Effect of $MgCl_2$ in Vapor-Phase Hydrogen Transfer Reaction between Acrolein and 2-Propanol over MgO Catalyst Systems

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Vapor-phase hydrogen transfer reaction between acrolein and 2-propanol over MgO catalyst systems has investigated. We found that, particularly at early reaction time, both the high activity and remarkable increase of allyl alcohol selectivity were achieved by the addition of a small amount of $MgCl_2$ on MgO catalyst.

In conventional hydrogenation of α,β-unsaturated carbonyl compounds, it is generally difficult to obtain a high selectivity to the corresponding allylic alcohols since olefinic groups are usually more easily hydrogenated than carbonyl groups. Some reports have been published concerning the hydrogen transfer reaction in vapor-phase between carbonyl compounds and alcohols over MgO-based catalysts.[1-5] Above all, Ueshima et al. have reported to obtain effectively the corresponding allylic alcohols in vapor-phase hydrogen transfer reaction between α,β-unsaturated aldehydes and alcohols over B_2O_3-MgO or ZrO_2-MgO catalyst.[4,5] We followed their catalytic reaction in our system and obtained the high allyl alcohol selectivity in vapor-phase hydrogen transfer between acrolein and 2-propanol over B_2O_3-MgO catalyst. However, the catalytic activity gradually decreased with the reaction time and eventually the difference of the activity was small between B_2O_3-MgO and MgO catalyst. In this work, we found that the title reaction could be performed with high catalytic activity and high allyl alcohol selectivity by adding a small amount of $MgCl_2$ on MgO catalyst.

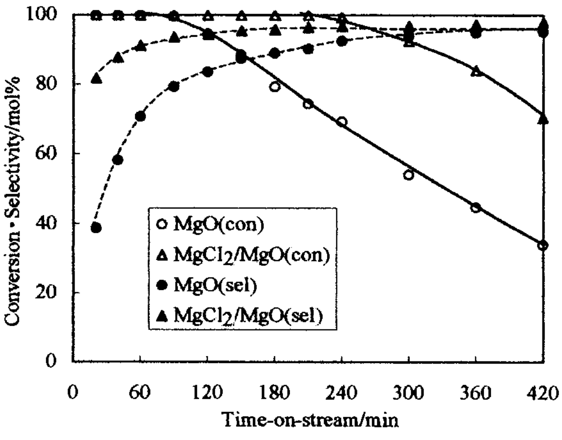
The MgO-based catalysts were prepared as follows. Into a mixture of dissolved B_2O_3 (0.13 g) and $MgCl_2 \cdot 6H_2O$ (usually 0.64 wt% to MgO) in 100ml of deionized water, $Mg(OH)_2$ (10.6 g) was added and the mixture was sufficiently stirred at room temperature. The above solution was vaporized in a water bath at ca. 80 °C and thereafter dried at 120 °C for 20 h in air. The dried sample was then ground and calcined at 600 °C for 2 h in air. The calcined powder was pressed and then pulverized (10-14 mesh) in order to use as a catalyst for some reactions in this work. All reactions were carried out in a conventional fixed bed flow system at atmospheric pressure, using a pyrex grass reactor (18Φ × 300 mm) at 270 °C. Using a microfeeder, a mixture (reactant) of acrolein (or allyl alcohol) and 2-propanol was introduced into a reactor immersed in a fluidized sand furnace with a dilute nitrogen gas. The volume ratio (2-propanol / acrolein (or allyl alcohol)) was 15. Reaction products were trapped in a dry ice-methanol and analyzed by gas chromatography.

The hydrogen transfer reaction is a reversible reaction. When acrolein is converted to allyl alcohol or 1-propanol in the reaction, 2-propanol is converted to acetone by dehydrogenation. In this study, liquid products were allyl alcohol, propanal, 1-propanol (derived from acrolein) and acetone (derived from 2-propanol). A relatively small amount of water derived from 2-propanol was also detected. We examined time course of acrolein conversion and allyl alcohol selectivity.

