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Article

Effect of metals on titanium silicalite TS-1 for butadiene epoxidation

WU Mei ^{a,b}, CHOU Lingjun ^a, SONG Huanling ^{a,*}^aState Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, Gansu, China^bUniversity of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 29 October 2012

Accepted 21 November 2012

Published 20 April 2013

Keywords:

Butadiene

Epoxidation

Vinylloxirane

Metal

Titanium silicalite-1

ABSTRACT

The titanium silicalite-1 (TS-1) modified by various metals (M-TS-1; M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, La, 1% metals loading) catalysts were employed to catalyze butadiene epoxidation. The metals influenced the TS-1 activity in various ways. V, Cr, and Mn caused H₂O₂ decomposition. Although the H₂O₂ conversion was high, its utilization was relatively low. The introduction of Fe, Co, Ni, and La into TS-1 promoted the vinylloxirane (VO) yield and H₂O₂ utilization to some extent. Cu and Zn modification inhibited the H₂O₂ conversion to VO, resulting in both low H₂O₂ utilization and conversion. We studied the influence of Cd on TS-1 and found that H₂O₂ was almost totally converted to VO over the Cd-TS-1 catalyst, and the turnover number of VO reached 1197. Powder X-ray diffraction, N₂ adsorption and desorption, X-ray photoelectron spectroscopy, and Fourier transformed infrared spectra were employed to characterize the specific metal role at the Ti site in the M-TS-1 catalysts. The TS-1 remained as MFI structure with doped metals. The added metals effectively changed the electron environment of the Ti active site. However, no universal trend in behavior was observed for these metals.

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1. Introduction

Epoxidation of alkenes, especially low olefins is of great interest. Ag/Al₂O₃ catalysts [1–6], transition metal oxide nanoparticles (TiO₂, MnO₂, NiO, CoO, etc.) and their modifying catalysts [7–11], along with all kinds of titanium silicalite materials such as TS-1, TS-2, Ti-β, Ti-MCM-41/48, and Ti-MWW [12–16] have been applied as catalysts for alkene epoxidation. TS-1 exhibits outstanding properties of shape selective catalysis oxidation for low olefin epoxidation (propylene [17], butadiene [18]), owing to its unique structure and highly activated tetrahedral Ti centers inside the skeleton. Epoxidation reactions over TS-1, which can be performed under mild reaction conditions (0–100 °C, low pressure) with high activity and selectivity, are environmentally benign. In the epoxidation of low ole-

fins, O₂, H₂/O₂, H₂O₂, and *tert*-butyl hydroperoxide are usually used as oxidants. The activated oxygen content of H₂O₂ reaches up to 47% and H₂O₂ is environmentally benign as it forms H₂O as the only by-product [19]. Therefore, H₂O₂ is considered as the best choice of oxidant in the TS-1 catalytic system. Methanol is usually employed as the solvent in alkene epoxidation. A five-membered-ring intermediate (Clerici-like cycle), in which the double bond of the olefin bonds well with the activated oxygen in the H₂O₂, can be formed from the tetrahedral Ti in TS-1, H₂O₂, and methanol. Generally, TS-1/H₂O₂/methanol provides an effective catalytic system for low olefin epoxidation.

Transition metals, whose unoccupied 3d orbitals are good electron acceptors, display superior catalytic performance in redox reactions. They have been exploited extensively to mod-

* Corresponding author. Tel: +86-931-4968066; Fax: +86-931-4968129; E-mail: songhl@licp.cas.cn

This work was supported by the National Natural Science Foundation of China (21133011).

DOI: 10.1016/S1872-2067(11)60498-1 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 4, April 2013

Scheme 1. Five-membered-ring intermediate of butadiene epoxidation catalyzed by M-TS-1.

ify TS-1 in recent years. For example, the activity of TS-1 had been improved effectively with Zn [20], Ni [21], Co [22], and V [23] modification. In our early studies [21], TS-1 zeolite modified with metal Ni effectively catalyzed butadiene epoxidation. The interaction between Ni and TS-1 changed the electronic environment of the Ti centers. The peripheral electronic cloud around the Ti center was attracted by an embedded Ni 3d orbital and the electrophilicity of the Ti center and active oxygen were enhanced. This activated the double bond epoxidation of butadiene (as shown in Scheme 1). In addition, rare earth metals commonly considered as electronic auxiliaries are widely used in the catalytic field.

In recent years, although the significance of metal modification has been of great interest, further studies on the modification effect of metals (transition or rare earth metals) on TS-1 need to be conducted systematically. Meanwhile, vinyl oxirane (VO) shows great value as an intermediate in synthesizing organic chemistry and chemical technology [19,24,25], and butadiene epoxidation is an attractive route to produce VO. Therefore, typical transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) and one rare earth metal (La) were exploited to modify TS-1 in this work. Butadiene (BD) epoxidation was used as a probe reaction, so as to explore the effect of metals on TS-1 catalytic performance.

