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Catalytic epoxidation of cyclohexene over mesoporous-silica immobilized Keggin-type tungstophosphoric acid

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ABSTRACT

A series of aminosilylated mesoporous silica (SBA-15) samples with different contents of (3-aminopropyl)triethoxysilane (APTES), synthesized using a simple one-pot method, were used as hosts for immobilization of Keggin-type 12-phosphotungstic acid ($H_3PW_{12}O_{40}$). The loading of $H_3PW_{12}O_{40}$ increased with increasing content of grafted APTES. The obtained materials were calcined at different temperatures, and the tungsten species were highly dispersed inside the SBA-15 channels. The catalytic activities of these samples were tested in heterogeneous oxidation of cyclohexene using H_2O_2 as the oxidant. The effects of different loadings and treatment temperatures on the activities of the catalysts were also investigated. The catalysts calcined at 400 °C showed high catalytic activities and reusabilities.

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1. Introduction

Tungsten-based catalysts have attracted much interest because they exhibit excellent catalytic activities in various reactions, such as epoxidation of alkenes [1–7], selective oxidation of alcohols [8–11], oxidative cleavage of olefins [12], and oxidative desulfurization of sulfur-containing organics [13]. Among these catalysts, materials based on Keggin-type 12-phosphotungstic acid ($H_3PW_{12}O_{40}$) have been extensively studied because of their high activity [14–23]. However, the high solubility of $H_3PW_{12}O_{40}$ in water and polar organic solvents and the low surface area of $H_3PW_{12}O_{40}$ limit practical applications. Heterogenization of the heteropoly acid is a feasible way of solving these problems. There have been a number of reports of heteropoly acids being highly dispersed on oxide supports such as SiO_2 , ZrO_2 , and TiO_2 [24–28]. In terms of “green chemistry”, however, high activity of the catalyst is not

the only concern, and good reusability and environmental friendliness are equally important.

Mesoporous silica SBA-15, which has an adjustable pore size and high thermal stability, is regarded as a good support for the accommodation of catalytic active species [29,30]. Furthermore, it is well documented that the surface of SBA-15 can be easily modified with different functional groups. Recently, the grafting of (3-aminopropyl)triethoxysilane (APTES) onto a silica surface was reported as a post-modification method for the introduction of functional amino groups onto a silica surface [31–33]. The surface-bonded amino groups can be used as a base to firmly anchor acidic species, e.g., iso- and hetero-poly acids, on the silica surface through electrostatic interactions [34,35].

Compared with the above conventional grafting method, the co-synthesis method offers a direct and easy way of modifying the surface of a mesoporous material in one pot by the copoly-

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merization of an organosilane with silica or organosilica precursors in the presence of a surfactant. This approach provides a higher content of functional organosilane groups. It is expected that as a result of the strong interactions between amino groups and polyacid species, the immobilized heteropoly acid/mesoporous silica composite materials will exhibit satisfactory reactivities and anti-leaching properties in epoxidation reactions involving H_2O_2 .

In this work, $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was immobilized on one-pot-synthesized aminosilylated mesoporous silica SBA-15 with various organosilane contents. The as-synthesized samples were characterized using various techniques, including X-ray diffraction (XRD), N_2 adsorption-desorption, transmission electron microscopy (TEM), nuclear magnetic resonance (NMR), and infrared (IR) spectroscopy. The effects of tungsten species loading and calcination temperature on the SBA-15 structure were investigated. In a model reaction, cyclohexene epoxidation with H_2O_2 as an oxidant, the SBA-15-incorporated tungstic species displayed high reactivity combined with good reusability.

2. Experimental

2.1. Preparation

The APTES-functionalized SBA-15 samples were synthesized according to the literature method [36,37]. Four grams of a surfactant, poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123), were dissolved in 125 g of 2.0 mol/L HCl solution at room temperature. After addition of 8.5 g of tetraethyl orthosilicate (TEOS), the solution was kept at 40 °C for prehydrolysis, and then a specific amount of APTES was slowly added to the solution. The resulting mixture was stirred at 40 °C for 20 h and then aged at 90 °C for 24 h. APTES-functionalized SBA-15 samples (APTES-SBA-15) were prepared with 0.1, 0.2, 0.5, 0.8, 1.0, and 1.6 g of APTES, and denoted by AS-*n* (*n* = 0.1, 0.2, 0.5, 0.8, 1.0, 1.6). The solid product was recovered by filtration and dried at room temperature overnight. Template removal from the as-synthesized material was conducted by refluxing in 95% ethanol for 24 h (1.5 g of as-synthesized material per 400 ml of ethanol). Finally, the samples were filtered, washed several times with water and ethanol, and dried at 50 °C.

