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EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL. TECHNICAL PROGRESS REPORT NO. 14, DECEMBER 16, 1990-MARCH 15, 1991

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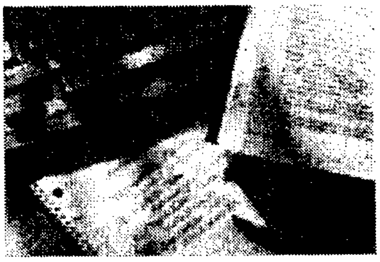

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

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SUMMARY

The objective of this research is to elucidate the role of additives on the methanol 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 additive 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 first quarter of 1991, the effect of Cu on the adsorption properties of Rh/SiO_2 catalysts was studied by temperature programmed desorption of hydrogen.

The presence of Cu on Rh/SiO_2 inhibited H_2 chemisorption at 303 K and suppressed CO hydrogenation. TPD study shows that chemisorption of H_2 on $Cu-Rh/SiO_2$ is an activated process.

INTRODUCTION

There have been numerous studies on supported group VIII metals, alloyed with group IB metals such as Cu, Ag and Au [1-5]. The group IB metals which have electronegativities similar to those of group VIII metals, are inactive components of catalysts for the Fischer-Tropsch (F-T) synthesis and alkane hydrogenolysis. These bimetallic catalysts have been employed for investigating geometric requirements of sites for specific reactions such as the F-T and alkane hydrogenolysis reactions [3-5]. Extensive studies have focused on the effects of alloying on the adsorptive and catalytic properties of Cu-Ni, Cu-Ru, and Cu-Fe [1-9]. Little is known about the effect of Cu on the the adsorptive property of Rh catalysts which are known to be active for C_2 oxygenate synthesis [5]. The purpose of this study is to examine adsorptive properties of $Cu-Rh/SiO_2$ using temperature-programmed desorption of hydrogen.

EXPERIMENTAL

$Cu-Rh/SiO_2$ containing 3 wt% Rh was prepared by coimpregnation of silica (Strem Chemicals, surface area: 350 m^2/g) using Cu and Rh nitrate solution. The molar ratios of Cu to Rh were 0, 0.25, and 1. After impregnation, the sample was dried overnight in air at 303 K, then reduced in flowing hydrogen at 673 K for 16 hours. The crystallite size of the resulting Cu and Rh metals was determined to be less than 30 ^{0}A by an X-ray diffraction (XRD) line-broadening technique. Details of temperature programmed desorption techniques and reaction studies have been reported elsewhere [10,11]. Following exposure of the catalyst to H_2, TPD experiments were carried out in an Altamira (AMI-1) TPD unit in flowing Ar from 303 K to 673 K at 20 K/min, and then maintained at 673 K for 15 min.

RESULTS AND DISCUSSION

Two types of spectra for hydrogen desorption were obtained. One following exposure of the catalysts to hydrogen during cooling of the reduced catalysts from 673 to 303 K is designated to TPD spectra (673-303); the other following exposure to hydrogen at 303 K is shown in TPD spectra (303). Fig. 1 shows various TPD spectra of hydrogen for Rh/SiO_2. Hydrogen desorbes from Rh/SiO_2 as a broad peak at 355 K followed by a wide shoulder ranging from 373 to 493 K. No distinct differences between TPD spectra (673-303) and (303) were observed except for a slightly smaller intensity for the spectra (303). All the repeated runs exhibited similar TPD spectra.

Figs. 2 and 3 show TPD spectra of H_2 for $Cu\text{-}Rh/SiO_2$ (Cu:Rh = 0.25:1) and $Cu\text{-}Rh/SiO_2$ (Cu:Rh = 1:1). TPD spectra (673-303) for the $Cu\text{-}Rh/SiO_2$ (0.25:1) consist of two low temperature peaks at 340 and 380 K and a high temperature peak at 668 while TPD spectra (303) show two low-temperature peaks with a slightly lower intensity relative to spectra (673-303).

TPD spectra (673-303) for $Cu\text{-}Rh/SiO_2$ (Cu:Rh=1:1) consist of a peak at 358 K with a higher temperature shoulder and a high-temperature peak at 653 K; the spectra (303) include two small bands at 343 and 417 K. The area under the TPD profile is equivalent to the total amount of hydrogen adsorbed before desorption. The area under the profile of spectra (673-303) is larger than that of spectra (303), indicating that the amount of hydrogen adsorbed in cooling from 673 K to 303 K is significantly greater than the quantity adsorbed at 303 K. The results suggest that hydrogen adsorption on $Cu\text{-}Rh/SiO_2$ (Cu:Rh=1:1) is highly activated.

