# Hydroformylation of 1-Hexene over Rhodium Supported on Active Carbon Catalyst

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Hydroformylation of 1-hexene on rhodium catalyst was studied under mild reaction conditions ($P = 3.0$ MPa, $CO/H_2 = 1/1$, $T = 403$ K). Its hydroformylation performances were investigated in a variety of solvent. It was found that the excellent activity for the heterogeneous catalyst was showed in the *n*-octane solvent, while poor activity in the alcoholic and $H_2O$ solvent.

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Because of their high efficiency and low emission, oxygenates has potentiality to be excellent transportation fuels. Our research group is devoted to the conversion of oxygenates from syngas (CO and $H_2$) and light olefin, where the latter is the main products in Fischer–Tropsch reaction.[1–3] Hydroformylation, a necessary tool in industry to produce aldehyde from syngas (CO and $H_2$) and olefins,[4] is basically operated in the homogeneous phase.[4,5] However, because of the separation problem in the reaction system, the conversion of homogeneous catalyst to heterogeneous system is favorable from the stand point of the industrial application. Thus the development of a practical heterogeneous catalyst would be desirable.[6–10] Among the research of heterogeneous catalyst, most of which has been concerned with supported rhodium catalyst due to its high activity and regioselectivities.[11–14] Particularly, the systems of Rh/C and $Rh/SiO_2$ have been extensively studied, but little systematic studies on the effects of solvents have been carried out yet.

Our interest in the hydroformylation of middle olefins under low pressure has guided us to investigate the effects of several solvents on the heterogeneous system.[15] It is of great importance when $\alpha$-olefin can be directly used as raw material at the completion stage of the Fischer-Tropsch reaction (2.0–3.0 MPa). This paper reports the results of a study on hydroformylation which was operated in several solvents over Rh supported on active carbon catalyst using 1-hexene as model material.

The Rh/active carbon (Rh/A.C.) catalysts were prepared by a conventional impregnation method.[15] 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 evacuated at 413 K for 2 h and then impregnated with aqueous solution of $Rh(NH_3)_2(NO_2)_2$ (Tanaka Noble Metal). The catalyst was dried in a rotary evaporator at 333 K and then calcined in nitrogen at 673 K for 4 h. The catalysts were reduced under $H_2$ at the same temperature for 6 h and passivated by 1% $O_2$ diluted by $N_2$ flow at room temperature before use.

Catalytic reactions were carried out in a flow–type semibatch autoclave slurry-phase reactor with an inner volume of 85 ml, where only synthesis gas flowed through while the catalyst and solvent were kept inside. The reaction conditions were $P$ (total) $= 3.0$ MPa, $T = 403$ K. The passivated catalyst of 0.2 g was used in the reaction without further pretreatment. 120 mmol (10.10 g) of 1-hexene was used as 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 80 ml/min.

The gaseous products were analyzed by an on-line equipped with an active charcoal column. Argon was employed as an internal standard with a concentration of 4.0% in the feed gas. The liquid products were analyzed by gas chromatography equipped with a DB-1 column of the J&W Scientific Co.

Table 1 gives the catalytic performance of 1-hexene hydroformylation over 1 wt% Rh/A.C. in various solvents, including the reaction result without any solvent for reference. At 3.0 MPa and 403 K the hydrogenation of 1-hexene is almost suppressed. The main products were C7-aldehyde and isomers of 1-hexene. Acetal was also detected as product when methanol was used as solvent.[15] Without any solvent, 1 wt% Rh/A.C. showed catalytic activity with 1-hexene conversion of about 95% and C7-aldehyde yield of about 40%. The yields of oxygenates were about 20% in $H_2O$ and about 25% (including C7-aldehyde and acetal) in methanol, respectively. The results indicate that the existences of $H_2O$ and methanol in the reaction system suppress the 1-hexene hydroformylation reaction. The higher catalytic activity was observed in the nonpolar solvent, such as *n*-octane and benzene solvents. The above results show that nonpolar and non protonic solvents are favorable for the reaction, contrary to the fact that alcohol is the best solvent for the Co/A.C. catalyst.[15]