2. Experimental

2.1. Catalyst preparation

The AR grade chemicals, NH_4VO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and methanol (CH_3OH) were supplied by a local vendor. All chemicals were used without further purification. Concentrations of H_2O_2 (50%; local vendor) were determined by iodometric titration prior to use. Titanium silicalite 1 (TS-1, $\text{SiO}_2/\text{TiO}_2 = 40$) with specific surface area $463.1 \text{ m}^2/\text{g}$ was from Shanghai Novel Chemical Technology Co. Ltd.

The typical synthesis process was as follows: 1.00 g of TS-1 was dissolved in 5 ml distilled water, and the required amount of metal nitrate solution was added into the resultant solution with vigorous stirring. The mixture was treated under ultrasound, placed into an infrared drying oven with vigorous stirring until it changed to dry powder and finally dried overnight at 120°C . The final powder was calcined at 550°C for 6 h.

2.2. Physicochemical characterization

Powder X-ray diffraction (XRD) measurements were performed using an X'Pert Pro multipurpose diffractometer (PANalytical, Inc.) with Ni-filtered $\text{Cu } K_\alpha$ radiation (0.15046 nm) from 10.0° to 80.0° . Measurements were conducted using a voltage of 40 kV, current setting of 40 mA, step size of 0.02° , and count time of 4 s.

The N_2 adsorption and desorption isotherms at -196°C were recorded on an Autosorb-iQ analyzer (Quantachrome Instruments, U.S.). Prior to the tests, samples were degassed at 200°C for 4 h. The specific surface areas were calculated via the BET method in the relative pressure range of 0.05–0.30; pore size distributions were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by Saito-Foley (SF) methods.

The oxidation state of titanium and metals was characterized over a Thermo Fisher Scientific K-Alpha X-ray photoelectron spectroscope (XPS). The M-TS-1 powder was pressed to form a self-supporting wafer prior to analysis.

Fourier transformed infrared (FT-IR) spectra of the M-TS-1 samples were recorded on an FT-IR spectrometer (Nicolet Nexus 870) with a resolution of 4 cm^{-1} and 64 scans in the region of $4000\text{--}400 \text{ cm}^{-1}$.

2.3. Catalytic reactions

The epoxidation of butadiene was performed in a 100 ml stainless-steel autoclave with magnetic stirrer. Typically, 0.40 g M-TS-1 and the designated amount of H_2O_2 were dispersed in 25.00 ml methanol solvent, and the autoclave was then sealed. Butadiene at 0.15 MPa was introduced into the autoclave through a needle valve. The slurry was heated to 40°C with vigorous stirring, maintained at 40°C for 60 min, and then quickly quenched in an ice water bath to around 0°C . The remaining H_2O_2 concentration was determined by standard iodometric titration. The liquid products that were formed were confirmed by gas chromatography-mass spectroscopy (GC-MS 5973, Agilent Technology Company). VO was confirmed as the main product, and the main by-products were small amounts of tetrahydro-2-furanmethanol and 4-ethenyl-cyclohexene. The quantity of products was determined using a gas chromatograph (SP-6800A GC) equipped with flame ionization detector and OV-1701 capillary column. The VO yield was determined

relating to methanol via an external standard method based on the GC results, while the concentrations of by-products were too low to be determined. The VO turnover number (TON, determined as the molar VO obtained per molar Ti atom) and the VO concentration in the final reaction mixture were utilized to evaluate and compare the activities of the different catalysts. The H₂O₂ conversion, H₂O₂ utilization, and VO TON were calculated from Eqs (1), (2), and (3), respectively:

$$X(\text{H}_2\text{O}_2) = (n_0(\text{H}_2\text{O}_2) - n(\text{H}_2\text{O}_2)) / n_0(\text{H}_2\text{O}_2) \times 100\% \quad (1)$$

$$U(\text{H}_2\text{O}_2) = n(\text{VO}) / n_0(\text{H}_2\text{O}_2) \times 100\% \quad (2)$$

$$\text{TON} = n(\text{VO}) / n(\text{Ti}) \quad (3)$$

In the above equations, n_{VO} represents the moles of VO obtained from the epoxidation of butadiene and $(n_{\text{H}_2\text{O}_2})_0$ and $n_{\text{H}_2\text{O}_2}$ represent the initial and remaining molar content of H₂O₂ after reaction, respectively.

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. XRD results

Figure 1 shows the XRD spectra of metals M used to modify TS-1. All M-TS-1 catalysts showed diffraction peaks at 7.8°, 8.8°, 23.2°, 23.8°, and 45°. Therefore, the introduction of metals did not change the TS-1 intrinsic MFI configuration. No diffraction peaks appeared at 24.5° and 29.5°. This suggests that the extra-framework anatase TiO₂ did not exist in the modified TS-1 catalysts and all Ti species were located inside the skeleton of the molecular sieve. No diffraction peak of metal oxides appeared in the XRD spectra. This could be explained by assuming that all metal oxides were well dispersed on the TS-1 surface owing to the low loading and ultrasonic immersion synthesis method.

