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EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL. TECHNICAL PROGRESS REPORT 17, SEPTEMBER 16, 1991--DECEMBER 15, 1991

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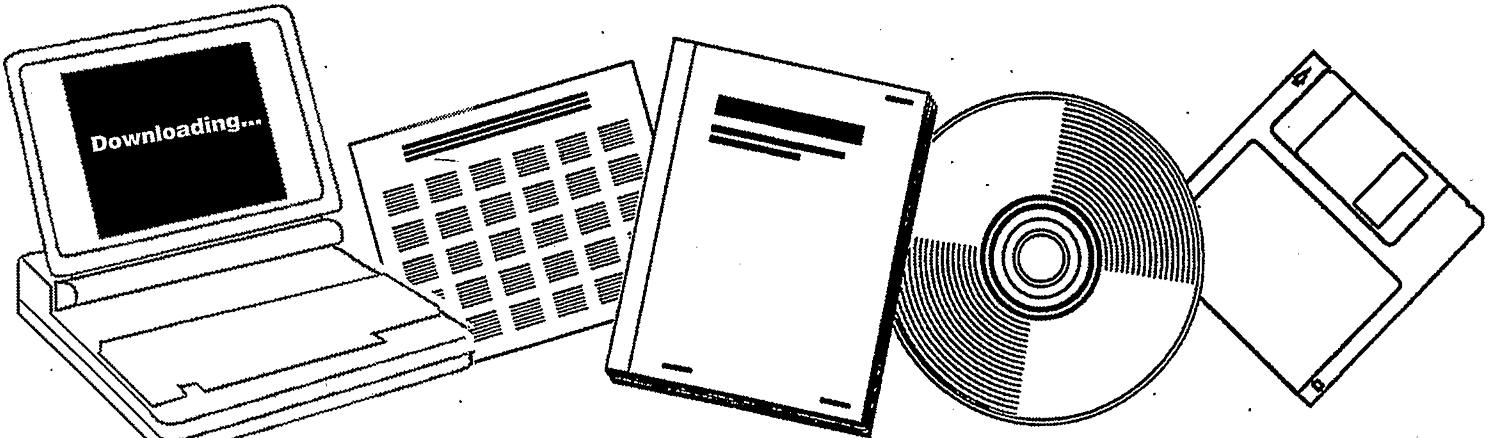
ENGINEERING

20 DEC 1991



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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

DOE/PC/79923--T10

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SUMMARY

The objective of this research is to elucidate the role of various chemical additives on ethanol synthesis over Rh- and Ni-based catalysts. Chemical additives used for this study will include S, P, Ag, Cu, Mn, and Na which have different electronegativities. The effect of additives on the surface state of the catalysts, heat of adsorption of reactant molecules, reaction intermediates, reaction pathways, reaction kinetics, and product distributions is/will be investigated by a series of experimental studies of NO adsorption, reaction probing, study state rate measurement, and transient kinetic study.

A better understanding of the role of additives on the synthesis reaction may allow us to use chemical additives to manipulate the catalytic properties of Rh- and Ni-based catalysts for producing high yields of ethanol from syngas.

RESULT TO DATE

During the fourth quarter of 1991, the interaction of C_3H_6/H_2 with adsorbed CO on Rh catalyst has been studied by in-situ infrared spectroscopy. A final report will be prepared in the next quarter and submitted by Feb. 15, 1992.

EXPERIMENTAL

Catalyst Preparation

Supported rhodium catalysts containing 3 wt% Rh were prepared by impregnation of silica (large pore, Strem chemicals) with an aqueous solution of $Rh(NO_3)_3.2H_2O$ (Alfa), respectively. The resulting silica supported rhodium nitrate was dried in air at 313 K and reduced in flowing hydrogen (10 cc/min) for 16 hours at 673 K. The sulfided Rh catalyst (S-Rh) was prepared by treating the reduced catalyst in H_2S (1000 ppm in H_2, 5 cc/min) at 673K for 4 hours. The bulk sulfur content of the S-Rh catalyst was measured by a Phillips PV 9550 X-ray fluorescence spectrometer.

