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Research Paper

Hydrogenation of levulinic acid to γ-valerolactone over anatase-supported Ru catalysts: Effect of catalyst synthesis protocols on activity

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ABSTRACT

γ-Valerolactone (GVL) is a value-added renewable chemical with great potential and can be obtained from biomass by the hydrogenation of levulinic acid (LA) using metal-based catalysts, such as Ru/TiO_2. We here report an in depth study of the effect of catalyst synthesis parameters on the performance of Ru/TiO_2 (anatase), varying the nature of the Ru-precursor and the conditions of the calcination and/or reduction step. Catalyst performance was evaluated under batch conditions at a hydrogen pressure of 45 bar and using either water (90 °C) or dioxane (150 °C) as solvent. The experiments showed that catalyst activity depends greatly on the Ru precursor used ($RuCl_3$, $RuNO(NO_3)_3$, $Ru(NH_3)_6Cl_3$). Best results when considering the turn-over frequencies (TOF) of the catalysts were obtained using the $RuNO(NO_3)_3$ precursor, whereas $RuCl_3$ performed better when considering the initial rate based on Ru intake. An intermediate calcination step and the use of a hydrogen-rich sweep gas during the final reduction step were shown to have a negative impact on catalyst activity. Characterization of the fresh catalysts by BET and TEM provided valuable insight in the relation between the catalyst structure and its activity.

1. Introduction

Levulinic acid (LA) is a major product of the controlled dehydration of the C6-sugars (D-glucose, D-mannose and D-galactose) in lignocellulosic biomass. It is recognized as an important carbohydrate-derived renewable platform molecule and has attracted considerable interest from a number of chemical companies [1,2]. The family of LA derivatives is large and some have much potential for commercialization. For instance, LA can be converted to 2-methyltetrahydrofuran (MTHF) and various levulinate esters, which may be used as gasoline and biodiesel additives, respectively [3–8]. δ-Aminolevulinic acid is a well-known herbicide and β-acetylacrylic acid has been proposed as a (co-)monomer for novel acrylate polymers [1]. Arguably, most attention has been devoted to the conversion of LA to γ-valerolactone (GVL), as GVL is considered as an important platform chemical in its own right and can be used as food additive, solvent and as precursor for fuel additives and bulk polymers [9–13]. The conventional way to produce GVL involves the hydrogenation of LA or its esters [14–16], with molecular hydrogen or an alternative hydrogen donor (e.g. formic acid), preferably using heterogeneous catalysts (Scheme 1). The intermediate 4-hydroxypentanoic acid (4-HPA) may be found in relatively high amounts when using water as the solvent, its exact amount depending on the relative rate of hydrogenation versus the rate of the intramolecular esterification reaction.

Recently, Liguori and Barbaro [17] published a comprehensive review on the direct catalytic conversion of renewable sources to GVL with an emphasis on the heterogeneous catalysts that have been used for this reaction. Noble metal-based catalysts are most commonly and successfully employed, with Ru-based ones in particular showing high activity and selectivity to GVL [14,18–21]. In addition to the nature of the active metal phase, the choice of support also has a large effect on catalyst performance, in particular on catalyst stability.

Activated carbons are the most widely used support for Ru in LA hydrogenation [22–24], mainly due to their good performance and availability [24–26], and as such Ru/C catalysts can be regarded as one of the benchmark catalysts for this reaction. Under continuous flow conditions and using water as the solvent, however, slow though irreversible deactivation of the Ru/C catalyst was observed, presumably due to Ru sintering and a reduction in specific surface area as a result of the deposition of carbonaceous deposits [15,22,25,27].

Various metal oxides, including SiO_2, Al_2O_3, Nb_2O_5, ZrO_2 and TiO_2, have been tested as a support for LA hydrogenation with Ru as the active metal [16,19,24,25]. A major advantage of such metal oxides over carbon supports is their mechanical and thermal stability, which

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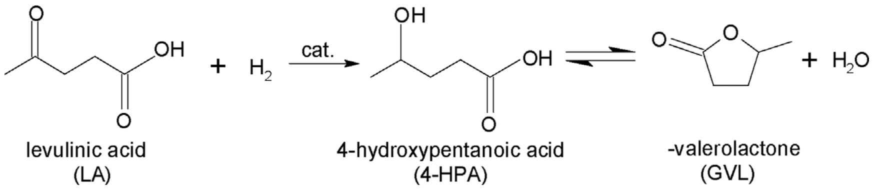

Scheme 1. Proposed reaction scheme for the catalytic hydrogenation of LA to GVL.