A typical process for the immobilization of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ within the modified SBA-15 channels was carried out as follows: AS-*n* samples (2 g) were stirred in 5 ml of an aqueous solution containing 6.5×10^{-4} mol of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (PW_{12}) at 60 °C for 8 h. The resulting solid ($\text{PW}_{12}/\text{AS}-n$) was then filtered, washed three times with methanol to remove unanchored PW_{12} , and dried at 100 °C for 3 h. To investigate the effects of calcination temperature, the immobilized samples were further separately treated at 100, 400, 600, and 800 °C. The calcined samples were denoted by $\text{PW}_{12}/\text{AS}-n-T$ (*T* = 100, 400, 600, 800 °C).

2.2. Characterization

Elemental analysis was carried out using a Thermo Ele-

mental IRIS Intrepid inductively coupled plasma atomic emission spectrometer and an Elementar Vario EL III microanalyzer. IR spectra were recorded on a Nicolet AVATAR 360 IR spectrometer using KBr pellets. The specific surface areas, pore diameters, and pore volumes of the samples were determined from N_2 adsorption isotherms measured using a Micromeritics Tristar 3000 instrument. The NMR experiments were obtained using a Bruker Avance DSX 300 spectrometer. ^{29}Si magic-angle spinning (MAS) NMR spectra were obtained at 59.6 MHz with a 90° pulse and a 600 s recycle delay at a spinning rate of ca. 4 kHz. ^1H -decoupled ^{31}P MAS NMR spectra were obtained at 121.5 MHz with a 30° pulse and a 20 s recycle delay at a spinning rate of ca. 12 kHz. XRD patterns were recorded on a Bruker D8 Advanced X-ray diffractometer using $\text{Cu } K_\alpha$ radiation with a voltage of 40 kV and a current of 40 mA. TEM measurements were performed on a JEOL JEM-2011 transmission electron microscopy. The identification of reaction products was performed on a Finnigan Voyager gas chromatography/mass spectrometer (GC-MS) instrument. Samples were quantified on a GC-122 with an Alltech EC-5 capillary column.

2.3. Catalytic reaction

Catalytic tests were performed by adding 7.5 g of acetonitrile, 2.5 ml (24.3 mmol) of 30% H_2O_2 , 0.838 g (10 mmol) of cyclohexene, 0.100 g of $\text{PW}_{12}/\text{AS}-n-T$, and 2 ml of *n*-hexane as the internal standard to a round-bottomed flask fitted with a reflux condenser. The mixture was stirred at 80 °C for 4 h. On completion of the reaction, the catalyst was separated by centrifugation. The liquid products were analyzed by GC.

3. Results and discussion

3.1. Characterization results of AS-*n* and $\text{PW}_{12}/\text{AS}-n-T$

The grafting of APTES in the SBA-15 channels was confirmed by NMR spectroscopy. A typical ^{29}Si MAS NMR spectrum of AS-1.0 before immobilization of PW_{12} is shown in Fig. 1. The three distinct resonance peaks at $\delta = -89.7$, -100.5 , and -109.7 are attributed to the Q^2 , Q^3 , and Q^4 silicon atoms ($\text{Q}^n = \text{Si}(\text{OSi})_n(\text{OH})_{4-n}$, $n = 2-4$), respectively, and the two other peaks, at $\delta = -55.7$ and -66.1 , are attributed to the T^2 and T^3 silicon atoms ($\text{T}^m = \text{RSi}(\text{OSi})_m(\text{OH})_{3-m}$, $m = 2, 3$), respectively [38,39].

Fig. 1. ^{29}Si MAS NMR spectrum of AS-1.0 before immobilization of PW_{12} .

