Catalysis Science & Technology

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ROYAL SOCIETY OF CHEMISTRY

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ARTICLE

Efficient aqueous hydrogenation of levulinic acid to γ-valerolactone over highly active and stable ruthenium catalyst

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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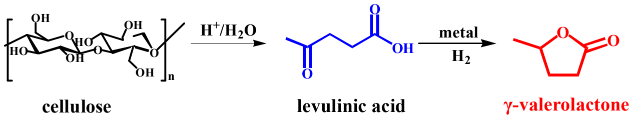
Efficient aqueous hydrogenation of levulinic acid over supported catalysts is of fundamental and industrial interests but highly challenging. For Ru/γ-Al_2O_3 catalysts, the primary problems are the low activity and stability aroused from the inhomogeneous dispersion of Ru and unstable nature of γ-Al_2O_3 in water. In this work, an integrated strategy was proposed for developing a highly active and stable catalyst for aqueous hydrogenation of LA to GVL. By modification with 3-aminopropyltriethoxysilane (KH550), the abundant surface Al-OH groups of γ-Al_2O_3 were transformed into stable Al-O-Si structure, while ruthenium active centres were bonded to γ-Al_2O_3 surface via coordination with amino ligands of KH550. This modification favours the formation of highly dispersed Ru centres with electron-rich state, leading to a superior activity at temperatures as low as 25 °C (GVL yield of 99.1%, TOF of 306 h^{-1}) and high stability.

Introduction

Currently, the development of economy and the progress of human society are at the expense of great consumption of non-renewable energy and the environmental pollution. It is becoming necessary to develop safe, sustainable and environment friendly resources for industrial production.[1] Biomasses are considered to be ideal complements to fossil resources in the production of chemicals and fuels.[2] Among them, levulinic acid (LA) is regarded as one of the most important renewable platform molecules, as it can be easily and economically produced from lignocellulose by an efficient hydrolysis,[3] and can further convert to many value-added products (as seen Scheme 1). The hydrogenation of LA to γ-valerolactone (GVL) is a key reaction in the sustainable biomass conversion,[4] since GVL is a sustainable liquid for widely producing fuel energy, carbon based chemicals and intermediate compounds for various solvents.[5]

In the process of LA production, water is essential as it acts as a solvent, a reactant or a product. The downstream solution from the conversion of cellulose to LA contains a great deal of water (typically more than 70%).[6] This indicates that the aqueous hydrogenation of LA is preferable due to the energy-intensive separation of LA from the upstream solution is not necessary. A series of homogenous catalysts with high activity was developed for aqueous hydrogenation of LA.[7] The heterogeneous catalysts, typically metal supported catalysts, are more favourable since they are easy to recycle from the products.[8-9]

However, many support materials including Al_2O_3, SiO_2, MCM-41, SBA-15, TiO_2 and CeO_2, are unstable in aqueous environment, especially in acidic aqueous environment due to the existence of surface hydroxyl groups (-OH)[10-11]. The instability of supports would lower the catalyst efficiency or even lead to the deactivation of catalysts. Particularly for γ-Al_2O_3, it readily rehydrates to form boehmite (γ-AlOOH) in the presence of water because the surface of γ-Al_2O_3 is rich in OH groups.[10a] This phase transformation is demonstrated to decline drastically the activity and stability of metal/γ-Al_2O_3 catalyst.[12-14] Meanwhile, the metal supported catalysts incline to suffer drastic deactivation for the industrial LA hydrogenation process due to the corrosion of H_2SO_4, which is typically used for the production LA from cellulose.[15] Moreover, the electronic properties of active metal centres on support were considered to be crucial for many reactions,[16] especially for the hydrogenation of carbonyl compounds. It has been reported that in the hydrogenation process of carbonyl groups (-C=O), the metal centres with electron-rich nature favour the activation of C=O bond, as the backbonding of d electron(s) from such metal centres to π orbitals of C=O bond are favorable.[17] Hence, it would be desirable but more challenging to prepare γ-Al_2O_3 supported metal catalysts with high stability and activity. We noticed that the feasible surface modification by silylation reaction,[18] which is a typical method to



