Low Pressure Hydroformylation in the Presence of Alcohol Promoters

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Active carbon supported cobalt catalyst was studied for the hydroformylation of 1-hexene in the presence of alcohol solvents at low pressure. The influence of various solvents on the hydroformylation and the CO conversion vs time on stream were investigated in detail. It was found that the heterogeneous catalyst shows excellent activity only in the alcohol solvents.

The emissions (smoke, particulate matter, CO, etc.) from diesel engine can be diminished by the addition of oxygen-containing compounds into hydrocarbon fuel. Our research group is aiming at the production of clean fuel from synthesis gas ($CO + H_2$) and olefins, which is the further utilization of products in the Fischer-Tropsch synthesis.[1,2] Olefin hydroformylation process is an old and fundamental route of the synthesis of aldehydes. The cobalt or rhodium carbonyls have been used as traditionally representative homogeneous catalyst in the hydroformylation industrial process.[3–5] The drawbacks of homogenous catalysis, such as the high pressure, the recovery of metal and the separation problem, inhibit their practical application in the wide fields. Therefore, most of the researches under low pressure conditions have been concerned with supported rhodium and cobalt catalyst.[6–11]

Our works focus on the exploration of low pressure process of hydroformylation. It is quite desirable that synthesis gas and lower olefins from F-T process can be utilized without any compression. In this work, hydroformylation was operated in alcohol solvent at lower pressure (3.0 MPa) over Co/active carbon using 1-hexene as model material.

The supported active carbon (20–40 mesh) was obtained from Kanto Chemical Co. with surface area of 1071.7 m^2/g and average pore volume of 0.43 cm^3/g. The support was impregnated with aqueous solution of cobalt nitrate. The weight percent of cobalt metal in catalyst was 10 wt%. The catalyst precursor was heated in nitrogen flow at 673 K for 4 h and reduced under hydrogen flow at 673 K for 6 h. The reduced catalyst was passivated by 1% O_2 diluted in N_2 flow before use.

Catalytic reactions were carried out in a semi–batch slurry–phase reactor with inner volume of 85 ml. The amount of catalyst was 0.2 g. 120 mmol of 1-hexene was used as a model olefin. Solvent/1-hexene = 2/1 (molar ratio). The flow rate of syngas ($CO/H_2/Ar = 47.8/48.2/4.0$) in the reaction was set to 80 ml/min.

The gaseous products were analyzed by an on-line GC equipped with an active charcoal column. The liquid products were analyzed by gas chromatography equipped with a DB-1 column of the J&W Scientific Co.

In the blank test without any solvents or catalyst, no 1-hexene conversion was observed at 3.0 MPa and 403 K over 10 wt% Co/A.C. The comparative effects of solvents on the hydroformylation of 1-hexene are compared in Table 1. In the solvents of benzene, hydrocarbon, toluene and THF over Co/A.C., only a small amount of 1-hexene was converted to 2-hexene, even when the catalyst was not passivated. The enhanced 1-hexene conversion was observed over Co/A.C. in alcohol solvents, suggesting that alcohol solvents dramatically promote the hydroformalytion reaction under the conditions of 3.0 MPa and 403 K. It is worthy to note that over the homogeneous catalyst, $Co_2(CO)_8$ exhibits high activity in both methanol and octane, while over the heterogeneous catalyst, high activities were observed only in alcohol.

Table 1. Hydroformylation of 1-hexene in various solvents[a]

Solvent	1-hexene	Yield/%					n/i[b]
	Conv./%	C_7-al	C_7-ol	acetal	ester	isomer	
Benzene	0.3	0.1	0.1	0	0	0.1	—
n-Heptane	0.1	0	0	0	0	0.1	—
n-Octane	0.2	0	0	0	0	0.2	—
n-Octane[c]	0.2	0	0	0	0	0.2	—
THF	0.1	0	0	0	0	0.1	—
Toluene	0.2	0.1	0	0	0	0.1	—
Methanol	49.2	8.8	0.4	24.8	0.3	14.9	0.3
Ethanol	72.9	28.9	3.8	31.8	0.8	7.6	0.4
1-Propanol	74.1	26.8	3.7	36.6	1.1	5.9	0.4
n-Octane[d]	84.4	67.8	0	0	0	16.6	1.0
Methanol[d]	80.6	27.4	1.6	38.5	1.3	11.8	0.4

[a]3.0 MPa; 403 K. [b]Ratio of normal C_7-aldehyde to i-C_7-aldehyde. [c]10 wt% Co/active carbon without passivation. [d]$Co_2(CO)_8$ (0.06 g) was used as catalyst.

For heterogeneous catalyst, the conversion of olefin and yield of oxygenates are largely related to the formation of active metal carbonyl species[6] and the formation of $Co_2(CO)_8$ requires a higher CO pressure,[5] usually above 7.0 MPa if without any solvent. Lower pressure such as 2.0 MPa was not suitable as the activity was very low under that condition. In case of $Co_2(CO)_8$, the catalyst reaction rate was high but the life was short. After reaction, the precipitate of Co metal was detected.

