



Short communication

Tuning the selectivity of phenol hydrogenation on Pd/C with acid and basic media

Mingming Li¹, Yi Li, Lu Jia, Yong Wang*

Advanced Materials and Catalysis Group, ZJU-NHU United R & D Center, Center for Chemistry of High-performance and Novel Materials, Department of Chemistry, Zhejiang University, Hangzhou 310028, PR China

ARTICLE INFO

Keywords:

Phenol hydrogenation
Pd/C
Selectivity
Acid-base property

ABSTRACT

The selectivity of phenol hydrogenation over Pd/C was successfully tuned by various Brønsted acid and base additives. Compared with neutral reaction condition, the basic condition witnessed decreased catalytic activity and cyclohexanone selectivity while the opposite trend was observed under acidic condition. Mechanistic studies indicated the varied interaction of substrate with acid and base is responsible for the activity difference, while the changed keto-enol tautomerization correlates directly to the selectivity variation.

1. Introduction

Selective hydrogenation of phenol has attracted great attention because of the importance of cyclohexanone in the synthesis of caprolactam and adipic acid, which is the intermediate for nylon 6 or nylon 66 [1]. To achieve high activity and product selectivity in phenol hydrogenation, researchers have made great efforts in the development of effective catalysts [2–8]. Among the various kinds of catalysts, metal supported catalysts have recently been the focus of researchers due to their controllable active centers (such as Pd, Pt, Rh, Ni) and diverse supports availability (such as metal oxides, zeolites, porous carbons) [2,9–12]. In view of the relatively low cost of Pd and its high activity in phenol hydrogenation, Pd based catalysts have attracted more attention.

Considering the great influence of catalyst supports on the reaction activity, efforts have been devoted to the controllable designing of catalyst supports. On the one hand, directly employing the various catalyst supports for the anchoring of Pd nanoparticles (NPs) was able to change the reaction activity and selectivity [4,13–16]. On the other, through controlling the acid-base property of the catalyst supports has also demonstrated its great influence on phenol hydrogenations [17–20]. For instance, the Han group reported that the introduction of Lewis acid such as AlCl₃ and ZnCl₂ in the Pd/C catalyzed liquid-phase phenol hydrogenation could effectively activate the benzene ring and stabilize the C=O group through acid-base interaction between the Lewis acid and cyclohexanone, thus ensuring the high activity and high cyclohexanone selectivity [21]. Based on above discussion, it can be concluded that the acid-base property of reaction system has a

significant influence on the reaction activity and product selectivity of phenol hydrogenation. Therefore, understanding the relationship between the acid-base property of the reaction solution and the product selectivity is of vital importance to the process. Unfortunately, there is no systematic investigation on the underlying mechanism of phenol hydrogenation under different acidity-alkalinity.

Herein, employing Pd/C as the catalyst, the effect of acid and basic media on the phenol hydrogenation of phenol was studied in detail through adjusting the acid-base property of the reaction media. The factors such as the reaction pH, acid-base additives and reaction solvent were studied. The reaction mechanisms of phenol hydrogenation in acid and basic aqueous media were investigated using density functional theory (DFT) calculations.

2. Experimental

2.1. Catalyst preparation and catalytic hydrogenations

The preparation method of Pd/C was modified from a previously reported one [22], with only the change of the support to activated carbon. Phenol hydrogenations were carried out in a stainless-steel autoclave with pressurized hydrogen. Detailed experimental procedures are described in Supplementary material.

2.2. Theoretical calculations

All the calculations in the present work were carried out on a Gaussian 03 [23]. The density functional theory, the B3LYP method and

* Corresponding author.

E-mail address: chemwy@zju.edu.cn (Y. Wang).¹ These authors contributed equally.

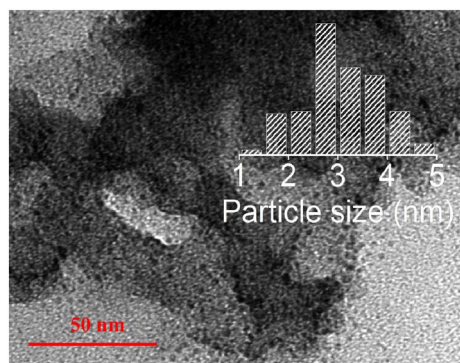


Fig. 1. TEM image and Pd particle size distribution of Pd/C catalyst.

basis set called 6-31G (2df, p) were used for all model compounds and reaction processes. Notably, the calculations were only considered on the organic molecules. Geometry optimizations, frequency and energy calculations were all carried out under this level of basis set. The stable points for all the optimized geometries were at the minimum energy point and no imaginary frequency was observed. For the transition state structures, only one imaginary frequency existed and the vibration direction were directed to the reactant and product respectively. The minimum energy paths for the transition state structures were further affirmed through intrinsic reaction coordinate (IRC).

3. Results and discussion

TEM characterization was firstly investigated. TEM image of Pd/C catalyst in Fig. 1 demonstrated that the small Pd NPs were uniformly distributed on the carbon support, showing an average Pd particle size around 3.1 nm (inset in Fig. 1). X-ray diffraction (XRD) pattern for Pd/C in Fig. S1A witnessed peaks at 40.1° , 46.6° and 68° which are typical patterns for Pd (111), Pd (200) and Pd (222), indicating the successful reduction of the Pd species. N_2 adsorption-desorption isotherms for Pd/C in Fig. S1B showed only a slight decrease of surface area ($813 \text{ m}^2/\text{g}$) compared with that of C ($892 \text{ m}^2/\text{g}$), indicating good maintenance of the pore structure of carbon support (pore volume of $0.77 \text{ cm}^3/\text{g}$ for Pd/C and $0.82 \text{ cm}^3/\text{g}$ for C).

