



# Article Tuning the Reaction Selectivity over MgAl Spinel-Supported Pt Catalyst in Furfuryl Alcohol Conversion to Pentanediols

Xinsheng Li <sup>1,2</sup>, Jifeng Pang <sup>1</sup>, Jingcai Zhang <sup>1</sup>, Xianquan Li <sup>1,2</sup>, Yu Jiang <sup>1</sup>, Yang Su <sup>1</sup>, Weizhen Li <sup>1</sup> and Mingyuan Zheng <sup>1,\*</sup>

- <sup>1</sup> Chinese Academy of Science Key Laboratory of Science and Technology on Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China; lixinsheng@dicp.ac.cn (X.L.); jfpang@dicp.ac.cn (J.P.); zjc@dicp.ac.cn (J.Z.); lixianquan@dicp.ac.cn (X.L.); jiangyu0825@dicp.ac.cn (Y.J.); suyang@dicp.ac.cn (Y.S.); weizhenli@dicp.ac.cn (W.L.)
- <sup>2</sup> University of Chinese Academy of Sciences, 19A Yuquan Road, Beijing 100049, China
- Correspondence: myzheng@dicp.ac.cn; Tel.: +86-411-84379738

**Abstract:** Catalytic conversion of biomass-derived feedstock to high-value chemicals is of remarkable significance for alleviating dependence on fossil energy resources. MgAl spinel-supported Pt catalysts were prepared and used in furfuryl alcohol conversion. The approaches to tune the reaction selectivity toward pentanediols (PeDs) were investigated and the catalytic performance was correlated to the catalysts' physicochemical properties based on comprehensive characterizations. It was found that 1–8 wt% Pt was highly dispersed on the MgAl<sub>2</sub>O<sub>4</sub> support as nanoparticles with small sizes of 1–3 nm. The reaction selectivity did not show dependence on the size of Pt nanoparticles. Introducing LiOH onto the support effectively steered the reaction products toward the PeDs at the expense of tetrahydrofurfuryl alcohol (THFA) selectivity. Meanwhile, the major product in PeDs was shifted from 1,5-PeD to 1,2-PeD. The reasons for the PeDs selectivity enhancement were attributed to the generation of a large number of medium-strong base sites on the Li-modified Pt catalyst. The reaction temperature is another effective factor to tune the reaction selectivity. At 230 °C, PeDs selectivity was enhanced to 77.4% with a 1,2-PeD to 1,5-PeD ratio of 3.7 over 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>. The Pt/Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst was robust to be reused five times without deactivation.

Keywords: biomass; furfuryl alcohol; lithium; platinum; spinel; pentanediol

## 1. Introduction

The fossil oil depletion and environmental problems have stimulated the exploration of carbon-neutral resources. Biomass is the only carbon-containing renewable feedstock, and is able to be upgraded into a variety of platform chemicals deeply involved in our life. As a group of newly emerged top chemicals for biorefinery, furfural and its derivatives are suitable to prepare value-added alcohols via catalytic hydrogenation or hydrogenolysis reactions [1–4]. Among these products, pentanediols (PeDs), specifically 1,2- and 1,5-pentanediols (1,2-PeD and 1,5-PeD), belong to important value-added chemicals for the synthesis of polyesters, cosmetics, and low-toxic microbicides [5,6]. Thus, great attentions have been dedicated to convert furfural or furfuryl alcohol (FFA) to PeDs [7–16].

There have been several types of catalysts developed for direct hydrogenolysis of furfural or FFA to PeDs [17–19]. For instance,  $CuCr_2O_4$  catalysts afforded 40% 1,2-PeD yield in furfural conversion at 150 °C [20]. Mizugaki et al. supported Pt on hydrotalcite for furfural conversion and obtained 73% selectivity to 1,2-PeD at 99% furfural conversion after a 4 h reaction at 150 °C [21]. Zhu et al. studied the effects of microstructure of Pt nanoparticles on the reaction selectivity and reported the dependence of reaction route on the Pt species state [22]. The coordination-unsaturated three-dimensional (3D) Pt-Pt sites efficiently cleaved the C-O bond in furan ring and contributed to the 1,2-PeD production, while the atomically dispersed Pt and coordination-unsaturated two-dimensional (2D)



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Pt-Pt sites favored 2-methylfuran and tetrahydrofurfuryl alcohol formation, respectively. Hydrogenation metal-incorporated hydrotalcite-based catalysts were explored for PeDs production. Over the Cu-MgAl oxide catalysts, ca. 50% selectivity to 1,2-PeD was obtained at 63.1% FFA conversion after an 8 h reaction at 140 °C [23]. The synergistic effect between Cu particles and the base sites enhanced adsorption of furan rings and facilitated the furan ring opening to form 1,2-PeD. Recently, Wang and coworkers reported a high-performance Pt/CeO<sub>2</sub> catalyst, which gave 77% yield of 1,2-PeD in the reaction at 438 K in 2 MPa H<sub>2</sub> [8,9]. According to the mechanism study, they supposed that water participated in the ring-opening process and significantly favored the 1,2-PeD production. In short, remarkable progress has been made in transforming FFA to PeDs. The catalytic processes are usually conducted at high temperatures (>120 °C) for a long time (>4 h in one-pot) and even under caustic hydrothermal conditions. Moreover, the complex reaction network requires the catalyst be able to finely control the selectivity to PeDs formation. Therefore, it is still highly desirable to develop more robust catalysts and elegant strategies to realize high reaction selectivity in FFA conversion.

