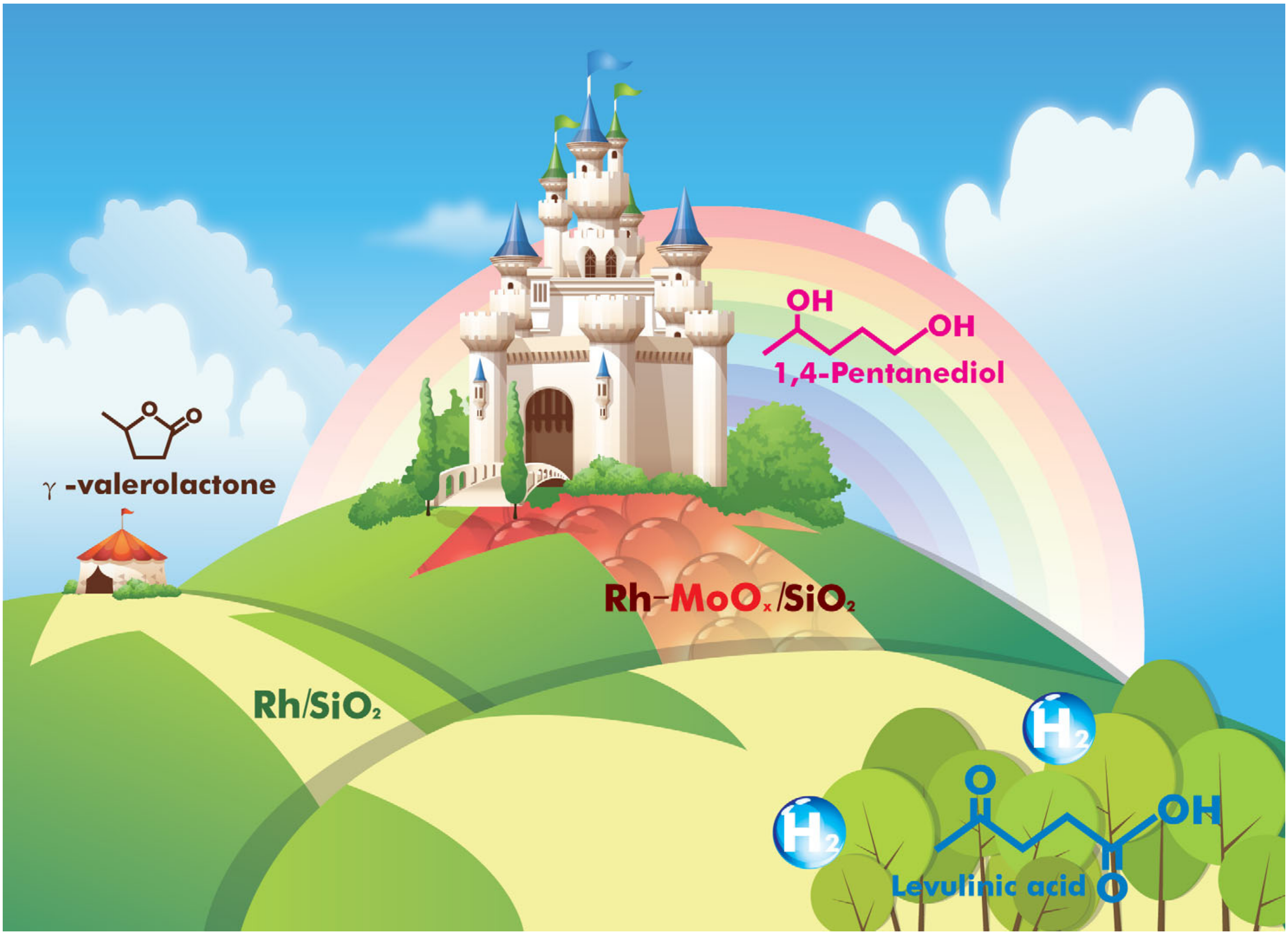

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Aqueous phase hydrogenation of levulinic acid to 1,4-pentanediol

Mo-modified Rh/SiO$_2$ was first reported to be effective for the aqueous-phase selective hydrogenation of levulinic acid to 1,4-pentanediol. Over this catalyst, high levulinic acid conversion (100%) and 1,4-pentanediol yield (70%) can be achieved at low temperature (353 K).

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Aqueous phase hydrogenation of levulinic acid to 1,4-pentanediol†

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For the first time, Mo modified Rh/SiO_2 was found to be an effective catalyst for the aqueous phase selective hydrogenation of levulinic acid to 1,4-pentanediol. Over such a catalyst, high levulinic acid conversion (100%) and 1,4-pentanediol yield (70%) can be achieved at low temperature (353 K).