Scheme 1 The reaction pathway of cellulose to γ-valerolactone

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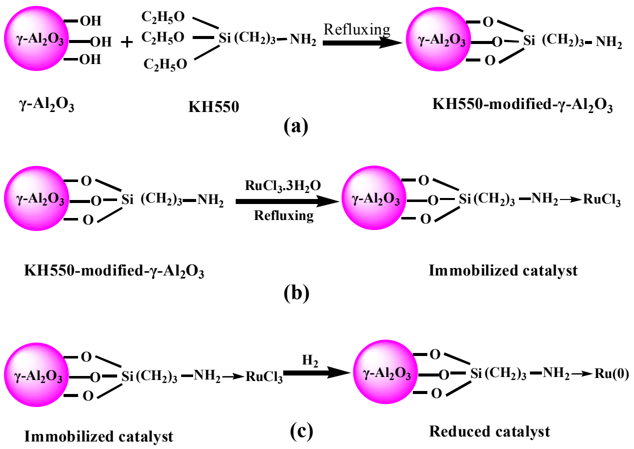
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x modulate the surface properties of metallic oxide, [19] can be applied for modification Ru/γ-Al_2O_3 catalyst to improve its catalytic properties and stability. Because of its special structure, the silane coupling agent 3-aminopropyltriethoxysilane (KH550) was gained more attention, which has two different functional groups, namely, triethoxy groups at one end, and functional group (-NH_2) at the other end.[20] By modification, the abundant Al-OH groups on the surface of γ-Al_2O_3 could form stable Al-O-Si structure via the chemical reaction with the triethoxy groups in KH550 (as shown in Scheme 2a). This would greatly alleviate the rehydration of γ-Al_2O_3 in water and improve its stability. More importantly, -NH_2 group can be introduced through this modification, which offers ideal hosts for uniformly distribution of Ru atom(s) to improve the dispersion of Ru NPs on the surface of the support (as shown in Scheme 2b). Specifically, the anchoring effect of -NH_2 groups favours the formation of electron-rich state of Ru as they are strong electron donors.

In this work, an integrated strategy for developing a highly active and stable Ru/γ-Al_2O_3 catalyst for aqueous hydrogenation of LA to GVL was developed. An immobilized ruthenium catalyst (i-Ru-NH_2-γ-Al_2O_3) was prepared by bonding ruthenium active sites on the surface of KH550-modified γ-Al_2O_3 through coordination with amino ligands. The reduced Ru-NH_2-γ-Al_2O_3 (r-Ru-NH_2-γ-Al_2O_3) catalyst displayed a superior low-temperature activity and high-temperature stability in the aqueous hydrogenation of LA to GVL. A TOF of 306 h^{-1} and a yield of 99.1% for GVL were obtained at room temperature (25 ^oC). Moreover, the activity of the r-Ru-NH_2-γ-Al_2O_3 catalyst was maintained at a high level after it was reused more than ten times under severe conditions (130 ^oC).

Results and discussion

To improve the stability of γ-Al_2O_3 and provide ligands for loading metal sites, γ-Al_2O_3 was firstly modified by a silylation reaction between the surface hydroxyl groups and -C_2H_5O groups in KH550 (as shown in Scheme 2a). The successful incorporation of organic carbon chain and amino-terminal silanes onto the surface of γ-Al_2O_3 was verified by Fourier transform infrared spectroscopy (FTIR) (as shown in Figure 1). In the spectrum of KH550-modified-γ-Al_2O_3, the strong stretching vibration of Si-O-Al bonds appeared at 960-1150 cm^{-1}, provide direct evidence for the efficient grafting of KH550 onto the surface of γ-Al_2O_3.[21a] Two bands at 2924 and 2850 cm^{-1} are assigned to the symmetric and antisymmetric vibration of -CH_2 connecting to the long silane chains, a pair of bands at 1483 and 1405 cm^{-1} are ascribed to -CH_2 bending vibrations.[22] The characteristic N-H bending vibration and C-N stretching vibration at 1570 and 1326 cm^{-1} reveal the introduction of amino groups.[23] This result is further verified by X-ray photoelectron spectroscopy (XPS) analysis (Figure S1). Additional signals of Si and N are clearly observed in the XPS spectrum of KH550-modified-γ-Al_2O_3 relative to γ-Al_2O_3. In addition to the above infrared absorption bands, the bands at 500-900, 3430 and 1640 cm^{-1} in the two samples are ascribed to the stretching vibration of Al-O bond, the stretching and bending vibrations of adsorbed water molecules, respectively.[21]



