Short communication

Recyclable Pd supported catalysts with low loading for efficient epoxidation of olefins at ambient conditions

Xiaohui He, Long Chen, Xiantai Zhou, Hongbing Ji *

School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

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ABSTRACT

Epoxides are a kind of useful synthetic intermediates. This work reports that activated carbon-supported Pd nanoparticles (Pd/C) efficiently catalyzed cyclohexene epoxidation in the presence of molecular oxygen and isobutyraldehyde with 91.5% conversion, 95.6% selectivity to cyclohexene oxide, ~400 h^{-1} activity and excellent stability for at least 5 catalytic runs. The epoxidation was examined on Pd catalysts supported on seven supports, and Pd/C exhibited superior catalytic performance possibly due to the inert support surface. The epoxidation reaction on Pd/C is via radical intermediate. Pd/C is also applicable to catalyze other olefins epoxidation.

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1. Introduction

Epoxidation of olefins has been widely concerned because the formed epoxides are value-added synthetic intermediates for various products including paints, epoxy resins, and surfactants [1,2]. Mostly, oxidants with active oxygen are employed as oxygen source in the ep-oxidation, including peracids [3], PhIO [4], H_2O_2 [5], and tert-BuOOH [6,7]. However, from economic and environmental-friendly perspective, the epoxidation process using molecular oxygen as oxygen atom donor is highly desirable. [8] Noble metals, (e.g., Au, Pt, Ru, Pd, and Rh) were suitable catalysts due to their high efficiency in molecular oxygen activation and organic aerobic oxidation [9–11], but suffers from the involvement of hydrogen in the epoxidation process which has safety risks [12,13]. Thus, hydrogen free aerobic epoxidation has been attempted, such as Pd, Ti-modified MCM-22 in presence of methanol for propylene epoxidation [14] and Pd/SiO_2 for olefin epoxidation [15]. However, they still require optimization due to low epoxide yield (19.5%) and high consumption of precious metal (10 wt%) to reach a satisfactory activity, respectively.

Here we report efficient epoxidation of olefins with a high yield of ~90% using 0.5 wt% Pd supported on activated carbon in the presence of molecular oxygen and isobutyraldehyde as coreductant, and the activity is as high as ~400 h^{-1}. The impacts of noble metals, supports, isobutyraldehyde concentrations, and solvents on the activity and

epoxide selectivity were examined. Pd/C is a stable and recyclable catalyst, applicable to catalyze epoxidation of other olefins.

2. Experimental

Activated carbon-supported catalysts (0.5 wt%) were prepared by incipient wetness impregnation. Activated carbon supplied by Kemiou was first treated at 393 K overnight, then added to aqueous solutions of $RuCl_3$-nH_2O (Aladdin), $RhCl_3$-nH_2O (Aladdin), H_2AuCl_4-nH_2O (Energy Chmical), H_2PtCl_6-nH_2O (Aladdin), and $PdCl_2$ (J&K) with ~0.5 mL concentrated hydrochloric acid solution, respectively. The samples were dried at 373 K overnight and subsequently reduced in hydrogen (Guangzhou Zhuozheng, 99.999%) at 673 K for 4 h. ZrO_2, Al_2O_3, CeO_2, TiO_2, H-ZSM-5(Si/Al = 25) and MgO supported Pd catalysts were prepared in the same way. ZrO_2, Al_2O_3, CeO_2, TiO_2, and MgO were purchased from Alfa Aesar, and H-ZSM-5(Si/Al = 25) was supplied by The Catalyst Plant of Nankai University.

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku's D/max 2200 v powder X-ray diffractometer using Cu Kα radiation source ($\lambda = 1.5406$ Å). Transmission electron microscopy (TEM) images were taken on a JEM2010-HR electron microscope. X-ray photoelectron spectroscopy (XPS) measurements were executed on an ESCALab250 XPS system with Al Kα source and a charge neutralizer, and all the binding energies were referenced to the contaminated C 1s peak at 284.8 eV.

