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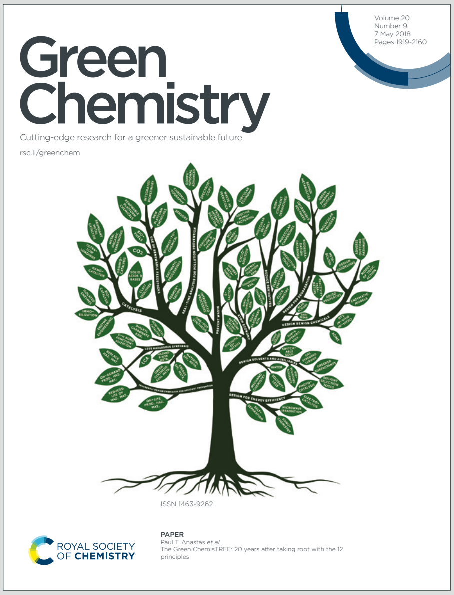

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ARTICLE

Selective Hydrogenation of Aromatic Furfurals into Aliphatic Tetrahydrofurfural Derivatives

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Youdi Yang,[a,b,c,d] Yanyan Wang,[a,b,c] Shaopeng Li,[a,b,c] Xiaojun Shen,[a,b,c] Bingfeng Chen,[a] Huizhen Liu*[a,b,c] and Buxing Han[a,b,c]

Tetrahydrofurfural (THFF) and 5-hydroxymethyltetrahydro-2-furaldehyde (5-HMTHFF) are important chemicals. Synthesis of THFF and 5-HMTHFF from the selective hydrogenation of furfural (FF) and 5-hydroxymethylfurfural (HMF) is highly desirable. However, it is a great challenge to hydrogenate furanyl ring while keeping C=O intact. Herein, we found that Pd/LDH-MgAl-NO_3 could efficiently catalyze the hydrogenation of FF to THFF and HMF to 5-HMTHFF in water. At near complete conversion of FF and HMF, the selectivities of THFF and 5-HMTHFF could reach 92.6% and 83.7%, respectively. A series of control experiments showed that both LDH-MgAl-NO_3 support and water solvent played important role for the unusual performance of the catalytic system. The hydrogenation of furanyl ring occurred on the surface of Pd. Water prohibited the hydrogenation of C=O group, and the special nature of LDH-MgAl-NO_3 prevented hydrogenation of C=O group on the support by the hydrogen spillover. Thus, the furanyl ring was selectively hydrogenated, and high selectivity of the desired product was successfully achieved. As far as we know, efficient hydrogenation of FF to THFF or HMF to 5-HMTHFF has not been reported. This work opens the way to selectively hydrogenate the furanyl ring while keeping C=O in the same molecule unchanged.

Introduction

Biomass is a very important renewable carbon resource [1-3] and can be used as feedstocks to prepare many valuable chemicals[4,5]. Selective hydrogenation[6-9] is a common strategy to achieve the transformation of biomass and its derivatives to valuable compounds. Since most biomass and its derivatives contain different kind of reducible functional groups in one compound, it is often a great challenge to control the selectivity for a desired product.

Furfural (FF) and 5-hydroxymethylfurfural (HMF), which can be produced from carbohydrates via hydrolysis and dehydration [10,11], are considered as platform chemicals for biomass conversion. Plenty of products have been obtained from the selective hydrogenation of FF and HMF [12-17]. However, in the reported work, the hydrogenation of aldehyde group was dominant (Scheme 1a). For example, Hronec and his co-workers reported the hydrogenation of FF to furfuryl alcohol (FA) over PdCu bimetal catalyst [14]. CuCo catalyst was used to catalyze the hydrogenation of FF to 2-methylfuran (2-MF) and the intermediate was FA[15]. The hydrogenation of HMF to 2,5-dimethylfuran (DMF) could proceed via hydrogenation of HMF to bis(hydroxymethyl)furan (BHMF) and then the hydrogenolysis of BHMF to DMF [16,17].