allows for repetitive regeneration and coke removal at elevated temperature. However, for some of these oxides, e.g. Al_2O_3 and SiO_2, the stability under hydrothermal, acidic conditions is known to be limited, which is of relevance for LA hydrogenations carried out in water or at high LA loadings [25,28]. Estimations of oxide support stability in pressurized water at 200 °C were recently provided by Lange using Pourbaix diagrams [2]. SiO_2 has the tendency to be converted into silica gel at all pH values, whereas Al_2O_3 is well-known to convert into boehmite (AlO(OH)) at pH values between 4.5 and 11.5. TiO_2, calculated to be stable over the entire pH range, and ZrO_2 are attractive alternatives [28], even though hydrated $Zr(OH)_4$ was found to be the thermodynamically most stable phase in water. Indeed, a screening study on LA hydrogenation involving 50 catalysts in a flow reactor system revealed that Pt on TiO_2 (P25 from Degussa) and ZrO_2 performed best, with constant GVL yields for runtimes exceeding 100 h (> 95 mol% at 200 °C and 40 bar H_2, 11 wt.% LA in GVL) [28]. LA hydrogenation studies in water as solvent comparing Ru/TiO_2 (P25) and Ru/ZrO_2 catalysts (both 1 wt.% Ru) in a batch set-up at 70 °C revealed that quantitative LA conversion could be achieved within 4 h with the Ru/TiO_2 catalysts, while Ru/ZrO_2 was less active and 92% LA conversion was observed after 6 h [29]. This enhanced hydrogenation activity of Ru/TiO_2 was attributed to a better Ru dispersion on TiO_2. Recently, some of us reported on a catalyst screening study for LA hydrogenation in water (90 °C, 45 bar H_2) using a wide range of supported Ru-catalysts (1 wt.% Ru on C, CNT, Al_2O_3, TiO_2, ZrO_2, Nb_2O_5 and H-Beta-12.5) and again found that TiO_2 (anatase form, A100) performed better than for Ru/ZrO_2 in this solvent [30]. The results listed above thus show the potential of TiO_2 as support for this reaction and an overview of titania-supported Ru catalysts for LA hydrogenation is given in Table 1.

Some of these studies have shown that the phase composition of the TiO_2 support (anatase, rutile and combinations thereof) influences catalyst performance. For example, Al-Shaal et al. investigated the hydrogenation of LA using Ru supported on rutile and P25 TiO_2 (a 75:25 mixture of anatase-rutile) supports in ethanol and ethanol–water mixtures [25]. The rutile-supported catalyst gave no LA conversion in neither ethanol nor ethanol–water, whereas Ru/TiO_2 (P25) showed much better performance. Furthermore, a comparison of the catalytic transfer hydrogenation of levulinate esters using $Ru(OH)_x/TiO_2$ [31], with anatase, rutile and anatase-rutile titanias, showed the anatase-rutile-based catalyst to perform best (86% for TiO_2(A); > 99% for TiO_2(R) and TiO_2(A75:R25)). Recently, Ruppert et al. reported a detailed study on the influence of various TiO_2 supports (anatase, rutile and mixtures thereof) on the Ru-catalyzed LA hydrogenation [32]. A

Table 1
Literature overview on LA hydrogenation using Ru/TiO_2 catalysts in batch and continuous flow set-ups.

Catalyst	TiO_2 support	Ruthenium precursor	Solvent	T (°C)	H_2 pressure (bar)	Reaction time (h)	LA conversion (%)	GVL Selectivity (%)	Ref.
	Batch								
$Ru_{1\%}/TiO_2$	P25 (A75:R25)[a]	$RuNO(NO_3)_3$	dioxane	200	40	4	100	92	[19]
$Ru_{1\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	dioxane	200	40	0.6	100	99	[20]
$Ru_{5\%}/TiO_2$	Tronox (R100)	$Ru(acac)_3$	ethanol	130	12	2.7	n.r.[d]-	–	[25]
			ethanol + H_2O				n.r.[d]-	–	
$Ru_{5\%}/TiO_2$	P25 (A75:R25)	$Ru(acac)_3$	ethanol	130	12	2.7	68	92	[25]
			ethanol + H_2O				81	88	
$Ru_{2\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	H_2O	130	40	0.5	100	99	[29]
$Ru_{1\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	H_2O	130	40	3	95	99	
$Ru_{0.5\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	H_2O	70	40	4	100	99	
$Ru_{1\%}/TiO_2$	(A100)	$RuCl_3$	H_2O	90	45	5	93	85	[30]
$Ru(OH)_x/TiO_2$	ST − 01[b] (A100)	$RuCl_3$	2-propanol	90	–	24	86	76	[31]
$Ru(OH)_x/TiO_2$	TTO − 55[c](R100)	$RuCl_3$					> 99	49	
$Ru(OH)_x/TiO_2$	P25 (A75:R25)	$RuCl_3$					> 99	80	
$Ru_{1\%}/TiO_2$	P25 (A75:R25)	$Ru(acac)_3$	H_2O	30	50	1	64	62	[32]
				70			99	95	
$Ru_{1\%}/TiO_2$	P90 (A90:R10)	$Ru(acac)_3$	H_2O	30	50	1	60	60	[32]
				70			100	100	
$Ru_{1\%}/TiO_2$	(R100)	$Ru(acac)_3$	H_2O	30	50	1	40	40	[32]
				70			95	83	
$Ru_{1\%}/TiO_2$	ST-01 (A100)	$Ru(acac)_3$	H_2O	30	50	1	54	48	[32]
				70			99	93	
	Continuous flow								
$Ru_{0.4\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	H_2O	50	24	–	7	36	[33]
$Ru_{5\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	H_2O	270	n.r.[d]-	n.r.[d]-	52.6	44.3	[34]
$Ru_{1\%}/TiO_2$	P25 (A75:R25)	$RuCl_3$	H_2O	90	45	6	25	54	[35]

[a] A: Anatase, R: rutile.

[b] ST-01: anatase TiO_2, $S_{BET} = 339\ m^2/g$ (Ishihara Sangyo Co., Ltd.).

[c] TTO-55: rutile TiO_2, $S_{BET} = 47\ m^2/g$ (Ishihara Sangyo Co., Ltd.).

[d] Not reported.