3.1.2. Physicochemical properties

The BET surface area and micropore volume of the M-TS-1 (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, La) catalysts were characterized by N₂ adsorption and desorption isotherms, with results

Table 1

Physicochemical properties of M-TS-1 obtained by BET method.

M	BET surface area (m ² /g)	Micropore volume (cm ³ /g)
—	463.1	0.175
V	466.4	0.175
Cr	469.5	0.177
Mn	474.4	0.170
Fe	472.1	0.177
Co	454.8	0.171
Ni	463.1	0.175
Cu	478.3	0.176
Zn	449.0	0.170
Cd	462.3	0.174
La	455.4	0.171

exhibited in Table 1. The introduction of various metals did not change the BET surface area and micropore volume, which remained around 460.0 m²/g and 0.175 cm³/g, respectively. As seen from the XRD characterization results, this occurs because all metal oxides were well-distributed on the TS-1 as a result of the low metal oxide loading (1%) and the ultrasonic immersion synthesis method. On the other hand, metal oxides did not sinter to block the TS-1 channel during the calcination process. This can also be confirmed by Fig. 2, which suggests that the pore size distribution of all metals modifying the catalysts remained around 0.56 nm.

3.1.3. XPS results

As shown in Fig. 3, the typical metals (Cr, Co, Cu, La, Cd) used to modify the TS-1 catalysts were characterized by XPS to indicate clearly the surface chemical state and electron environment of the Ti 2p_{3/2} and Ti 2p_{1/2} orbitals. The binding energy of Ti 2p_{3/2} was 460.0 eV in the reference TS-1, and the characteristic peak of 458.5 eV did not exist in the XPS spectrum. This further certified that Ti was presented in the tetrahedral configuration in the TS-1 skeleton and excluded the existence of TiO₂ outside of the TS-1 framework, which agreed with the XRD results. An identical result was obtained from the diffused reflection ultraviolet visible spectrum (DR UV-Vis) of TS-1 in our earlier work [21]. Besides the characteristic peak of 460.0

Fig. 1. XRD patterns of various M-TS-1 catalysts.

Fig. 2. Pore size distribution of M-TS-1 catalysts.

Fig. 3. Ti 2p XPS spectra of the M-TS-1 samples.

eV, a new peak appeared at 459.0 eV after TS-1 was modified with metal. The introduction of metals caused the excursion of an electron cloud of the Ti 2p orbital and reduced the electron cloud density around the Ti active site. As a result, the Ti 2p orbital binding energy declined completely. Owing to the interactions between supporting metal and TS-1, the electrophilicity of the Ti center and the active oxygen in H_2O_2 was strengthened, as shown in the five-membered-ring intermediate (Scheme 1). However, the relative intensity of the characteristic peaks at 460.0 and 459.0 eV varied in the TS-1 modified catalysts. The intensity of the characteristic peak at 459.0 eV was lower than that at 460.0 eV in the Cr and Cu modified catalysts. The reverse feature was observed in the Co, Cd, and La modified TS-1 catalysts, that is, the peaks at 459.0 eV were higher. It is believed that the Co, Cd, and La decreased the electron cloud density around the Ti centers to a greater extent and the electrophilicity of more Ti centers increased. The latter metals could therefore better promote epoxidation.

3.1.4. FT-IR results

The FT-IR spectrum of the TS-1 zeolite lattice vibration is depicted between 4000 and 500 cm^{-1} (Fig. 4). Absorption bands at around 1100, 800, and 450 cm^{-1} were lattice modes associated with internal linkages in $[\text{SiO}_4]$ tetrahedra. Absorption bands at around 1230 and 547 cm^{-1} were characteristic peaks of the MFI type zeolite structure, which is in accordance with the XRD results. The peak around 970 cm^{-1} could be considered as the stretching mode of the $[\text{SiO}_4]$ tetrahedral bond with Ti atoms and the fingerprint of the framework titanium [26–29]. The introduction of metals caused a deviation in the IR absorption bands around 970 cm^{-1} to lower wavenumbers. This illustrated that the strength of the titanium oxygen bond decreased, thus the electron cloud density of the surrounding Ti decreased. Interactions between metals and the TS-1 thereby increased the electrophilicity of the Ti center. In the different metals used to modify the TS-1 catalysts, the wavenumber migration was in the order of $\text{Cd} > \text{La} > \text{Co} > \text{Cu} > \text{Cr}$ (wavenumbers declined from 976 to 968, 970, 971, 973, and 974

Fig. 4. FT-IR spectra of M-TS-1 catalysts.

cm^{-1} , respectively).