Tetrahydrofurfural (THFF) and 5-hydroxymethyltetrahydro-2-furaldehyde (5-HMTHFF) are important intermediates for the furan-based drugs, such as ranitidine, prazosin, furosemide, and cefuroxime, and have been widely used in pharmaceutical industry[18,19]. Traditionally, THFF was synthesized by the hydroformylation of dihydrofurans using Rh(acac)CO_2, HRh(CO)$(PPh_3)_3$ or RhCl(CO)$(PPh_3)_2$ as the catalysts[20-22]. In addition, THFF could also be obtained by the reaction of lithium derivatives of furfural with CO[23]. 5-HMTHFF was synthesized by the oxidation of 4-acetoxy-1,5-dibromopentane derivatives with silver nitrate[24]. Obviously, the traditional methods are complex and not environmentally benign (Scheme 1b). It is highly desirable to obtain THFF from FF and 5-HMTHFF from HMF by selective hydrogenation, but this is a great challenge because hydrogenation of C=O is easier than furanyl ring over commonly used catalysts.

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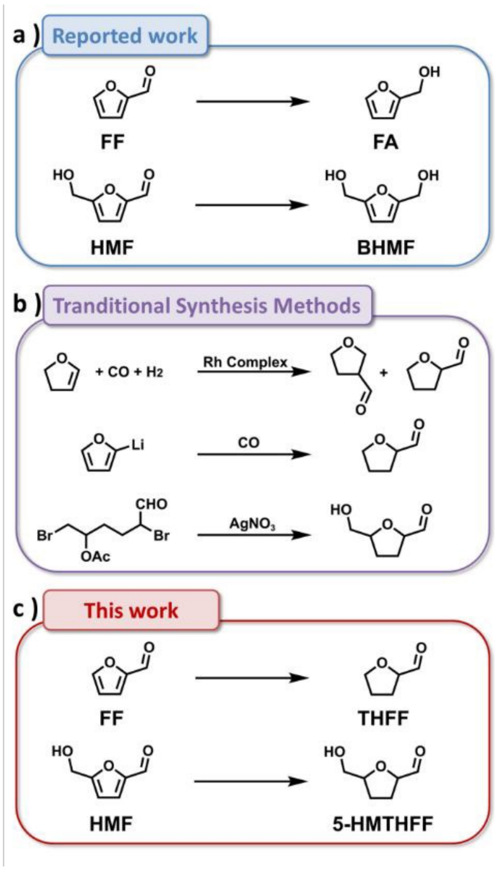
[a] *Beijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid and Interface and Thermodynamics, CAS Research/Education Centre for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.*
[b] *School of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.*
[c] *Physical Science Laboratory, Huairou National Comprehensive Science Centre, Beijing 101407, P. R. China.*
[d] *College of Science, Beijing Forestry University, Beijing 100083, China.*
**Correspondence to: liuhz@iccas.ac.cn (Huizhen Liu).*

Electronic Supplementary Information (ESI) available: [Materials and Methods, Table S1-S2 and Fig. S1-S4]. See DOI: 10.1039/x0xx00000x



Scheme 1 The reaction routes of (a) reported work for hydrogenation FF and HMF, (b) traditional methods to synthesize THFF and 5-HMTHFF, (c) this work to synthesize THFF and 5-HMTHFF.

Layered double hydroxides (LDHs) are a class of highly ordered two-dimensional anionic clays and their properties can be adjusted by changing the metallic ions and the interlaminar anion, which makes it a tunable heterogeneous catalyst support[25-27]. On the other hand, Pd based catalyst has been widely used to catalyze hydrogenation reactions[6-7, 28-29] In addition, it has been reported that support and solvent could significantly influence the performance of the catalyst[30-32]. In this work, we discover that Pd/LDH-MgAl-NO_3 could efficiently catalyze the selective hydrogenation of FF to THFF and HMF to 5-HMTHFF in water (Scheme 1c). At near complete conversion, the selectivities of THFF and 5-HMTHFF could reach 92.6% and 83.7%, respectively. Detailed study indicates that the solvent water and LDH-MgAl-NO_3 synergistically promotes the selectivity of the reaction. The reaction occurred on the surface of Pd in Pd/LDH-MgAl-NO_3. Water prohibited the adsorption of C=O on the metal surface that made the active sites unfavorable for the hydrogenation of C=O.