Scheme 2 (a) mechanism of surface modification by silane coupling agent,(b)synthesis of immobilized Ru-based catalyst,(c) immobilized Ru-based catalyst was reduced

The hydrothermal stability of KH550-modified γ-Al_2O_3 was tested and compared with unmodified γ-Al_2O_3 (Figure 2). The significant phase transformation of unmodified γ-Al_2O_3 to γ-AlOOH (Figure 2e) was observed after a hydrothermal process under 150 ^oC for 24 h, whereas KH550-modified-γ-Al_2O_3 maintained its structure under the same conditions (Figure 2b). Moreover, prolonging the hydrothermal treating time to 48 h at 150 ^oC, the phase evolution of KH550-modified-γ-Al_2O_3 (Figure 2c) to γ-AlOOH was also not detected. This result indicates that the hydrothermal stability of KH550-modified-γ-Al_2O_3 was greatly improved with respect to the unmodified γ-Al_2O_3. In addition, the ability of resistance to high temperature was investigated. The KH550-modified-γ-Al_2O_3 was calcined under 300 ^oC for 2 h, followed by a hydrothermal processing for 48 h under 150 ^oC. The samples did not convert to γ-AlOOH after the treatments (Figure 2d), suggesting the superior stability of KH550-modified-γ-Al_2O_3.

The surface of KH550-modified-γ-Al_2O_3 has amino functional

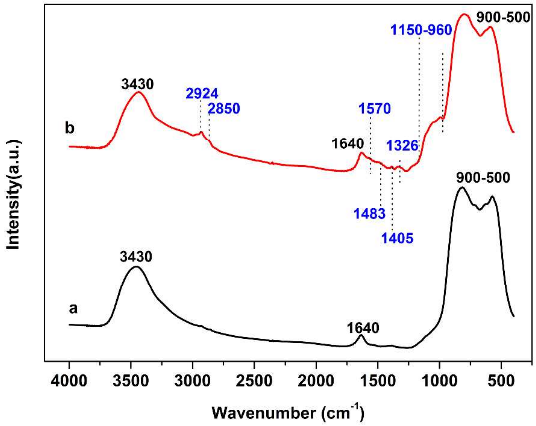


Figure 1 The FTIR spectra of (a): unmodified γ-Al_2O_3 (b) KH550-modified-γ-Al_2O_3

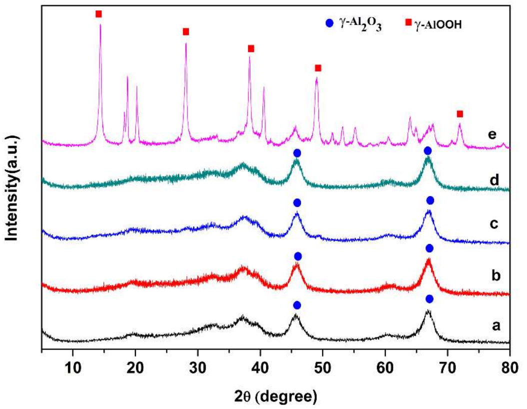


Figure 2 The stability of γ-Al_2O_3 and the KH550-modified-γ-Al_2O_3. a: γ-Al_2O_3; b: KH550-modified-γ-Al_2O_3 hydrothermal at 150 °C for 24 h; c: KH550-modified-γ-Al_2O_3 hydrothermal at 150 °C for 48 h; d: KH550-modified-γ-Al_2O_3 calcined at 300 °C for 2 h, hydrothermal at 150 °C for 48 h; e: γ-Al_2O_3 hydrothermal at 150 °C for 24 h.

