO is considered as being typically a π acceptor. The back donation of electrons from the metal surface orbitals to the anti-symmetric unoccupied $2\pi^*$ of CO would result in lowering of the CO stretching frequency (5). However our results show an increase in the CO stretching frequency in the alcohol region. Chini and Co-workers (6) report that when the number of metal atoms in a cluster increase, the stretching frequencies of CO also increase. The magnetization results clearly indicate that cobalt is well reduced in the alcohol selective catalysts increasing the number of metal atoms in given cluster. Hence in structure IVa the cluster mechanism seems to be responsible for observed increase in the frequencies instead of a drop as suggested by Dalmon et.al.(7).

The high frequency bands in the 1900 cm^{-1} region is observed only in the hydrocarbon and methanol selective catalysts. These are the only bands that disappeared upon desorption of gaseous CO. These may be due to the cobalt carbonyl formations, $\text{Co}(\text{CO})_4^-$, that have transiently formed due to the CO_2 stabilization on the matrix as CO_3^{2-} species according to the reaction (8).

This gradual disappearance is a consequence of gradual modification in the adsorbate-adsorbent interaction when the surface becomes covered by the adsorbed carbon (carbided surface). We designate these bands as physisorbed distinct from the carbonate like species bands which persist even after desorption and may be considered as resulting from the chemisorption process.

Future Plans:

The present studies provided some understanding of the mechanism involved and the role of CO in the catalytic process. We plan to correlate the FTIR data, NMR and Magnetization results along with the catalytic studies and prepare the final report in the next few months.

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. The engineering major is currently enrolled at an engineering school. 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.

Table 1
Vibrational frequencies of Cu-Co-Cr Catalysts

SAMPLE ID	Metal ratio Cu/Co	CO on Cr ₂ O ₃ 800-900	$\nu_s\text{CO}_3^-/\nu\text{C-O}$ II/III 1040-1080	$\nu_s\text{COO}^-$ III 1300-1370	$\nu_{as}\text{CO}_3^{2-}$ II 1420-1450	$\nu\text{CO=O}$ IV a 1530-1620	$\nu\text{C=O}$ IV b 1620-1670	Carbonyls (CO) ₄ ⁻ 1800-2000
32-64-4	0.5	860 (879)	1056 (1058)	1358 (1344)	1434 (1446)	1544 (1556)	1673	1928
37-37-26	1.0	859 (845)	1056 (1058)	1328 (1316)	—	1544 (1598)	1673	1925
43-28-29	1.5	898 (877)	1024 (1031)	1392 (1377)	—	1580 (1603)	—	—
58-29-13	2.0	822 (834)	1020	1392 (1359)	—	1598 (1648)	—	—
54-22-24	2.5	850	—	—	1415 (1453)	— (1676,1538)	—	—
60-20-20	3.0	—	1036 (1035)	1352 (1344)	1454	1598 (1606)	1670	—
74-21-5	3.5	823 (840)	1017 (1044)	1383	1455	1539 (1591)	1688	1937
63-16-21	4.0	850 (844)	1019 (1035)	1351 (1352)	1408	1604 (1588)	—	—
80-18-2	4.5	823	—	1352 (1371)	—	1597 (1518)	—	1941
50-10-40	5.0	878 (878)	1025 (1025)	—	1445 (1445)	1541 (1545)	1672	—

Table 2
Comparison of vibrational frequencies of Co/Cr catalyst

Modes of Vib.	1			3			8			16		
	Co/Cr	Co/Cu	Co/Cr/Cu	Co/Cr	Co/Cu	Co/Cr/Cu	Co/Cr	Co/Cu	Co/Cu/Cu	Co/Cr	Co/Cu	Co/Cr/Cu
Unknown	844	—	850	846	—	—	849	—	823	858	—	860
(820-900)	(844)	—	(844)	(851)	—	(986)	(846)	—	(936)	(846)	—	(879)
$\nu(\text{CO}_3)^{2-}/\nu\text{C-O}$	1064	—	1019	1065	—	1036	1056	—	—	1049	1015	1056
II III	(1053)	(1075)	—	(1054)	(1046)	—	(1056)	—	—	(1043)	—	(1058)
(1040-1080)												
$\nu_s\text{COO}^-$	1364	—	1351	1371	1335	1362	1354	—	1352	1369	1354	1358
III	(1343)	—	(1352)	(1362)	(1350)	(1359)	(1368)	—	(1371)	(1352)	(1329)	(1344)
(1300-1378)												
$\nu(\text{CO}_3)^{2-}$	—	1450	1408	—	1442	1454	—	1454	—	—	—	1434
II	—	(1451)	—	—	—	—	—	—	—	—	—	(1446)
(1420-1450)												
$\nu\text{C=O}$	1599	1535	1604	1585	1602	1598	1549	1532	1597	1576	1595	1544
IV a	(1605)	(1535)	—	(1597)	(1596)	(1595)	(1561)	—	—	(1580)	—	(1556)
(1530-1620)												
$\nu\text{C=O}$	1657	1692	—	1645	—	1670	1635	1697	—	—	1642	1673
IV b	—	—	—	—	—	(1648)	(1648)	—	—	—	—	—
(1620-1670)												
$\nu(\text{CO})_4^-$	2002	1821	—	2004	—	—	1902	—	—	1863	1883	—
	—	—	—	—	—	—	1959	—	—	1932	(1884)	1928
(1800-2000)							2031	—	—	2028	—	—

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