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GAS PHASE HYDROFORMYLATION OF PROPYLENE OVER
SUPPORTED Ru-Fe BIMETALLIC CATALYSTS

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Bimetallic catalysts consisting of Ru-Fe prepared on SiO_2 and carbon (sibunit) supports were found to be catalytically active and selective in the formation of C_4 -aldehydes and alcohols in hydroformylation of propylene at 433 K and 2 atm. of $\text{CO} + \text{H}_2 + \text{C}_3\text{H}_6$ (1:1:1). The addition of Fe to Ru altered the activity of monometallic Ru catalyst and favored the hydrogenation of CO to methanol.

INTRODUCTION

Transition metals in the form of heterogeneous and homogeneous metal complexes have been shown to exhibit hydroformylation activities to give oxygenates [1-3]. Supported metal catalysts are of interest because these can be prepared in a highly dispersed form and are less costly for use in industrial applications. In such catalyst systems, the metal exists as well as very small crystallites dispersed on the surface of a carrier, which is commonly a porous material. Development of cost effective and economically viable catalyst systems for industrial applications needs a study of parameters which are responsible for the catalytic activity under laboratory conditions. Though

work has been done extensively using transition metal based catalyst systems [4-9], we are now trying to insert Fe into the Ru system so that the system becomes cost effective. Our study on the activity and selectivity parameters of these Ru-Fe bimetallic catalyst systems prepared using SiO_2 and carbon (sibunit) supports in the gas phase hydroformylation of propylene are reported in this paper.

EXPERIMENTAL

1. Catalyst preparation

Bimetallic catalysts consisting of Ru along with Fe having a total metal content of 5 wt.% were prepared by coimpregnation method using SiO_2 and carbon (sibunit) supports (supplied by the Institute of Catalysis, Novosibirsk). $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and FeCl_3 (anhydrous) dissolved in 38% HCl solution were interacted with known amounts of supports. The excess solvent was removed by heating on a water bath. The solid mass thus obtained was dried under vacuum at 378 K for 2 h. The samples were charged into a stainless steel tubular reactor preheated to reduction temperature of 723 K and reduced with purified H_2 at a flow rate of 100 mL/min at atmospheric pressure for 3 h just before contact with the hydroformylation gaseous reaction mixture.

2. Catalytic activity measurements

The premixed hydroformylation gaseous reaction mixture $\text{CO} + \text{H}_2 + \text{C}_3\text{H}_6$ (1:1:1) was purified by passing through a purification unit consisting of reduced $\text{MnO}_2/\text{SiO}_2$ (to remove O_2 impurity) and activated molecular sieve (to remove moisture content) before it is allowed to interact with the previously reduced (stored in the reactor itself) catalyst system in a preheated stainless steel tubular reactor. The reaction was carried out at 2 atm of hydroformylation gaseous reaction mixture with the flow rate of 30 mL/min at 433 K. The products of hydroformylation of propylene such as methanol, butyraldehydes and butanols were collected by bubbling the effluent gas through ice cold

water. The activities (mmol of products per mol of metal per min) of the catalysts were calculated from the yields of the hydroformylation products determined by gas chromatography. The gaseous products of propylene hydroformylation experiments were not estimated in our studies but confirmed as propane and methane by comparing with standards.

RESULTS AND DISCUSSION

Gas phase hydroformylation of propylene at 433 K and 2 atm $\text{CO} + \text{H}_2 + \text{C}_3\text{H}_6$ (1:1:1) gave liquid products such as methanol, n-butyraldehyde, iso-butyraldehyde, n-butanol and iso-butanol. The amount of products and selectivities for n-isomers estimated with different catalyst systems are presented in Table 1.

It is seen from the data in Table 1 that the activities of carbon supported Ru and Ru-Fe catalyst systems show higher activities than the corresponding SiO_2 systems. The activities of Ru/carbon or Fe/carbon are nearly two times higher than the corresponding SiO_2 supported systems. The selectivities for n-isomers decreased with increasing Fe content in both SiO_2 and carbon supported systems. It is interesting to observe that methanol is formed in all the other systems studied except for the Ru/ SiO_2 catalyst, which is mainly due to the Fe content and partially due to the carbon support of the different catalyst systems. In general it is found that irrespective of the supports the activities of the corresponding bimetallic systems are intermediate between those obtained with the monometallic systems. As n- and iso-butanol are formed by the hydrogenation of initially formed aldehydes, their yields depend on the corresponding aldehydes formed at any time of the reaction. Based on the yields of alcohols presented in Table 1 it is found that the rates of formation of alcohols via hydrogenation of the corresponding aldehydes are much slower than the hydroformylation rates in the hydroformylation of propylene.