Results and discussion

Preparation and characterization of Pd based catalysts. MgAl-LDH with anion NO_3^- was obtained according to the procedure reported[33]. The Pd/LDH-MgAl catalyst was prepared by impregnation method and the procedure is shown in the Supporting Information. Transmission electron microscopy (TEM) image of the Pd/LDH-MgAl-NO_3 catalyst is presented in Fig. 1a. The Pd nanoparticles about 2.3 nm were immobilized on the support. The catalyst was also characterized by X-ray diffraction (XRD) method. No peaks of Pd were observed because of the small size of the particles (Fig. 1b). A series of diffraction peaks with 2θ values at 11.4°, 22.8°, 34.6°, 38.7°, 45.2°, 60.6° and 61.8° are related to the (003), (006), (012), (015), (018), (110) and (113) crystal planes of the MgAl-LDH. The basal spacing of Pd/LDH-MgAl-NO_3 calculated from (003) peak is 8.16 Å. Considering the thickness of brucite-like sheet is about 4.8 Å, the interlayer spacing of the LDH-MgAl-NO_3 was known to be 3.36 Å [34]. Moreover, it can be known from TEM and XRD characterizations that the lamellar structure of LDH was maintained after loading Pd nanoparticles. The Pd content obtained by ICP was 2.76%. Besides Pd/LDH-MgAl-NO_3 catalyst, Pd/SiO_2, Pd/TiO_2 and Pd/ZrO_2 were also fabricated and the TEM characterizations are shown in Fig S1. The Pd contents obtained by ICP were 2.58%, 2.66% and 2.98%, respectively (Table S1).

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Performances of the catalysts for selective hydrogenation of FF and HMF. The performances of the catalysts were studied by selective hydrogenation of FF and the results are shown in Table 1. LDH-MgAl-NO_3 could not catalyze the hydrogenation of FF and no product was detected (Table 1, entry 1). Using water as the solvent, the conversion of FF could reach 97.5% in 2 h at room temperature with 92.6% selectivity of THFF over Pd/LDH-MgAl-NO_3 (Table 1, entry 2). The conversion of FF and the selectivity of THFF were both very low over Pd/ZrO_2 and Pd/SiO_2 and the yield of THFF was only 3.3% and 1.5%, respectively (Table 1, entries 3 and 4). Although the activity of Pd/TiO_2 was very high with 95.2% conversion of FF in 3 h, the selectivity of THFF was only 19.4%, and much coupling product was formed (Table 1, entry 5). Very interestingly, no FA, which was produced by hydrogenating the C=O prior to furanyl ring, was detected over Pd/LDH-MgAl-NO_3 catalyst, while it was produced over Pd/SiO_2, Pd/ZrO_2, and Pd/TiO_2. These results indicate that the supports of the catalysts played an important role for the reaction, and the activity of Pd/LDH-MgAl-NO_3 for the hydrogenation of furanyl ring was much higher than that for C=O. The effect of time on the reaction was also investigated (Fig. S2). No FA was detected at lower conversion. Only 3.3% of FF was converted in 0.25 h and the selectivity of THFF was 100% (Table 1, entry 6). It further indicates that the hydrogenation of furanyl ring was prior to C=O. However, the C=O group in the desired product THFF could be hydrogenated to form tetrahydrofurfuryl alcohol (THFA) with longer time, and the selectivity of THFF dropped to 75.6% in 3 h (Table 1, entry 7).

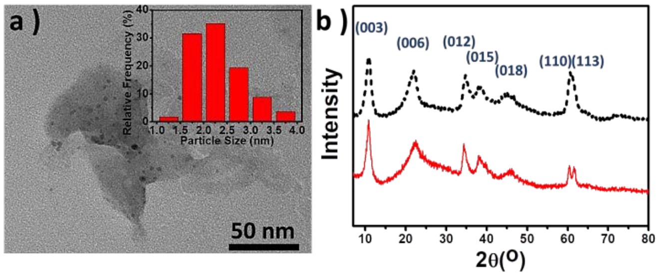

Fig. 1 (a) The TEM image of Pd/LDH-MgAl-NO_3; (b) The XRD patterns of LDH-MgAl-NO_3 (dash line) and Pd/LDH-MgAl-NO_3 (solid line).

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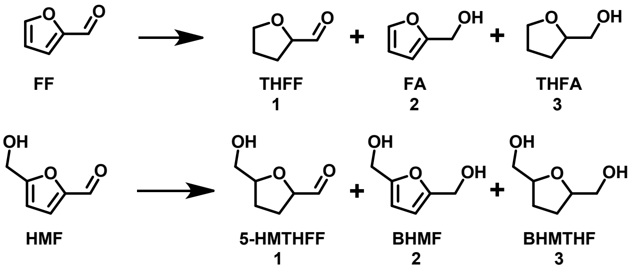
The solvent affected the performance of the catalyst significantly (Table 1, entries 2 and 8-10). The selectivity of THFF was 69.2%, 39.8% and 8.2% in EtOH, THF and n-hexane, respectively. Moreover, FA was detected in EtOH, THF and n-hexane. Thus, it can be deduced that in the organic solvents examined, the C=O could be hydrogenated prior to the furanyl ring, which was obviously different from the reaction in water.