groups ($-NH_2$) located at the end of organic chains. The amino group ($-NH_2$) is a strong ligand for metal centres due to the existence of isolated electron pairs. Hence, $-NH_2$ groups on the surface of KH550-modified-γ-Al_2O_3 can interact with metal complexes and act as anchoring sites for metal complexes, facilitating the high dispersion of Ru complex on the surface of support (as seen in Scheme 2b).

FTIR and XPS were carried out to understand the structure of i-Ru-NH_2-γ-Al_2O_3 catalyst. The FTIR spectrum of i-Ru-NH_2-γ-Al_2O_3 (Figure 3A (b)) is similar to that of KH550-modified-γ-Al_2O_3 (Figure 1b). The amino-terminal silanes (at 1570 and 1326 cm^{-1}) and organic carbon chain (at 2924, 2850, 1405 and 1483 cm^{-1}) were observed in the spectrum of i-Ru-NH_2-γ-Al_2O_3, whereas these groups are absence in that of Ru/γ-Al_2O_3 (Figure 3A (a)). XPS results also corroborate the presence of NH_2-Si-O-Al structure after loading Ru. As shown in Figure 3B (b), the N and Si signals appear in the spectrum of i-Ru-NH_2-γ-Al_2O_3 catalyst, while these two additional signals are absence in that of Ru/γ-Al_2O_3 (Figure 3B (a)). Additionally, a positive shift of 0.24 eV for N1s XPS signal (Figure S 2b) was observed in i-Ru-NH_2-γ-Al_2O_3 compared with the N 1s XPS of KH550-modified-γ-Al_2O_3 (Figure S2a), indicating the coordination of Ru^{3+} and $-NH_2$ group.[24]

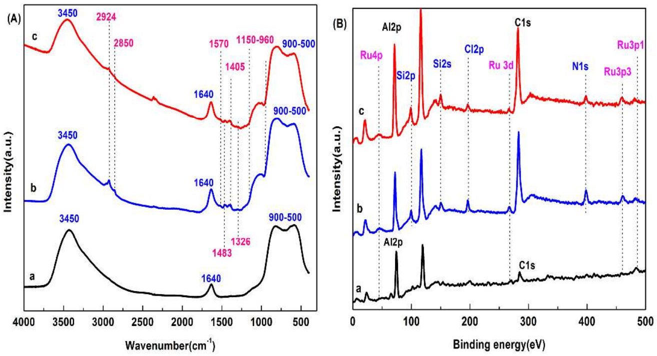


Figure 3 FTIR spectra (A) a: Ru/γ-Al_2O_3, b: fresh Ru-NH_2-γ-Al_2O_3, c: reduced Ru-NH_2-γ-Al_2O_3 and Full range XPS spectrum (B) a: Ru/γ-Al_2O_3, b: fresh Ru-NH_2-γ-Al_2O_3, c: reduced Ru-NH_2-γ-Al_2O_3

