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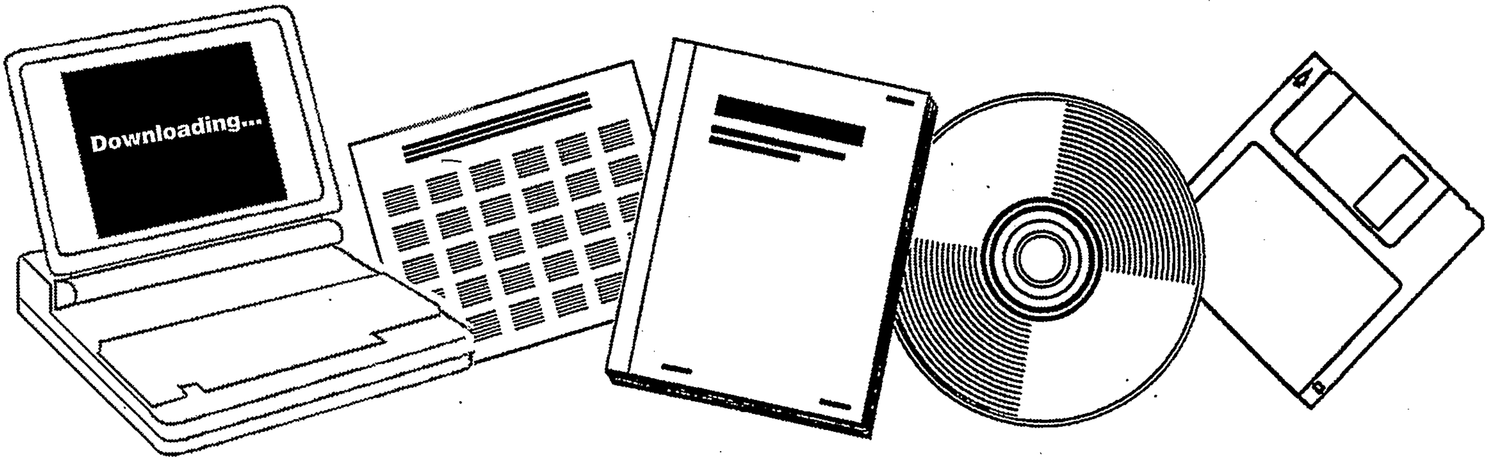

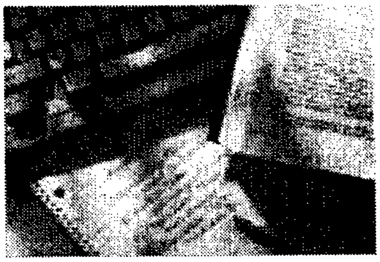

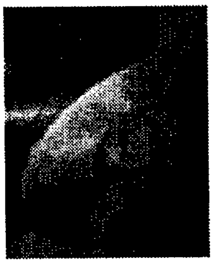

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THE EFFECT OF CHEMICAL ADDITIVES ON THE SYNTHESIS OF ETHANOL

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Technical Progress Report 10

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by

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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 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 1990, the CO insertion activity of sulfided Group VIII metals was studied by using ethylene hydroformylation as a probe reaction.

ABSTRACT

NiS and sulfided group VIII metals including Ni, Co, Fe, Ru, Ir, and Os have been found to exhibit hydroformylation activities in 150 - 300 °C and 10 atm.

Key word listing

Hydroformylation, Aldehyde, Synthesis Gas (CO/ H_2)
Ethylene, Propionaldehyde, Sulfided Group VIII Metals, NiS

INTRODUCTION

Hydroformylation, a reaction of olefin with carbon monoxide and hydrogen for the production of aldehydes and alcohols, is well known to be a homogeneously catalyzed reaction [1-5]. Metal carbonyls and their modified forms have long been employed for the commercial hydroformylation process. The major disadvantage of the homogeneous process is the expensive separation steps after hydroformylation stage for catalyst recovery and product purification [5-6]. To avoid the separation steps, various heterogeneous hydroformylation catalysts have been prepared by the use of polymer or oxides for anchoring metal complex catalyst as well as mixed metal oxides as catalysts. However, most of these catalysts exhibit poor thermal stability and activity [6-7].

Supported Rh has been found to be one of the most active catalyst for heterogeneous hydroformylation [8,9]. Recent studies have shown that H_2S fails to poison hydroformylation over Rh/SiO_2 [10,11] while H_2S enhances hydroformylation on Ni/SiO_2 [12]. These observations have led to investigation of hydroformylation on other sulfided Group VIII metals. We report here a new finding that NiS, sulfided Co, Fe, Ru, Ir, and Os exhibit a wide range of hydroformylation activities. Results of hydroformylation on the sulfided Rh and Ni are also included for comparison.

EXPERIMENTAL

Supported Ni, Co, Ru, Rh, Os, and Ir catalysts were prepared by impregnation of SiO_2 (large pore, Strem Chemicals) with $Ni(NO_3)_2$ $6H_2O$, $Co(NO_3)_2$ $6H_2O$, $RuCl_3$ $3H_2O$, $RhCl_3$ $3H_2O$, H_2OsCl_6 $6H_2O$, and $IrCl_3$ $3H_2O$, respectively. Fe/SiO_2 was prepared by precipitating $FeCl_3$ solution with Na_2CO_3. The precipitate was filtered and washed with water at room temperature. Following the impregnation or precipitation, the catalysts were dried at 30 °C and reduced in flowing hydrogen at 400 °C for 16 hrs. The metal crystallite size was determined by X ray diffraction-line broadening. The resulting catalysts were sulfided by 1000 ppm H_2S in H_2 at 400 °C. The bulk ratio of sulfur to metal was determined by energy-dispersive spectroscopy. It was found that sulfidation with either 240 or 400 °C resulted in the catalysts exhibiting the same activity and selectivity.