As shown in Scheme 1, by combining the characterization results of XPS with that of FT-IR, it can be seen that interactions between metals and Ti decreased the electron cloud density of the activated Ti center, where the metals attract the electrons around Ti by the oxygen atom, and thus the electrophilicity of the Ti center increases. The electron cloud density of O1 or O2 decreased indirectly and their electrophilicity increased, making it easier for the O1 or O2 to react with the butadiene double bond. However, the modification effects between various metals on TS-1 were different. The early transition metals represented as Cr and ds group metals represented as Cu had a weak influence on the electron environment of the Ti sites. The metal Cd, the VIII group transition metals represented by Co and the rare earth metals represented by La increased the electrophilicity of the Ti active center significantly.

3.2. Effects of metals on TS-1 for butadiene epoxidation

Various metals used to modify the TS-1 catalysts were exploited to catalyze the liquid epoxidation of butadiene. The effect of metal modification on TS-1 was diverse, and the reaction results of butadiene epoxidation over modified catalysts are displayed in Table 2.

Relative to TS-1, the introduction of the early transition metals, V, Cr, and Mn, suppressed the H_2O_2 utilization. Although the H_2O_2 conversion remained above 90%, H_2O_2 utilization and VO yield were lower than 76.0% and 0.41 mol/L, respectively. The TON of VO also declined from 953 to 256. We studied the H_2O_2 blank reference conversion of the metals V, Cr, and Mn used to modify the TS-1. Reaction conditions were kept consistent except for the existence of butadiene. The reaction results revealed that the H_2O_2 blank conversion of these catalysts was 76.5%, 40.6%, and 31.1%, respectively. This indicates that the ability of the metal oxides (V_2O_5 , Cr_2O_3 , MnO_2) to be oxidized was so strong that H_2O_2 was decomposed to H_2O and O_2 . On the other hand, as seen from Table 2, H_2O_2 utilization, VO yield, and VO TON increased with decreasing potential for oxi-

Table 2
Effect of metals (M) on butadiene epoxidation over M-TS-1 catalysts.

M	H ₂ O ₂ conversion (%)	H ₂ O ₂ utilization (%)	TON	VO yield (mol/L)
—	98.8	76.0	953	0.41
V	94.6	21.6	256	0.11
V	76.5*	—	—	—
Cr	99.5	64.1	766	0.33
Cr	40.6*	—	—	—
Mn	91.4	75.1	848	0.36
Mn	31.1*	—	—	—
Fe	99.0	95.9	1141	0.49
Co	98.8	84.9	1013	0.44
Ni	98.3	82.9	1010	0.43
Cu	79.0	67.3	750	0.32
Zn	83.9	85.1	962	0.41
Cd	~100	~100	1197	0.51
La	98.8	93.4	1105	0.48

Reaction conditions: 40 °C, butadiene 0.15 MPa, H₂O₂ (50%) 0.51 mol/L, M-TS-1 0.40 g, CH₃OH 25.00 ml.

* H₂O₂ conversion of blank without butadiene reference experiment.

dation of the metal oxides.

The introduction of the VIII group transition metals, Fe, Co, and Ni, promoted H₂O₂ conversion effectively: H₂O₂ conversion was maintained above 98.3% and the H₂O₂ utilization, VO TON, and VO yield were increased to some extent. Moreover, compared to the reference TS-1, H₂O₂ utilization was increased significantly with modification by the rare earth metal La. The VO yield and VO TON were increased to 93.4% and 1105. XPS and FT-IR characterization results revealed that the metals, Fe, Co, Ni, and La, increased the electrophilicity of TS-1 and therefore H₂O₂ was converted effectively to VO.

However, the ds group metals Cu and Zn suppressed the H₂O₂ conversion: H₂O₂ conversion decreased from 98.8% to 79.0% and 83.9%, respectively. The H₂O₂ utilization of the Cu-TS-1 catalyst was lower than Zn-TS-1. Cu introduction decreased the yield and TON of VO from 0.41 mol/L and 953 to 0.32 mol/L and 750, respectively. For the Zn-TS-1 catalyst, the H₂O₂ utilization increased from 76.0% to 85.1%. This indicates that the existence of Zn contributes to the formation of VO, which was in accordance with the propylene epoxidation results over Zn treated TS-1 catalysts [20]. XPS and FT-IR characterization results indicate that the interaction between Cu and Ti was relatively weak.

TS-1 modified with Cd, which was in the same group with Zn, exhibited excellent catalytic performance for butadiene epoxidation. H₂O₂ utilization and conversion were promoted greatly, H₂O₂ was almost completely translated to the target product VO. As shown from the XPS and FT-IR results, compared with other metals, Cd introduction decreased the electron cloud density around the Ti centers effectively. The electrophilicity of the Ti active site was improved noticeably. As a result, H₂O₂ conversion was promoted by Cd to the largest degree over the modified TS-1 catalysts.