This catalytic system also could catalyze the selective hydrogenation of HMF to 5-HMTHFF, and the selectivity of 5-HMTHFF could reach 83.7% when HMF conversion was 97.2% (Table 1, entries 13). In addition, no BHMF was detected, indicating that the hydrogenation of furanyl ring also occurred prior to the hydrogenation of C=O for the selective hydrogenation of HMF over Pd/LDH-MgAl-NO$_3$.

Table 1 Results for the selective hydrogenation of FF and HMF over different catalysts**.**



Entry	Catalyst	Solvent	t (h)	Conversion (%)	Yield (%)				Selectivity of **1** (%)
					1	**2**	**3**	**others**	
Substrate: FF									
1	LDH-MgAl-NO$_3$	H_2O	2	0	0	0	0	0	-
2	Pd/LDH-MgAl-NO$_3$	H_2O	2	97.5	90.3	0	7.1	0	92.6
3	Pd/SiO$_2$	H_2O	3	39.1	3.3	18.0	4.4	13.4	8.5
4	Pd/ZrO$_2$	H_2O	3	13.6	1.5	6.5	1.6	4.0	10.9
5	Pd/TiO$_2$	H_2O	3	95.2	18.5	11.1	19.9	45.7	19.4
6	Pd/LDH-MgAl-NO$_3$	H_2O	0.25	3.3	3.3	0	0	0	100
7	Pd/LDH-MgAl-NO$_3$	H_2O	3	100	75.6	0	24.3	0.1	75.6
8	Pd/LDH-MgAl-NO$_3$	EtOH	2	73.3	50.8	11.1	9.4	1.9	69.2
9	Pd/LDH-MgAl-NO$_3$	THF	2	6.3	2.5	2.5	1.2	0.1	39.8
10	Pd/LDH-MgAl-NO$_3$	Hex	2	9.9	0.8	3.6	5.4	0.1	8.2
11[a]	Pd/LDH-MgAl-NO$_3$+ ZrO$_2$	H_2O	2	57.1	43.6	7.1	4.4	2.0	76.3
12[b]	Pd/ZrO$_2$+LDH	H_2O	3	24.6	13.0	4.3	1.6	5.7	52.8
Substrate: HMF									
13	Pd/LDH-MgAl-NO$_3$	H_2O	4	97.2	81.4	0	8.8	7.0	83.7

Reaction conditions: FF: (1 mmol) or HMF (0.5 mmol), catalyst (10 mg), solvent (2 mL); 30°C; H_2 pressure, 1 MPa; and stirring speed, 800 rpm. [a] ZrO$_2$ (10 mg). [b] LDH-MgAl-NO$_3$ (10 mg).

Hydrogen spillover on the catalysts. On the surface of supported catalysts, it is a common phenomenon that the activated hydrogen atoms on the surface of the metal particles can further migrate to the support, which makes the support become the active center as well, which is called as hydrogen spillover. Hydrogen spillover can be proved by mixing various catalysts with WO_3[35-37]. The migrated activated hydrogen can react with WO_3 to form H_xWO_3, and the color of sample changes from yellow to dark blue. We studied the hydrogen spillover of the catalysts in this work using the reported method. In our experiment, 20 mg of catalyst and 1 g of WO_3 were mixed and ground, and then put into a transparent double-pass quartz tube. The photos of the samples obtained after treatment with H_2 at room temperature for 10 min are shown in Fig. S3. Pure WO_3 exhibited pale yellow and the color remained unchanged after hydrogen treatment. However, the treated mixture of WO_3 and Pd/LDH-MgAl-NO_3 turned from pale yellow to dark green. The same phenomenon occurred for the treated mixtures consisting of WO_3 and Pd/SiO_2, Pd/TiO_2, Pd/ZrO_2. The results indicate that WO_3 reacted with activated hydrogen and H_xWO_3 was formed, confirming the existence of hydrogen spillover on the surface of the catalysts.