With the increasing social concern about the energy and environmental problems, the catalytic conversion of renewable biomass to fuel[1,2] and chemicals[3,4] has drawn a lot of attention. Carboxylic acids are a family of chemicals which can be produced by the biological and chemical treatment of biomass. The selective hydrogenation of carboxylic acids to their corresponding alcohols or diols is a very important reaction in the biomass refinery. For example, the selective hydrogenation of acetic acid, propanoic acid, lactic acid and succinic acid from the fermentation of biomass can produce ethanol,[5] propanol,[6] 1,2-propanediol[7] and 1,4-butanediol.[8–10] These compounds can be used as biofuel or as monomers for the production of polyesters. Secondly, the selective hydrogenation of fatty acids from the hydrolysis of triglycerides can produce fatty alcohols which are widely used in lubricants, non-ionic surfactants, perfumes, resins, cosmetics, and conditioners.[11,12] As the third application, the selective hydrogenation can be used for the removal of carboxylic acids in the bio-oil from the pyrolysis or liquefaction of biomass. These acids increase the acid value of bio-oil and make it corrosive. As a result, the bio-oil cannot be directly used as fuel without hydrotreating. In some reports in the literature,[13] the hydrogenation of carboxylic acids was considered to be one of the slowest steps in the hydrotreatment of bio-oils. To fulfill the need for a real application, more effective catalysts should be developed.

Levulinic acid is a very important platform chemical which can be produced by the chemical treatment of lignocellulose.[14,15] As the product of the simultaneous hydrogenation of the carbonyl and carboxyl groups in levulinic acid, 1,4-pentanediol can be used as a potential monomer for the production of polyesters.[4,16] However, due to the preferable intermolecular esterification, most of the research regarding the hydrogenation of levulinic acid was focused on its conversion to γ-valerolactone (GVL)[16,17] which can be used as fuel additive or feedstock for biojet fuels.[18] For the selective hydrogenation of levulinic acid to 1,4-pentanediol, only homogenous organometallic catalysts based on $Ru(acac)_3$ and a triphos ligand have been reported.[19–21] This system has drawbacks of non-reusability, special handling of metal complexes and the high cost of phosphine ligands. As a solution, Cao *et al.*[22] found that 1,4-pentanediol can be produced by the selective hydrogenation of GVL over a copper zirconia catalyst. To the best of our knowledge, there is no report about the direct selective hydrogenation of levulinic acid to 1,4-pentanediol over a heterogeneous catalyst. In this work, a Mo modified Rh/SiO_2 (Rh–MoO_x/SiO_2) catalyst was first used for the aqueous phase hydrogenation of levulinic acid and exhibited high selectivity to 1,4-pentanediol at low temperature (353 K). The reaction pathway and the reason for the promotion effect of Mo were explored. The possibility of using the Rh–MoO_x/SiO_2 catalyst for the aqueous phase selective hydrogenation of other biomass derived carboxylic acids was also investigated.

From the results shown in Table 1, we can see that the Rh/SiO_2 catalyst is very active for the aqueous phase hydrogenation of levulinic acid. Under the investigated conditions (353 K, 6 MPa), the levulinic acid is completely converted with GVL as the major product. The yield of 1,4-pentanediol in the liquid product was very low (1%). After modification with a small amount of Mo, the levulinic acid conversion over the Rh/SiO_2 catalyst was unchanged

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Table 1 Results for the hydrogenation of levulinic acid or GVL over different catalysts. Reaction conditions: 353 K, 6 MPa, 2.0 g catalyst, 10% levulinic acid (or GVL) aqueous solution flow rate 0.08 mL min^{-1}, H_2 flow rate 60 mL min^{-1}

Entry	Catalyst	Mo/M atomic ratio (M: Rh, Ir, Pt, Pd, Ru)	Conversion of levulinic acid or GVL (%)	Selectivity[a] (%)					
				1,4-PeD	2-Peol	1-Peol	GVL	MTHF	Others
1	4%Rh/SiO_2	0	100	1.2	0.4	0	76.8	0.1	21.5
2	4%Rh–MoO_x/SiO_2	0.07	100	45.3	8.9	5.2	34.9	2.0	3.7
3	4%Rh–MoO_x/SiO_2	0.13	100	70.0	13.2	2.6	1.1	4.7	8.4
4	4%Rh–MoO_x/SiO_2	0.25	100	65.2	5.8	0.7	20.2	1.3	6.7
5	4%Rh–MoO_x/SiO_2	0.50	100	38.5	3.4	0.3	24.5	1.7	31.5
6	MoO_x/SiO_2	—	1.5	0	0	0	0	0	100
7	4%Rh/SiO_2 + MoO_x/SiO_2[b]	0.13	100	1.8	0.4	0.1	80.8	0.2	16.9
8	4%Ir–MoO_x/SiO_2	0.13	100	52.9	15.1	0.3	18.0	0.4	13.2
9	4%Pt–MoO_x/SiO_2	0.13	100	13.3	0.8	0.2	56.8	0.0	28.9
10	4%Ru–MoO_x/SiO_2	0.13	100	15.8	1.6	0	79.2	2.5	0.9
11	4%Pd–MoO_x/SiO_2	0.13	100	0.3	0	0.1	77.2	0.5	21.9
12[c]	4%Rh–MoO_x/SiO_2	0.13	100	28.3	8.9	1.7	58.1	1.9	1.1
13[c]	4%Rh–MoO_x/SiO_2	0.13	86.2	7.8	2.6	0.5	87.5	0.5	1.1
14[d]	4%Rh–MoO_x/SiO_2	0.13	68.2	61.8	9.0	4.7	—	5.5	19.0

