Applied Catalysis B: Environmental 212 (2017) 15–22

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

The role of water on the selective decarbonylation of 5-hydroxymethylfurfural over Pd/Al_2O_3 catalyst: Experimental and DFT studies

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ARTICLE INFO

Article history:
Received 13 January 2017
Received in revised form 23 April 2017
Accepted 25 April 2017
Available online 26 April 2017

Keywords:
Hydrogen bond
Water
Pd/Al_2O_3
5-Hydroxymethylfurfural
Decarbonylation

ABSTRACT

Highly selective decarbonylation of 5-hydroxymethylfurfural (HMF) to furfuryl alcohol (FOL) was originally realized by adding water to organic solvent. Side reactions such as hydrogenolysis, dehydrogenation and etherification could be effectively suppressed by introducing appropriate amount of water in pure organic solvent. Based on DFT calculations, hydrogen bonds between hydroxymethyl groups and water hinder the dehydrogenation of FOL to furfural (FAL) and furan. On the other hand, in situ water-pyridine-FTIR measurements revealed that the hydrogen bonding interaction between water and the hydroxyl groups on γ-Al_2O_3 surface decrease the acidity of Pd/Al_2O_3 and suppresses side reactions such as hydrogenolysis and etherification. Therefore, adding water to organic solvent could be a strategy for the protection of hydroxyl groups.

1. Introduction

As an abundant carbon resource and an ideal replacement for fossil fuels, biomass has attracted more and more research and application attentions. Furfuryl alcohol (FOL) is an important biomass-derived chemical, and it can be used for the manufacture of resins, rubbers and fibres [1–3]. Presently, FOL is produced by hydrogenation of furfural (FAL) [4,5]. However, FOL can be produced alternatively by the decarbonylation of 5-hydroxymethylfurfural (HMF, from C6 sugar) due to the greater availability and versatility of C_6 than C_5 sugars in biomass feedstock.

It has been reported that homogeneous $[IrCl(cod)]_2PCy_3$ [6] and heterogeneous Pd/SBA-15 [7] catalysts catalyze the decarbonylation of HMF under inert atmosphere or air efficiently. However, the high costs and anhydrous operating conditions restrict the large-scale application of these catalysts. In comparison, Pd/Al_2O_3 is effective but less expensive for HMF decarbonylation [8,9], although the acidic support could lead to dehydrogenation, hydrogenolysis etc. side reactions even under N_2 atmosphere [9]. We have increased the selectivity of FOL to 92% by suppressing the acidity of Pd/Al_2O_3 catalyst using alkali earth metal [8], but simple and operable method is desirable. Water, with Lewis base character, has been reported to have a detrimental effect on Lewis acid reactivity [10], which may thus influence the decarbonylation selectivity. In fact, water is produced in the process of HMF production, or the hydrolysis of cellulose to hexose and the dehydration of hexose to HMF. Therefore, it would be advantageous to achieve transformation of HMF in the presence of water.

Solvent effect is an important issue for liquid phase reactions. As the most important green solvent, water could also serve as a reaction promoter. Compared with many other organic solvents, its remarkable superiority could be its great ability to form hydrogen bond, which has been demonstrated in homogeneous catalysis systems [11–13]. At the interface of the aqueous and organic phases, water is supposed to interact with the organic substrates through hydrogen bond and promote their activity accordingly. This has been demonstrated by computer simulations that hydrogen bonds between water molecules and hydrogen-bond accepting groups in the complex could lower the energy of activation for Diels-Alder reaction [14]. The solvent effect of water in heterogeneous catalysts

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http://dx.doi.org/10.1016/j.apcatb.2017.04.069
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has also been reported in a few publications [15,16]. The activity of hydrogenation of acetophenone to 1-phenylethanol was promoted significantly when water was used as the solvent over Rh/Al_2O_3 and Rh/C [15]. This was achieved by the interactions between the carbonyl groups of substrates and water through hydrogen bonds on Rh/C, and the hydrogen bonds between water and the hydroxyl groups on the catalyst surfaces of Rh/Al_2O_3. Water is also useful as effective multiphase reaction media for modification of selectivity. For example, the *n*-hexane-CO_2-water medium promoted the selectivity for the hydrogenation of benzyl cyanide to 2-phenylethylamine over Pd/Al_2O_3 [16]. However, the hydrogen-bonding functional mechanism of water and the solvation effect has not been investigated in detail in heterogeneous catalysis, where solid-liquid interfaces exist.

Herein, a combined and water-containing solvent system is originally reported for the selective decarbonylation of HMF using a Pd/Al_2O_3 catalyst, and the selectivity of FOL is increased significantly to 97% with a water content of 28 wt%. The functional mechanism of water is carefully explored by the help of DFT and in situ water-pyridine-FTIR with the solvation effect considered. It is proved that the hydrogen bonding interaction between water and hydroxyl in FOL inhibits the hydroxymethyl group from dehydrogenation side reaction. Moreover, the water, with Lewis base character, could coordinate onto Lewis acid sites of γ-Al_2O_3, decrease the acidity of Pd/Al_2O_3 and suppress side reactions such as hydrogenolysis and etherification.