XRD, TEM and HRTEM characterizations were performed (Figure 4) to understand the dispersion and morphology of Ru/γ-Al_2O_3 and i(r)-Ru-NH_2-γ-Al_2O_3 catalysts. The sizes of Ru species are below the detection limit of XRD in fresh and reduced Ru-NH_2-γ-Al_2O_3 catalyst (Figure 4A), while the diffraction peaks of RuO_2 or Ru NPs in fresh and reduced Ru/γ-Al_2O_3 were observed respectively (Figure 4B). This result indicates that the Ru species in i(r)-Ru-NH_2-γ-Al_2O_3 are highly dispersed. HRTEM analysis exhibits that the Ru NPs are smaller on the surface of KH550-modified-γ-Al_2O_3 than those on γ-Al_2O_3 (Figure 4C and D). The corresponding size distribution histogram of Ru NPs shows that r-Ru-NH_2-γ-Al_2O_3 owns a super small average size of 1.2 nm, while a large average size of 12.3 nm was observed on Ru/γ-Al_2O_3, although the surface areas and pore volumes of the two supports are at the same level (Table S1). Primo et al. demonstrated that Ru NPs with small size are more active than larger Ru NPs in the hydrogenation of -C=O group.[25]

The hydrogenation of LA to GVL over r-Ru-NH_2-γ-Al_2O_3 and Ru/γ-Al_2O_3 catalysts was investigated (Table 1). All Ru-based catalysts enable a quantitative conversion of LA to GVL at 130 °C (Table 1, entries 1, 2). However, a drastic difference appeared in the catalytic activity as the reaction temperature decreased to 70 °C (entries 3, 4). The r-Ru-NH_2-γ-Al_2O_3 catalyst exhibits a much higher activity than Ru/γ-Al_2O_3 catalyst. The TOF value on r-Ru-NH_2-γ-Al_2O_3 catalyst is 3355 h^{-1}, which is about 8 times of the value on

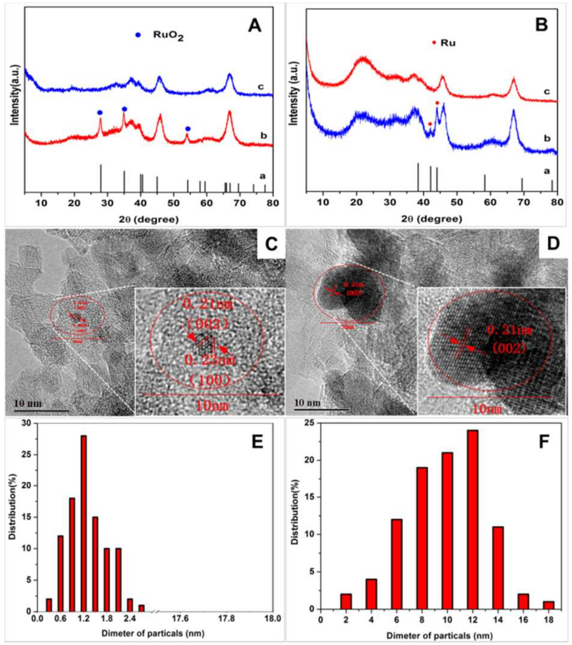


Figure 4 XRD of (A) : (a) RuO_2 (b) Fresh Ru/γ-Al_2O_3 (c) Fresh Ru-NH_2-γ-Al_2O_3; (B): (a) Ru metal (b) Reduced-Ru/γ-Al_2O_3 (c) Reduced- Ru-NH_2-γ-Al_2O_3; HRTEM and particle size distribution histogram of r-Ru-NH_2-γ-Al_2O_3 catalyst(C,E) and Ru/γ-Al_2O_3 (D,F)

Table 1. Catalytic hydrogenation of LA to GVL[a]

Entry	Catalyst	T/°C	H_2(MPa)	t/h	LA Conversion%	GVL Selectivity%
1[b]	r-Ru-NH_2-γ-Al_2O_3	130	4	0.5	100	99.8
2[b]	Ru/γ-Al_2O_3	130	4	0.5	100	99.9
3	r-Ru-NH_2-γ-Al_2O_3	70	4	1.0	100	99.9
4	Ru/γ-Al_2O_3	70	4	1.0	25.7	99.8
5	r-Ru-NH_2-γ-Al_2O_3	40	4	4	99.0	99.9
6	Ru/γ-Al_2O_3	40	4	4	39.5	99.8
7	r-Ru-NH_2-γ-Al_2O_3	25	4	13	99.1	99.9
8	Ru/γ-Al_2O_3	25	4	13	43.1	99.9

Reaction conditions: 0.1 g 2 wt% reduced Ru-catalyst, a: 12 g 16.7 wt% LA/water solution, b: 15 g 33.3 wt% LA/water solution, the carbon balance for each run exceeds 96%. The effect of hydrogen pressure on LA conversion was displayed in Figure S3.