As reported by Ueshima et al.[4], the catalytic activity was somewhat increased by the addition of a small amount of B_2O_3 on MgO under our reaction condition. According to Aramendia et al., BET surface area, acidity and basicity were almost the same between MgO and B_2O_3-MgO catalyst, although acidity was slightly increased for B_2O_3-MgO.[6] Shimasaki et al. have reported that the increase of the catalytic activity was caused by the addition of acidic oxides such as ZrO_2, SiO_2, B_2O_3, or TiO_2 on MgO.[5] For MgO and B_2O_3-MgO catalysts, we performed the reaction at 270 °C, with contact time 28.8 g-cat h/mol, and nitrogen flow rate 10 L/h. The results were consistent with Shimasaki et al.'s report.[5]

Aramendia et al. have also pointed out that the hydrogenation of α,β-unsaturated aldehyde to the corresponding unsaturated alcohol is related to Lewis acidity, which activates the carbonyl group by inducing a positive charge on the carbon atom.[7] They have also revealed that the number of Lewis acid sites of B_2O_3-MgO is slightly larger than that of MgO. The increase of the number of Lewis acid sites due to the addition of B_2O_3 was about twice of the number of Brønsted acid sites.[6] Therefore, these facts may explain the higher conversion and increase of selectivity of allyl alcohol, particularly at early reaction time. So, we examined the effect of the addition of $MgCl_2$, which is a Lewis acid material, on MgO catalyst. The results are shown in Figure 1.

From the results of Figure 1, a higher conversion after some reaction time and remarkable increase (from 39 mol% to 82 mol%) of selectivity of allyl alcohol at early reaction time, were observed for $MgCl_2$/MgO. This effect may be due to the effective increase of Lewis acidity by the addition of $MgCl_2$.



(con : conversion, sel : selectivity)

Figure 1. Effect of $MgCl_2$ on the vapor-phase hydrogen transfer reaction over MgO-based catalysts.
reaction temperature : 270 ℃, contact time : 28.8 g-cat h/mol, nitrogen flow rate : 10 L/h.