The catalyst was pressed into a self supporting disk (10 mm in diameter, 1 mm in thickness and 15-20 mg). The disk was placed in an infrared (IR) cell which consists of four stainless steel flanges and two CaF_2 step windows that minimize the IR pathlength for the gaseous species. The path lengths for the infrared beam in the cell is slightly less than 2 mm and the net reactor volume is 0.2 cm^3. The cell can be used upto 6 MPa and in the temperature range of 293 to 563 K. Infrared spectra were obtained by a Nicolet 5XSC Fourier Transform Infrared spectrometer at a resolution of 4 cm^{-1}.

Reaction of adsorbed CO with C_3H_6/H_2

CO (5 cc/min) was admitted into the reactor at 303 K and 1 atm for 2-3 minutes and the catalyst was then flushed with N_2 (5-10 cc/min) for 5 minutes to remove any gaseous species before the IR spectra were taken. The IR spectra of adsorbed CO were used to determine the surface state of the catalysts. The reaction of adsorbed CO with C_3H_6/H_2 was carried out by admission of a mixture of C_3H_6/H_2 (5 cc/min each, at 1 atm) for 1 minute to the adsorbed CO with the outlet of the reactor kept closed. The batch reaction was allowed to take place. The IR spectra of the reaction of C_3H_6/H_2 with CO adsorbed on Rh were taken as a function of reaction time and temperature. The temperature increase was achieved at a steady rate of 4-5 ° C/minute. The same reaction was performed on the sulfided Rh catalyst. Closed system reaction refers to the reaction in the IR cell operated in the batch mode.

RESULTS

Reaction of Propylene and Hydrogen with CO Adsorbed on Rh/SiO$_2$

Figure 1 shows the IR spectra of the reaction of C_3H_6/H_2 with CO adsorbed at 303 K over Rh/SiO$_2$, as a function of time. The spectra taken just before admitting the C_3H_6/H_2 into the reactor showed linear CO at 2070 cm^{-1}, bridge CO at 1894 cm^{-1} and the dicarbonyl species at 2100 and 2036 cm^{-1}. Upon admitting the C_3H_6/H_2 mixture, the intensity of the linearly adsorbed CO band at 2070 cm^{-1} decreased. There was a gradual downward shift of the linear CO band from 2070 to 2059 cm^{-1} and of the bridge bonded CO from 1894 to 1879 cm^{-1}. These shifts are attributed to a decrease in the dipole-dipole coupling between adsorbed CO [32] as a result of the formation of the adsorbed alkene species. The twin carbonyl bands at 2100 and 2036 cm^{-1} did not change in intensity. Intense bands at 1453, 1641, 2953, and 3081 cm^{-1} due to propylene [33] did not show any obvious change in intensity with reaction time. The small band at 2980 cm^{-1} can be attributed to one of the propane bands [33].

