Hydrogenation of benzylpyridine over Ru/γ-Al$_2$O$_3$ catalysts: Use of Ru$_3$(CO)$_{12}$ as a Ru precursor

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Liquid organic hydrogen carrier (LOHC) has the ability to store hydrogen under ambient conditions [1]. When N atom is introduced into molecular structure of possible LOHC compounds, dehydrogenation efficiency would be improved owing to the decrease of dehydrogenation enthalpy. However, this adversely affects hydrogenation. Therefore, it is necessary to develop a highly efficient catalyst in the hydrogenation of N-containing molecules, e.g., benzylpyridine in this work.

Among various noble metals used for the hydrogenation of N-containing molecules, Ru is reported the most efficient and cheapest compared to Pt, Pd and Rh metals [2]. Generally, RuCl$_3$ has been used as a precursor for Ru catalysts, but complete removal of chloride ion is inevitably needed. When we searched for another Ru precursor, Ru$_3$(CO)$_{12}$ was found to have the highest dispersion [3]. In order to convert Ru$_3$(CO)$_{12}$ to Ru metal, thermal decomposition of carbonyl group is essential. However, an effect of heat treatment on the hydrogenation activity has been seldom studied because Ru$_3$(CO)$_{12}$ is quite a new Ru precursor in the literature.

Thus, Ru$_3$(CO)$_{12}$ of 5 wt% Ru was loaded onto γ-Al$_2$O$_3$ (Strem Chemicals, 185 m^2 g^{-1}) and then thermally treated under H$_2$, N$_2$ or air at 500 and 700 or 800 °C. The prepared Ru catalysts were tested for the hydrogenation of benzylpyridine (BPy) in a Parr batch reactor at 150 °C and 40 barg. For explaining the activity results, the following characterizations were conducted: TG-MS, FT-IR, TPR, TPO, PXRD, CO chemisorption, and TEM. The results of hydrogenation activity and CO chemisorption were summarized in Table 1.

When prepared by decomposing Ru$_3$(CO)$_{12}$ under air at 500 and 700 °C, Ru/γ-Al$_2$O$_3$ catalysts (after H$_2$ reduction at 250 °C) showed the BPy conversion of 31–33%. Such a low catalytic activity originates from larger Ru particles identified by lower CO chemisorption values as well as more intense reflections of RuO$_2$. This is due to low Hüttig temperature of RuO$_2$ (168.9 °C). In contrast, Ru/γ-Al$_2$O$_3$ catalysts prepared under H$_2$ and N$_2$ at 500 °C exhibited the high BPy conversions of 85–90%, where the results were similar irrespective of the thermal atmosphere. This indicates that tiny Ru particles of almost similar sizes are formed by decomposition under H$_2$ and N$_2$. Temperature-programmed decomposition with a MS detector revealed that the carbonyl group is decomposed to CH$_4$ under H$_2$ but it is transformed into CO and CO$_2$ under N$_2$. However, the BPy conversion was dropped to 38.4% when Ru catalysts were treated under N$_2$ at 800 °C, which is very different from the case under H$_2$ at 800 °C. This is presumed to be caused by the formation of RuO$_2$ under N$_2$. This assumption was confirmed by PXRD and TPR. In conclusion, our study will help us selecting an optimal treatment condition for the preparation of an active Ru catalyst when Ru$_3$(CO)$_{12}$ is used as a Ru precursor.

Table 1. Hydrogenation activities and properties of the prepared Ru catalysts

Heat treatment	BPy Conv. (%)	D_{CO}[b] (%)	d[c] (nm)
500 °C under air[a]	33.2	8.8	15.3
700 °C under air[a]	31.2	7.7	17.5
500 °C under H$_2$	89.7	89.1	1.0
800 °C under H$_2$	86.9	50.7	2.1
500 °C under N$_2$[a]	84.9	88.1	1.0
500 °C under N$_2$	86.8	88.1	1.0
800 °C under N$_2$	38.4	3.3	41.5

[a] Reduction at 250 °C for 3 h.
[b] Metal dispersion measured by CO chemisorption.
[c] Particle size calculated by CO chemisorption.
[d] Reaction condition: catalyst 36 mg (5 wt% Ru), benzylpyridine 3 g, solvent (decalin) 27 g, 150 °C, 40 barg, 400 rpm, 2 h.

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