Table 1

N and W contents and molar ratios of APTES to PW_{12} of $\text{PW}_{12}/\text{AS}-n-100$ samples.

Sample	Element content (wt%)		APTES/ PW_{12} molar ratio
	N	W	
$\text{PW}_{12}/\text{AS}-0.1-100$	0.17	6.20	4.32
$\text{PW}_{12}/\text{AS}-0.2-100$	0.49	12.00	6.43
$\text{PW}_{12}/\text{AS}-0.5-100$	0.92	14.51	9.99
$\text{PW}_{12}/\text{AS}-0.8-100$	1.57	18.07	13.68
$\text{PW}_{12}/\text{AS}-1.0-100$	1.82	21.90	13.09
$\text{PW}_{12}/\text{AS}-1.6-100$	2.58	36.40	11.16

The appearance of T^m peaks confirms that the silane organic moieties are incorporated as part of the silica wall structure and most of the grafted functional groups are bound to the surface. The intensity ratio $T^m/(T^m + Q^n)$ is ca. 0.13 for AS-1.0, in good agreement with that theoretically expected on the basis of the APTES content in the initial mixture, suggesting that nearly all the APTES was incorporated with the TEOS to form APTES-SBA-15.

Elemental analysis was performed to determine the amount of APTES incorporated in SBA-15 and to confirm whether PW_{12} was introduced onto APTES-SBA-15. The N and W contents and the molar ratios of APTES to PW_{12} deduced from the N/W ratios are listed in Table 1. The amount of PW_{12} clusters attached to the aminosilylated support increased with increasing content of amino groups. This indicates that the polyacids are held on the silica surface via electrostatic interactions. A considerable amount of APTES is not combined well with the PW_{12} clusters because of the steric hindrance of the Keggin polyanions, which leads to molar ratios of APTES to PW_{12} greater than the theoretical value of 3.

IR spectroscopy was used to determine the presence of PW_{12} clusters within the SBA-15 channels [40]. The characteristic IR fingerprints of bulk PW_{12} and $\text{PW}_{12}/\text{AS}-1.6-T$ in the region from 1100 to 700 cm^{-1} (Table 2) are attributed to the vibrations of P–O in the central PO_4 unit, and of W=O and W–O–W in PW_{12} . The bands at 900–1050 cm^{-1} are partially obscured by the presence of silica [41]. These characteristic IR absorption data are very useful in identifying the structural features of polyoxometalates (POMs) incorporated into the mesoporous channels. It can be seen that the vibration bands of $\text{PW}_{12}/\text{AS}-1.6-T$ ($T = 100, 400$ °C) are similar to those of the corresponding bulk PW_{12} , suggesting that the Keggin structures of the POMs remained intact after immobilization on the mesoporous silica surface and calcining at a low temperature (Fig. 2). For the $\text{PW}_{12}/\text{AS}-1.6-600$ sample, the specific bands shift obviously, indicating that the Keggin structure has changed after being calcined at 600 °C.

The ^{31}P MAS NMR spectra of $\text{PW}_{12}/\text{AS}-1.6-100$ and $\text{PW}_{12}/\text{AS}-1.6-400$ are shown in Fig. 3. The peak at ca. $\delta = -15$ in

Fig. 2. IR spectra of bulk PW_{12} and $\text{PW}_{12}/\text{AS}-1.6-T$.

both samples is slightly perturbed from that of pure $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [42], indicating retention of the Keggin structure. An additional weak peak at $\delta = -13.0$ in $\text{PW}_{12}/\text{AS}-1.6-100$ may be assigned to a small portion of a partially degraded cluster, which is possibly formed as a result of the basicity of the surface amines. This additional peak becomes stronger and broader after treatment at higher temperatures, which is possibly the result of complicated interactions between the POM and the support. However, the ^{31}P MAS NMR results indicate that $\text{PW}_{12}/\text{AS}-1.6-400$ retains a high content of phosphorus and the majority of the Keggin structure.