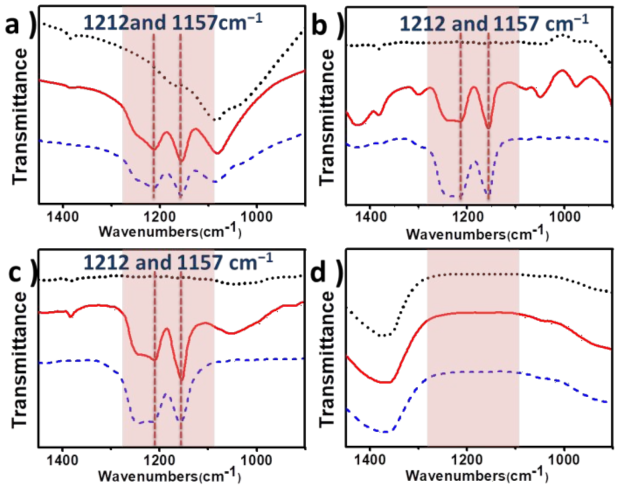


Fig. 2 (a-d) The FT-IR spectra of unmodified (dot line) and aldehyde-modified supports (stirring in H_2O, solid line; stirring in n-hexane, dash line). (a) SiO_2, (b) TiO_2 (c) ZrO_2 and (d) LDH-MgAl-NO_3.

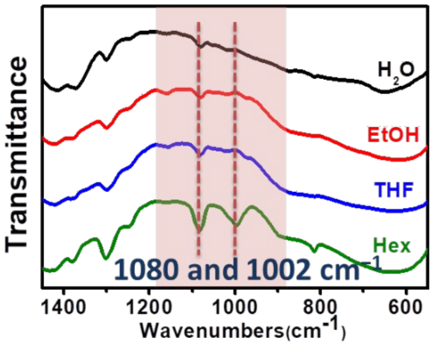


Fig. 3 The FT-IR spectra of aldehyde-modified Pd/LDH-MgAl-NO_3 in H_2O, EtOH, THF and n-hexane.

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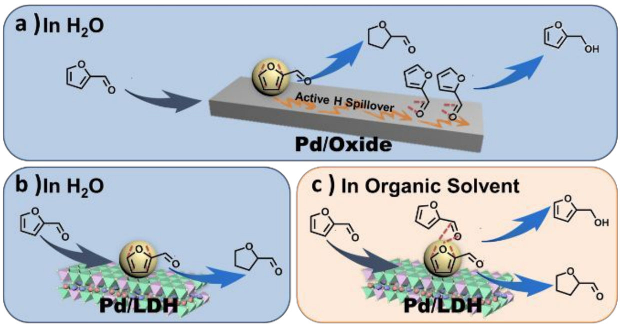
The effect of the support. As discussed above, support of the catalysts influences the reaction significantly. The mode of the substrate adsorbed on different supports in H_2O and n-hexane was investigated by Fourier transform infrared spectroscopy (FT-IR) according to the reported work[38-40]. Propyl aldehyde was used as the model compound in order to verify the adsorption of C=O on the surface of the supports. The support SiO_2, ZrO_2, TiO_2 and LDH-MgAl-NO_3 were treated by the solution of propyl aldehyde in H_2O or n-hexane, and the physically adsorbed propyl aldehyde was removed. As shown in Fig. 2a-2c, the peaks at 1157 and 1212 cm^{-1}, assigned to the ν(C-O) bands of the on-top and bridged sites, respectively, were observed on the support SiO_2, TiO_2, ZrO_2, while these peaks were not observed on LDH-MgAl-NO_3 support (Fig. 2d). The results indicate that, C=O group could be chemically adsorbed on SiO_2, ZrO_2, TiO_2 in both water and n-hexane, but not on LDH-MgAl-NO_3.

Hydrogen spillover affected the performance of the catalyst significantly. The performance of the physically mixed Pd/LDH-MgAl-NO_3 and ZrO_2 was checked. The yield of THFF decreased to 43.6%, and 7.1% of FA was generated (Table 1, entry 11). It suggests that the active hydrogen generated on Pd of Pd/LDH-MgAl-NO_3 migrated to ZrO_2 because of hydrogen spillover, and the adsorbed C=O group on ZrO_2 was hydrogenated. The yield of THFF over physically mixed catalysts of Pd/ZrO_2 and LDH-MgAl-NO_3 was obviously higher than that over Pd/ZrO_2 (Table 1, entries 4 and 12), indicating that the active hydrogen generated on Pd of Pd/ZrO_2 migrated to LDH-MgAl-NO_3 because of hydrogen spillover, and the C=O group could not be hydrogenated on LDH-MgAl-NO_3 because it cannot chemically adsorb the C=O group[41]. These results further illustrate the existence of hydrogen spillover and the importance of the support.