Spinels are reported to be good carriers for many transition metal-based catalysts. They can realize ultrahigh-dispersion of active sites via the strong interaction with the loaded metals and afford outstanding anti-sintering stability [24–27]. Moreover, the acid-base properties of spinels' surface are tunable, e.g., by altering the composition of spinels or introducing alkalies. Therefore, they may serve as suitable supports for constructing high-performance catalysts applied in the acid-base sensitive reaction, like FFA conversion to PeDs. According to these considerations, we developed a promising MgAl spinel-supported Pt catalyst, over which the product distribution was successfully tuned to 77.4% PeDs selectivity. The catalyst exhibited robust performance in five-cycle runs without deactivation. On the basis of the comprehensive characterizations of catalysts, the correlation between the catalyst structure and catalytic performance was revealed. The robust catalyst and the effective strategy to tune the reaction selectivity would give good reference for exploring high-performance catalysts and methods for biomass and FFA conversion to high-value products.

## 2. Results and Discussion

## 2.1. Catalytic Conversion of FFA over Different Catalysts

#### 2.1.1. Performance of Pt/MgAl<sub>2</sub>O<sub>4</sub> Catalysts in FFA Conversion

In view of the high thermal stability and readily obtained high dispersion of metals, the spinel of MgAl<sub>2</sub>O<sub>4</sub> was employed to load noble metals for the catalytic conversion of FFA. The performance of various noble metal catalysts was first screened. As shown in Table 1, Entries 1–5, compared to Pd, Rh, and Ru catalysts, which gave much higher selectivity to THFA (tetrahydrofurfuryl alcohol), the MgAl<sub>2</sub>O<sub>4</sub>-supported Pt catalyst showed highest selectivity to 1,2-PeD and 1,5-PeD. Over 4Pt/MgAl<sub>2</sub>O<sub>4</sub>, the total selectivity to PeDs reached 48.2%, with a 1,2-PeD to 1,5-PeD ratio of ca. 1:1.5 at 100% FFA conversion. Thus, the Pt catalyst was deemed as the promising one for further investigation in this study.

It is reported that FFA conversion to PeDs is a structure-sensitive reaction over the Pt catalysts [22]. THFA is preferentially formed over the Pt-Pt in 2D clusters and the terrace Pt-Pt in nanoparticles, while 1,2-PeD is readily formed over the Pt-Pt in 3D clusters. We varied the Pt loading from 1% to 8% to probe the particle size effects and tune the reaction selectivity toward PeDs. As the Pt loading increased in this wide range, the catalyst activity was improved from 55.4% to 100%, but neither variation of product distribution nor enhancement in PeDs selectivity was obtained. The overall PeD selectivity was ca. 50%, with the ratio of 1,2-PeD to 1,5-PeD at ca. 1:1–1:1.5. This is quite different from the performance of 1.67%Pt/Mg(Al)O@Al<sub>2</sub>O<sub>3</sub>, which gave a high ratio of 1,2-PeD to 1,5-PeD at ca. 9:1, as reported by Zhu et al. [22]. In contrast, Tomishige et al. conducted extensive investigations on 1,5-PeD production from furfural-based substrates by using Ir-Re- and Rh-Re-based catalysts and obtained specifically high selectivity to 1,5-PeD in most of the cases [12,13]. Evidently, the product distribution in the present study may provide two

types of PeDs at similar yields and also has great potential to be tuned to obtain the one single desired product. On the other hand, the direct hydrogenation product THFA was always obtained at a high selectivity of ca. 45% (Table 1, Entries 6–8). This may suggest that 1–8 wt% Pt was dispersed on the MgAl spinel in a similar 3D nanoparticle structure. However, as seen from the XRD and TEM analyses discussed in the following section, the morphologies of Pt nanoparticles were quite different among the catalysts with low to high loadings of Pt. Therefore, correlating to the results reported by Zhu et al. [22], we conjecture that besides the size and structure of Pt nanoparticles, other factors, e.g., reactor type (batch reactor vs. fixed-bed reactor), reaction solvent (water vs. ethanol), and catalyst support (MgAl spinel and MgAl layered double oxides) also essentially determine the catalytic behavior of Pt catalysts in FFA conversion.

Entry	Catalyst	Conversion %	Selectivity/%				С
			1,2-PeD	1,5-PeD	THFA	Pol	Balance/%
1	4Pt/MgAl <sub>2</sub> O <sub>4</sub>	100	19.2	29.0	45.9	0.7	94.8
2	$4Pd/MgAl_2O_4$	67.7	2.3	2.3	70.3	0	74.9
3	$4 Ir/MgAl_2O_4$	13.6	5.4	5.4	20.5	0	31.3
4	$4Rh/MgAl_2O_4$	91.3	0.4	0.4	99.4	0	100
5	$4Ru/MgAl_2O_4$	84.2	9.5	9.5	61.0	0	80.0
6	$1Pt/MgAl_2O_4$	55.4	20.3	32.1	43.1	0.7	96.1
7	$2Pt/MgAl_2O_4$	83.6	23.3	28.4	43.9	0.6	96.2

Table 1. Catalytic conversion of FFA over different catalysts.

100

Reaction conditions: 20 g 5 wt% furfuryl alcohol, 0.1 g catalyst, 4 MPa H<sub>2</sub>, 140 °C, 4 h; FFA, Con., Sel., 1,2-PeD, 1,5-PeD, THFA, and Pol. are abbreviations for furfuryl alcohol, conversion, selectivity, 1,2-pentanediol, 1,5-pentanediol, tetrahydrofurfuryl alcohol, and 1-pentanol, respectively.