3.2. Effects of different loadings and treatment temperatures

Typical low-angle XRD patterns of catalysts with the same PW_{12} loading but treated at different temperatures, $\text{PW}_{12}/\text{AS}-0.2-T$ ($T = 100, 400, 600, 800$), are shown in Fig. 4. All four samples have the same APTES and PW_{12} contents. The $\text{PW}_{12}/\text{AS}-0.2-T$ ($T = 100, 400, 600$ °C) samples exhibit three peaks, which can be indexed as the characteristic (100), (110), and (200) diffractions of hexagonal mesoporous SBA-15, indicating that these samples consist of well-ordered channels [29]. The $\text{PW}_{12}/\text{AS}-0.2-800$ sample shows the weakest peaks, and the intensities of all the diffraction peaks drop significantly; this

Fig. 3. ^{31}P MAS NMR spectra of $\text{PW}_{12}/\text{AS}-1.6-100$ (1) and $\text{PW}_{12}/\text{AS}-1.6-400$ (2).**Table 2**

IR bands of PW_{12} and $\text{PW}_{12}/\text{AS}-1.6-T$.

Sample	$\nu_{\text{as}}(\text{P}-\text{O})/\text{cm}^{-1}$	$\nu_{\text{as}}(\text{W}=\text{O})/\text{cm}^{-1}$	$\nu_{\text{as}}(\text{W}-\text{O}-\text{W})/\text{cm}^{-1}$	
PW_{12}	1081	983	893	814
$\text{PW}_{12}/\text{AS}-1.6-100$	1083	982	897	810
$\text{PW}_{12}/\text{AS}-1.6-400$	1082	979	901	814
$\text{PW}_{12}/\text{AS}-1.6-600$	1092	921	816	776

Fig. 4. Low-angle XRD patterns of $\text{PW}_{12}/\text{AS-0.2-}T$ and $\text{PW}_{12}/\text{AS-}n\text{-400}$.

could be caused by the collapse of the typical SBA-15 ordered structure under high-temperature treatment. With increasing treatment temperature, the diffraction peaks shift slightly towards larger angles, indicating a slight shrinkage of the cell dimensions during calcination.

The effects of different contents of APTES and PW_{12} on the mesoporous structure are also shown in Fig. 4. Three samples, $\text{PW}_{12}/\text{AS-}n\text{-400}$ ($n = 0.2, 0.5, 1.0$), were treated at the same temperature (400 °C). On increasing the APTES and PW_{12} contents, the diffraction peaks shift towards larger angles and their intensities decrease. It can be concluded that the primary structure of SBA-15 is well maintained after aminosilylation and immobilization of PW_{12} , but an increase in the PW_{12} loading inside the SBA-15 channels results in pore filling of the host material with PW_{12} .

High-angle XRD patterns of typical samples, $\text{PW}_{12}/\text{AS-0.5-}T$ ($T = 400, 600, 800$ °C), are displayed in Fig. 5. It can be clearly observed that several diffraction peaks appear when the samples are treated at high temperatures (600 and 800 °C), indicating decomposition of PW_{12} to form monoclinic tungstic oxide ($a = 0.7306$ nm, $b = 0.7540$ nm, $c = 0.7692$ nm; JCPDS 72-0677). However, there is no diffraction peak in the $\text{PW}_{12}/\text{AS-0.5-400}$ sample, which means that the Keggin struc-

Fig. 5. XRD patterns of $\text{PW}_{12}/\text{AS-0.5-}T$.

Fig. 6. N_2 adsorption-desorption isotherms of $\text{PW}_{12}/\text{AS-0.2-}T$ and $\text{PW}_{12}/\text{AS-}n\text{-400}$.

ture remains intact, as observed in the IR spectra.

