

## Remarkable Support Effects of Gallium Compounds on the Activity and Selectivity of Ru Metal Catalyst for Liquid-phase Citral Hydrogenation

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Various types of p-block metal oxides and nitrides were employed as catalyst supports for Ru metal in liquid-phase citral hydrogenation. Compounds containing  $\text{Ga}^{3+}$  ions, in particular GaOOH, were found to exhibit remarkable support effects on the enhancement of catalytic activity and reaction selectivity for the production of  $\alpha,\beta$ -unsaturated alcohols (nerol and geraniol).

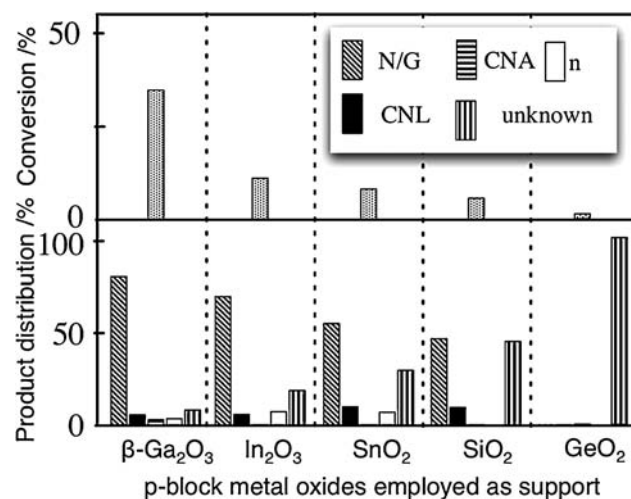
The selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to unsaturated alcohols on heterogeneous catalysts is of great synthetic importance for the production of various fine chemicals in the flavor, fragrance, and pharmaceutical industries. In particular, the  $\alpha,\beta$ -unsaturated alcohols nerol and geraniol are important in the perfume industry and are obtained in the hydrogenation of the  $\alpha,\beta$ -unsaturated aldehyde citral (3,7-dimethyl-2,6-octadienal), which contains three unsaturated bonds; i.e., conjugated C=O and C=C bonds and an isolated C=C bond. Difficulty in selective hydrogenation to nerol/geraniol is due to the fact that the hydrogenation of a C=C bond is thermodynamically more favorable than C=O hydrogenation.

Ruthenium is a potentially useful metal as a catalyst for selective C=O bond hydrogenation because of its wide d band character which favors interactions between the metal surface and the C=O bond.<sup>1</sup> It has been established that the supports for metal-supporting catalysts play an important role in the improvement of catalytic performance. The citral hydrogenation has been examined with Ru metals dispersed on various supports such as  $\text{Al}_2\text{O}_3$ ,<sup>2-4</sup> carbon,<sup>2-4</sup>  $\text{SiO}_2$ ,<sup>1</sup> KL zeolite ( $\text{K}_9\text{Al}_9\text{Si}_{27}\text{O}_{72}$ ),<sup>5</sup> and  $\text{TiO}_2$ ,<sup>6</sup> however, significant support effects on nerol/geraniol production have not been reported. The conventional supports lead to poor performance with low yields of the desired products. Therefore, the discovery of supports that have strong enhancing effects on Ru metal for the citral hydrogenation is an important issue. In the present study, we have investigated various p-block metal oxides and nitrides for use as supports and found that compounds containing  $\text{Ga}^{3+}$  ions, in particular GaOOH, make excellent supports that significantly enhance the ability of Ru to promote the selective hydrogenation of citral for nerol/geraniol production.