22.3

24.3

0.9

46.0

93.5

#### 2.1.2. Alkali-Modified Pt/MgAl<sub>2</sub>O<sub>4</sub> Catalysts

8Pt/MgAl<sub>2</sub>O<sub>4</sub>

8

To enhance PeDs' proportion in products, it is necessary to enhance the furan ring opening and depress the direct hydrogenation over catalysts. Base sites were reported to be effective in improving 1,2-PeD production owing to their activation on the OH group of FFA during the catalytic hydrogenolysis [8,23,28]. We introduced the group of alkalies onto Pt/MgAl<sub>2</sub>O<sub>4</sub> to compare their performance in the reaction. As shown in Table 2, Entry 1, with the presence of LiOH on 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>, the THFA yield was slightly depressed from 45.9% to 41.8%, accompanied with a 4% increase in 1,2-PeD selectivity. Considering the water solvent may leach the alkali from the catalyst and compromise the effect of base modification on tuning the reaction selectivity, we changed the reaction solvent to organics for FFA conversion. In an aprotic solvent of 1,4-dioxane, merely 1,5-PeD and THFA were obtained, but without 1,2-PeD formation (Table 2, Entry 2). Differently, in low-polar protic solvents of iso-propanol (iPA) and MeOH (Table 2, Entries 3–4), the selectivity to PeDs was significantly improved to 64% in spite of the fact that FFA conversions over 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> decreased to <24%. Interestingly, the ratio of 1,2-PeD to 1,5-PeD was reversed (2:1 in iPA vs. 1:1.3 in water), with 1,2-PeD as the dominant product.

Then, the effects of other alkali-modified  $Pt/MgAl_2O_4$  catalysts were evaluated in iPA in view of its advantages in giving high reaction selectivity to PeDs. As shown in Table 2, Entries 5–7, with the increase in the atomic number and the basicity strength, the alkali-modified  $Pt/MgAl_2O_4$  catalysts gave significantly decreased FFA conversion and PeDs selectivity. Especially over the K- and Cs-modified  $Pt/MgAl_2O_4$  catalysts, no FFA conversion was observed. These results demonstrate that both base type and strength are crucial for FFA hydrogenolysis to produce PeDs. The  $Pt/Li/MgAl_2O_4$  was the best one among the alkali-modified catalysts under the present reaction conditions. Xu et al. prepared Pt catalysts loaded on a mesoporous Co-Al spinel with high surface area and suitable basicity for furfural hydrogenation to PeDs [29]. They found that with the introduction of a small amount of Li on the catalyst, the yields of 1,2-PeD and 1,5-PeD were concurrently improved, from 9.3% to 16.2% for the former and from 27.2% to 34.9% for the latter after a 24 h reaction at 140 °C in ethanol. However, over  $4Pt/10Li/MgAl_2O_4$  studied herein, the enhancement

by Li was more remarkable for 1,2-PeD production, of which selectivity was doubled from 22.0% to 42.4%, but with almost unchanged 1,5-PeD selectivity (Table 2, Entries 10 and 4). Therefore, the modification effect of Li or other alkalies should also be related to the support properties.

Table 2. Results of FFA conversions on alkali-modified 4Pt/MgAl<sub>2</sub>O<sub>4</sub> catalysts <sup>[a]</sup>.

Entry	Catalyst	Conversion %	Selectivity/%				С
			1,2-PeD	1,5-PeD	THFA	Pol	Balance/%
1	4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> <sup>[b]</sup>	100	23.1	29.1	41.8	0	94.0
2	4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> <sup>[c]</sup>	5.6	-	30.0	63.3	-	93.4
3	4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> <sup>[d]</sup>	12.6	37.0	25.5	32.9	1.2	96.6
4	4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub>	24.4	42.4	21.6	31.0	1.0	95.9
5	4Pt/10Na/MgAl <sub>2</sub> O <sub>4</sub>	11.8	22.8	15.7	57.0	0.9	96.2
6	4Pt/10K/MgAl <sub>2</sub> O <sub>4</sub>	0	-	-	-	-	-
7	4Pt/10Cs/MgAl <sub>2</sub> O <sub>4</sub>	0	-	-	-	-	-
8	4Pt/2Li/MgAl <sub>2</sub> O <sub>4</sub>	54.4	36.6	20.5	41.4	0.6	99.2
9	4Pt/6Li/MgAl <sub>2</sub> O <sub>4</sub>	42.1	43.0	20.4	35.9	0.4	99.7
10	$4Pt/MgAl_2O_4$	18.7	22.0	17.2	48.5	2.2	89.9
11	8Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub>	83.9	40.8	20.1	34.4	0.4	95.8
12	$8Pt/MgAl_2O_4$	100	11.3	24.4	50.0	5.4	91.2
13	4Pt/MgAl <sub>2</sub> O <sub>4</sub> +LiOH <sup>[e]</sup>	22.8	15.1	21.4	43.3	4.0	83.7

<sup>[a]</sup> Reaction conditions: 20 g 5 wt % furfuryl alcohol in iPA solvent, 0.1 g catalyst, 4 MPa H<sub>2</sub>, 140 °C, 4 h. <sup>[b], [c], and [d]</sup> Reactions in solvents of H<sub>2</sub>O, 1,4-dioxane and methanol, respectively. <sup>[e]</sup> 0.1 g catalyst with 0.028 g LiOH. FFA, Con., Sel., 1,2-PeD, 1,5-PeD, THFA, Pol., and iPA are abbreviations of furfuryl alcohol, conversion, selectivity, 1,2-pentanediol, 1,5-pentanediol, tetrahydrofurfuryl alcohol, 1-pentanol, and iso-propanol, respectively.