[a] 1,4-PeD = 1,4-pentanediol; 2-peol = 2-pentanol; 1-peol = 1-pentanol; GVL = γ-valerolactone; MTHF = 2-methyl-tetrahydrofuran; others means alkanes and some unidentified products (detailed information is provided in Table S1 of ESI). [b] 4%Rh/SiO_2 + MoO_x/SiO_2 means the physical mixture of the 4%Rh/SiO_2 and MoO_x/SiO_2 at the mass ratio of 1 : 1. [c] Experiment 12 and 13 were carried out with 0.5 g and 0.2 g 4%Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) catalyst, respectively. [d] Experiment 14 was carried out with 10% GVL aqueous solution.

but the main hydrogenation product shifted from GVL to 1,4-pentanediol. The promotion effect of Mo was most evident when the Mo/Rh atomic ratio was between 0.13 and 0.25. Further increase of Mo/Rh atomic ratio led to the decrease of selectivity towards 1,4-pentanediol and the increase of the GVL yield. Moreover, we also studied the catalytic performances of MoO_x/SiO_2 and its physical mixture with Rh/SiO_2. To facilitate the comparison, the Rh and/or Mo content in these catalysts were kept the same as the ones in 4%Rh–MoO_x/SiO_2 (Mo/Rh = 0.13). As shown in Table 1, the MoO_x/SiO_2 catalyst is inactive for the hydrogenation of levulinic acid, while the catalytic performance of the physical mixture of Rh/SiO_2 and MoO_x/SiO_2 is almost the same as that of Rh/SiO_2. From these results, the excellent catalytic performance of Rh–MoO_x/SiO_2 for the hydrogenation of levulinic acid can be explained by the synergy effect between the closely contacting Rh and Mo species.

The performances of various Mo modified noble metal (M–MoO_x/SiO_2, M = Rh, Ir, Pt, Ru, Pd) catalysts in the aqueous phase hydrogenation of levulinic acid were compared (entries 3, 8–11 in Table 1). Among these catalysts, Rh–MoO_x/SiO_2 exhibited the highest selectivity to 1,4-pentanediol. Besides Rh–MoO_x/SiO_2, the Ir–MoO_x/SiO_2 catalyst was also selective for the hydrogenation of levulinic acid to 1,4-pentanediol, but the selectivity to 1,4-pentanediol over this catalyst is slightly lower than that of Rh–MoO_x/SiO_2. Pt–MoO_x/SiO_2 and Ru–MoO_x/SiO_2 have lower selectivity to 1,4-pentanediol. In contrast, Pd–MoO_x/SiO_2 is totally unselective for the production of 1,4-pentanediol.

The reaction pathway for the conversion of levulinic acid to 1,4-pentanediol over Rh–MoO_x/SiO_2 was explored. With the decrease of catalyst loading (see entries 3, 12 and 13 in Table 1), the main product from the hydrogenation of levulinic acid over the 4%Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) catalyst shifted from 1,4-pentanediol to GVL. This phenomenon is more evident at lower catalyst loading. Moreover, we also investigated the aqueous phase hydrogenation of GVL over the Rh–MoO_x/SiO_2 catalyst (see entry 14 in Table 1). It was found that GVL can be converted to 1,4-pentanediol over the Rh–MoO_x/SiO_2 catalyst under similar conditions. As suggested in the literature,[19,21] GVL may be a possible intermediate for the hydrogenation of levulinic acid to 1,4-pentanediol over the Rh–MoO_x/SiO_2 catalyst.