The special structure of LDH is the primary reason for the unfavorable chemical adsorption of C=O. To get further information on this, LDH-MgAl-NO_3 was calcined to form the corresponding metal oxides MgO-Al_2O_3 at 500 °C. The XRD pattern, which is given in Fig. S4a, is consistent with the pattern of periclase MgO. The substrate adsorbed on the MgO-Al_2O_3 in H_2O and n-hexane was also checked by FT-IR using the method discussed above. It was found that MgO-Al_2O_3 could chemically adsorb C=O bonds in n-hexane, but not in water (Fig. S4b). It has been reported that the MgO-Al_2O_3 could restore the structure of LDHs in water.[42] The material of MgO-Al_2O_3 treated in water was characterized by XRD and the characteristic peaks of LDHs appeared (Fig. S4a). The MgO-Al_2O_3 could not chemically adsorb C=O in water because it changed back into LDHs. The catalytic performance of Pd/MgO-Al_2O_3 in water was also checked (Table S2). The selectivity of THFF could reach 71.4%.

The effect of the solvent. The solvent influenced the reaction significantly. In order to get some evidence to explain the solvent effect, we studied the adsorption mode of C=O in different solvents on Pd/LDH-MgAl-NO_3 by FT-IR (Fig.3). Pd/LDH-MgAl-NO_3 was treated by the solution of propyl aldehyde in different solvents and the physically adsorbed propyl aldehyde was removed by centrifugation and vacuum drying. The peaks observed at 1080 and 1002 cm^{-1} in Fig. 3 were assigned to the ν(C–O), which indicated the chemically adsorption of C=O occurred on the surface of catalyst in EtOH, THF and n-hexane. The peaks of the catalyst treated in n-hexane were strongest, while that of the catalyst treated in water were very weak. The results suggest that H_2O prohibited the adsorption of C=O group on Pd metal surfaces, which is not favorable to the hydrogenation of C=O. The results were consistent with the fact that the selectivity of THFF in water was much higher.

The main reaction pathways. From the results above and the knowledge in the literature, we can discuss the main reaction pathways of the reaction over different catalysts in different solvents, which are shown schematically in Scheme 2. On one hand, the adsorption ability of support influences the selectivity significantly. The activated hydrogen on Pd surface can migrate to the supports and hydrogenate the substrates activated by the supports[43-45]. In water, Pd/SiO_2, Pd/TiO_2 and Pd/ZrO_2, Pd particles promote the hydrogenation of furanyl ring to produce desired product THFF. At the same time the supports could adsorb and activate the C=O group (Figure 3a-3c), and the hydrogenation of C=O took place on support to produce by-product FA via hydrogen spillover. Thus, both THFF and FA were obtained (Scheme 2a). The low selectivity of THFF (Table 1, entries 3-5) suggests that hydrogenation of C=O group on the support via hydrogen spillover is a dominant reaction. When the reaction occurred over the Pd/LDH-MgAl-NO_3 in water, the selectivity of the desired product was very high because the ability of both Pd particle and the support to adsorb C=O group was very weak (Figure 3d and 4), and thus mainly the furanyl ring was hydrogenated to generate THFF (Scheme 2b). When the reaction took place over the Pd/LDH-MgAl-NO_3 in organic solvents, the Pd particles could adsorb C=O group, and thus both C=O group and furanyl ring could be hydrogenated (Scheme 2c). Hence, the selectivity in the organic solvents was lower than that in water. The ability of the catalyst to adsorb the C=O in the organic solvents varied in the order of n-hexane>THF>EtOH (Fig. 3), and selectivity of THFF decreased with the increase of the adsorption ability. All the results are consistent with the proposed reaction pathway, and both LDH-MgAl-NO_3 support and water are crucial for the very high selectivity of THFF.