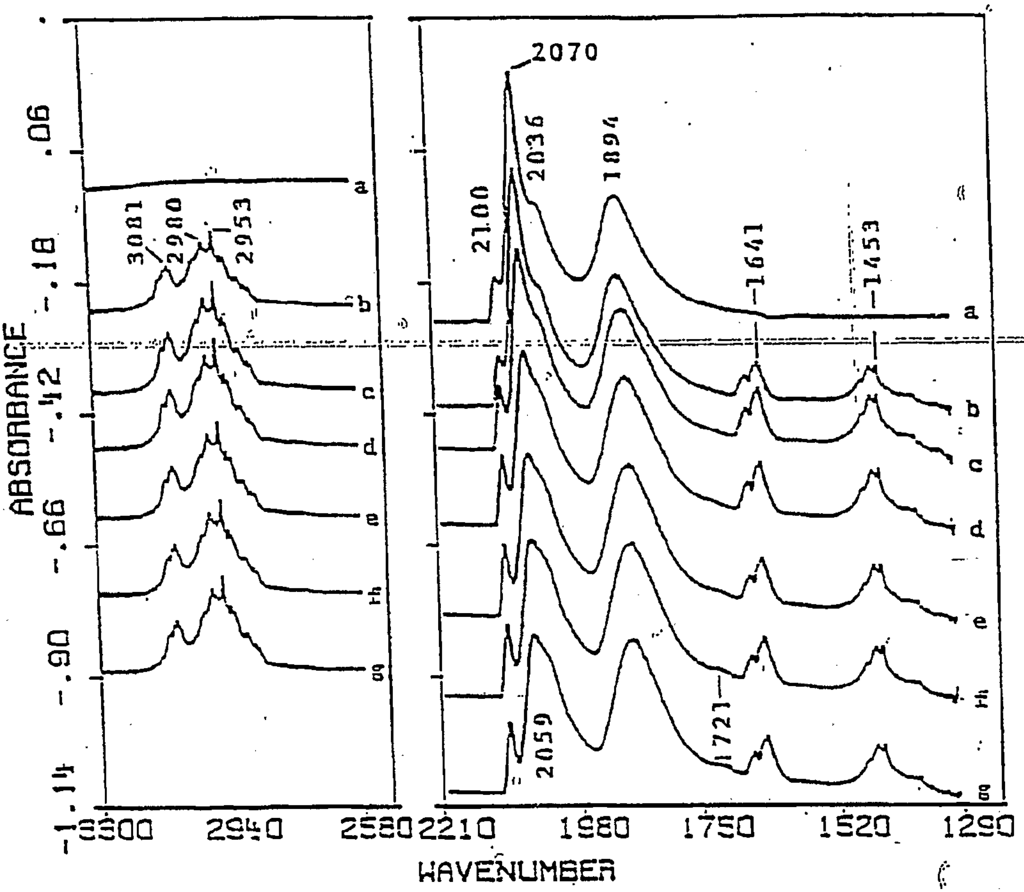
A small band emerged at 1721 cm^{-1}, 19 minutes after the isothermal batch reaction had proceeded and became prominent as the reaction time increased further. This band can be assigned to the adsorbed butyraldehyde species [34]. The distinction between the 'n' and 'iso' butyraldehyde species could not be made form the IR spectra. Figure 2 shows the difference spectra of Figure 1, taken to discern the involvement of the adsorbed CO species in the formation of the aldehyde. The difference spectra were consecutive spectra taken and subtracted from the original spectra obtained before the alkene and hydrogen species were admitted into the reactor. A gradual negative increase in the intensity of the band at 2070 cm^{-1} was observed; with a slight growth in the butyraldehyde band at 1721 cm^{-1}. The increase in the intensity of the bridge CO band at 1894 cm^{-1}, and the gem dicarbonyl bands indicate that these species are not directly related to the formation of butyraldehyde. The simultaneous consumption of linear CO and the formation of butyraldehyde suggest that linear CO is the active species that takes part in the reaction to form butyraldehyde.

Reaction of Propylene and Hydrogen with CO Adsorbed on Sulfided Rh/SiO₂

Figure 3 shows the IR spectra of the reaction of C_3H_6/H_2 with CO adsorbed on sulfided Rh/SiO_2 at 30° C. The spectra taken prior to admitting the C_3H_6/H_2 mixture showed the linear CO band at 2067 cm^{-1}, the the $Rh^+(CO)$ band at 2092 cm^{-1}, the asymmetric gem dicarbonyl band at 2038 cm^{-1} and a weak bridge CO band at 1854 cm^{-1}. The addition of C_3H_6/H_2 to CO adsorbed on sulfided Rh/SiO_2 resulted in the following spectral developments: (a) the appearance of the propylene bands at 1453, 1640, 2950 and 3081 cm^{-1} and propane band at 2977 cm^{-1}, (b) a gradual decrease in the intensity of the band at 2092 cm^{-1} with reaction time, (c) an increase in the intensity of the butyraldehyde band at 1715 cm^{-1}, and (d) a gradual increase in the intensity of the bridge CO band at 1854 cm^{-1}.