2. Experimental section

2.1. Catalyst preparation and evaluation

Pd/Al_2O_3 and Pd/Al_2O_3-AlOOH with 1 wt% of nominal Pd loading were prepared using an incipient wetness impregnation method. Firstly, Al_2O_3 (Aluminum Co., Ltd, of China) or Al_2O_3-AlOOH powders were impregnated with calculated amount of $Pd(NO_3)_2$ (Sinopharm Chemical Reagent Co., Ltd) aqueous solution containing 10 mg/mL of Pd for 5 h, followed by drying at 80 °C for 16 h and calcinating at 400 °C for 2 h. Prior to the reactions, the catalysts were reduced off-line with an H_2 flow at 250 °C for 2 h. The tests were performed in a 50 mL stainless steel autoclave with an inserted Teflon vessel. Typically, 1.2 g HMF (Shang Hai DEMO Medical Tech. Co., Ltd, China), 25 g solvent and 0.12 g catalysts were introduced into the autoclave. Afterwards, the reactor was purged with H_2 for several times to remove the air, and then heated to 180 °C. After the reactions are complete, the autoclave was cooled down rapidly by ice-water bath. The tail gas was collected and analyzed off-line by two gas chromatographs (models 6890N, Agilent, USA) equipped with a FID and a TCD detector respectively. The furan-derived compounds in the gaseous phase were less than 1% (mol) and could be neglected. The liquid products were filtered to remove the solid catalysts and were analyzed by another gas chromatograph (models 6890N, Agilent, USA) equipped with a DB-WAXETR capillary column (30 m × 0.32 mm × 0.5 um). The conversion and the selectivity were determined by the area normalization method. The content of FOL and HMF were also tested by external standard method normalized by the area of the solvent. The results calculated by the two methods were consistent. The conversion and selectivity of products for the reactions were calculated based on the following equations (Note: the actual selectivity of difurfuryl ether is two times of the calculated value from the equation below):

$$\text{Conversion}\,(\%) = 100 - \frac{\text{Amount of HMF after reaction (mol)}}{\text{Total amount of HMF (mol)}} \times 100$$

$$\text{Selectivity}\,(\%) = \frac{\text{Amount of a product (mol)}}{\text{Total amount of HMF converted (mol)}} \times 100$$

2.2. Catalyst characterization

The influence of water on the acidity of the catalyst was examined by the *in situ* FTIR measurements using a VERTEX70 Bruker FTIR Spectrometer. Typically, the catalyst was reduced in situ with flowing H_2 at 250 °C for 2 h prior to the measurement. Then the sample was degassed in vacuum (1×10^{-2} Pa) at 300 °C for 30 min and then cooled to 30 °C. After that, the catalyst was exposed to the water vapor for 30 min, repeating for several times. Finally, the sample was exposed to pyridine for 30 min. The spectra were recorded at 30 °C, 150 °C and 300 °C after vacuuming for 30 min.

2.3. Methods and models for DFT calculations

The plane-wave DFT calculations were carried out using the Vienna ab initio simulation package (VASP), version 5.3 [17,18]. The electron-ion interaction was described with the projector augmented wave (PAW) method [19,20]. The generalized gradient approximation and the Perdew-Burke-Ernzerhof functional (GGA-PBE) [21] were used to describe the exchange and correlation energies for all systems, and considering the long-range dispersion correction PBE-D3 functional for vdW interaction [22–24]. In the computations, an energy cutoff of 400 eV was chosen for the plane-wave basis set.

A 4 × 4 Pd(111) surface with a thickness of four atom layers was employed for all calculations. The bottom two layers were frozen, and the top two layers were allowed to relax. The vacuum layer between periodically repeated slabs was set as 20 Å to avoid interactions among slabs. The Brillouin zone was sampled with a 3 × 3 × 1 k-point grid. Surface relaxation was performed until all forces were smaller than 0.05 eV/Å. To locate the transition states of decarbonylation of HMF on Pd(111), the nudged elastic band (NEB) method [25] was applied and the stretching frequencies were analyzed to characterize transition state with only one imaginary frequency.

The adsorption energy was defined as $E_{ads} = E_{slab+i} - E_{slab} - E_i$, where E_{slab+i} is the total energy of the adsorbate/slab system, E_{slab} is the total energy of the clear slab and E_i is the total energy of the adsorbate in gas phase. The reaction barrier (E_a) and reaction energy (E_r) are defined as $E_a = E_{TS} - E_{IS}$ and $E_r = E_{FS} - E_{IS}$, where E_{IS}, E_{TS}, and E_{FS} are the energies of the corresponding initial state (IS), transition state (TS) and the final state (FS).

The solvation energy and solvation effect on reaction energy and barrier are calculated with VASPsol software [26].

3. Results and discussion

3.1. Decarbonylation performance of HMF over Pd/Al_2O_3 catalyst in different media

Decarbonylation of HMF was studied with Pd/Al_2O_3 catalyst in different reaction media at 180 °C. Under these conditions, a series of products were produced, including desired product FOL; side products: FAL and furan, 2-methylfuran (2-MF), 2, 5-dimethylfuran (DMF) and 5-methylfurfural (MFAL), and etherification products. The reaction pathways of the products are shown in Scheme 1 as previously reported [9]. The sources of side products fall into three categories: hydrogenolysis, dehydrogenation and etherification reactions. In the solvent of 1, 4-dioxane, difurfuryl ether (DFE) was the main etherification product. When methanol or ethanol was added into 1, 4-dioxane, large amount of ether 5-methoxymethylfurfuryl alcohol (MOMFOL) or 5-ethoxymethylfurfuryl alcohol (EOMFOL) appeared. MOMFOL and EOMFOL are likely produced respectively by etherification of