Scheme 2 The reaction pathways of the reaction over different catalysts in different solvents. (a) Pd/ZrO_2, Pd/TiO_2 and Pd/SiO_2 in water. (b) Pd/LDH-MgAl-NO_3 in water. (c) Pd/LDH-MgAl-NO_3 in organic solvents.

Conclusions

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In summary, Pd/LDH-MgAl-NO_3 could efficiently catalyze the selective hydrogenation of FF to THFF and HMF to 5-HMTHFF in water, respectively. In water, the support and water worked cooperatively to improve the selectivity. The furanyl ring was hydrogenated on the surface of Pd and water prohibited the reaction of C=O on the metal surface, and the support could not activate C=O group, resulting in high selectivity to the desired product. By comparison, in organic solvents, both the C=O and furanyl ring could be hydrogenated and the selectivity was low. In addition, the selectivity of reaction over Pd/SiO_2, Pd/ZrO_2 and Pd/TiO_2 was very low because the support could activate C=O and hydrogenation of C=O took place on the support via hydrogen spillover. This work makes the breakthrough in that furanyl ring is selectively hydrogenated while the C=O in the same molecule remains unchanged, which is a significant progress in hydrogenation chemistry, and new, efficient, greener routes to prepare THFF and 5-HMTHFF are provided. We believe that the protocol can be used to design other efficient catalytic systems for selective hydrogenation of substances with two or more reducible groups.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgements

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Notes and references

1. P. Gallezot, *Chem. Soc. Rev.* 2012, **41**, 1538-1558.
2. C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, *Science* 2012, **337**, 695-699.
3. L. T. Mika, E. Cséfalvay, A. Németh, *Chem. Rev.* 2018, **118**, 505-613.
4. M. J. Climent, A. Corma, S. Iborra, *Green Chem.* 2014, **16**, 516-547.
5. A. A. Rosatella, S. P. Simeonov, R. F. Frade, C. A. Afonso, *Green Chem.* 2011, **13**, 754-793.
6. H. Liu, T. Jiang, B. Han, S. Liang, Y. Zhou, *Science*, 2009, **326**, 1250-1252.
7. Q. Meng, M. Hou, H. Liu, J. Song, B. Han, *Nat. Comm.* 2017, **8**, 14190.
8. H. Liu, Q. Mei, S. Li, Y. Yang, Y. Wang, H. Liu, L. Zheng, P. An, J. Zhang, Han, B, *Chem. Commun.* 2018, **54**, 908-911.
9 Y. Yang, S. Li, C. Xie, H. Liu, Y. Wang, Q. Mei, H. Liu, B. Han, *Chinese Chem. Lett.* 2018, **30,** 203-206.
10 C. Chiappe, M. J. Rodriguez Douton, A. Mezzetta, C. S. Pomelli, G. Assanelli, A. R. de Angelis, *ACS Sustainable Chem. Eng.* 2017, **5**, 5529-5536.
11 J. P. Lange, *Biofuels, Bioprod. Biorefin.* 2007, **1**, 39-48.
12 G. H. Wang, J. Hilgert, F. H. Richter, F. Wang, H. Bongard, B. Spliethoff, C. Weidenthaler, F. Schüth, *Nat. Mater.* 2014, **13**, 293-300.