Figure 4 shows the difference spectra of Figure 3. A negative increase in the intensity of the $Rh^+(CO)$ band at 2092 cm^{-1} was observed with a corresponding increase in the butyraldehyde band at 1715 cm^{-1}. No significant change in the intensities of the linear CO and gem dicarbonyl bands were observed. The negative increase in the $Rh^+(CO)$ band and the increase in the butyraldehyde band at 1715 cm^{-1} showed that the CO bonded to the Rh^+ site was involved in the CO insertion. The appearance of the bridge CO band in Figures 3 and 4 indicates that a part of the sulfur was removed from the catalyst surface resulting in the formation of Rh crystallite surface that chemisorbs bridge CO.

LIST OF FIGURES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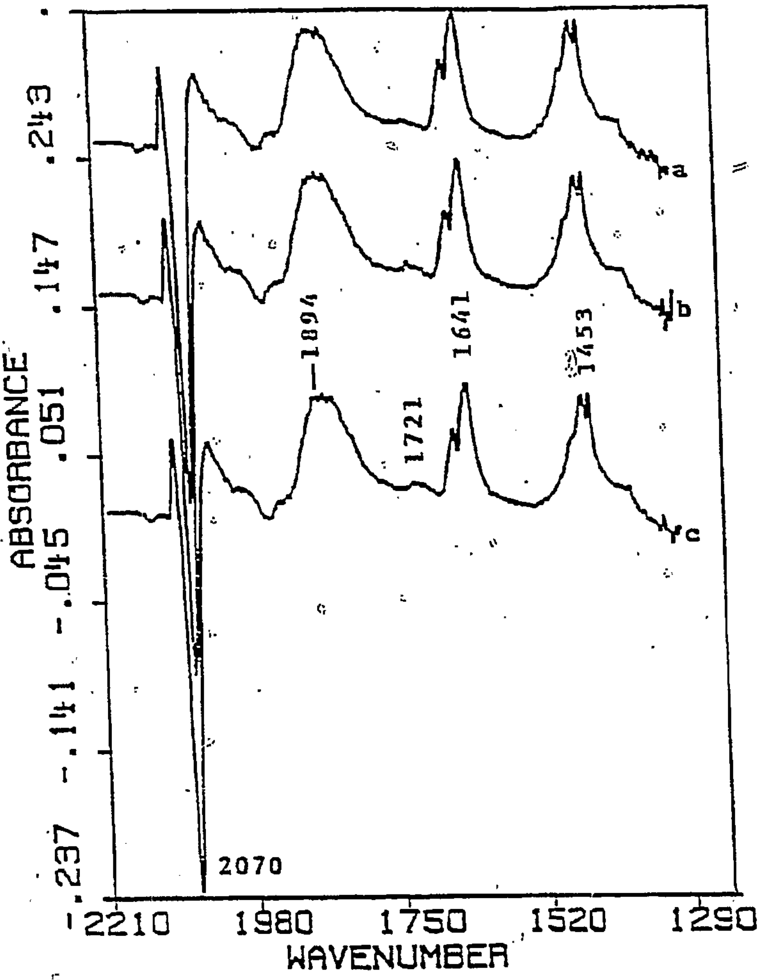
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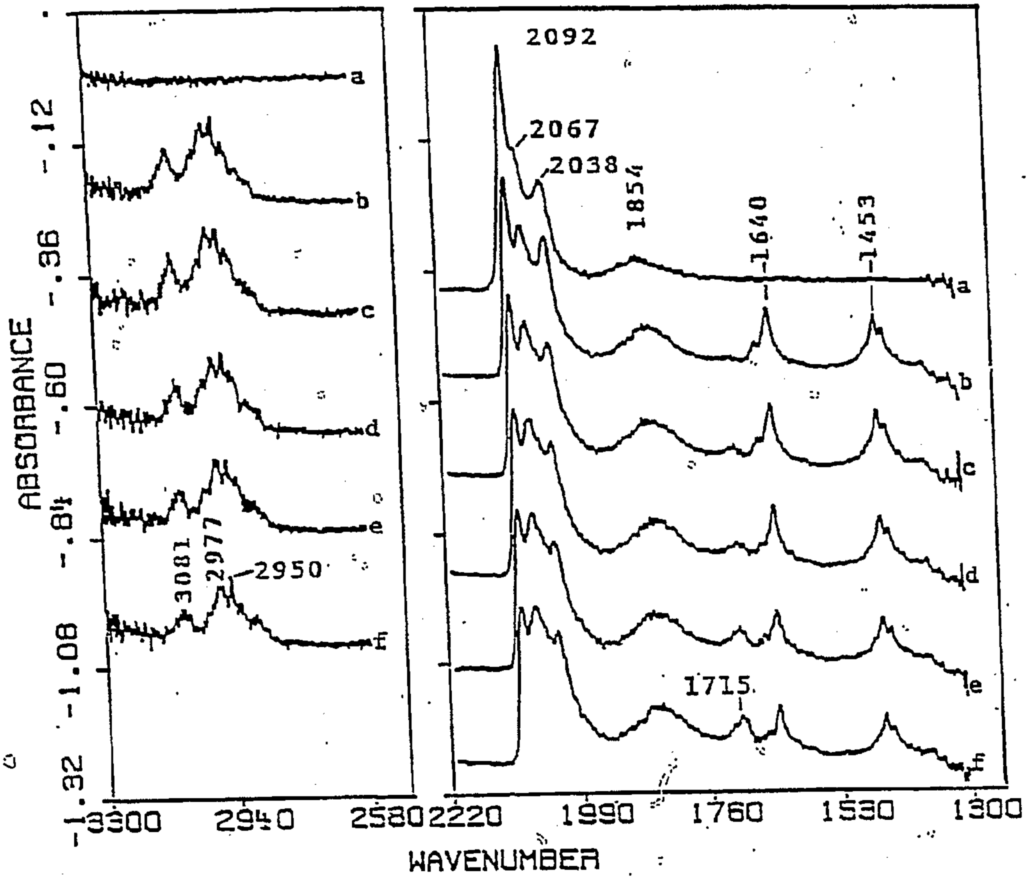
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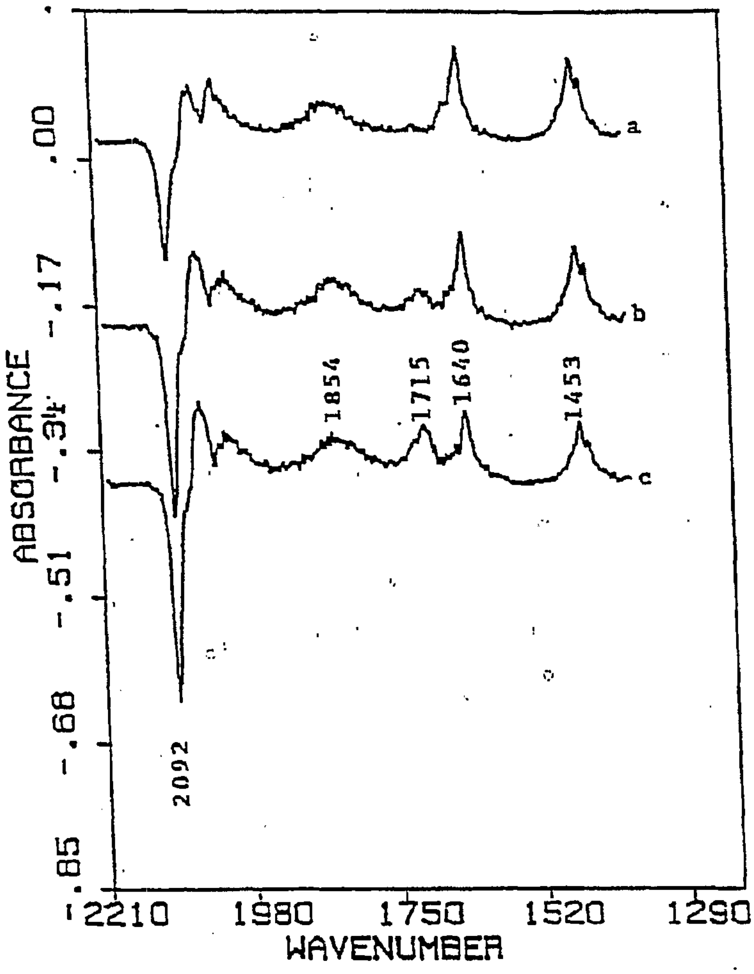
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