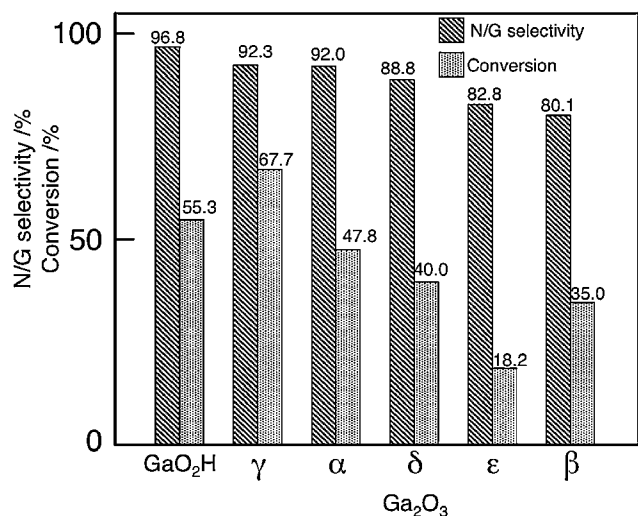
The p-block metal oxides employed were commercially available  $\text{Ga}_2\text{O}_3$  (99.99% pure, Soekawa Chem.),  $\text{In}_2\text{O}_3$  (99.999%, Nacalai Tesque),  $\text{SnO}_2$  (ER, Nacalai Tesque),  $\text{SiO}_2$  (GR, Nacalai Tesque),  $\text{GeO}_2$  (99.99%, Nacalai Tesque), and the metal nitrides were BN (>99%, Kojundo Chem. Lab.), GaN (>99.99%, Aldrich), InN (99.9%, Aldrich),  $\text{Si}_3\text{N}_4$  (>99.9%, Kojundo Chem. Lab.), AlN (98%, Aldrich), and  $\text{Ge}_3\text{N}_4$  (>99.99%, Aldrich). Ruthenium metal (2.5 wt %) was loaded on the supports using a liquid-phase reduction method. Ruthenium chloride ( $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ ) as a starting material and the supports were dispersed in water, and then  $\text{NaBH}_4$  aqueous

solution as a reducing agent was added to the solution. After reduction, the catalysts were recovered by filtration, washed with water and acetone, and dried at room temperature. The liquid-phase hydrogenation of citral was carried out at a hydrogen pressure of 1.3 MPa and at 393 K under constant stirring conditions in an autoclave equipped with a thermocouple, heater and a rotator. About 2.0 g of catalyst and 130 mL of citral (98.0% pure) were loaded without solvent into the autoclave. The reaction products were analyzed by a gas chromatograph with an FID detector. The conversion was taken as a measure of catalytic activity and determined by the consumption of citral at a given reaction time, whereas the selectivity was defined as the percentage of nerol/geraniol to the total of the other products.

Under the present reaction conditions, the products identified were nerol/geraniol (N/G), citronellal (CNL), isogeraniol (n), and citronellol (CNA). Figure 1 shows the activity and selectivity of citral hydrogenation on Ru metals loaded on various p-block metal oxides. Both the activity of the catalysts and the selectivity for N/G production were larger in the order  $\beta\text{-Ga}_2\text{O}_3 > \text{In}_2\text{O}_3 > \text{SnO}_2 > \text{SiO}_2 > \text{GeO}_2$ . Previously reported high selectivities for N/G production on supported Ru metal catalysts were 87.8% at a conversion of 21% for Ru-Sn/ $\text{TiO}_2$  ( $\text{TiO}_2$  was subjected to high-temperature reduction at 673 K)<sup>6</sup> and 82% at 70% conversion for Ru-Ce/active carbon<sup>3</sup> in which heptane and 2-propanol were used as solvents, respectively. The result that Ru/ $\beta\text{-Ga}_2\text{O}_3$  catalyst provided a selectivity of 80% at 35% conversion under solvent-free reaction conditions was indicative of compatible support effects of  $\beta\text{-Ga}_2\text{O}_3$  on the selectivity for Ru-catalyzed C=O hydrogenation. The transition-metal



**Figure 1.** Conversion and selectivity of liquid phase citral hydrogenation over Ru metal loaded on various p-block metal oxide supports. Reaction time: 6 h.



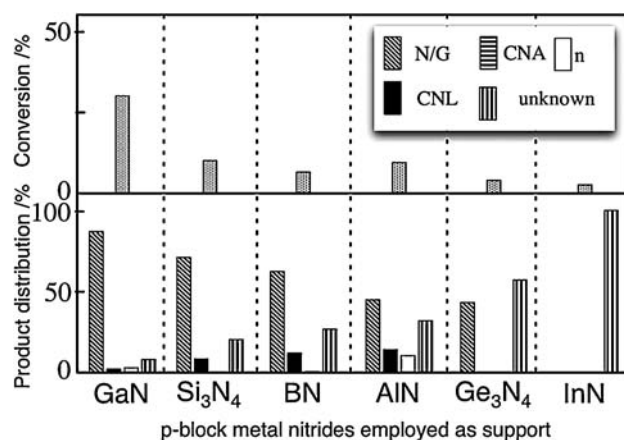
**Figure 2.** Selectivity for nerol/geraniol production and conversion in liquid phase citral hydrogenation over Ru metal supported on  $\text{Ga}_2\text{O}_3$  and  $\text{GaOOH}$ . Reaction time: 6 h.

oxides of  $\text{Nb}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  were also used here as supports for comparison purposes, and the selectivity remained low at levels of 55.7 and 14.7%, respectively, under similar reaction conditions as employed for the Ru/ $\beta$ - $\text{Ga}_2\text{O}_3$  catalyst.