**Table 1.** Effects of solvents on the 1-hexene hydroformylation

| Solvents | 1-hexene conv./% | Yield/% | | | |
|---|---|---|---|---|---|
| | | Oxygenates | C7-al | acetal | isomer |
| None | 93.6 | 38.5 | 38.5 | 0 | 52.8 |
| Methanol | 88.2 | 24.8 | 9.3 | 15.2 | 61.9 |
| $H_2O$ | 91.4 | 19.4 | 19.4 | 0 | 70.7 |
| Benzene | 94.2 | 46.7 | 46.7 | 0 | 45.3 |
| n-Octane | 93.7 | 56.8 | 56.8 | 0 | 34.1 |
| n-Octane[b] | 91.7 | 48.0 | 48.0 | 0 | 43.7 |

Reaction conditions: [a]1 wt% Rh/A.C.; 3.0 MPa; 403 K; 6 h; [b]1 wt% Rh/Q-6 as catalyst.

The reverse effect of alcohol solvent on cobalt catalyst (promotive) and rhodium catalyst (suppressive) should be explained as follows. The cobalt catalyst is easy to be oxidized compared to noble metals. The reduction of $Co^{n+}$ species by $H_2$ under the reaction conditions is hard to occur but is promoted by alcohol. For example, the promotive effect of alcohol is in the order: $i\text{-}C_3H_7OH > n\text{-}C_3H_7OH > C_2H_5OH > CH_3OH$, which is the order of the generation of reactive hydrogen. On the Rh-catalyst, however, since Rh can be reduced by $H_2$ under reaction conditions, alcohol promoter is not necessary. The protonic solvent (alcohol or water) will be dissociatively adsorbed (oxidative addition). This effect will reduce the electron density of Rh and then retard the CO adsorption because of the insufficient contribution of back donation of electron from Rh to CO.

In the similar solvent, Rh supported on silica support (Rh/Q-6) also showed good catalytic activity for hydroformylation of 1-hexene, whose level was not as high as that of the Rh/A.C. catalyst.

Results of 1-hexene hydroformylation over Rh/A.C. as a function of temperatures are shown in Figure 1. The yield of target product (C7-aldehyde) was very low at 343 K and 423 K. High temperature accelerated the isomerization. The high yields of oxygenate were obtained between 363 K–403 K. Compared with

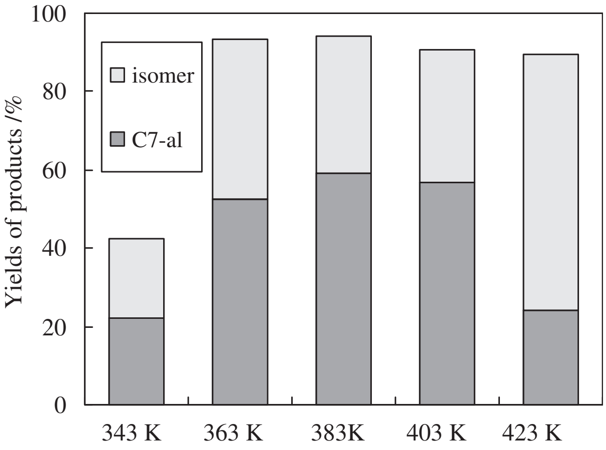

**Figure 1.** Effect of reaction temperature on 1-hexene hydroformylation (1 wt% Rh/A.C.; *n*-octane as solvent; 3.0 MPa; 6 h.)

cobalt catalyst, on which we reported previously,[15] rhodium catalyst shows a rather high aldehyde yield over a wide temperature range in spite of the lower metal content.

The effect of CO/$H_2$ (1:1) pressure on the hydroformylation was also investigated at 403 K over 1 wt% Rh/A.C catalyst (Table 2). When the pressure varied from 2.0 MPa to 4.0 MPa, the yield of C7-al increased from 13% to 65%, while that of isomer decreased from 74% to 29%. The results show that high pressure is very favorable for hydroformylation reaction, probably because of the high CO concentration on the active site. The ratio of $n/i$ is also increased from 0.54 to 0.66.

**Table 2.** Effects of pressure on the hydroformylation of 1-hexene

| Pressure /MPa | 1-hexene Conv./% | Yield/% |  | *n/iso*[a] |
|---|---|---|---|---|
|  |  | C7-al | isomer |  |
| 2.0 | 87.9 | 13.4 | 74.5 | 0.54 |
| 3.0 | 90.9 | 56.8 | 34.1 | 0.57 |
| 4.0 | 93.5 | 64.8 | 28.7 | 0.66 |

Reaction conditions: 1 wt% Rh/A.C.; *n*-octane solvent; 403 K; 6 h; [a]Ratio of normal $C_7$-aldehyde to *iso*-$C_7$-aldehyde.