The effect of Li loading amount on the catalytic performance of Pt/Li/MgAl<sub>2</sub>O<sub>4</sub> was examined. As shown in Table 2, Entries 4, 8, and 9, increasing the Li loading from 2% to 10% suppressed the FFA conversion from 54.4% to 24.4%. On the contrary, the 1,2-PeD selectivity increased from 36.6% to 42.4%, with a stable selectivity to 1,5-PeD (ca. 20%). Compared to the 4Pt/MgAl<sub>2</sub>O<sub>4</sub> catalyst used in iPA without Li modification (Table 2, Entry 10), the 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst gave notably higher PeDs selectivity (64.0% vs. 39.2%). A similar enhancing effect on PeDs production was also observed on the 8Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts. We further tested the performance of physically mixed catalysts of 4Pt/MgAl<sub>2</sub>O<sub>4</sub> and LiOH in the reaction (Table 2, Entry 13). The mixed catalysts gave 36.5% PeDs selectivity, merely one half of that over the 4Pt/10Li/Mgl<sub>2</sub>O<sub>4</sub> catalyst. Therefore, the close interaction between Pt and base sites is necessary for 1,2-PeD yield enhancement in the FFA hydrogenolysis.

#### 2.1.3. Effects of Reaction Temperature on Product Selectivity

The effects of reaction temperature on FFA conversion over  $4Pt/10Li/MgAl_2O_4$  were investigated and shown in Figure 1. As the reaction temperature increased from 110 to 230 °C, the FFA conversion monotonically increased from 20.3% to 47.5%. In the meantime, the selectivity of PeDs rose up from 60.8% to 77.4%, at the expense of THFA selectivity decreasing from 34.7% to 18.2%. This catalytic selectivity to PeDs is superior to that of 55.5% obtained for 1,5-PeD (40.3%) and 1,2-Ped (15.2%) over Cu-LaCoO<sub>3</sub> catalysts [28]. The 1,5-PeD selectivity also decreased slightly, leading to the ratio of 1,2-PeD to 1,5-PeD amplified from 1.5 to 3.7. These results suggest that the apparent activation energies for the three major products are different, largely following an order of Ea <sub>1,2-PeD</sub> > Ea <sub>1,5-PeD</sub> ~ Ea <sub>THFA</sub>, which can be utilized to steer the product selectivity toward 1,2-PeD.



**Figure 1.** Catalytic conversion of FFA over 4%Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> at different temperatures (Reaction conditions: 20 g 5 wt% reactant in isopropanol solution, 0.1 g catalyst, 4 MPa H<sub>2</sub>, 4 h).

We monitored the reaction product distribution as a function of reaction time. As shown in Figure 2, in the course of a 240 min reaction at 230 °C, the 1,2-PeD, 1,5-PeD, and THFA yields concurrently increased without a peak appearance on the profiles. This suggests that the catalytic conversion of FFA to form the three major products follows parallel ways. This argument was further verified by the conditional experiment that no THFA conversion was obtained when it was used as the feedstock. In addition, less than 2.5% yield of 1-pentanol was formed in the reaction, suggesting that the PeDs were stable over the  $Pt/Li/MgAl_2O_4$  catalyst and were not prone to undergo further hydrogenolysis.



**Figure 2.** FFA conversion and product yields over 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> as a function of reaction time (Reaction conditions: 20 g 5 wt% reactant in isopropanol solution, 0.1 g catalyst, 4 MPa H<sub>2</sub>, 230 °C).

## 2.1.4. Catalyst Stability

The reusability of the 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst was evaluated at 230 °C. As shown in Figure 3, the catalyst activity was retained well in five-cycle runs. FFA conversion levelled off at 47–56% with nearly constant selectivities of 1,2-PeD and 1,5-PeD, demonstrating the good stability of 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> under the harsh reaction conditions. The XRD and TEM analyses of the spent 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst discussed below exhibited the intact crystalline structure of catalyst and the unchanged Pt nanoparticle size distribution, which supported the robust performance of the catalyst.



**Figure 3.** Reusability of the  $4Pt/10Li/MgAl_2O_4$  catalyst in FFA conversion (Reaction conditions: 20 g 5 wt% reactant in isopropanol solution, 0.1 g catalyst, 4 MPa H<sub>2</sub>, 230 °C, 4 h).

## 2.2. Physicochemical Properties of Catalysts

## 2.2.1. Physical Properties of Catalysts

The texture properties of MgAl<sub>2</sub>O<sub>4</sub> spinel and the supported Pt catalysts were measured by N<sub>2</sub> adsorption. As shown in Figure 4, the N<sub>2</sub> adsorption-desorption isotherms of these samples belong to type IV with H3 hysteresis loop according to the IUPAC (International Union of Pure and Applied Chemistry) classification [30]. This suggests that the pore structures of MgAl<sub>2</sub>O<sub>4</sub> spinel and the supported Pt catalysts belonged to the macropore network or were formed by the non-rigid aggregates of plate-like particles with ca. 12 nm average pore sizes. The introduction of Pt or Li did not change the pore structure of MgAl<sub>2</sub>O<sub>4</sub> and 82 m<sup>2</sup>/g over 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> with the introduction of Pt and Li. After being used 1–5 times, the pore structure and the specific surface areas of the spent 4Pt/MgAl<sub>2</sub>O<sub>4</sub> (one time) and 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> (five times) remained, demonstrating the high structure stability of the MgAl spinel-supported catalysts. In addition, we measured Pt and Li loadings over the spent 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst but did not find the loss of Pt (3.9 wt% vs. 3.9 wt%) and Li (4.2 wt% vs. 4.1 wt%) comparing the fresh and spent catalysts.



**Figure 4.** N<sub>2</sub> sorption isotherms of MgAl<sub>2</sub>O<sub>4</sub> and the supported Pt catalysts (Inset is the pore size distribution of  $4Pt/10Li/MgAl_2O_4$  which was obtained by the BJH (Barrett-Joyner-Halenda) method according to the branch of N<sub>2</sub> desorption isotherms).