Ru/γ-Al_2O_3 (Figure 5). To further investigate the low temperature activities of the r-Ru-NH_2-γ-Al_2O_3 catalyst, the reactions were performed at 40 °C and 25 °C, respectively (Table 1 and Figure S4). The r-Ru-NH_2-γ-Al_2O_3 catalyst maintained a high catalytic efficiency (Table 1, entries 5, 7), whereas a drastic decrease in the activity was observed for Ru/γ-Al_2O_3 (Table 1, entries 4, 8). Moreover, the attained TOF values over r-Ru-NH_2-γ-Al_2O_3 are about 7 times of those over Ru/γ-Al_2O_3 (Figure 5). This result clearly revealed the higher intrinsic activity of r-Ru-NH_2-γ-Al_2O_3 catalyst. Efficient conversion of LA to GVL on r-Ru-NH_2-γ-Al_2O_3 catalyst at low temperature is considerably significant as the corrosion of LA/water solution to the reactor would be greatly alleviated.

The superior hydrogenation activity of r-Ru-NH_2-γ-Al_2O_3 catalyst was attributed to the excellent dispersion of Ru NPs on the surface of KH550-modified-γ-Al_2O_3. Moreover, we noticed that the organic carbon chains $(CH_2)_3$- and amino groups (-NH_2) of i-Ru-NH_2-γ-Al_2O_3 were reserved after reduction, (Figure 3A (c) and Figure3B (c)).The presence of amino ligands might promote the catalytic behaviour by increasing the electron cloud density of Ru centers.[24] To confirm this hypothesis, the chemistry of metallic Ru NPs (Ru^0) on KH550-modified γ-Al_2O_3 and γ-Al_2O_3 were studied by XPS (Figure 6). The $Ru3d_{5/2}$ XPS peak for Ru^0 is reported to be at 280.2 eV.[26] Interestingly, a negative correlation between low-temperature activity and the binding energy (BE) values of Ru^0 NPs were observed. The BE value of Ru^0 NPs on KH550-modified γ-Al_2O_3 is 279.55 eV (Figure 6a), while that on γ-Al_2O_3 is 280.74 eV (Figure 6b). Additionally, a positive shift of 0.21 eV was obtained for N1s in r-Ru-NH_2-γ-Al_2O_3 (Figure S2d). This result reflected that a few electrons were transferred from amino ligands to Ru^0. The sufficient electrons on Ru sites are in favour of π-back bonding to C=O, which is effective for the activation of C=O bonds.

The catalyst stability is a primary challenge for the aqueous hydrogenation of LA over Ru/γ-Al_2O_3 catalyst for the unstable

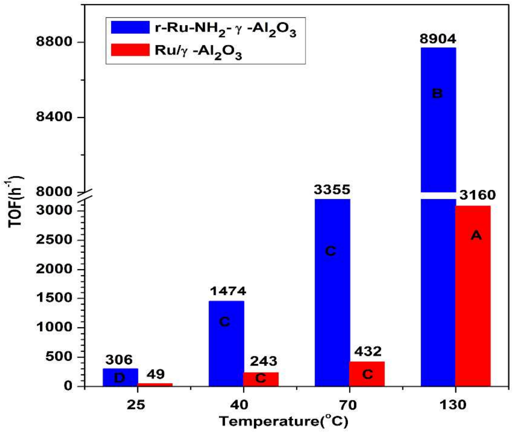


Figure 5 The TOF values of r-Ru-NH_2-γ-Al_2O_3 and Ru/γ-Al_2O_3 Reaction conditions: 0.1 g 2 wt% Ru-catalyst, 4.0 MPa H_2 (A) 15 g 33.3 wt% LA/water solution, t=15 min, (B): 15 g 33.3 wt% LA/water solution, t=10 min; (C): 12 g 16.7 wt% LA/water solution, t=15 min; (D): 12 g 16.7 wt% LA/water solution, t=90 min