To find out the intrinsic reason for the excellent performance of the Rh–MoO_x/SiO_2 catalyst in the selective hydrogenation of levulinic acid to 1,4-pentanediol, we compared the activities of Rh/SiO_2 and Rh–MoO_x/SiO_2 for the aqueous phase hydrogenation of carboxyl group using acetic acid as the model compound. From Fig. 1, the Rh/SiO_2 is inactive for the hydrogenation of acetic acid under the investigated conditions. This result is consistent with the previous work of Huber group.[5] In contrast, higher acetic acid conversion (100%) and ethanol yield (83%) can be achieved over Rh–MoO_x/SiO_2. From this result, we can see that the modification of Mo promoted the hydrogenation of carboxyl group over the Rh catalyst, which may be the reason for the higher selectivity of the

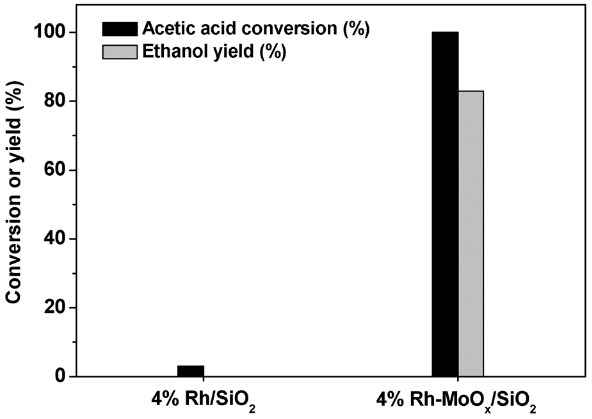

Fig. 1 Hydrogenation of acetic acid over 4%Rh/SiO_2 and 4%Rh–MoO_x/SiO_2 (Mo/Rh = 0.13). Reaction conditions: 353 K, 6 MPa, 2.0 g catalyst, 10% acetic acid aqueous solution flow rate: 0.08 mL min^{-1}, H_2 flow rate: 60 mL min^{-1}.

Table 2 Results for the hydrogenation of different biomass derived carboxylic acids over the 4%Rh–MoO_x/SiO_2 (Mo/Rh = 0.13). Reaction conditions: 353 K, 6 MPa, 2.0 g catalyst, 10% carboxylic acid aqueous solutions flow rate 0.08 mL min^{-1}, H_2 flow rate 60 mL min^{-1}

Reactant	Conversion (%)	Product	Selectivity (%)
Propanoic acid	100	Propanol	76.2
		Others[a]	23.8
Butanoic acid	100	Butanol	68.4
		Others[a]	31.6
Lactic acid	76.9	1,2-Propanediol	58.8
		1-Propanol	14.2
		Others[a]	27.0
Malonic acid	96.2	1,3-Propanediol	46.1
		1-Propanol	13.9
		Others[a]	40.0
Succinic acid[b]	99.0	1,4-Butanediol	42.0
		1-Butanol	17.4
		Others[a]	40.6

[a] Others means light alkanes and some unidentified products (see Table S2 of ESI). [b] 5% aqueous solution of succinic acid was used as feedstock.

Rh–MoO_x/SiO_2 to 1,4-pentanediol. Analogous to what the Tomoshige group found in their recent work about the selective hydrogenolysis of tetrahydrofurfuryl alcohol,[23,24] the modification of Rh catalysts with Mo may promote the adsorption of carboxyl acid (by interaction with the lone electron pair of hydroxyl and/or carbonyl group oxygen), which is very important for the hydrogenation of carboxylic acid.[11]

Subsequently, we also explored the possibility of using the Rh–MoO_x/SiO_2 catalyst for the aqueous phase hydrogenation of other biomass derived carboxylic acids. Under the same reaction conditions that we used for the hydrogenation of levulinic acid, high conversion and good selectivity were achieved for the aqueous phase hydrogenation of different organic acids to their corresponding alcohols or diols (Table 2). To our knowledge, this is the first report about the aqueous hydrogenation of carboxylic acid at such a low temperature (353 K). In our future work, the optimization of the catalyst and reaction conditions will be carried out to obtain a higher yield of alcohol or diol.

Finally, we studied the stability of 4%Rh–MoO_x/SiO_2 (Mo/Rh = 0.13) catalyst in aqueous phase hydrogenation of acetic acid and levulinic acid (see Fig. S1 and Table S3 in ESI†). During the 30 h continuous test, no evident change of activity and/or selectivity was observed. Based on the excellent performance and good stability of Rh–MoO_x/SiO_2, we believe that it is a promising catalyst for future applications.

Mo modified Rh/SiO_2 (Rh–MoO_x/SiO_2) is a promising catalyst for the low-temperature aqueous phase selective hydrogenation of levulinic acid to 1,4-pentanediol (a potential monomer for the synthesis of polyester). The synergism between the closely contacted Rh and Mo species is necessary for the high selectivity of 1,4-pentanediol over the Rh–MoO_x/SiO_2 catalyst. From the reactions of some model compounds, it was found that the modification of Mo promoted the hydrogenation of the carboxyl group over the Rh/SiO_2 catalyst, which was responsible for the higher selectivity of 1,4-pentanediol over the Rh–MoO_x/SiO_2 catalyst.

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