XRD patterns of MgAl<sub>2</sub>O<sub>4</sub> support and its supported Pt catalysts are shown in Figure 5. The MgAl<sub>2</sub>O<sub>4</sub> demonstrated typical diffraction peaks belonging to crystalline phase of spinel MgAl<sub>2</sub>O<sub>4</sub>. After the loadings of 1–4 wt% Pt and LiOH, no new peak was observed, indicating the high dispersion of Pt and Li on the MgAl<sub>2</sub>O<sub>4</sub> support. At a higher Pt loading of 8 wt%, the diffraction peaks belonging to metallic Pt crystallites were present, demonstrating that Pt nanoparticles were enlarged on the support.



Figure 5. XRD patterns of MgAl<sub>2</sub>O<sub>4</sub> and supported Pt catalysts.

The dispersion of Pt species with different loadings on MgAl<sub>2</sub>O<sub>4</sub> and 10Li/MgAl<sub>2</sub>O<sub>4</sub> supports was visualized by HAADF-STEM (high-angle annular dark field scanning transmission electron microscopy) images. As shown in Figure 6a, the Pt particles on 1Pt/MgAl<sub>2</sub>O<sub>4</sub> were uniformly distributed with an average diameter of ca. 1.5 nm. Increasing the Pt loading to 2% and 4% enlarged the average diameters of Pt particles to ca 2.1 nm and widened the particle distributions slightly (Figure 6b,c). For Li-modified 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst, the presence of LiOH on the support seemed not to change the Pt particles' size distribution, which centered at 2.2 nm (Figure 6e). According to the HRTEM (high resolution transmission electron microscopy) image of 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> in Figure 6h, the lattice spacing of Pt particles was 0.226 nm, indexed to the Pt(111) plane [31]. However, from the images of 8Pt/MgAl<sub>2</sub>O<sub>4</sub> and 8Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts (Figure 6d,g), it is readily found that LiOH enhanced Pt dispersion on the support (2.6 vs. 3.0 nm). In short, as the Pt loading was varied in the range of 1-8 wt%, the Pt species on the spinel support correspondingly formed nanoparticles in sizes of 1-3 nm, giving different structures of Pt-Pt bond on the surface. In addition, the MgAl<sub>2</sub>O<sub>4</sub>-supported Pt catalysts were robust in the reaction. As shown in Figure 6f, i, the morphologies of Pt particles on both  $MgAl_2O_4$ and 10Li/MgAl<sub>2</sub>O<sub>4</sub> supports were well retained after the catalyst one- to five-cycle use under the harsh reaction conditions.



**Figure 6.** HAADF-STEM images of (**a**) 1Pt/MgAl<sub>2</sub>O<sub>4</sub>, (**b**) 2Pt/MgAl<sub>2</sub>O<sub>4</sub>, (**c**) 4Pt/MgAl<sub>2</sub>O<sub>4</sub>, (**d**) 8Pt/MgAl<sub>2</sub>O<sub>4</sub>, (**e**) 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>-Fresh, (**f**) 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>-Used, (**g**) 8Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>, (**i**) 4Pt/MgAl<sub>2</sub>O<sub>4</sub>-Used, and HRTEM image of (**h**) 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>.

## 2.2.2. Chemical Properties of Catalysts

 $H_2$ -TPR (Temperature-programmed reduction) profiles of  $4Pt/MgAl_2O_4$  and  $4Pt/10Li/MgAl_2O_4$  catalysts are shown in Figure 7. The major reduction peak (with  $H_2O$  formation) appeared at 355 °C on the profile of  $Pt/MgAl_2O_4$ . With the introduction of LiOH in the catalyst, two major peaks were detected at 242 and 375 °C, respectively. This suggests that two types of Pt particles existed on  $4Pt/10Li/MgAl_2O_4$ , which interacted with the support in weak and strong modes, respectively. In addition, the mass spectra analysis shows that some amounts of CO, CO<sub>2</sub> and CH<sub>4</sub> were present at 288–380 °C in the off-gas during the  $H_2$ -TPR experiment (Figure 8b). This should be attributed to the reduction of lithium carbonate on the catalyst, which derived from LiOH-adsorbed CO<sub>2</sub> from the air during catalyst storage.

The dispersion of Pt over the MgAl<sub>2</sub>O<sub>4</sub>-supported catalysts was determined by CO chemisorption. As listed in Table 3, the dispersion of Pt on  $1Pt/MgAl_2O_4$  was 49.1% with an estimated Pt particle size of 2.0 nm. Increasing the Pt loading to 2–4 wt% slightly decreased the Pt dispersion to 22–35%. With the introduction of LiOH on the  $4Pt/MgAl_2O_4$  catalyst, the Pt dispersion was improved to 39.6% on the support. The changing trend of Pt dispersion with respect to the metal loading and Li introduction is consistent with that observed in TEM images discussed above.



Figure 7. H<sub>2</sub>-TPR profiles of 4Pt/MgAl<sub>2</sub>O<sub>4</sub> and 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts monitored with mass spectra.



**Figure 8.** CO-DRIFT spectra of 1Pt/MgAl<sub>2</sub>O<sub>4</sub>, 4Pt/MgAl<sub>2</sub>O<sub>4</sub>, and 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts. **Table 3.** Pt dispersion over various catalysts as determined by CO chemisorption.

