



Silylated Pd/Ti-MCM-41 catalyst for the selective production of propylene oxide from the oxidation of propylene with cumene hydroperoxide

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ARTICLE INFO

Article history:

Received 29 September 2017

Received in revised form 2 January 2018

Accepted 23 January 2018

Available online 31 January 2018

Keywords:

Porous materials

Structural

Ti-MCM-41

Palladium

Silylation

Propylene epoxidation

ABSTRACT

Titanium-containing mesoporous molecular sieves with regular pore structure, high specific surface area, tunable pore size and suitable active sites have attracted great attention in the epoxidation of alkenes. Herein, we report the silylated Pd/Ti-MCM-41 (PdTM-ZS) catalysts prepared by treating the series Ti-MCM-41 samples (Si/Ti molar ratio = 10, 15, 20, 25 and 30) with palladium loading followed by surface silylation with trimethylchlorosilane. Reaction results show that the PdTM-ZS catalysts can be applied as efficient catalysts for the selective production of propylene oxide from the oxidation of propylene with cumene hydroperoxide as the oxidant. The PdTM-20S catalyst exhibits an excellent catalytic performance with the selectivity of propylene oxide approaching 100%, which can be attributed to the synergistic effect of abundant active sites, palladium loading and surface silylation.

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1. Introduction

The catalytic oxidation of hydrocarbons is a very important process in the chemical industry [1–4]. As a key propylene derivative, propylene oxide (PO), is an important chemical feedstock for producing fine chemicals [5–8]. PO is commonly produced by the chlorohydrin process and the hydrogen peroxide/propylene oxide (HPPO) process in industry [9,10]. However, the chlorohydrin method is environmentally unfriendly, producing a lot of chlorine containing waste water and chlorinated organics [9–11]. And although the HPPO process is environmentally friendly, it usually generates multiple by-products and requires the production of hydrogen peroxide on site to guarantee economic benefits [8,10]. Recently, the selective oxidation of propylene to PO by the cumene hydroperoxide/propylene oxide (CHPO) process has aroused much attention academically and industrially since the cumyl alcohol formed after epoxidation can be easily recycled on a large scale [12–14].

The conventional microporous zeolite catalysts such as TS-1 cannot be applied in the CHPO process with large organic hydroperoxide molecules due to the limited diffusion efficiency of products and reactants in the small zeolite pores [8,15–18]. To address this problem, titanium-containing mesoporous molecular sieves with regular pore structure, high specific surface area and tunable pore size, such as Ti-MCM-41, have been employed [8,12,19]. However, the catalytic performance of

Ti-MCM-41 in the CHPO process is unsatisfactory with low catalytic activity and PO selectivity. In this study, we attempt to optimize the traditional Ti-MCM-41 catalyst by employing it as a support for palladium followed by the silylation treatment. The reaction results show that the PdTM-ZS catalysts are highly efficient for the selective production of PO from the CHPO process.

2. Experimental

2.1. Catalyst preparation

Firstly, solution A was prepared by dissolving 5.7 g of $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ into 34 mL of deionized (DI) water; solution B was prepared by dissolving 1.85 g of CTAB into 10 mL of DI water; and solution C was prepared by dissolving a certain mass of $\text{Ti}(\text{SO}_4)_2$ into 10 mL of DI water at room temperature. Solution A and B were then thoroughly mixed with 0.5 h of vigorous stirring, and then the pH of the solution was adjusted to 7. Secondly, solution C was added to the mixed solution and the pH of the mixture was adjusted to 9.5. The resulting mixture was stirred at 40 °C for 2 h, and then was transferred to a 150 mL polytetrafluoroethylene autoclave. The hydrothermal reaction was performed at 120 °C for 72 h. After reaction, the product was separated by filtration, washed thoroughly with DI water, and dried at 100 °C for 10 h. Afterwards, the dried powder was calcined in air at 550 °C for 5 h at a temperature ramping rate of 2 °C/min to obtain Ti-MCM-41. The prepared Ti-MCM-41 samples with different Si/Ti molar ratios were denoted as TM-Z, where Z was the molar ratio of Si/Ti.

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The TM-Z samples were employed as supports for the preparation of Pd/Ti-MCM-41 catalysts with nominal 0.2 wt% palladium loading. In this procedure, PdCl₂ were firstly dissolved in the hydrochloric acid solution. Then the supports were impregnated with the PdCl₂ solution. Afterwards, the samples were dried at 100 °C for 10 h and calcined at 450 °C for 4 h. The obtained samples were denoted as PdTM-Z. For the silylation process, 0.2 g of PdTM-Z samples were added to 0.08 g of trimethylchlorosilane and 3.0 g acetone under stirring. Then the mixture was transferred to a 100 mL polytetrafluoroethylene autoclave, placed at 120 °C for 5 h. After reaction, the product was separated by filtration, washed with ethanol and dried at 100 °C for 2 h. The silylated samples were denoted as PdTM-ZS.