Table 1

Activities of Ru-Fe bimetallic catalysts supported on SiO₂ and carbon (sibunit) in gas phase hydroformylation of propylene at 433 K and 2 atm CO+H₂+C₃H₆ (1:1:1) after 3 h contact time

1. SiO₂, surface area= 110 m²/g, density=0.3 g/cm³ particle size=150-500 nm, and porosity=1.7 cm²
2. Carbon (sibunit), surface area=500 m²/g, density=0.6 g/cm³ particle size=200-250 nm, porosity=0.6 cm² (metal loading total in all the cases=5 wt.%)

Catalyst	Activity*	Products (mmol)					Selectivity n-
		Meth.	n-ald.	n-alc.	iso-ald.	iso-alc.	
Ru/SiO ₂	1.2	-	0.092	0.030	0.0150	0.002	88
Fe/SiO ₂	0.47	0.046	0.030	0.011	0.005	0.0007	45
		(50)					
Ru-Fe/SiO ₂ (2.5%+2.5%)	0.99	0.034	0.067	0.023	0.021	0.003	62
		(24)					
Ru/carbon	2.04	0.033	0.115	0.038	0.0097	0.0013	77
		(15)					
Fe/carbon	0.67	0.078	0.031	0.011	0.0088	0.0012	32
		(60)					
Ru-Fe/carbon (2.5%+2.5%)	1.16	0.069	0.065	0.021	0.0150	0.0020	50
		(40)					

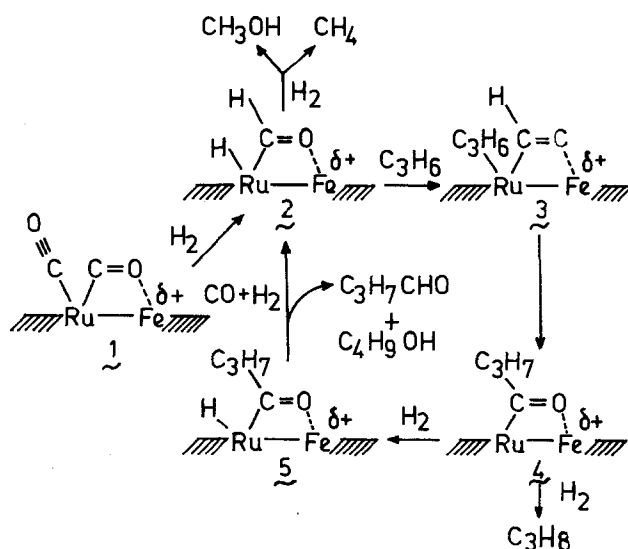
$$\text{Activity}^* = \frac{\text{mol of (n- and iso-(aldehydes+alcohols)+methanol)}}{\text{mol of metal min}}$$

Activity unit = mmol of products per mol of metal per min

$$\text{Selectivity} = \frac{\text{mol of (n-ald. + n-alc.)}}{\text{total mol of products}} \times 100$$

Mechanism

The possible mechanism proposed for the Ru-Fe bimetallic (supported on SiO_2 and carbon) catalyst systems in hydroformylation of propylene under gas phase conditions is shown in Scheme I.



It is reported in the literature that in gas phase hydroformylation catalyzed by supported metal catalysts CO is adsorbed in two modes such as linear and bridged, as shown in Scheme I [10]. In bimetallic catalysts it is believed that Ru-Fe would have two sites for CO activation to give intermediate species 1 Ru-C=O-Fe. Species 1 on hydrogenation would give formyl HC(=O) species 2 which undergoes hydrogenation to give methanol and methane. Simultaneously, the formyl species 2 interacts with propylene and undergoes hydride transfer to the olefinic bond of propylene to form acyl intermediate 4. The acyl species 4 gets reduced to aldehyde intermediate 5 and pro-

pane. Species 5 in the presence of CO + H₂ forms aldehydes and alcohols while regenerating the active intermediate species 2 in the catalytic cycle. This mechanism is similar to the one proposed by Ichikawa et al. [7].

In the proposed mechanism shown in Scheme I, the carbon of chemisorbed CO is bonded to two or more Ru atoms and its oxygen to Fe ions. Thus when carbon and oxygen ends of CO are bonded to two different metals, the $M_{Ru}-C=O-M_{Fe}$ species formed could be treated as a precursor state for the dissociation of CO [11]. As a result of this, the activity of the adsorbed CO species is dramatically enhanced because of lowering of the activation energy for CO dissociation, which is reflected by a large enhancement of CO dissociation. Hence, the effect of addition of Fe to Ru would decrease in the bridging carbonyl chemisorption on Ru. Such a surface promotes CO dissociation giving methane and the hydrogenation of nondissociating chemisorbed CO into methanol. From our results presented in Table 1, it is concluded that Fe catalyst systems are more active for CO dissociation while Ru systems are more selective for CO insertion to give C₄ products in gas phase hydroformylation of propylene under the reaction conditions studied.

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