Entry	Catalyst	Dispersion/%	Pt diameter/nm
1	1Pt/MgAl <sub>2</sub> O <sub>4</sub>	49.1	2.0
2	$2Pt/MgAl_2O_4$	35.3	2.8
3	4Pt/MgAl <sub>2</sub> O <sub>4</sub>	22.3	4.5
4	4Pt/MgAl <sub>2</sub> O <sub>4</sub> -Used	18.1	5.5
5	4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> -Fresh	39.6	2.5
6	4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> -Used	31.0	3.2

The chemical states of Pt on the catalysts were further probed with in-situ CO-DRIFTS (CO-diffuse reflectance infrared Fourier transform spectra) (Figure 8). In the case of  $4Pt/MgAl_2O_4$ , two bands at 2056 and  $1818 \text{ cm}^{-1}$  were observed, corresponding to the CO linear and bridge bonding on Pt<sup>0</sup> species, respectively [32–34]. In contrast, on the spectra of  $1Pt/MgAl_2O_4$ , the band shifted to a higher wavenumber at 2064 cm<sup>-1</sup>, suggesting that Pt species at the lower loading were slightly electron-deficient as compared to that over  $4Pt/MgAl_2O_4$ . Moreover, the band belonging to CO bridge adsorption sites almost vanished. Correlating to the above TEM analysis, we supposed that both the microstructure and the morphology of Pt species were different among the catalysts with different Pt loadings.

With the introduction of Li on the catalyst, the band at high frequency was shifted to 2072 cm<sup>-1</sup> accompanied with a remarkable shoulder at 2026 cm<sup>-1</sup>, and the band at low frequency was lowered to 1788 cm<sup>-1</sup>. The blue shift of wavenumber indicates that  $Pt^{\delta+}$  sites were present on  $4Pt/10Li/MgAl_2O_4$ , which belong to the partially reduced Pt oxide [35]. The lowered wavenumbers should be assigned to the Pt<sup>0</sup> species with slightly enriched electrons due to the contribution from alkali modification [36]. In addition, the peak area of the bridge-bonded CO was remarkably enhanced as compared to that of the linearly bonded. Further correlating to the H<sub>2</sub>-TPR result and TEM analysis, we supposed that the introduction of Li on the support made Pt species dispersion more coarse.

After five-cycle use, the spent  $4Pt/10Li/MgAl_2O_4$  catalyst showed one large and widened CO adsorption band at 2040 cm<sup>-1</sup> on the spectra. Meanwhile, the peak area at 1800 cm<sup>-1</sup> belonging to CO bridge bonding sites was also decreased. This suggests that during the reaction, the Pt valence was decreased toward Pt<sup>0</sup> and the microstructure of Pt became more uniform. Correlating to the stable reaction selectivity and activity in the recycling experiments, we conjectured that the Pt valence and the microstructure of Pt clusters or nanoparticles did not affect the reaction selectivity remarkably, which is different from the argument reported previously [22].

The valences of Pt on the 4Pt/MgAl<sub>2</sub>O<sub>4</sub> and 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts were analyzed with XPS (X-ray photoelectron spectroscopy) (Figure 9). As shown in Figure 9 and Table 4, Pt species on the 4Pt/MgAl<sub>2</sub>O<sub>4</sub> catalyst existed in forms of Pt<sup>0</sup> and low-valence Pt<sup>2+</sup>. With the introduction of Li, 17% of Pt<sup>4+</sup> species occurred on 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>. This is consistent with the analysis of H<sub>2</sub>-TPR and CO-DRIFTS that the presence of Li on the spinel support made a part of Pt more difficult to be reduced. After five-time run in the reaction, the valence of Pt species on the spinel catalyst was reduced and very similar to that over the 4Pt/MgAl<sub>2</sub>O<sub>4</sub> catalyst. This is also consistent to that observed on CO-DRIFTS.



Figure 9. XPS spectra of 4Pt/MgAl<sub>2</sub>O<sub>4</sub>, fresh, and used 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts.

Catalyst	Pt <sup>0</sup> 7/2		P <sup>2+</sup> <sub>7/2</sub>		$P^{4+}_{7/2}$	
Catalyst	B.E./eV	Ratio/%	B.E./eV	Ratio/%	B.E./eV	Ratio%
4Pt/MgAl <sub>2</sub> O <sub>4</sub>	71.1	70.7	72.9	29.3	-	-
4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> -Fresh	71.4	49.1	72.8	66.4	74.9	17.5
4Pt/10Li/MgAl <sub>2</sub> O <sub>4</sub> -Used	71.2	71.2	73.1	29.5	-	-

Table 4. XPS analysis of MgAl<sub>2</sub>O<sub>4</sub>-supported Pt catalysts.

B.E. is the abbreviation of binding energy.

Due to the significant role of base sites in conversion of FFA to PeDs, CO<sub>2</sub>-TPD (temperature-programmed desorption) experiments were conducted to probe the basicity of MgAl<sub>2</sub>O<sub>4</sub> and its supported catalysts. As shown in Figure 10, the MgAl<sub>2</sub>O<sub>4</sub> support presented the sole CO<sub>2</sub> desorption peak at 80 °C, which belongs to weak base sites (294 umol/g). With the loading of Pt, the number of weak base sites were significantly suppressed on the 4Pt/MgAl<sub>2</sub>O<sub>4</sub> (47 umol/g), accompanied with a small amount of newly formed medium-strong base sites (24 umol/g) and notable strong base sites (desorption peaks at 400 and 660 °C, respectively). Upon the introduction of LiOH, the catalyst basicity was greatly enhanced. Two large peaks emerged at 277 and 408 °C (150 and 124 umol/g, respectively), demonstrating that a large number of medium-strong base sites were formed on the 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst.



Figure 10. CO<sub>2</sub>-TPD profiles of MgAl<sub>2</sub>O<sub>4</sub>, 4Pt/MgAl<sub>2</sub>O<sub>4</sub>, and 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>.