Having successfully prepared the Pd/C catalyst, the effect of acid or base additives on the performance of phenol hydrogenation over Pd/C in aqueous media was thus studied. The results were shown in Table 1. In the absence of additive, 37% of phenol conversion and 82% cyclohexanone selectivity was obtained (entry 1, Table 1). When protonic acid (entries 2–4, Table 1) or acid salt (entry 5, Table 1) were added into, apparently increased cyclohexanone selectivity (90–95%) was

Table 1
Catalytic results of different additives in hydrogenation of phenol.

Entry	Additive	Conv. (%)	Sel. (%)	
			Cyclohexanone	Cyclohexanol
1	–	37	82	17
2	HCOOH	36	95	5
3	CH ₃ COOH	61	91	8
4	HCl	38	95	5
5	NH ₄ Cl	39	90	10
6	NaCl	38	82	17
7	Na ₂ SO ₄	36	83	16
8	NaOH	33	61	39
9	NaHCO ₃	35	69	31
10	Na ₂ CO ₃	32	64	36
11	CH ₃ COONa	35	71	29

Reaction condition: phenol 1 g (10.6 mmol), Pd/C 25 mg, additive 40 mg, H₂O 20 mL, H₂ pressure 1.0 MPa, temperature 100 °C, reaction time 2 h.

observed. Notably, much increased activity was observed when CH₃COOH was used as an additive. When the additive was neutral, phenol hydrogenation was not affected (entries 6–7, Table 1). However, when it comes to basic additives such as inorganic bases (entries 8–11, Table 1), slightly decreased activity was seen while sharply decreased cyclohexanone selectivity was observed. From these results, we deduced that the changed acid-base property of the reaction solution may be responsible for the activity and selectivity changes.

Firstly, the hydrogenation processes as a function of time in both acidic and basic media were thus investigated, as shown in Fig. S2. As can be seen, the activity was much higher in CH₃COOH solution than that in NaOH aqueous media. Although both decreased cyclohexanone selectivity was observed, the selectivity in acidic media dropped much slower, showing much higher selectivity towards cyclohexanone at equal phenol conversion. These results well illustrated the great influence of the acid-base property of the reaction solution on the activity and selectivity changes. After the reaction, the used catalyst in the above two reaction media was further characterized. XRD patterns in Fig. S3 demonstrated that the reduced Pd nanoparticles were not oxidized, still showing typical peaks for Pd⁰ species. HRTEM images in Fig. S4 showed that, in both acidic and basic reaction media, Pd particle size growth and local Pd agglomerations were observed. Although both Pd/C catalysts saw particle size growth after the hydrogenations, however, they saw very similar trend. These results thus excluded the influence of catalyst changes difference on the catalytic performance in different reaction media, which well proved the major influence of the reaction media on the hydrogenation process.

Afterwards, a series of aqueous solutions with pH values ranging from 1 to 14 were prepared using HCl or NaOH, and the results were shown in Fig. 2. As is observed, under acid conditions, phenol conversion was not affected while cyclohexanone selectivity saw obvious increase when the pH value is below 4. In contrary, when the pH value of the reaction condition was above 10, both activity and selectivity saw apparent decrease along with the increased pH value. Therefore, we concluded that the changed acid-base environment around phenol greatly affects its reaction activity, showing totally different trends in acid and basic aqueous media. To further prove this hypothesis, phenol hydrogenation in a nonpolar solvent-cyclohexane was then conducted, and the results were shown in Table S1. It was found that in cyclohexane, the product selectivity was not affected regardless of the addition of acidic CH₃COOH or basic NaOH, although slightly increased activity were both observed. These control experiments thus well confirmed that the H⁺ or OH[–] in aqueous media may correlate closely with the varied activity and selectivity, the reasons for which will be further illustrated in the following.

In basic media, the reason for the greatly decreased activity was firstly investigated. It is known that phenol is a weak acid, and may react with the base to form phenolate [24]. Sodium phenolate was thus

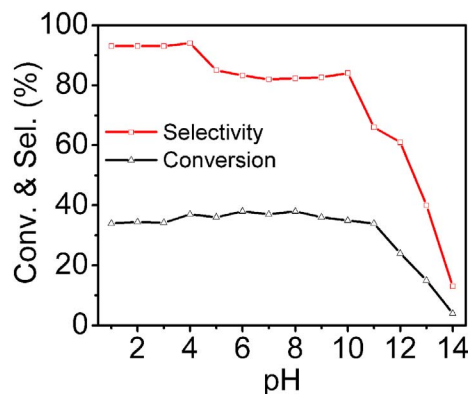


Fig. 2. The effect of pH on the activity and cyclohexanone selectivity of phenol hydrogenation.

Download English Version:

<https://daneshyari.com/en/article/4756280>

Download Persian Version:

<https://daneshyari.com/article/4756280>

[Daneshyari.com](https://daneshyari.com)