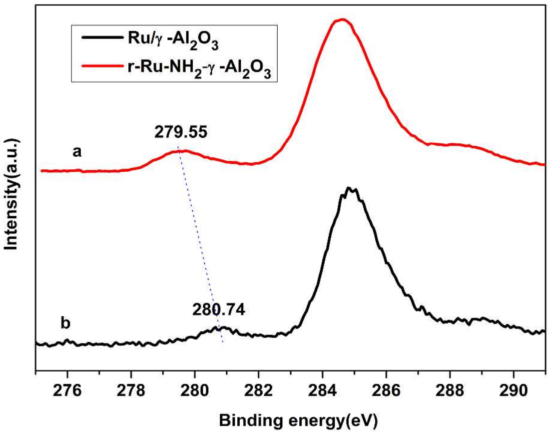


Figure 6 XPS spectra of $Ru3d_{5/2}$ in (a) r-Ru-NH_2-γ-Al_2O_3 (b) Ru/γ-Al_2O_3

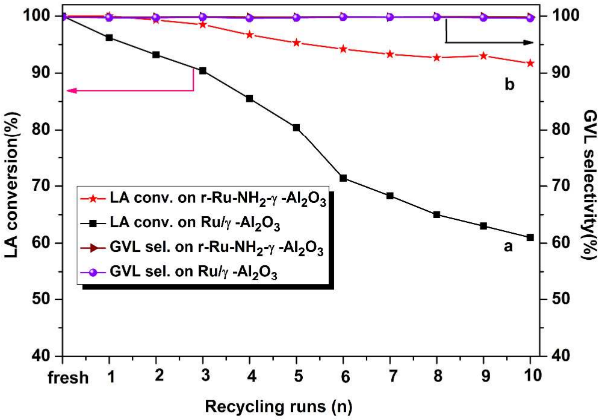


Figure 7 Stability of (a) r-Ru-NH$_2$-γ-Al$_2$O$_3$ and (b) Ru/γ-Al$_2$O$_3$ Reaction conditions: Cat. 0.1 g, LA 5 g, H$_2$O 10 g, H$_2$= 4.0 MPa, T=130°C t=0.5 h

nature of γ-Al$_2$O$_3$. The recyclability of r-Ru-NH$_2$-γ-Al$_2$O$_3$ and Ru/γ-Al$_2$O$_3$ catalysts was investigated. At ambient temperature the r-Ru-NH$_2$-γ-Al$_2$O$_3$ exhibited excellent stability and no decline in the activity was observed after running for 9 recycles (Figure S5; the selectivity was 99.9% Figure S6). To further investigate the stability of r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst under severe conditions, the reactions were performed at 130 °C and the results are illustrated in Figure 7. Compared with Ru/γ-Al$_2$O$_3$ catalyst, the r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst displayed a more excellent stability under the reaction conditions. The activity was maintained at a high level after it was reused more than ten successive recycling runs. Nevertheless, the activity of Ru/γ-Al$_2$O$_3$ catalyst was decreased drastically after second runs under the same reaction conditions. To investigate the possible metal leaching during the reaction, the Ru contents of r-Ru-NH$_2$-γ-Al$_2$O$_3$ and Ru/γ-Al$_2$O$_3$ catalysts before and after 10 runs were detected by ICP-OES (Table S2). As shown in Table S2, a slight leaching of Ru for both catalysts was observed. Furthermore, a comparison of the XRD patterns of the spent catalyst used for ten runs (r-Ru-NH$_2$-γ-Al$_2$O$_3$) with that of the fresh one suggested that the conversion of KH550-modified-γ-Al$_2$O$_3$ to γ-AlOOH was negligible (Figure S7d), while the support of γ-Al$_2$O$_3$ in Ru/γ-Al$_2$O$_3$ catalyst transformed into γ-AlOOH completely after second runs (Figure S7e). Formic acid is formed in the production process of LA from cellulose, while sulfuric acid is a commonly-applied acid catalyst in the conversion of cellulose into LA. Hence, formic acid and sulfuric acid were chosen to investigate the acid resistance of the r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst (Table S3 in ESI). The activity of r-Ru-NH$_2$-γ-Al$_2$O$_3$ maintained after the addition of HCOOH (Table S3 entries 3-5). Moreover, the activity decreased slightly with the increasing concentration of H$_2$SO$_4$ in the reaction system (Table S3 entries 6-9). Typically, the concentration of 0.5 M for H$_2$SO$_4$ is commonly applied in the production process of LA from cellulose [15]. Notably, a high LA conversion can be achieved over the r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst with 0.5 M H$_2$SO$_4$ in the reaction. These results showed the potential of the r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst in the industrial LA hydrogenation process. It is hence conclude that r-Ru-NH$_2$-γ-Al$_2$O$_3$ is a more outstanding hydrogenation catalyst in terms of its reactivity and reusability.