We tried to associate the influence of various metals on TS-1 catalytic performance with their intrinsic properties (such as metal ion electronic structure, redox potential, ion radius, etc.), to determine whether a universal law exists for the behavior. However, the method of interaction between the metals and

TS-1 were influenced by many factors, although the properties of all the metals applied in this work were consistent. The introduction of transition and rare earth metals decreased the electron cloud density around the Ti centers and increased the electrophilicity of the Ti centers and active oxygen sites. The modification of these metals affected the epoxidation performance of the TS-1 to some extent.

4. Conclusions

Transition metals (V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) and one rare earth metal (La) were used to modify TS-1 via the ultrasonic immersion synthesis method. The BET surface area and micropore volume of TS-1 were unchanged by metal treatment, and modified TS-1 remained the intrinsic MFI configuration of TS-1. The effect of various metals on the electronic environment of the Ti center was diverse. However, the similarities were that all metal modifications caused the electron cloud density of the Ti active site to decline. The electrophilicity of the Ti center and active oxygen in H₂O₂ were enhanced. The introduction of Fe, Co, Ni, Cd, and La promoted TS-1 activity in butadiene epoxidation to some extent. Especially for catalysts modified with Cd, H₂O₂ was almost totally converted to VO, and the VO TON reached up to 1197.

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Graphical Abstract

Chin. J. Catal., 2013, 34: 789–797 doi: 10.1016/S1872-2067(11)60491-8

Effect of metals on titanium silicalite TS-1 for butadiene epoxidation

WU Mei, CHOU Lingjun, SONG Huanling*

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences; University of Chinese Academy of Sciences

The various metals modified TS-1 (M-TS-1) catalysts were applied to catalyze butadiene epoxidation. The effect of the modified metals on TS-1 was diverse. All metals changed the electronic environment of the Ti active site in TS-1 to some extent via a five-membered-ring intermediate.

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金属对钛硅分子筛TS-1催化丁二烯环氧化性能的影响

吴 妹^{a,b}, 丑凌军^a, 宋焕玲^{a,*}

^a中国科学院兰州化学物理研究所羰基合成与选择氧化国家重点实验室 甘肃兰州730000

^b中国科学院大学, 北京10049

摘要: 制备了不同金属改性的钛硅分子筛样品M-TS-1 (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, La, 负载量为1%), 并研究了其催化丁二烯环氧化反应的性能. 结果表明, V, Cr, Mn的加入导致H₂O₂无效分解, 因而在丁二烯环氧化反应中表现出较高的H₂O₂转化率和较低有效利用率; Fe, Co, Ni以及稀土金属La均在一定程度上促进了TS-1对H₂O₂的有效利用; Cu, Zn抑制了H₂O₂的转化, 使得H₂O₂转化率和有效利用率都较低; Cd有效提高了TS-1的催化活性, H₂O₂转化率和有效利用率均接近100%. 采用X射线衍射、N₂吸附-脱附、X射线光电子能谱、傅里叶变换红外光谱等手段表征了上述各金属的改性对TS-1骨架结构以及Ti活性中心周围电子环境的影响. 结果表明, 各M-TS-1样品的骨架结构都仍保持原有的MFI构型, 但是TS-1中Ti活性中心周围的电子环境受到来自各种金属的不同程度影响, 关联催化活性时没有特定的规律性.

关键词: 丁二烯; 环氧化; 乙烯基环氧乙烷; 金属; 钛硅分子筛

收稿日期: 2012-10-29. 接受日期: 2012-11-21. 出版日期: 2013-04-20.

*通讯联系人. 电话: (0931)4968066; 传真: (0931)4968129; 电子信箱: songhl@licp.cas.cn

基金来源: 国家自然科学基金(21133011).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

烯烃特别是低级烯烃环氧化反应一直备受关注. 所采用的催化剂包括Ag/Al₂O₃负载催化剂^[1-6]、过渡金属氧

化物(TiO₂, MnO₂, NiO, CoO等)纳米颗粒及其负载催化剂^[7-11]、以及各种钛硅多孔材料, 如TS-1, TS-2, Ti-β, Ti-MCM-41/48和Ti-MWW等^[12-16]均曾被尝试用于催化烯烃环氧化反应. 其中钛硅分子筛TS-1具有独特的疏水

性孔道结构以及高活性的骨架内四面体Ti中心,因而对低级烯烃(如丙烯^[17]、丁二烯^[18])表现出良好的择形催化氧化功能,不仅反应条件温和(0~100 °C, 低压)、反应速率快、而且产物选择性高(不易深度氧化)。在低级烯烃环氧化反应中,一般使用的氧化剂有O₂、H₂/O₂、H₂O₂或叔丁基过氧化氢(TBHP)等。其中H₂O₂中有效氧含量达到47%,氧化副产物只有水,环境友好^[19],是TS-1催化体系中良好的氧化剂。当以甲醇为溶剂时,TS-1的四面体Ti中心、H₂O₂、甲醇可以形成五元环中间体(Clerici-like cycle),使得低级烯烃的双键有效地与H₂O₂中活性氧结合形成环氧化产物。因此,TS-1/H₂O₂/甲醇成为低级烯烃环氧化良好的催化反应体系。