Gallium oxides have five kinds of polymorphic metal oxides ( $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -, and  $\epsilon$ - $\text{Ga}_2\text{O}_3$ ). A preliminary study has been done to further examine their support effects, together with that of  $\text{GaOOH}$ . Figure 2 shows their selectivity for N/G. The selectivity was higher in the order of  $\text{GaOOH} > \gamma$ ,  $\alpha > \delta > \epsilon > \beta$ - $\text{Ga}_2\text{O}_3$ . Interestingly,  $\text{GaOOH}$  provided a selectivity as high as 96.8%, which is remarkably high under solvent-free conditions. The selectivity of 96.4% was obtained even at a conversion of 85%.

Figure 3 shows the activity and selectivity of Ru metal loaded on various metal nitrides. The activity increased in the order  $\text{GaN} > \text{Si}_3\text{N}_4 > \text{AlN} > \text{BN} > \text{Ge}_3\text{N}_4 \gg \text{InN}$ . The selectivity was higher in the same order except for the reversal of AlN and BN. Once again, GaN exhibited the highest performance as a support among the various metal nitrides, which was in line with the advantageous position of  $\text{Ga}_2\text{O}_3$  and  $\text{GaOOH}$  in the p-block metal oxides. These results indicate that compounds involving  $\text{Ga}^{3+}$  ions have remarkably positive effects on Ru metal as a support for C=O hydrogenation.

Mercadante et al.<sup>4</sup> showed that in liquid-phase citral hydrogenation over Ru/ $\text{Al}_2\text{O}_3$  and Ru/carbon, the selectivity (15%) for N/G production remained constant in all ranges of H/Ru dispersion from 0.05 to 0.88, indicating the absence of Ru particle size effects. Other catalyst systems such as Pt/ $\text{SiO}_2$ <sup>7</sup> and Pd/ $\text{SiO}_2$ <sup>1</sup> also showed no effect of the crystallite size on the activity and product distribution. These findings suggest that the geometry and coordination number of the Ru sites are not important in the hydrogenation of citral to unsaturated alcohols. This is apparently due to the structure of the citral molecule which has a very bulky aliphatic substituent in the  $\beta$ -carbon position. These results show that particle size differences in Ru metal are not likely to be responsible for its different catalytic behavior with various metal oxides and nitride supports.



**Figure 3.** Conversion and reaction selectivity of liquid phase citral hydrogenation over Ru metal loaded on various p-block metal nitride supports. Reaction time: 6 h.

To explain the positive support effects of  $\text{Ga}^{3+}$  ion-containing compounds, two models associated with the polarized surface states are considered. The first is the effect of charge transfer from the support to the Ru metal, which increases its electron density. This decreases the probability of C=C hydrogenation. The second is the role of surface Lewis acidic sites that are involved in the activation of the C=O bond. The addition of  $\text{SnO}_2$  on Ru/ $\text{TiO}_2$  catalyst<sup>6</sup> was reported to cause considerable changes in the selectivity of N/G production, which indicates that the active site is composed of Ru metal in direct contact with  $\text{SnO}_2$ . This shows that the promotion effect of the support is due to a positively charged cationic site. Thus, Ru supported on Ga-containing compounds provides bifunctional surfaces which induce the chemical bond formation of the citral molecule to the  $\text{Ga}^{3+}$  cation through the C=O bond and the interactions of the carbon atom of C=O with Ru metals dispersed on the supports.

In the present study,  $\text{GaOOH}$  was found to have the most useful support effects compared to other Ga compounds and other metal oxide supports. Although we need to fully characterize its properties, such as stability with reaction conversion, the findings are encouraging for the development of high performance catalysts for the selective hydrogenation of the C=O bond.

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