Reverse Water Gas Shift Reaction Using Supported Ionic Liquid Phase Type Catalyst Systems

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Although carbon monoxide (CO), which is industrially produced from coke, biomass and so on and is transformed to chemical product such as aldehyde, is significant material, it's serious toxic nature acts as high hurdle to employ it in industrial plants. One approach to solve such situation is producing CO in plant and successively converting it to chemical products.

Recently, we have studied reverse water gas shift reaction (RWGSR), which is hydrogenation reaction of CO_2 to produce CO, using homogeneous Ru catalyst at low temperature and found that $[RuCl_2(CO)_3]_2$ showed good activity for RWGSR among studied Ru catalysts, while $Ru_3(CO)_{12}$ can promote both RWGSR and following hydroformylation reaction.[1, 2]

Supported ionic liquid phase (SILP) type catalyst consists of nano-porous support which surface is covered with ionic liquid (IL) thin layer including homogeneous catalyst (**Fig. 1**). By using SILP type catalyst system, homogeneous catalyst can be treated like a heterogeneous catalyst and mass transport of reaction gases can be improved due to large surface area derived from the nano-porous support.[3] In this study, we studied about RWGSR using SILP type Ru catalyst system.

$[RuCl_2(CO)_3]_2$, $Ru_3(CO)_{12}$, and $RuCl_3$ were employed as catalyst for RWGSR. Typical procedure of preparation of SILP is as follows. 10.0 g of silica gel (Wakosil-C200) which was previously heat-treated at 500 °C and stored in grove box are added to CH_2Cl_2 solution consisting 60 mg of $[RuCl_2(CO)_3]_2$, 1600 mg of [C4mim]Cl and 15 mL of distilled CH_2Cl_2. From the suspension, CH_2Cl_2 was removed under reduced pressure with vigorously stirring and resulting powder materials was dried under vacuum and stored in grove box. RWGSR was performed at 170 °C under high pressure of reaction gases (P_{CO2}/P_{H2} = 6 MPa/2MPa). After the reaction, resulting gases are analyzed by GC.

The results of RWGSR performed using SILP for various reaction times are shown in **Fig. 2**. Among studied Ru catalysts, $[RuCl_2(CO)_3]_2$ showed best performance even in SILP system and after 40 h TON reached to ca. 400 which is corresponding to ca. 14 % of CO_2 conversion. Besides, $RuCl_3$ shows good performance comparable to $Ru_3(CO)_{12}$ after heat-treatment under CO atmosphere. In this presentation, cycle performances will be also reported.
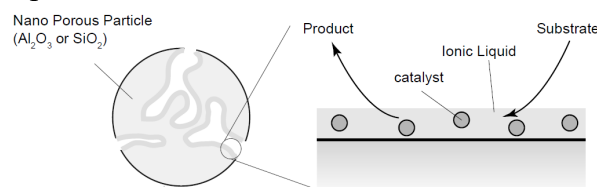

Fig. 1 Description of SILP catalyst. Ionic liquid dissolving homogeneous catalyst forms nano-layer in the pore of support.
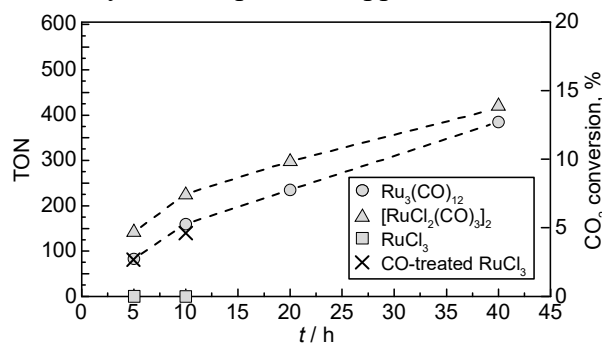

Fig. 2 Results of RWGSR using SILP based on various catalysts. Reaction time was 10 h. TON was calculated by dividing mole of produced CO by that of Ru atom. Before the reaction, CO treatment of $RuCl_3$ based SILP was also performed at 170 °C for 10 h under 1 MPa CO atmosphere to generate active species.

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