过渡金属大部分具有变价,在氧化还原反应中具有较好的催化性能。另外,由于过渡金属一般具有空的3d轨道,可以接受电子,因而可用于修饰TS-1,以期通过改变Ti活性中心的电子环境来提高其催化活性。例如,经金属Zn^[20]、Ni^[21]、Co^[22]、V^[23]修饰后,TS-1的催化效果均有所改善。我们也发现,特定金属与Ti中心的相互作用使得Ti活性位点周围的电子趋向于金属的3d空轨道,降低了Ti中心的电子云密度,从而产生亲电性更强的Ti中心和活性氧,使双键环氧化更加容易发生(见图式1)^[21]。另外,稀土金属也是常用的电子助剂。

然而,有关过渡金属或稀土金属对TS-1的改性研究还缺乏系统性;同时,乙烯基环氧乙烷(VO)作为一种新型的精细化工中间体,可制备上百种重要的后续产品,涉及大宗化学品、精细化学品和特种化学品等多个领域^[19,24,25]。而制备VO的最佳途径就是通过丁二烯环氧化。因此,我们选择代表性的过渡金属(V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd)以及稀土金属(La)对TS-1进行改性,以丁二烯环氧化作为探针反应,探索过渡金属以及稀土金属对TS-1催化活性的影响。

2. 实验部分

2.1. 催化剂的制备

Cu(NO₃)₂·3H₂O, Mn(NO₃)₂·6H₂O (天津光复科技发展有限公司), Ni(NO₃)₂·6H₂O, Zn(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, La(NO₃)₃·6H₂O, Fe(NO₃)₃·9H₂O (国药集团化学试剂有限公司), NH₄VO₃, Cd(NO₃)₂·4H₂O, Co(NO₃)₂·6H₂O (北京化工厂), 甲醇(烟台双双试剂公司)均为分析纯,且在使用之前未经进一步处理。

TS-1 (SiO₂/TiO₂ = 40, 上海卓悦化工科技有限公司)在使用前于450 °C焙烧4 h,以除去残留模板剂及其他杂

质。H₂O₂ (50%, 上海三友试剂厂)使用之前用标准碘量法标定其准确浓度。

在5 ml去离子水中加入1.00 g TS-1和适量的金属硝酸盐水溶液,所得混合液在超声条件下浸渍3 h,再在红外灯下边搅拌边快速干燥,将得到的粉末催化剂在120 °C干燥过夜,最后在550 °C (升温速率1 °C/min)焙烧6 h,即为不同金属修饰的TS-1催化剂,记为M-TS-1 (M = V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, La),其负载量均为1%。

2.2. 催化剂的表征

催化剂的物相结构分析在X'Pert Pro多功能X射线衍射仪上进行,Cu K_α射线(λ = 0.154184 nm),X光管电压40 kV,电流40 mA,扫描范围2θ = 5°~80°,扫描步宽0.02°,扫描速度4°/min。N₂吸附-脱附测定在Autosorb-iQ型测定仪(美国康塔公司)上进行。测试之前,将样品在200 °C脱气4 h。计算样品BET比表面时的相对压力范围为0.005~0.05;根据Saito-Foley (SF)方法用N₂吸附-脱附等温线计算材料的孔径分布。傅里叶变换红外光谱(FT-IR)测试在美国Nicolet公司Nexus 870型红外光谱仪上进行,固体粉末用KBr压片法。X射线光电子能谱(XPS)测试在热电K-Alpha X-射线光电子能谱上进行。

2.3. 丁二烯环氧化反应

丁二烯环氧化反应在带磁力搅拌的100 ml不锈钢反应釜中进行。将0.40 g M-TS-1样品和50% H₂O₂ (0.51 mol/L)投入到装有25.00 ml甲醇溶剂的反应釜中,密封反应釜后,充入0.15 MPa丁二烯气体,最后在40 °C、充分搅拌的条件下反应1 h。反应后离心分离催化剂和液相产物,液相组分用气质联用仪(GC-MS 5973)定性,反应后生成的VO用气相色谱仪(GC SP-6800A)内标法定量,少量副产物不予定量。反应剩余的H₂O₂浓度用标准碘量法标定。H₂O₂转化率X(H₂O₂),利用率U(H₂O₂)以及VO的转化频数TON通过以下公式计算:

$$X(\text{H}_2\text{O}_2) = (n_0(\text{H}_2\text{O}_2) - n(\text{H}_2\text{O}_2))/n_0(\text{H}_2\text{O}_2) \times 100\% \quad (1)$$

$$U(\text{H}_2\text{O}_2) = n(\text{VO})/n_0(\text{H}_2\text{O}_2) \times 100\% \quad (2)$$

$$\text{TON} = n(\text{VO})/n(\text{Ti}) \quad (3)$$

其中n₀(H₂O₂)为用标准碘量法标定出的初始H₂O₂浓度,n₀(H₂O₂)为用标准碘量法标定出的反应后剩余H₂O₂浓度,n(VO)为反应中产生的VO的摩尔数(由气相色谱确定),n(Ti)为反应所用催化剂中Ti的摩尔数。