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13 Y. Deng, R. Gao, L. Lin, T. Liu, X. D. Wen, S. Wang, D. Ma, *J. Am. Chem. Soc.* 2018, **140**, 14481-14489.
14 K. Fulajtárova, T. Soták, M. Hronec, I. Vávra, E. Dobročka, M. Omastová, *Appl. Catal. A-Gen.* 2015, **502**, 78-85.
15 C. Nguyen-Huy, H. Lee, J. Lee, J. H. Kwak, K. An, *Appl. Catal. A-Gen.* 2019, **571**, 118-126.
16 W. Guo, H. Liu, S. Zhang, H. Han, H. Liu, T. Jiang, B. Han, T. Wu, *Green Chem.* 2016, **18**, 6222-6228.
17 Y. Yang, H. Liu, S. Li, C. Chen, T. Wu, Q. Mei, Y. Wang, B. Chen, H. Liu, B. Han, *ACS Sustainable Chem. Eng.* 2019, **7**, 5711-5716.
18 J. C. L. Erve, S. C. Vashishtha, W. DeMaio, R. E. Talaat, *Drug Metab. Dispos.* 2007, **35**, 908-916.
19 N. Can, G. Altiokka, Y. Hassan, A. Enein, *Anal. Chim. Acta* 2006, **576**, 246-252.
20 X. Zheng, K. Xu, X. Zhang, *Tetrahedron Lett.* 2015, **56**, 1149-1152.
21 S. H. Chikkali, R. Bellini, B. de Bruin, J. I. van der Vlugt, J. N. H. Reek, *J. Am. Chem. Soc.* 2012, **134**, 6607-6616.
22 M. D. Khokhar, R. S. Shukla, R. V. Jasra, *J. Mol. Catal. A-Chem.* 2015, **400**, 1-6.
23 G. G. E. Linares, N. S. Nudelman, *J. Phys. Org. Chem.* 2003, **16**, 569-576.
24 M. Mitani, H. Takeuchi, K. Koyam, *Chem. Lett.* 1987, **16**, 2335-2336.
25 G. Fan, F. Li, D. G. Evans, X. Duan, *Chem. Soc. Rev.* 2014, **43**, 7040-7066.
26 T. Yatabe, X. Jin, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* 2015, **54**, 13302-13306.
27 Y. Wang, B. Chen, S. Liu, X. Shen, S. Li, Y. Yang, H. Liu, B. Han, *ChemCatChem* 2018, **10**, 5124-5127.
28 F. Zhao, Y. Ikushimaa, M. Chatterjeea, M. Shiraia, M. Arai, *Green Chem.* 2003, **5**, 76-79.
29 D. Wang, Y. Zhu, C. Tian, L. Wang, W. Zhou, Y. Dong, H. Yan, H. Fu, *ChemCatChem* 2016, **8**, 1718-1726.
30 L. M. Estevesa, M. H. Brijaldob, E. G. Oliveiraa, J. J. Martinezc, H. Rojasc, A. Caytueroa, F. B. Passos, *Fuel*, 2020, **270**, 117524.
31 C. Li, H. Cai, B. Zhang, W. Li, G. Pei, T. Dai, A. Wang, T. Zhang, *Chinese J. Catal.* 2015, **36**, 1638–1646.
32 G. Sun, J. An, H. Hu, C. Li, S. Zuo, H. Xia, *Catal. Sci. Technol.* 2019, **9**, 1238-1244.
33 Z. Hu, X. Song, C. Wei, J. Liu, *Chemosphere* 2017, **187**, 196-205.
34 K. H. Goha, T. T. Lima, Z. Dong, *Water Res.* 2008, **42**, 1343-1368.
35 J. M. Sinfelt, P. J. Lucchesi, *J. Am. Chem. Soc.* 1963, **85**, 3365-3367.
36 S. Khoobiar, *J. Phys. Chem.* 1964, **68**, 411-412.
37 C. Wang, E. Guan, L. Wang, X. Chu, Z. Wu, J. Zhang, Z. Yang, Y. Jiang, L. Zhang, X. Meng, B. C. Gates, F. S. Xiao, *J. Am. Chem. Soc.* 2019, **141**, 8482-8488.
38 X. Jia, J. Ma, F. Xia, Y. Xu, J. Gao, J. Xu, *Nat. Commun.* 2018, **9**, 933.
39 M. Tamura, K. Tomishige, *Angew. Chem., Int. Ed.* 2015, **54**, 864-867.
40 A. Badri, C. Binet, J. C. Lavalley, *J. Chem. Soc., Faraday Trans.* 1997, **93**, 1159-1168.
41 R. Liu, Y. Yu, K. Yoshida, G. Li, H. Jiang, M. Zhang, F. Zhao, S. Fujita, M. Arai, *J. Catal.* 2010, **269,** 191–200.
42 Z. M. Ni, S. J. Xia, L. G. Wang, F. F. Xing, G. X. Pan, *J. Colloid Interface Sci.* 2007, **316**, 284-291.
43 W. C. Conner Jr, J. L. Falconer, *Chem. Rev.* 1995, **95**, 759-788.
44 L. R. Merte, G. Peng, R. Bechstein, F. Rieboldt, C. A. Farberow, L. C. Grabow, W. Kudernatsch, S. Wendt, E. Lægsgaard, M. Mavrikakis, F. Besenbacher, *Science* 2012, **336**, 889-893
45 W. Karim, C. Spreafico, A. Kleibert, J. Gobrecht, J. VandeVondele, Y. Ekinci, J. A. van Bokhoven, *Nature* 2017, **541**, 68-71.