The increase in the $n/i$ ratio with increased reaction pressure should be attributed to the ligand effect of adsorbed CO (steric effect). As the case of homogeneous catalyst, the added ligands, such as phosphine, strongly promote the $n/i$ ratio. The high density of CO on the metal under high pressure should promote the primary co-ordination (*n*-type) of olefin rather than the secondary co-ordination (*i*-type).

Figure 2 summarizes the effects of Rh loading on 1-hexene hydroformylation over Rh/A.C. catalysts. The CO conversion describing the CO insertion activity greatly increased with the increase in the Rh loading up to 1 wt%. It is noteworthy that with the decreasing Rh content, the induction period increased. Since the interaction between the Rh and active carbon should be stronger for the lower loading Rh catalyst, which may cause the slow activation.

It is also shown in Figure 2 that over Rh/A.C. catalysts, CO conversion rate sharply decreased from the peak value with the reaction time. This decrease in CO conversion rate is thought not due to the deactivation of the catalyst, but due to the decrease in 1-hexene concentration (with over 90% 1-hexene conversion after 6 h reaction),[15] the same case for cobalt catalyst.

The liquid compositions of supported rhodium catalysts with different loading are displayed in Table 3. Increased Rh loading did not remarkably change the conversion of 1-hexene, but significantly promoted the oxygenate formation. With increasing rhodium loading from 0.1 wt% to 1.0 wt%, the yield of C7-aldehyde increased from 25% to 58%, while the yield of isomer decreased from 61% to 34%.

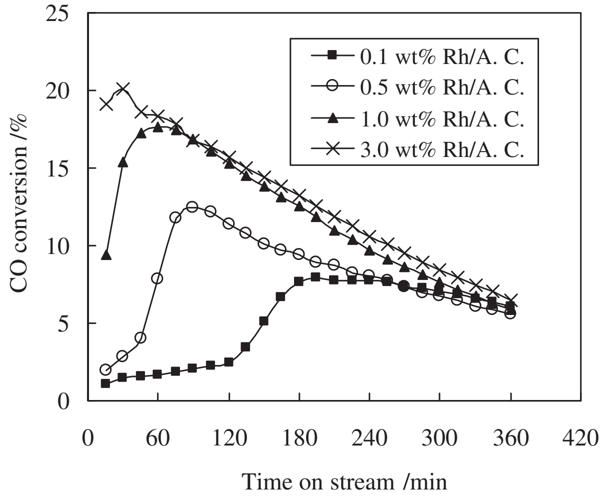

**Figure 2.** Effect of Rh loading on the 1-hexene hydroformylation (*n*-octane as solvent; 403 K; 3.0 MPa.)

**Table 3.** Effects of Rh loading on 1-hexene hydroformylation

| Rh /wt% | 1-hexene Conv./% | Yield/% |  | *n/iso*[a] |
|---|---|---|---|---|
|  |  | C7-al | isomer |  |
| 0.1 | 86.2 | 25.4 | 60.8 | 0.61 |
| 0.5 | 92.1 | 41.2 | 50.9 | 0.57 |
| 1.0 | 90.9 | 56.8 | 34.1 | 0.56 |
| 3.0 | 88.9 | 58.6 | 30.3 | 0.56 |

Reaction conditions: *n*-octane; 3.0 MPa; 403 K. [a]Ratio of normal $C_7$-aldehyde to *iso*-$C_7$-aldehyde.

The high catalytic activity of the high Rh-loading catalyst should be attributed to the larger number of metal site, which is demonstrated by $H_2$ adsorption. (2.37 μmol/g for 1 wt% Rh catalyst and 0.26 μmol/g for 0.1 wt% Rh catalyst.)

In conclusion, a novel low pressure process of solid catalyzed hydroformylation was developed by utilizing low loading rhodium supported on active carbon catalyst. At lower reaction pressure of 3.0 MPa, the catalytic performance of rhodium supported on active carbon catalyst was greatly promoted in nonpolar solvent. 403 K is a suitable reaction temperature for the hydroformylation of 1-hexene under the pressure of 3.0 MPa.

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