#### 2.3. Discussion

We have prepared various MgAl<sub>2</sub>O<sub>4</sub>-supported Pt catalysts and used them for the FFA conversion. The spinel showed its advantage in loading Pt with high dispersion. As the Pt loading varied in a wide range of 1–8 wt%, the sizes of Pt nanoparticles were tuned in 1–3 nm and the microstructures and morphorgies of Pt species were also slightly different. FFA hydrogenation was reported to be structure-sensitive over the Pt/MgAlOx catalysts. Over coordination-unsaturated 3D Pt-Pt sites in the nanoparticles, 1,2-PeD was preferentially produced, while 2-methylfuran and tetrahydrofurfuryl alcohol were favored over the coordination-unsaturated 2D Pt-Pt sites [22]. However, the reaction selectivity in FFA conversion presented herein did not show the dependence on the microstructure of Pt species. The reasons might be related to the different reaction conditions between these studies.

Introducing LiOH onto the support is an effective way to improve the reaction selectivity to PeDs over the Pt/Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts. Catalyst characterizations of TEM and CO chemosorption showed that the presence of Li on the spinel support enhanced the Pt dispersion. Moreover, it modified the valence of the Pt species and led to more  $Pt^{4+}$  and  $Pt^{2+}$  formation according to CO-DRIFTS and XPS analysis. However, during the reaction, the valence of Pt species over Pt/Li/MgAl<sub>2</sub>O<sub>4</sub> was gradually reduced and close to  $Pt^0$ , which widely existed on Pt/MgAl<sub>2</sub>O<sub>4</sub> without Li modification. Correlating to the stable reaction selectivity in the five-cycle runs of the 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst, we conjectured that the minor difference in the valence of Pt species could not affect the reaction selectivity remarkably. In addition, both 4Pt/MgAl<sub>2</sub>O<sub>4</sub> and 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub> catalysts showed high stability of structures during the running, as shown in Figures 4–6 and Table 3. The dominant factor determining the reaction selectivity should be the catalyst basicity. Among the various alkalies applied to modify the catalyst, LiOH was the most distinguished one, possibly owing to its capability to generate abundant medium-strong base sites on the catalyst, as revealed by CO<sub>2</sub>-TPD analysis. The Pt nanoparticles and base sites contacted closely on the support and played synergistic roles in improving PeDs selectivity in the reaction.

Another validated way to alter the PeDs selectivity is changing the reaction temperature. With the temperature increasing from 110 to 230 °C, the PeDs selectivity increased from 60.8% to 77.4%, with THFA selectivity depressed from 34.7% to 18.2%. Additionally, the ratio of 1,2-PeD to 1,5-PeD was improved from 1.5 to 3.7. This indicates that the apparent activation energies increase in an order of THFA~1,5-PeD < 1,2-PeD, which is the fundamental reason for tuning reaction selectivity by changing reaction temperature.

## 3. Materials and Methods

## 3.1. Catalysts Preparation

## 3.1.1. Synthesis of MgAl<sub>2</sub>O<sub>4</sub> Support

The MgAl<sub>2</sub>O<sub>4</sub> support was prepared by the ethanol pyrolysis method as reported previously [25]. In detail, 0.02 mol of magnesium nitrate and 0.04 mol of aluminum isopropoxide were dissolved in 160 mL of ethanol. Then, the mixture was transferred into a 300 mL parr reactor and heated to 160 °C in 0.5 MPa N<sub>2</sub> for 10 h under stirring at 1000 rpm. The solid was then filtered, washed, and dried at 120 °C overnight. Finally, it was calcined at 800 °C for 5 h.

### 3.1.2. Synthesis of MgAl<sub>2</sub>O<sub>4</sub>-Supported Catalysts

The MgAl<sub>2</sub>O<sub>4</sub>-supported noble metal catalysts were prepared by an incipient wetness impregnation method. Briefly, a noble metal chloride aqueous solution was impregnated on the MgAl<sub>2</sub>O<sub>4</sub> support, followed with drying at 120 °C for 8 h and calcination at 300 °C for 3 h. Then, the catalyst was reduced in a H<sub>2</sub> flow under 300 °C for 1 h and passivated with 1% O<sub>2</sub>/N<sub>2</sub> at room temperature before exposure to air. The obtained catalyst was labeled as M<sub>1</sub>/MgAl<sub>2</sub>O<sub>4</sub> (M<sub>1</sub> is the noble metal).

For the alkali-modified Pt catalysts, alkali and Pt precursors were introduced to the MgAl<sub>2</sub>O<sub>4</sub> support by the incipient wetness impregnation way in two steps. In detail, a desired amount of alkali hydroxide was dissolved in water and then MgAl<sub>2</sub>O<sub>4</sub> was added, followed with 10 min of stirring. After drying at 120 °C for 8 h, it was calcined at 550 °C for 3 h to get an alkali-modified support. Afterward, Pt was loaded on the as-modified support and treated with the same process as mentioned above to obtain the Pt-based catalyst. The obtained catalyst was labeled as Pt/M<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> (M<sub>2</sub> is the alkali)

#### 3.2. Catalyst Characterization

Brunauer–Emmett–Teller (BET) surface areas of catalysts were measured using Micromeritics Chemisorb S (Micromeritics, Atlanta, GA, USA) with nitrogen as the adsorbent at 77K. Prior to nitrogen adsorption, the sample was pre-treated at 300  $^{\circ}$ C under vacuum for 3 h.

X-ray diffraction (XRD) patterns of catalysts were measured on a PW 3040/60 X'Pert PRO (PANAlytical) diffractometer (Almelo, Netherlands) equipped with a Cu K $\alpha$  radiation

source ( $\lambda = 0.15432$  nm) operated at 40 kV and 40 mA. The spectra were recorded in 2 $\theta$  range of 5–80° at a scan speed of 5°/min.