Cyclohexene epoxidation reactions were carried out in tailored tubes. Typically, 10 mL dichloromethane, 4 mmol olefin, 20 mmol

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* Corresponding author.
E-mail address: jihb@mail.sysu.edu.cn (H. Ji).

isobutylaldehyde, 0.1 g catalysts and 2 mmol naphthalene (as internal standard) were mixed with stirring at 303 K. Then, dioxygen (Guangzhou Zhuozheng, 99.999%) was bubbled through the solution. For recycling, the catalyst was simply reduced in hydrogen at 673 K for 1 h. The reactants and products were analyzed by GC (Shimadzu GC2010 plus) and GC–MS (Shimadzu GCMS-QP2010). Activities were reported as molar cyclohexene conversion rates per mole of Pd per hour (h^{-1}).

3. Results and discussion

3.1. Conversions and product selectivities in epoxidation of cyclohexene on supported Pd catalysts

Seven different supports, including C, ZrO_2, Al_2O_3, CeO_2, TiO_2, H-ZSM-5, and MgO with different surface acid-basicity and reducibility, were employed to support Pd clusters for the cyclohexene epoxidation. Activated carbon is an inert support [9], as confirmed by the controlled experiment (entry 13, Table 1). MgO is regarded as solid base, while Al_2O_3 and H-ZSM-5(25) as solid acids. TiO_2, CeO_2, and ZrO_2 are typical metal oxides with redox properties. XRD patterns (Fig. S1) showed no Pd diffraction peak in these catalysts indicating that Pd was well dispersed on all these supports. Compared at the same reaction conditions (303 K, 0.1 g catalyst, 4 mmol cyclohexene, 20 mmol isobutyraldehyde, 2 mmol naphthalene, 10 mL CH_2Cl_2, O_2 bubbling, 2 h), Pd/C exhibited both superior conversion (91.5%) and selectivity to cyclohexene oxide (95.6%). However, Pd supported on other supports exhibited much lower conversions (<65%). These results implied that C was the most suitable support among the seven supports, possibly due to its inert surface. To examine the effect of the Pd oxidation state on the epoxidation reaction, PdO_x/C (binding energy of Pd 3d5/2: 337.3 eV, the average particle size: 2 nm, Fig. S3) was prepared by treating Pd/C at 473 K for 2 h under air and compared with Pd/C (binding energy of Pd 3d5/2: 335.8 eV, the average particle size: 1.7 nm, Fig. 2a) under identical conditions. As shown in Table 1 entry 1 and entry 8, the conversion declined from 91.5% on Pd/C to 59.1% on PdO_x/C, indicating that the Pd^0 species are the main active sites for the epoxidation of cyclohexene under the conditions employed in this work. The epoxidation reactions on other supported noble metal catalysts, including Ru/C, Au/C, Pt/C, and Rh/C, were also conducted, as shown in Table 1 entries 9–12. XRD for these catalysts (Fig. S2) shows that no obvious noble metal diffraction peak in these catalysts, which implies that all the noble metals were well dispersed on activated carbon. Ru/C showed superior activity for the
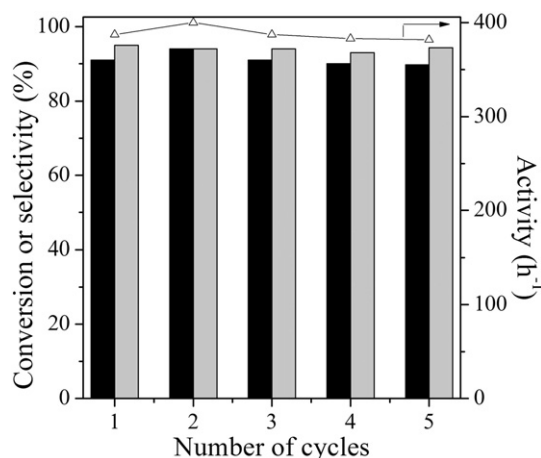