The N_2 adsorption isotherms of $\text{PW}_{12}/\text{AS-0.2-}T$ ($T = 100, 400, 600, 800$ °C) in Fig. 6 are classified as type IV, which is the typical hysteresis loop of mesoporous materials [29]. The surface-modified and PW_{12} -introduced samples retain the same isotherm shape for the samples from $\text{PW}_{12}/\text{AS-0.2-100}$ to $\text{PW}_{12}/\text{AS-0.2-600}$. However, the shape of the hysteresis loop of $\text{PW}_{12}/\text{AS-0.2-800}$ changes significantly; this is caused by loss of the ordered SBA-15 structure. The inflection point of the step is shifted to low p/p_0 with increasing calcination temperature, attributed to a decrease in pore size. Contraction of the channels at high temperature accounted for the decreases in pore volume, pore size, and surface area, listed in Table 3. The effects of different APTES and PW_{12} contents on the mesoporous structure are shown in Fig. 6. The hysteresis loops of $\text{PW}_{12}/\text{AS-0.5-400}$ and $\text{PW}_{12}/\text{AS-1.0-400}$ decrease obviously in comparison with that of $\text{PW}_{12}/\text{AS-0.2-400}$; this is caused by filling of the channels with larger amounts of APTES and PW_{12} . The variations in the physicochemical parameters listed in Table 3 indicate that the amino groups of APTES and PW_{12} are impregnated into the SBA-15 pore channels. These results are consistent with the low-angle XRD patterns.

The TEM images of $\text{PW}_{12}/\text{AS-1.0-400}$ further demonstrate that the hexagonal ordered channel structure of SBA-15 was not significantly changed after aminosilylation, immobilization of PW_{12} in the channels, and thermal treatment. It can be clearly seen in Fig. 7 that the PW_{12} clusters were highly dispersed inside the modified SBA-15 host.

Table 3

Physicochemical properties of $\text{PW}_{12}/\text{AS-0.2-}T$ and $\text{PW}_{12}/\text{AS-}n\text{-400}$.

Sample	BET surface area (m^2/g)	BJH pore diameter (nm)	BJH pore volume (ml/g)
$\text{PW}_{12}/\text{AS-0.2-100}$	585	7.7	1.02
$\text{PW}_{12}/\text{AS-0.2-400}$	573	6.9	0.89
$\text{PW}_{12}/\text{AS-0.5-400}$	384	5.6	0.48
$\text{PW}_{12}/\text{AS-1.0-400}$	225	5.4	0.27
$\text{PW}_{12}/\text{AS-0.2-600}$	493	6.7	0.82
$\text{PW}_{12}/\text{AS-0.2-800}$	132	10.2	0.43

Fig. 7. TEM images of $\text{PW}_{12}/\text{AS}-1.0-400$, perpendicular (a) and parallel (b) to the channel direction of SBA-15.

The IR and ^{31}P MAS NMR spectra show interactions between the PW_{12} clusters and the supports and retention of the Keggin structure. TEM images supply direct proof of distribution of the PW_{12} clusters inside the mesoporous silica. The XRD patterns and N_2 adsorption isotherms show that the support preserves its ordered mesoporous structure under thermal treatment up to 600 °C.

3.3. Catalytic tests

The epoxidation of cyclohexene with 30% H_2O_2 was chosen as a model reaction to compare the behaviors of different catalysts. The yields of cyclohexene oxide after 4 h are shown in Fig.

Fig. 8. Comparison of catalytic activities in epoxidation of cyclohexene with 30% H_2O_2 over $\text{PW}_{12}/\text{AS}-n-T$ catalysts. (a) Two sets of $\text{PW}_{12}/\text{AS}-n-100$ and $\text{PW}_{12}/\text{AS}-n-400$ ($n = 0.1, 0.2, 0.5, 0.8, 1.0, 1.6$) catalysts with different PW_{12} loadings; (b) Two sets of $\text{PW}_{12}/\text{AS}-0.5-T$ and $\text{PW}_{12}/\text{AS}-0.8-T$ ($T = 100, 400, 600, 800$ °C) catalysts calcined at different temperatures. Reaction conditions: 7.5 g of acetonitrile, 2.5 ml (24.3 mmol) of H_2O_2 , 0.838 g (10 mmol) of cyclohexene, 0.100 g of $\text{PW}_{12}/\text{AS}-n-T$, 2 ml of *n*-hexane (internal standard), 80 °C, 4 h. *Recycled after the fifth run.

8. The samples exhibit remarkable catalytic activities. No other oxidation product was observed, indicating that the selectivity for cyclohexene oxide was almost 100% [43]. The yields of cyclohexene oxide using the $\text{PW}_{12}/\text{AS}-n-100$ ($n = 0.1, 0.2, 0.5, 0.8, 1.0, 1.6$) samples (Fig. 8(a)) are higher than those over Aerosil-Ti(OiPr), TiSBA-15, and Ti-MCM-41 reported in the literature [44–46].