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and high resolution transmission electron microscopy (HRTEM) images of the catalysts were obtained on JEM-2100F (JEOL, Akishima, Tokyo, Japan) at 200 kV. Before characterization, the samples were dispersed in ethanol under ultrasonic conditions. The prepared suspension was dropped on carbon-coated Cu grids followed by a slow evaporation of ethanol at room temperature.

Temperature-programmed reduction (TPR) of H<sub>2</sub> and temperature-programmed desorption (TPD) of CO<sub>2</sub>/CO were performed on a Micromeritics AutoChem 2910 (Micromeritics, Atlanta, GA, USA). For the H<sub>2</sub>-TPR experiment, samples were pretreated in a He flow at 200 °C for 1 h and then cooled at 25 °C. After changing the gas flow to 5% H<sub>2</sub>/He and cooling sample to -50 °C, temperature was increased to 800 °C at a rate of 10 °C/min. During this procedure, both TCD (thermal conductivity detector) and MS (mass spectrum) signals were collected. For CO<sub>2</sub>-TPD experiments, samples were pretreated with 5% H<sub>2</sub>/He at 300 °C for 1 h, followed by purging with He at 310 °C for 30 min and then cooling to 25 °C. Afterward, 5% CO<sub>2</sub>/He pulse was introduced to reach CO<sub>2</sub>-saturated adsorption. Finally, the temperature was increased to 800 °C at 10 °C/min. CO-TPD experiments were conducted following the same procedure, and the Pt dispersion was calculated according to the moles of CO adsorbed and the metal loaded.

CO-diffuse reflectance infrared Fourier transform spectra (CO-DRIFTS) were collected on a BRUKER Equinox 70 spectrometer (BRUKER, Karlsruhe, Baden-Wurttemberg, Germany) equipped with a MCT (mercury chromium tellurium) detector and operated at a resolution of 4 cm<sup>-1</sup> and 32 scans. The sample was pretreated with 5% H<sub>2</sub>/He at 300 °C for 1 h, followed by purging with He at 310 °C for 30 min. After the temperature decreased to 25 °C, the background spectrum was collected. Then, CO flow was introduced for 5 min to reach the CO-saturated adsorption. Again, the gas was changed to He flow, and the spectra of adsorbed CO were collected after 10 min of purging.

X-ray photoelectron spectroscopy (XPS) of different catalysts were recorded on a Thermo Fisher spectrometer (Thermo Fisher Scientific, Waltham, MA, USA)using an Al K $\alpha$  (h $\nu$  = 1486.6 eV) X-ray source with a pass energy of 30 eV, and a base pressure of  $5 \times 10^{-9}$  mbar in the analysis chamber. All samples were etched by Ar<sup>+</sup> for 10 s to obtain a fresh surface of catalysts. Binding energy (BE) values were referenced to the binding energy of the C 1s core level at 284.6 eV.

#### 3.3. Catalytic Reaction

The catalytic conversion of FFA was performed in a 50 mL autoclave. In a typical experiment, 5 wt% FFA aqueous solution (total ca. 20 g) was charged into the reactor with 0.1 g of catalyst. Then, the autoclave was sealed and purged with  $H_2$  3 times to exclude air. After 4 MPa  $H_2$  was charged into the reactor, the reaction was conducted at the desired temperature for 4 h with magnetic stirring at 800 rpm.

#### 3.4. Products' Analysis

The products were collected by filtration method and diluted with iso-propanol (1,2-propanediol as the internal standard). Then, the products were analyzed by a gas chromatograph (Agilent, 7890 B) (Agilent Technologies, Palo Alto, CA, USA) equipped with a FFAP (free fatty acid phase) column and a flame ionization detector.

#### 4. Conclusions

We synthesized MgAl spinel-supported Pt catalysts for the FFA conversion. Compared to other noble metal catalysts which readily afforded the direct hydrogen product THFA, Pt/MgAl<sub>2</sub>O<sub>4</sub> showed the highest selectivity to 1,2-PeD and 1,5-PeD. The Pt was highly dispersed on the spinel support as nanoparticles in sizes of 1–3 nm when its loading was altered in a large range of 1–8 wt%. The reaction selectivity over Pt/MgAl<sub>2</sub>O<sub>4</sub> in FFA

conversion did not show the dependence on the size of Pt nanoparticles, consistently reaching ca. 50% for PeDs and ca. 45% for THFA at 140 °C. Introducing alkali onto the support effectively steered the reaction products, particularly over the LiOH-modified catalyst. The PeDs selectivity was enhanced from 39.2% to 64.0% at the expense of THFA selectivity decreased from 48.5% to 31.0% over 4Pt/10Li/MgAl<sub>2</sub>O<sub>4</sub>. Meanwhile, the major product in PeDs was shifted from 1,5-PeD to 1,2-PeD. Catalyst characterizations revealed that LiOH introduction promoted Pt dispersion and increased the valence of Pt species to some extent. However, the reasons for the PeDs selectivity enhancement over the Li-modified Pt catalyst should be attributed to the presence of a large number of medium-strong base sites on the catalyst. The reaction temperature is an alternative factor to effectively tune the reaction selectivity. At 230 °C, the PeDs selectivity was enhanced to 77.4% with a 1,2-PeD to 1,5-PeD ratio of 3.7. The catalyst showed stable performance in five-cycle runs. The robust Pt/Li/MgAl<sub>2</sub>O<sub>4</sub> catalyst and the strategy to tune reaction selectivity developed herein would give inspiration for catalytic conversion of furfural-based biomass to high-value chemicals.

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