Fig. 1. Conversions (■), selectivities (▨), and activities (△) for the five cycles of cyclohexene epoxidation on Pd/C with Pd loading of 0.5 wt% (303 K, 0.1 g Pd/C, 4 mmol cyclohexene, 20 mmol isobutyraldehyde, 10 mL CH_2Cl_2, 2 mmol naphthalene as internal standard, O_2 bubbling, 2 h).

epoxidation (97.3% conversion) but relatively lower selectivity to cyclohexene oxide (82.2%). In contrast, Au/C, Pt/C, and Rh/C exhibited high selectivity to cyclohexene oxide (97.4%, 94.7%, and 94.1%, respectively) but lower conversions (68.8%, 84.1%, and 87.0%, respectively) than Pd/C. Based on these results, Pd/C was the most suitable catalyst in this epoxidation reaction for its excellent catalytic performance.

As shown in Fig. 1, recycling Pd/C catalyst for five runs exhibited no essential decline of cyclohexene conversions (~90%), selectivities to cyclohexene oxide (~95%), and the activities (~400 h^{-1}). TEM images before and after five runs showed no essential change in the size distribution of the Pd nanoparticles (1.7 ± 0.3 nm vs. 1.9 ± 0.4 nm, Fig. 2).

3.2. Effects of reaction parameters on cyclohexene epoxidation

Fig. 3 displays the cyclohexene conversions and the selectivities to cyclohexene oxide as a function of the reaction time on Pd/C at 303 K. The selectivity slightly decreased from 98.8% to 95.6% with the conversion increasing from 11.0% to 92.0%, indicating that the high epoxide selectivity can be kept even at high cyclohexene conversion.

The effect of isobutyraldehyde concentration on the reaction rates was also discussed (Fig. S4). The cyclohexene conversion increased sharply from 5.1% to the maximum value of 91.5% with increasing the molar ratio of isobutyraldehyde to cyclohexene from 0 to 5.0, and then kept almost unchanged (90.0%) afterwards to molar ratio to 6.0. Therefore, 20 mmol isobutyraldehyde was enough in this reaction of 4 mmol cyclohexene.

Table S1 shows the catalytic performance of the Pd/C catalyst for the epoxidation of cyclohexene in a serious of solvents with varying polarity represented by their empirical parameters E_T. [16] The cyclohexene conversion increased from 0% to the maximum of 91.5% with the decrease of the E_T value from 0.762 (methanol) to 0.309 (dichloromethane), and then decreased to 16.1% with further decreasing the E_T value to 0.006 (cyclohexane). Polar solvents exhibited poor performance in this radical oxidation reaction mainly because of the low solubility and thus the low actual concentration of oxygen. [17] On the other hand, in the non-polar solvent the cleavage of the peroxo bond of the intermediate and the transfer of active oxygen atom to olefin may become difficult. [18] These results implied that the solvent polarity is crucial for the epoxidation reactions and solvents with moderate polarity (e.g. CH_2Cl_2) were optimal.

Table 1
Conversions and product selectivities in epoxidation of cyclohexene on different Pd catalysts and on activated carbon-supported Ru, Au, Pt, and Rh.[a]

Entry	Catalysts	Conversion (%)	Selectivity (%)
1	Pd/C	91.5	95.6
2	Pd/MgO	23.9	88.3
3	Pd/Al_2O_3	25.2	88.5
4	Pd/H-ZSM-5(25)	3.3	99.8
5	Pd/ZrO_2	31.4	90.1
6	Pd/CeO_2	64.7	82.4
7	Pd/TiO_2	28.5	60.7
8	PdO_x/C[b]	59.1	92.6
9	Ru/C	97.3	82.2
10	Au/C	68.8	97.4
11	Pt/C	84.1	94.7
12	Rh/C	87.0	94.1
13	C	25.4	85.7
14	Blank	11.2	93.4

[a] Reaction conditions: 303 K, 0.1 g catalyst, 4 mmol cyclohexene, 20 mmol isobutyraldehyde, 2 mmol naphthalene as internal standard, 10 mL CH_2Cl_2, O_2 bubbling, 2 h.
[b] Prepared by Pd/C calcined at 473 K for 2 h under air.