Ethylene hydroformylation ($CO:H_2:C_2H_4 = 1:1:1$) over sulfided metals was studied in a differential reactor at 10 atm and 150 - 300 °C. The reaction product was analyzed by a gas chromatograph using a 6 ft Porapak PS column in series with 6 ft Porapak QS column. The combination of these two columns permits a good on-line separation of all C_1-C_7 hydrocarbons, aldehyde, and alcohols. Due to the heterogeneity of the surface of sulfided metals and the lack of information on the site for the reaction, the rate will be reported on the basis of mol/kg hr. rather than turnover number.

RESULTS AND DISCUSSION

Table 1 shows the rate of ethylene conversion and product selectivity for ethylene hydroformylation over sulfided metals. Although all the sulfided metals were sulfided under the same condition, the ratio of sulfur to metal for the sulfided metals appears to depend on the type of metals and their thermodynamic properties [13,14]. It would be very difficulty to maintain the same ratio of sulfur to metal for all the catalysts in this study. The sulfur content of the catalyst remains about the same during the entire course of reaction studies.

Ethane and propionaldehyde are major products while CH_4, C_{3+} hydrocarbons, and C_3H_7OH are minor products. Variation of the H_2S concentration in the reactant stream from 0 - 1000 ppm did not affect the catalyst activity and selectivity. The rates of formation of CH_4 and C_{3+} hydrocarbons in ethylene hydroformylation are comparable to those from CO hydrogenation on the sulfided metals indicating that the formation of theses minor products from CO hydrogenation were inhibited by sulfur [15,16]. The inability of sulfur to completely poison ethylene hydrogenation is not surprising since most transition metal sulfides are active for olefin hydrogenation in 120 - 400 °C [17].

Variation of reaction temperature and pressure showed that decreasing reaction temperature shifted the product selectivity toward propionaldehyde for all the sulfided catalysts; while decreasing the reaction pressure enhanced the ethane selectivity. Infrared studies of CO adsorption on the sulfided Ni, Rh, and Ru showed that sulfidation led the disruption of bridge-CO site resulting in the formation isolated atom site for linearly adsorbed CO [15]. It is likely that the isolated atom site is responsible for the hydroformylation reaction.

Comparison of the product selectivity in Table 1 shows that the sulfided Ni is the most selective catalyst for ethylene hydroformylation. Thus, we further investigated hydroformylation activity of NiS (Johnson Matthey). The results are presented in Table 2. Propionaldehyde slectivity on NiS is significantly higher than those on the sulfided metals. In contrast to sulfided Ni, methane is the major product at temperature below 210 °C; increasing reaction temperature from 210 to 288 °C shifts the selectivity toward propionaldehyde.

MoS_2 modified with Li, K, and Mg has been reported to exhibit hydroformylation activity [18]. However, pure MoS_2 showed only hydrogenation activity at 10 atm and 210 - 300 °C. Studies on other metal sulfides such as MnS and CrS also revealed that these sulfides are inactive for hydroformylation but active for hydrogenation at 10 atm and 210 - 300 °C [19].

In conclusion, sulfided Group VIII metals exhibit hydroformylation activities. Sulfided Ni appears to be the most active sulfide catalyst for the reaction.

ACKNOWLEDGEMENT

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Table 1 Ethylene Hydroformylation on Sulfided Metals

Catalyst (the ratio of Sulfur to Metal)	Metal Loading (wt%)	Rate of C_2H_4 Convsersion (mol/kg hr)	Product Selectivity (mol %)				
			CH_4	C_{3+}	C_2H_4	C_2H_5CHO	C_3H_7OH
S-Fe 0.21	10	0.31	0.9	1	80.1	18	0
S-Co 0.3	5	9.2	0.2	0.3	83	16.5	0
S-Ni 0.46	15	4.5	0.4	0.01	59	37.1	1.5
S-Ru 0.12	3	0.65	3	1.3	84	11	0.7
S-Rh 0.14	3	52.4	1	0	68	29.3	1.7
S-Os 0.11	3	1.1	0	0	94	6	0
S-Ir 0.12	3	10.1	2	0	88	10	0

Reaction Condition: 10 atm, 270 °C

$$\text{Product Selectivity} = \frac{\text{Rate of Formation of a Specific Product}}{\text{Rate of Formation of all Products}}$$

Table 2 Ethylene Hydroformylation on NiS

Reaction Temperature (°C)	Product Distribution CH_4	C_2H_4	C_2H_5CHO
	(mol %)		
210	47.1	12.3 (0.02)[a]	40.5 (0.066)
230	12.2	3.7 (0.025)[a]	82.9 (0.53)
275	8.9	4.8 (0.06)[a]	87.6 (1.07)
288	9.4	5.6 (0.054)[a]	84.6 (0.82)

Reaction Pressure: 10 atm
a: rate of product formation in mol./kg hr.

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