As shown in Fig. 8(b), for catalysts with the same PW_{12} contents, different calcination temperatures affect the catalytic performance significantly. The yields over $\text{PW}_{12}/\text{AS}-0.5-T$ and $\text{PW}_{12}/\text{AS}-0.8-T$ ($T = 100, 400, 600, 800$) were chosen to compare the different catalytic behaviors. The catalysts calcined at 100 °C always gave relatively low yields, but the yields increased quickly for those calcined at 400 °C. When the calcination temperature was increased to 600 °C, the yields decreased significantly, and the catalysts calcined at 800 °C exhibited similar activities to those calcined at 600 °C. As shown in Fig. 5, the Keggin structures of the POMs remained intact on the support when the calcination temperature was 400 °C, whereas the samples treated at 600 and 800 °C decomposed to the crystalline phase of WO_3 . The above catalytic results clearly demonstrate that PW_{12} could be the most active species under the present reaction conditions. Thus, as shown in Fig. 8(a), the conversion and epoxide yield increase with increasing PW_{12} loading.

Catalyst recycling tests were carried out on $\text{PW}_{12}/\text{AS}-0.5-400$ and $\text{PW}_{12}/\text{AS}-0.8-400$. After the reaction, the catalyst was separated from the reaction mixture by centrifugation and calcined at 400 °C for reuse. As shown in Fig. 8(b), there was nearly no loss of activity after five cycles, indicating that the catalysts have high reusability. In the ^{31}P NMR study, no signal was detected in the solution after reaction for 4 h with $\text{PW}_{12}/\text{AS}-0.5-400$ and $\text{PW}_{12}/\text{AS}-0.8-400$, showing that the loss of active species was negligible. In contrast, under the same reaction conditions, the conversion of cyclohexene decreased significantly over $\text{PW}_{12}/\text{AS}-0.5-100$, and the ^{31}P NMR signal, although weak, could be detected in the filtered reaction solution. Calcination therefore not only enhances the catalytic activity, but also prevents catalyst leaching.

4. Conclusions

A series of mesoporous-SBA-15-immobilized 12-phosphotungstic acids ($\text{H}_3\text{PW}_{12}\text{O}_{40}$), with various amounts of incorporated heteropoly acid, were fabricated by directly immobilizing $\text{H}_3\text{PW}_{12}\text{O}_{40}$ on the channels of SBA-15 co-synthesized with APTES. In this preparation method, the calcination temperature plays an important role in increasing the catalytic activity. The catalysts calcined at 400 °C showed high reactivities and reusabilities in the liquid-phase epoxidation of cyclohexene with H_2O_2 as the oxidant. These results are promising for further applications in other reactions because of the heterogenized homogeneous characters of the heteropoly acids.

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Graphical Abstract

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Catalytic epoxidation of cyclohexene over mesoporous-silica immobilized Keggin-type tungstophosphoric acid

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A simple method was used to prepare mesoporous-silica-immobilized Keggin-type tungstophosphoric acid. The resulting catalysts showed high catalytic activities and reusabilities in heterogeneous oxidation of cyclohexene using H_2O_2 as the oxidant.

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介孔硅负载 Keggin 型钨磷酸催化环己烯环氧化

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摘要: 采用共合成法制备了一系列不同硅氨基含量的介孔氧化硅 SBA-15, 在其孔道中引入 Keggin 型钨磷酸, 且其含量随硅氨基含量的增加而增加. 考察了不同处理温度下杂多酸的热稳定性, 发现焙烧后钨物种能在 SBA-15 孔道内高度分散. 以 H_2O_2 为氧化剂, 研究了该催化剂在环己烯环氧化反应中的催化活性, 考察了杂多酸负载量和焙烧温度对催化活性的影响. 结果表明, 400 °C 处理后的钨磷酸催化剂具有高的反应活性和重复使用性能.

关键词: 12-磷钨酸; 硅氨基化; SBA-15; 环氧化; 环己烯

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2nd International Congress on Catalysis for Biorefineries (CatBior 2013)

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