2.2. Catalyst characterization

The small-angle X-ray diffraction patterns (SA-XRD) and the wide-angle X-ray diffraction patterns (WA-XRD) were recorded on a D8 Advance diffractometer with Cu K α radiation ($\lambda = 0.154056$ nm). The Fourier-transform infrared (FT-IR) spectra were obtained with a Bruker Tensor 27 spectrometer. The UV–vis absorption spectra were recorded on a CARY 5000 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo, Fisher Scientific ESCALAB 250Xi spectrometer. The morphology and structure of the samples were examined by scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, Tecnai 12) equipped with an energy-diffusive X-ray spectroscopy (EDS) attachment. The N₂ adsorption and desorption isotherms were collected at 77 K on a Quantachrome Autosorb-iQ3.

2.3. Catalyst test

For the epoxidation of propylene with cumene hydroperoxide (CHP), in a typical process, a mixture of 166 mmol of cumene and 0.2 g of catalyst were heated at 80 °C in a three-necked flask. Then, propylene (22.5 mL/min) is introduced into the reactor, and CHP (2.2×10^{-3} mol/min) was added dropwise by a constant pressure dropping funnel.

The effluent gas released from the reactor was analyzed by a gas chromatography (FULI 9790) with a KB-1 column and N₂ as a carrier gas. The propylene conversion and PO selectivity were calculated by the following equations:

$$\text{Propylene Conversion (\%)} = \frac{\text{(formed derivatives of propylene in molar/initial propylene in molar)}}{\times 100\%}$$

$$\text{PO Selectivity (\%)} = \frac{\text{(PO in the product in molar/formed derivatives of propylene in molar)}}{\times 100\%}$$

3. Result and discussions

The WA-XRD patterns of the samples are shown in Fig. 1a. All the samples show a broad peak from 20° to 30°, which can be indexed to the typical amorphous silica [15]. For the PdTM-10S and PdTM-15S, however, a tiny peak centered at ca. 25°, corresponding to anatase titanium oxide, can be observed. This indicates that a small part of Ti atoms crystallized and aggregated due to the high titanium usage during the preparation of these two samples. For the other samples, as expected, almost all the Ti atoms have been incorporated into the MCM-41 framework. In addition, none of these samples shows the diffraction peaks of PdO, suggesting that the PdO particle size is quite small and should be highly dispersed within the mesoporous channels. Fig. 1b shows the SA-XRD patterns of the samples. All the samples exhibit three peaks indexed to the (100), (110), (200) planes, indicating a uniform hexagonal pore structure [20]. With the decrease of the Si/Ti molar ratio, the intensity of the (100) peak gradually reduces, suggesting the lowering in the structure regularity due to the incorporation of Ti into the framework [21].

Fig. 1c shows the FT-TR spectra of the samples. Compared with the unsilylated samples, the silylated samples present significantly lower intensity of the peaks assigned to the stretching of hydroxyl at 3400–3700 cm⁻¹ and the Si–OH bending vibration at 1633 cm⁻¹.

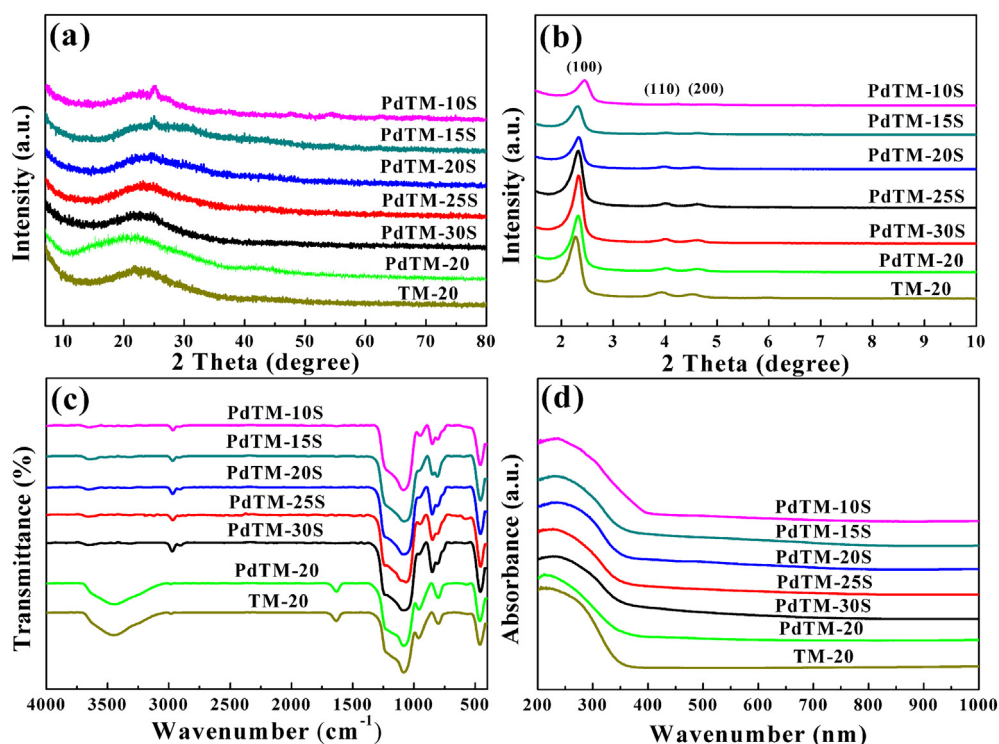


Fig. 1. WA-XRD patterns (a), SA-XRD patterns (b), FT-IR spectra (c) and UV–vis spectra (d) of the samples.

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