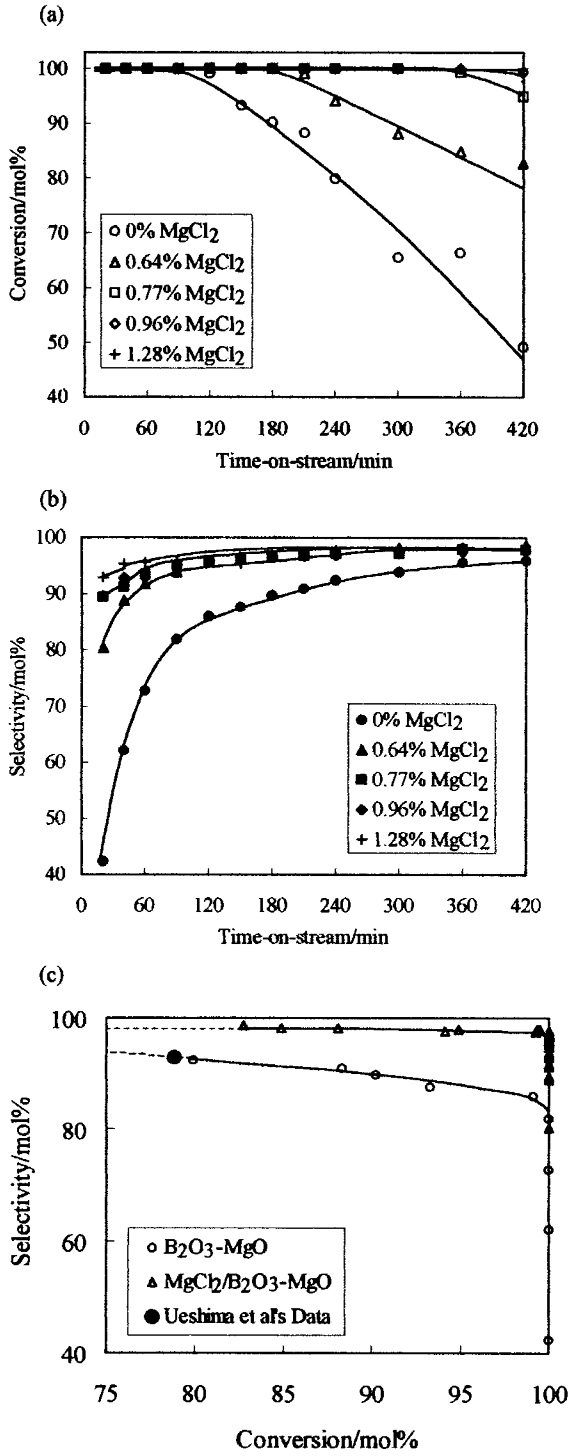


Figure 2. Effect of the amount of $MgCl_2$ over B_2O_3-MgO catalyst. reaction temperature : 270℃,
contact time : 28.8 g-cat h/mol, nitrogen flow rate : 10 L/h.

Also, we studied the effect of $MgCl_2$ addition on B_2O_3-MgO catalyst. The results are shown in Figure 2. As shown in Figure 2 (a), the degradation of the activity was suppressed by the addition of $MgCl_2$. On the other hand, the selectivity of allyl alcohol increased by the addition of $MgCl_2$ in the beginning of the reaction as shown in Figure 2 (b), although the difference was not so much between 0.64 wt% and 1.28 wt% of $MgCl_2$.

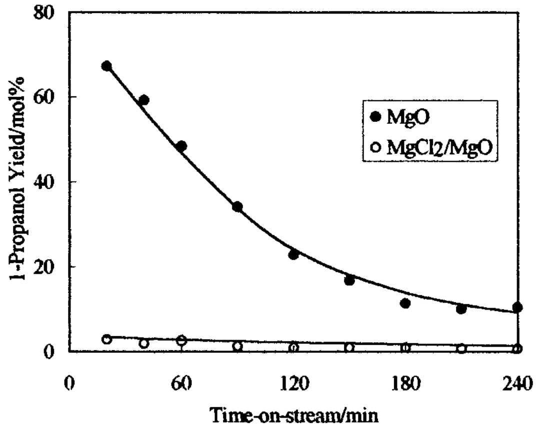


Figure 3. Effect of $MgCl_2$ on the hydrogen transfer reaction between allyl alcohol and isopropanol over MgO catalyst.
reaction temperature : 270 ℃, contact time : 28.8 g-cat h/mol,
nitrogen flow rate : 10 L/h.

Next, we examined the effect of the addition of $MgCl_2$ on MgO catalyst in the hydrogen transfer reaction between allyl alcohol and 2-propanol. The allyl alcohol is supposed to be an intermediate spacies of hydrogen transfer reaction between acrolein and 2-propanol.

As shown in Figure 3, the product from allyl alcohol was only 1-propanol for both cases, but the reactivities of 1-propanol formation were clearly different. Due to the addition of $MgCl_2$ on MgO catalyst, we found 1-propanol formation was markedly suppressed. This may explain the higher selectivity of allyl alcohol on $MgCl_2$ added catalysts.

Also, the effect of the additives such as $FeCl_2$, ZnO and AgCl, which have Lewis acidity, on MgO catalyst was examined (although not shown). We found that these additives also caused high selectivity with high conversion, such as shown in Figure 2 (c). These results indicate that the hydrogenation of the carbonyl group was enhanced and the hydrogenation of the olefinic group was suppressed by the addition of a small amount of Lewis acid type additives. It is supposed the favorable effect may be caused by introducing an appropriate Lewis acid character to a solid-base MgO, the factors of these effects are not clear at present.

References and Notes

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