Conclusions

In summary, an integrated strategy for developing a superior active and stable catalyst for aqueous hydrogenation of LA to GVL was proposed. By modification with KH550, the abundant surface Al-OH groups of γ-Al$_2$O$_3$ were transformed into stable Al-O-Si structure, which enhances largely the stability of γ-Al$_2$O$_3$ in water. More importantly, there exists a strong coordination between the amino groups at the end of KH550 and ruthenium species, namely, the -NH$_2$ groups offered ideal hosts for dispersing Ru species and modifying their electronic properties. As a result, highly dispersed subnano sized Ru centers with electron-rich state were formed on the surface of KH550-modified-γ-Al$_2$O$_3$. These Ru centers exhibit superior activities in the aqueous hydrogenation of LA to GVL at temperatures as low as 25 °C. A yield of 99.1% to GVL was obtained at ambient temperature (25 °C), leading to a TOF of 306 h^{-1}. Besides its effectiveness, the r-Ru-NH$_2$-γ-Al$_2$O$_3$ catalyst displayed an excellent stability compared with the Ru/γ-Al$_2$O$_3$ catalyst in the hydrogenation process. It can be reused at least ten times without deactivation under drastic reaction conditions (130 °C).

Acknowledgements

The authors gratefully acknowledge the financial support of the Major State Basic Research Development Program of China (973 Program) (no. 2012CB215305).

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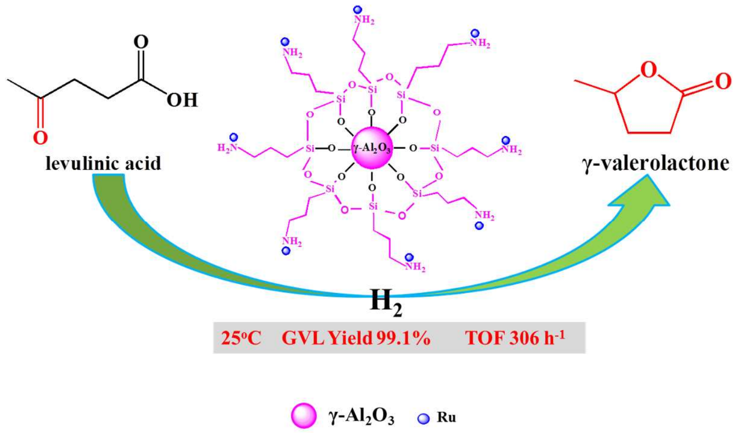

Efficient aqueous hydrogenation of levulinic acid to γ-valerolactone over highly active and stable immobilized ruthenium catalyst with a GVL yield of 99.1 mol% at 25 ^{o}C .