When methanol was used as solvent, aldehydes and acetal (1,1-dimethoxy heptane) were main products. Trace amount of ester (heptanoic acid methyl ester) were also formed. The formations of acetal and ester are shown as follows:

$$RCHO + 2CH_3OH \rightarrow RCH(OCH_3)_2 + H_2O \qquad (1)$$

$$R\text{-}CO\text{-}Co + CH_3OH \rightarrow R\text{-}CO\text{-}OCH_3 + CoH \qquad (2)$$

The CO conversion as a function of reaction time is presented in Figure 1. For the passivated 10 wt% Co/A.C, an induction period exists at the beginning of the reaction, while no such period was showed over 10 wt% Co/A.C. without passivation under the same reaction condition. We can assume that the induction period partly involves a reduction process in the presence of methanol solvent and synthesis gas, which provides more active metallic

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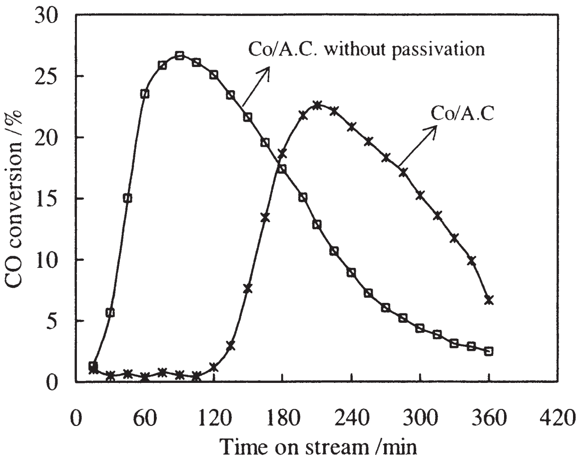

Figure 1. CO conversion vs time on stream in methanol over 10 wt% Co/active carbon. Reaction conditions are the same as in Table 1.

sites available for the hydroformylation.

Figure 2 compares the yield of products over Co/A.C. with and without passivation. The yields of desired C7-al and acetal over 10 wt% Co/A.C. without passivation are 20.6% and 35.9%, respectively, which are both higher than the yields of products over passivated catalyst, 8.8% and 24.8%, respectively.

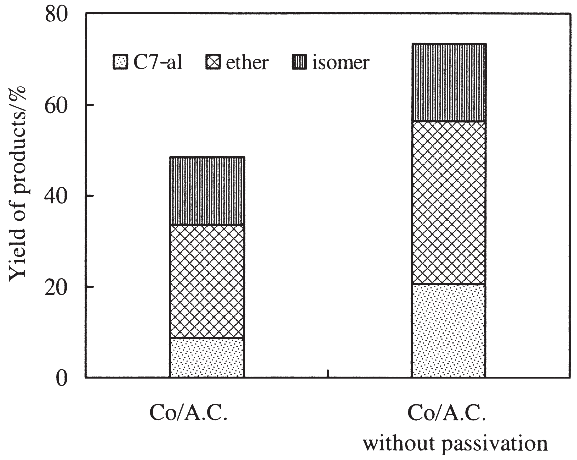

Figure 2. Comparison of yield of products over 10 wt% cobalt supported on active carbon with and without passivation. 3.0 MPa, 403 K.

In Figure 1, over 10 wt% Co/A.C, CO conversion gradually decreases from the peak value of 22.6% to 6.9%. This decrease in CO conversion is thought due to the decrease of the 1-hexene and methanol. After 6 hour-reaction, about 60 mmol of 1-hexene is converted to products (49.2% conversion). It may cause the decrease in the rate of hydroformylation. In order to verify this assumption, about 3 g (36 mmol) of 1-hexene through micro liquid pump was added to the solution at the point of CO conversion of 6.9%. The effect of 1-hexene addition is displayed in Figure 3, which showed drastic increase in CO conversion from 6.9% to 28.9%. This is a good indication that the decrease in CO conversion is not because of the deactivation of the catalyst, but of the decrease in reactant.

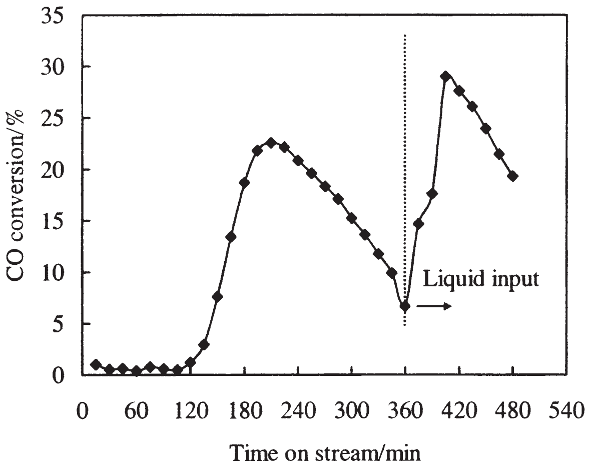

Figure 3. Hydroformylation of 1-hexene in methanol with 10 wt% Co/active carbon after liquid input. 403 K, 3.0 MPa.

In conclusion, we developed a novel solid catalyzed low pressure process of hydroformylation of 1-hexene. At 3.0 MPa and 403 K, carbon-supported cobalt significantly promoted the hydroformylation reaction, giving acetal and aldehydes only in the presence of alcohols, while inert solvents such as paraffin gave no reaction. In the CO conversion vs time on stream, the induction period was observed for the passivated catalyst while the non-passsivated catalyst showed no induction period. Although the reason is not clear yet, lower alcohols promoted not only the reduction of cobalt, but also hydroformylation on the solid catalyst itself. However, the activity level is still lower than that of $Co_2(CO)_8$, especially without alcohols. It suggests that Co/A.C. make some special active species.

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