3. 结果与讨论

3.1. 催化剂的物化性质

3.1.1. XRD结果

图1为M-TS-1样品的XRD谱. 催化剂均在 $2\theta = 7.8^\circ$, 8.8° , 23.2° , 23.8° 和 45° 处出现强特征衍射峰. 由图可见, 金属的引入没有改变TS-1的原有骨架结构, 仍为MFI构型. 同时, 未出现锐钛矿型 TiO_2 , 表明Ti完全存在于分子筛骨架内^[20]. 各样品均未出现所掺杂的金属氧化物的特征衍射峰. 这是由于金属氧化物的负载量较低, 且使用了超声浸渍法, 因而很好地分散在载体TS-1上.

3.1.2. 织构性质

表1为M-TS-1催化剂的比表面积和微孔孔体积. 各金属的引入对TS-1的比表面积和微孔孔体积影响较小, 分别保持在 $460.0 \text{ m}^2/\text{g}$ 和 $0.175 \text{ cm}^3/\text{g}$ 左右. 结合XRD可认为, 这是由于金属氧化物分散度较好; 且在焙烧过程中, 没有烧结而堵塞孔道所致. 图2为各样品的孔径分布图. 由图可见, 各种金属负载后, TS-1的孔径分布不变, 分布在 0.56 nm 左右.

3.1.3. XPS结果

图3为M-TS-1催化剂的XPS谱. 由图可见, 未被修饰的TS-1的Ti $2p_{3/2}$ 特征结合能为 460.0 eV , 在 458.5 eV 处没有出现明显的特征峰, 进一步证明Ti基本以骨架内四面体构型存在, 与XRD表征结果一致. 我们曾对所用载体TS-1进行漫反射紫外可见光谱(DR UV-Vis)表征^[21], 结果同样表明TS-1中只存在骨架内四面体Ti物种. 引入金属M后, 除了 460.0 eV 处的特征峰外, 均还于 459.0 eV 处出现另一特征峰. 这可能是由于金属的引入导致骨架内部分Ti $2p$ 轨道电子云发生偏移, 使得Ti中心周围电子云密度降低, 从而总体上降低了Ti $2p$ 轨道的结合能. 负载金属与TS-1之间的相互作用降低了Ti中心 $2p$ 轨道结合能, 提高了Ti中心的亲电性, 从而有利于活化 H_2O_2 中的活性氧, 形成活性五元环中间体(见图式1). 然而, 在这几种金属修饰的TS-1中, 处于 460.0 和 459.0 eV 的特征峰相对强度却有所不同. 经Cr, Cu修饰后, 459.0 eV 处特征峰的强度低于 460.0 eV 处的; 而在金属Co, Cd, La修饰的TS-1中, 459.0 eV 处特征峰的强度相对较强. 这说明金属Co, Cd, La的加入降低了TS-1中Ti中心周围的电子云密度, 使得更多的Ti中心的亲电性增强, 对TS-1环氧化活性提高效果最明显.

综上所述, 过渡金属和稀土金属的引入都可以提高TS-1中活性Ti中心的亲电性; 但相对于Cr和Cu, 而Co, Cd, La对Ti中心的电子环境影响更加明显, 因此对TS-1的改性作用更加显著.

3.1.4. FT-IR结果

图4为M-TS-1样品的FT-IR谱. 位于 1100 , 800 和 450

cm^{-1} 左右处吸收峰归属为TS-1骨架中四面体构型的 $[\text{SiO}_4]$ 的骨架振动. 1230 和 547 cm^{-1} 左右处吸收峰对应于分子筛的MFI构型, 与XRD结果一致; 970 cm^{-1} 左右处的振动吸收峰则一般被看作为TS-1骨架内Ti与四面体构型的 $[\text{SiO}_4]$ 协同伸缩振动的结果, 这也是判断Ti是否进入TS-1骨架内的一个依据^[26–29]. 由图4可见, 金属的引入造成骨架内Ti活性中心吸收峰蓝移, 说明 $[\text{Ti-O}]$ 键强度降低, Ti周围的电子云密度降低, 这也意味着金属与TS-1间相互作用提高了Ti中心的亲电性. 结合XPS结果发现, M-TS-1催化剂中 $[\text{Ti-O}]$ 键红外吸收峰蓝移的程度依次为: $\text{Cd} > \text{La} > \text{Co} > \text{Cu} > \text{Cr}$, 相应地, 红外吸收峰分别从 976 cm^{-1} 降至 968 , 970 , 971 , 973 和 974 cm^{-1} .

