

Conversion of levulinate esters to γ -valerolactone by catalytic transfer hydrogenation over supported ruthenium hydroxide catalysts

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Introduction

Due to increasing global energy consumption and gradual depletion of fossil fuel resources, use of lignocellulosic biomass to produce chemicals, fuels, and energy has attracted considerable attention. Among various chemicals synthesized from lignocellulosic biomass, γ -valerolactone (GVL) is suggested as the most promising molecules, as it can be used as a fuel additive, solvent, as well as an ideal precursor for the production of alkanes, alkenes and valuable chemicals.^{1,2} GVL can conventionally be produced from cellulosic biomass-derived levulinic acid (LA) and its esters via i) the hydrogenation (using H₂) or ii) the catalytic transfer hydrogenation (CTH) process (using alcohols as hydrogen donors). Recent research on this reaction has mainly focused on the former process. CTH method is another viable option for the production of GVL, since the reaction proceeds under ambient conditions and without the need of flammable, high-pressure H₂. For the production of GVL via a CTH process, several catalytic systems have recently been reported.³ However, the system still requires high temperature/pressure conditions and suffers from catalytic deactivation during the reaction. In this presentation, we report efficient production of GVL from levulinate esters and several alcohols via a CTH process over supported ruthenium hydroxide catalysts, which are reusable over multiple cycles without loss of catalytic performance.

Materials and Methods

Supported Ru(OH)_x catalysts were prepared by precipitation method in aqueous RuCl₃ solution.⁴ Various kinds of metal oxide such as Al₂O₃, TiO₂, ZrO₂, CeO₂, MgO, CaO were used as support materials. Ru loading was varied to 0.8, 2.0, 4.0 wt.%. X-ray diffraction (XRD) and N₂ adsorption measurement were used for the structure identification. X-ray absorption fine structure (XAFS) analysis was used to investigate the local structure of Ru species. GVL production via a CTH process was performed in a quartz glass reactor with a reflux condenser at 90 °C in Ar atmosphere. Yields of GVL and other products were determined by GC using biphenyl as an internal standard.

Results and Discussion

Table 1 shows the results of the CTH reaction of methyl levulinate using 2-PrOH as a hydrogen donor at 90 °C. When the same amount of Ru was used, Ru(OH)_x catalysts supported on TiO₂ provided the highest yield of GVL, which far outperformed that given by unsupported Ru(OH)_x. On the other hand, Ru(OH)_x catalysts supported on γ -Al₂O₃, α -Al₂O₃, ZrO₂ showed modest catalytic activity (entries 1–2), and those supported on MgO, CaO, CeO₂ were almost inactive for this reaction (entry 8). Interestingly, Ru(OH)_x supported on high-surface-area TiO₂ (ST-01) provided an increased yield of GVL as increasing the Ru loading

from 0.8 to 4.0 wt.% (entries 5–6), and the highest GVL yield of 89% with >99% conversion was attained at 4.0 wt.% Ru loading. The XRD patterns of the catalysts indicated that Ru species are highly dispersed on the support surface in all cases. XAFS analysis evidenced that Ru species are mostly present as monomeric Ru(OH)_x species on TiO₂ surface, and suggested a clear relationship between the Ru–O–Ru shell signals in the radial distribution functions and the reaction rates in the CTH reactions was observed.

A further faster GVL production rate was attained by the addition of bases. Among several bases, solid bases such as MgO and hydrotalcite (HT) were found to be effective, affording GVL in almost quantitative yields within 24 h (Table 1, entry 7). Other secondary alcohols such as 2-BuOH and cyclohexanol also acted as efficient hydrogen donors, whereas primary alcohols such as methanol, ethanol and 1-PrOH gave similar performances to the blank experiments. In addition, the prepared Ru(OH)_x/TiO₂ catalyst was at least four times repeatedly used without loss of catalytic activity and GVL selectivity (Table 1, entry 6).

Table 1. Production of γ -valerolactone (GVL) from methyl levulinate using supported Ru(OH)_x catalysts.

Entry ^a	Catalyst	Ru loading (wt%)	S _{BET} (m ² /g)	Solvent / Additive ^b	Conversion (%)	GVL yield (%)
1	Ru(OH) _x / α -Al ₂ O ₃	0.8	6.7	2-PrOH / -	76	38
2	Ru(OH) _x / γ -Al ₂ O ₃	0.8	236	2-PrOH / -	66	64
3	Ru(OH) _x /TiO ₂ (P25)	0.8	53	2-PrOH / -	>99	80
4	Ru(OH) _x /TiO ₂ (P25)	4.2	61	2-PrOH / -	96	48
5	Ru(OH) _x /TiO ₂ (ST-01)	0.8	336	2-PrOH / -	84	75
6	Ru(OH) _x /TiO ₂ (ST-01)	4.0	214	2-PrOH / -	>99	89 (90) ^c
7	Ru(OH) _x /TiO ₂ (ST-01)	4.0	214	2-PrOH / MgO	>99	98
8	Ru(OH) _x /MgO	0.8	346	2-PrOH / -	0.7	0.7

^a catalyst (Ru 0.8 mol%), methyl levulinate (1 mmol), 2-PrOH (5 mL), 90 °C, in Ar, 24 h.

^b additive (100 mg). ^c 2nd use.

Significance

GVL, an important feedstock chemical, was produced from biomass-derived levulinate esters and secondary alcohols as H-donors via a mild catalytic transfer hydrogenation process over supported Ru(OH)_x catalysts. Among the catalysts examined, Ru(OH)_x supported on high-surface-area TiO₂ consisting of isolated Ru(OH)_x species was demonstrated to be highly active for CTH process, and GVL production rate was accelerated by the addition of solid bases. The catalyst is reusable over multiple cycles without loss of catalytic performance, making this material a potential candidate for efficient GVL production.

References

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