

# Hydrogen Charge of LOHC Compounds over Al<sub>2</sub>O<sub>3</sub>- and MgO-supported Ru Nanoparticles

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## Introduction

Liquid organic hydrogen carrier (LOHC) systems have recently attracted a great deal of attention in storing and releasing hydrogen under a mild condition. Marlotherm<sup>®</sup>-type heat transfer fluids (monobenzyl toluene or dibenzyl toluene) supplied by Sasol company are an interesting LOHC material with a hydrogen storage capacity of 6.2 wt%, a high boiling point of more than 280 °C and a low melting point of less than −30 °C [1]. Although the dehydrogenation of H<sub>2</sub>-rich LOHC compounds generally requires a high reaction temperature of more than 270 °C [2,3], the hydrogenation reaction is also important for fast H<sub>2</sub> storage at low temperatures. Thus, we focused on the development of an active catalyst for the hydrogen charge of monobenzyl toluene (H<sub>0</sub>-MBT) and dibenzyl toluene (H<sub>0</sub>-DBT) at low temperatures.

In most studies the hydrogenation of LOHC compounds was performed over Ru catalysts supported on Al<sub>2</sub>O<sub>3</sub> with Lewis acidity [4]. Recently, Ru/MgO catalyst has been also investigated for the hydrogenation reaction due to heterolytic hydrogen splitting by aid of basic character of MgO support [5]. Hence, we have herein compared the hydrogenation activity of Ru/Al<sub>2</sub>O<sub>3</sub> and Ru/MgO catalysts with respect to the time to charge full H<sub>2</sub> for H<sub>0</sub>-MBT and H<sub>0</sub>-DBT, which will serve as a recommendation for the hydrogenation catalyst.

## Materials and Methods

Al<sub>2</sub>O<sub>3</sub>- and MgO-supported Ru catalysts were prepared by impregnating the commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Strem Chemicals) and the lab-made Mg(OH)<sub>2</sub> with a solution of Ru<sub>3</sub>(CO)<sub>12</sub> (Sigma-Aldrich Co.) in tetrahydrofuran, respectively. After the suspension was stirred at room temperature, the solvent was removed in a rotary evaporator (EYELA) under a reduced pressure at 45 °C. The obtained sample was dried for 8 h at 105 °C followed by thermal activation for 6 h at 500 °C (5 °C/min) in a H<sub>2</sub> flow (100 ml/min).

The hydrogenation activity was tested in a Parr reactor equipped with a glass liner (volume 100 ml). The substrate H<sub>0</sub>-MBT or H<sub>0</sub>-DBT (15 g) and a supported Ru catalyst (0.045 mol% Ru/H<sub>0</sub>-MBT and 0.10 mol% Ru/H<sub>0</sub>-DBT) were added into the reactor. After sufficient N<sub>2</sub> purge, the reactor was pressurized with 99.99% hydrogen to 50 bar that was maintained throughout the reaction using a back pressured regulator. Then, the reactor was heated to a desired temperature while stirring at a rate of 1200 rpm. Finally, the time to obtain the full hydrogenation product H<sub>12</sub>-MBT or H<sub>18</sub>-DBT by GC analysis of liquid products was measured.

## Results and Discussion

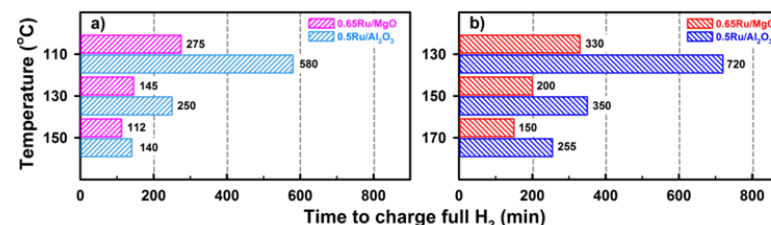
0.5Ru/Al<sub>2</sub>O<sub>3</sub> (0.5 wt% Ru by ICP) and 0.65Ru/MgO (0.65 wt% Ru by ICP) samples showed the average Ru particle size of 1.1 and 1.4 nm, respectively (Table 1). When the

hydrogenation reaction was performed at 150, 130 and 110 °C, the time required for full charge of H<sub>0</sub>-MBT was estimated to be 112, 145, and 275 min over 0.65Ru/MgO and 140, 250, and 580 min over 0.5Ru/Al<sub>2</sub>O<sub>3</sub>, respectively (Fig. 1). The tests for full conversion of H<sub>0</sub>-DBT to H<sub>18</sub>-DBT at 170, 150 and 130 °C also verified the superior catalytic performance of 0.5Ru/MgO to 0.65Ru/MgO. Notably, the activity difference between the two catalysts was much larger at lower reaction temperatures. This phenomenon was associated with a stronger adsorption of the substrate onto Ru/MgO and, importantly, a higher H<sub>2</sub> abstraction by heterolytic hydrogen splitting taking place in Ru/MgO. The characterization results will be presented on the symposium site.

**Table 1. Properties of Al<sub>2</sub>O<sub>3</sub>- and MgO-supported Ru catalysts**

Sample	Ru <sup>a</sup> [wt%]	S <sub>BET</sub> <sup>b</sup> [m <sup>2</sup> /g]	d <sub>Ru</sub> <sup>c</sup> [nm]
0.5Ru/Al <sub>2</sub> O <sub>3</sub>	0.50	270	1.1
0.65Ru/MgO	0.65	196	1.4

[a] Actual Ru loading measured by ICP-OES. [b] BET surface area measured by N<sub>2</sub> physisorption at 77 K. [c] Ru<sup>0</sup> particle size measured by CO chemisorption.



**Figure 1.** The time required to fully H<sub>2</sub> charge in a) H<sub>0</sub>-MBT or b) H<sub>0</sub>-DBT over Ru/MgO (red bars) and Ru/Al<sub>2</sub>O<sub>3</sub> (blue bars).

## Significance

Ru/MgO catalyst exhibited the fast hydrogenation kinetics in H<sub>2</sub> charge into homocyclic Marlotherm-type LOHC compounds at lower temperatures compared to Ru/Al<sub>2</sub>O<sub>3</sub>, which was supported by the facile adsorption of the substrate and the higher H<sub>2</sub> abstraction over Ru/MgO.

## References

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