综合XPS和FT-IR结果可见, 金属与载体中Ti活性中心的相互作用使得金属通过氧吸引Ti周围的电子, 降低了Ti周围的电子云密度, 提高了Ti中心的亲电性, 间接也使O1或O2周围的电子云密度降低, 从而提高了O1或O2的亲电性, 使它们更容易和丁二烯的双键结合发生环氧化反应. 但是, 各种金属对TS-1修饰作用的程度有很大差异. 以Cr为代表的前过渡金属以及以Cu为代表的ds区金属对TS-1中Ti中心周围的电子环境影响较弱, 以Co为代表的第VIII族过渡金属, 金属Cd, 以及以La为代表的稀土金属对Ti活性中心亲电性提高作用较为明显.

3.2. M-TS-1催化剂上丁二烯环氧化反应性能

表2为各M-TS-1催化剂上丁二烯环氧化反应结果. 由表可见, 前过渡金属V, Cr, Mn的引入对 H_2O_2 的利用有一定的抑制作用, H_2O_2 转化率虽然均在90%以上, 但其有效利用率和反应后VO的浓度分别低于76.0%和 0.41 mol/L , VO的转化频数也从953最低降至256. 我们考察了V, Cr, Mn修饰的TS-1对 H_2O_2 的空白转化率, 发现在不加入丁二烯时, 这几种催化剂对 H_2O_2 的空白转化率分别为76.5%, 40.6%和31.1%. 这说明 V_2O_5 , Cr_xO_y , MnO_2 的氧化性过强, H_2O_2 被无效分解为 H_2O 和 O_2 . 还可以看出, 随着金属氧化物氧化性的减弱($\text{V}_2\text{O}_5 > \text{Cr}_x\text{O}_y > \text{MnO}_2$), H_2O_2 有效利用率、VO浓度和转化频数都有所上升.

第VIII族过渡金属Fe, Co, Ni的引入促进了 H_2O_2 向VO的有效转化, H_2O_2 转化率基本保持在98.3%以上, H_2O_2 有效利用率、环氧化产物的TON和产量均有所提高. 另外, 在丁二烯环氧化反应中, 稀土金属La的修饰使 H_2O_2 有效利用率显著提高, 同时VO的产量和TON也分别提高到93.4%和1105. 结合XPS和FT-IR结果可知, 这是因为在上述M-TS-1催化剂中, 金属M对Ti活性中心

亲电性的增强效应促进了TS-1催化 H_2O_2 向VO的有效转化能力.

但是, 经ds区金属Cu, Zn修饰后, H_2O_2 转化率从98.8%分别降低至79.0%和83.9%. 同时, Cu-TS-1催化 H_2O_2 有效转化为VO的能力显然小于Zn-TS-1催化剂, Cu的引入使VO的浓度和TON分别从0.41 mol/L和953降至0.32 mol/L和750, H_2O_2 利用率从76%降低至67.3%; 而在Zn-TS-1催化剂中, H_2O_2 利用率从76.0%提高至85.1%, 说明Zn的存在有助于环氧化产物的生成, 正如Zn处理TS-1后使得丙烯环氧化选择性提高^[20]. XPS和FI-IR结果显示, 与第VIII族过渡金属相比, 金属Cu对TS-1的Ti中心周围的电子环境虽有类似作用, 但这种作用较小.

TS-1经过与Zn同族的金属Cd修饰后, 表现出优异的丁二烯环氧化性能, H_2O_2 几乎完全被转化为目标产物VO. 这是由于金属Cd的引入有效减小了Ti 2p轨道的电子云密度, 对Ti活性中心亲电性的增强作用最明显, 因而也最大程度上提高了TS-1催化 H_2O_2 转化为VO的能力.

我们试图把各种金属对TS-1催化性能的影响与金属本身的性质(如: 金属离子的电子结构、氧化还原电

位、离子半径等)关联起来, 但发现并不存在规律性. 虽然各种金属之间的性质是有递变规律的, 但是当它们被引入TS-1中后, 与TS-1的相互作用方式受到很多因素的影响, 很难呈现出统一的规律. 可以肯定的是, 过渡金属和稀土金属的引入的确对TS-1中Ti活性中心周围的电子环境有影响, 从而在不同程度上增强了Ti中心和活性氧的亲电性, 使得TS-1催化活性改变.

4. 结论

通过超声浸渍法将过渡金属(V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd)以及稀土金属(La)负载于TS-1上. 结果表明, 各金属的加入并未改变TS-1的比表面积、微孔孔体积以及骨架结构, 但各种金属对Ti中心周围电子环境的影响程度不同, 均在不同程度上降低了Ti活性中心周围的电子云密度, 增强了Ti中心和活性氧的亲电性. 其中金属Co, Cd和La对Ti中心活化程度较高, Cd改性后的TS-1催化剂在丁二烯环氧化反应表现出良好的催化效果, 能够将投入的0.51 mol/L H_2O_2 完全转化为目标产物VO, VO的TON也达到1197.