Comparison of TPD spectra for Rh/SiO_2 and $Cu\text{-}Rh/SiO_2$ shows that the presence of Cu on the Rh/SiO_2 produced an additional peak in 653-668 K. This high temperature peak is probably due to hydrogen desorbed from spillover sites. Cu has been found to promote spillover of hydrogen from Ru to Cu

[3]. These spillover sites on Cu-Rh/SiO_2 (0.25:1) were eliminated by by repeating the TPD runs following by H_2 reduction at 676 K as indicated by the disappearance of the high temperature peak as shown in Fig. 2 and 3. The spectra of repeated runs appear to resemble to those of Rh/SiO_2.

Recent studies [10] have shown that the presence of Cu on Rh/SiO_2 resulted in a marked reduction in the CO hydrogenation activity of the catalysts and only slight difference in C_2 oxygenate selectivity. The decrease in CO hydrogenation activity brought about by Cu may relate to the activated chemisorption of H_2 on Cu-Rh/SiO_2.

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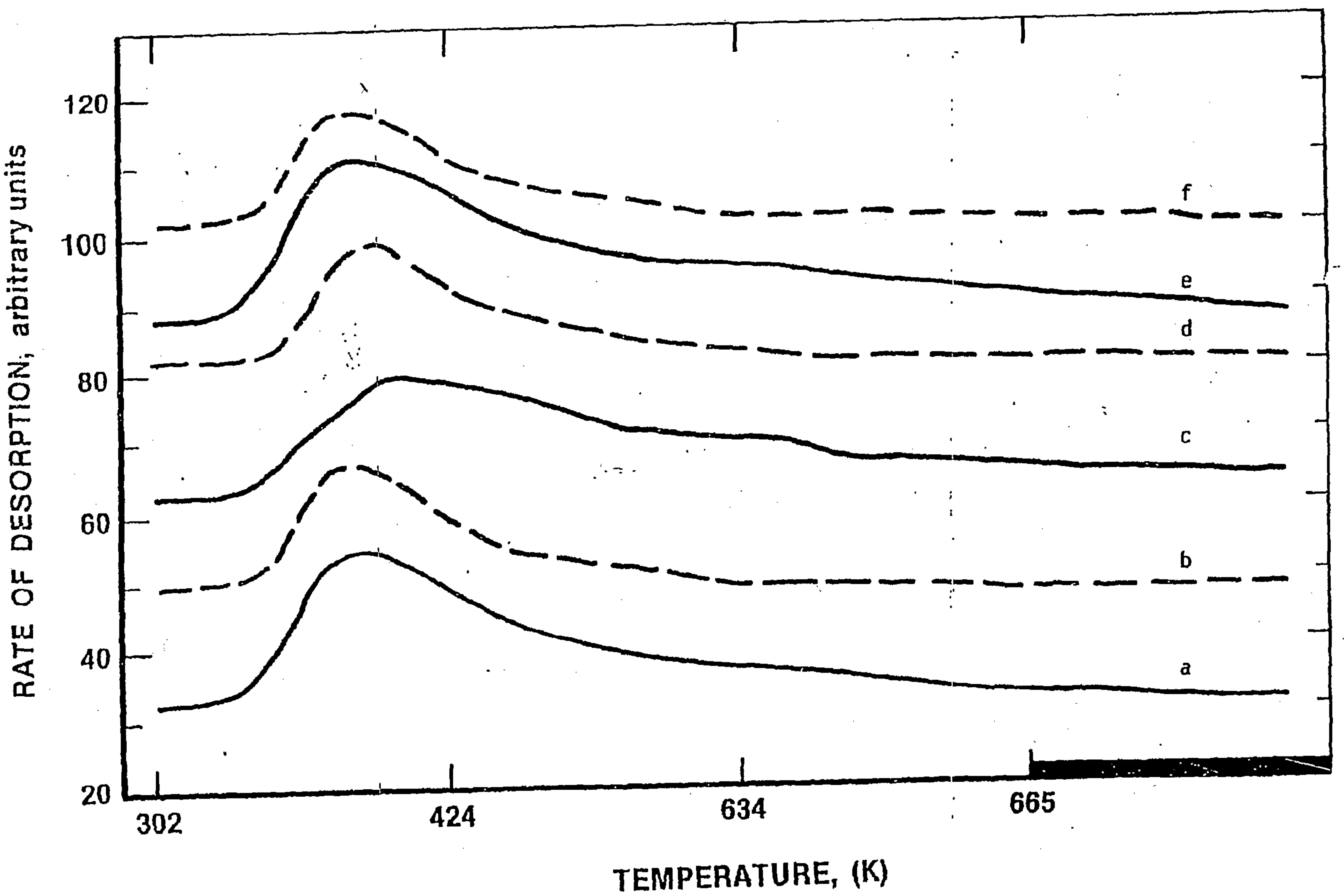
LIST OF FIGURES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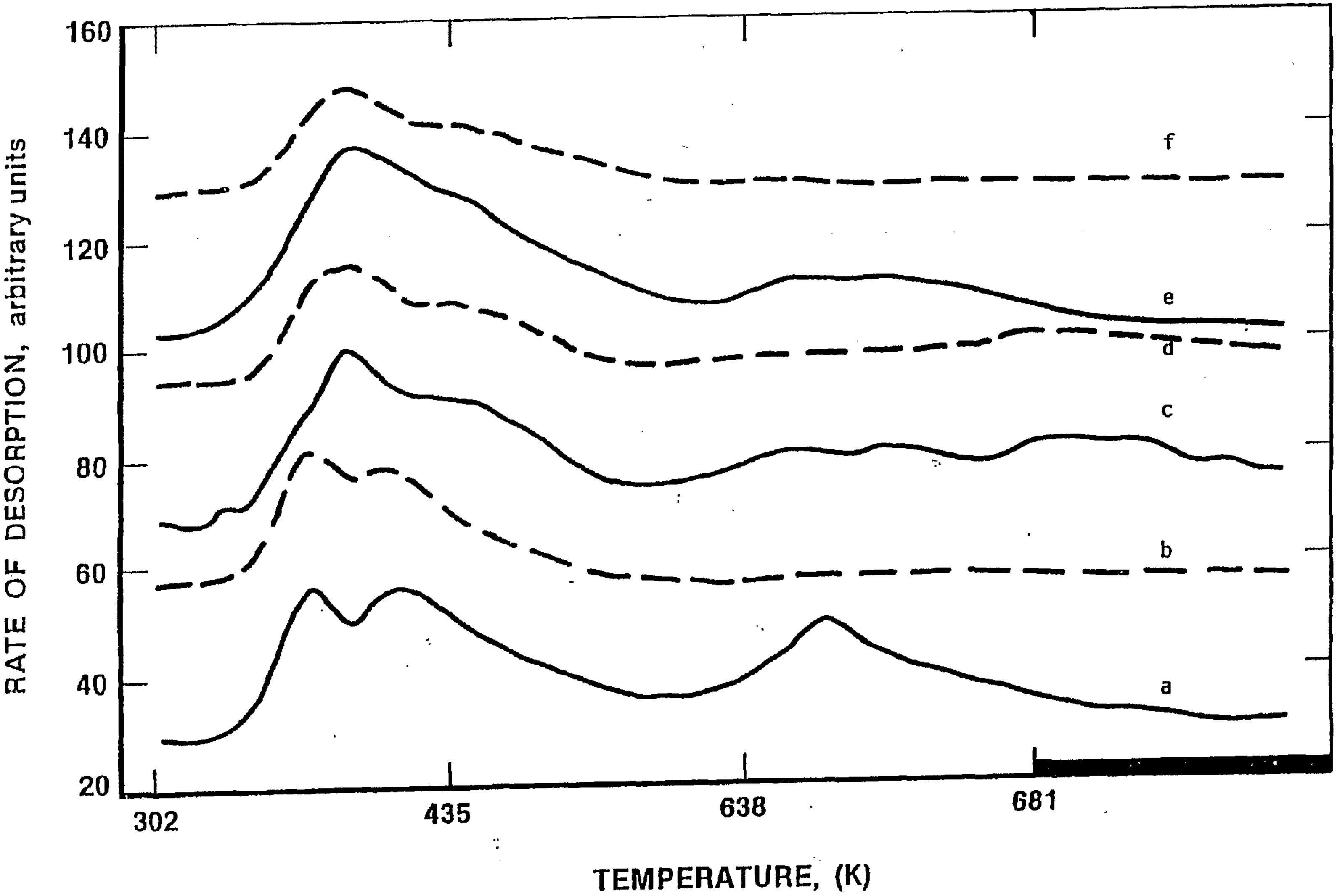
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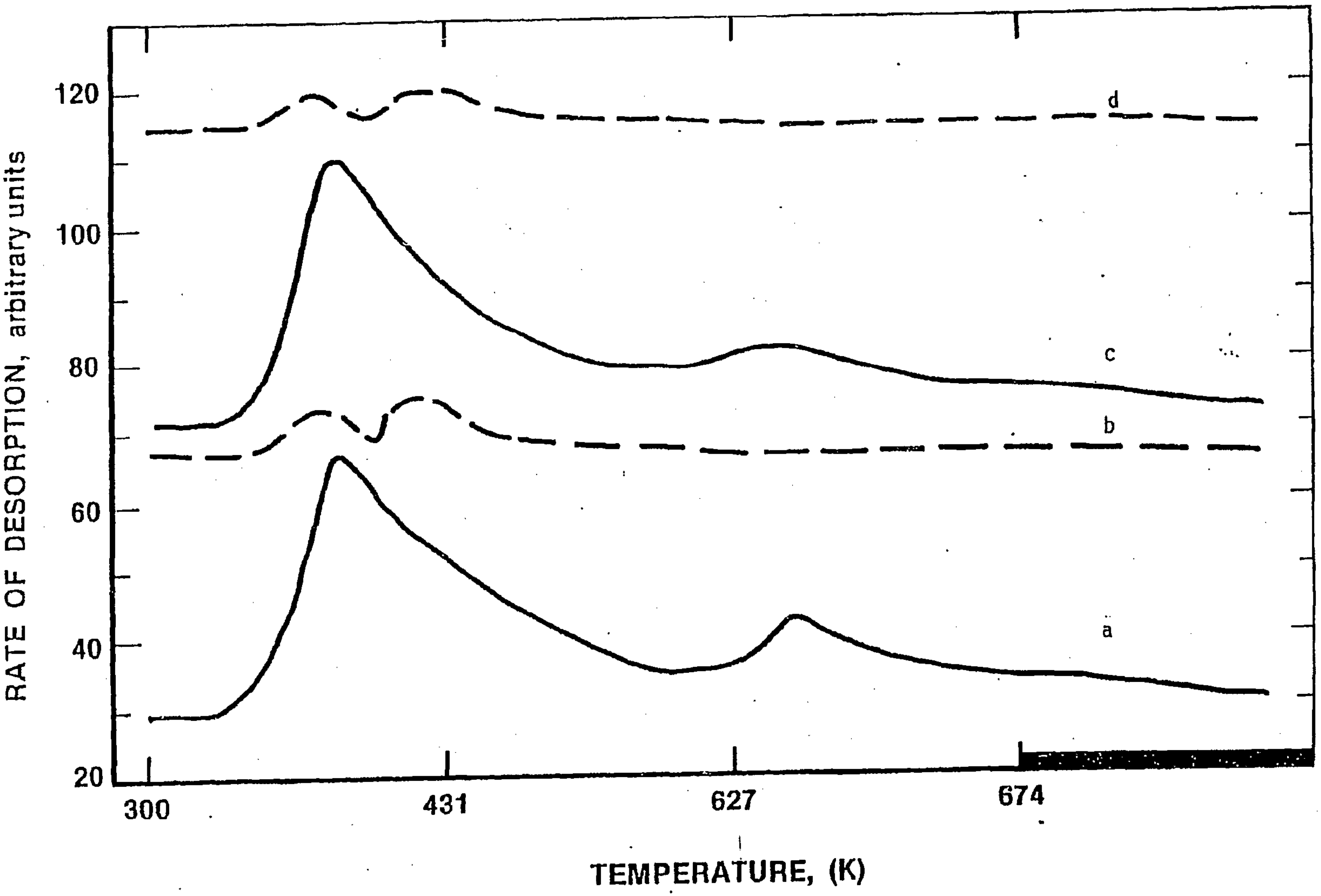
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