稀土负载钛-硅沸石 ETS-10 的制备及其光催化性质

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摘要: 以水玻璃和四氯化钛为原料, 在不使用有机模板剂、氟离子和晶种的条件下, 用水热法合成了钛-硅沸石 ETS-10, 将 La、Ce、Pr 和 Nd 四种稀土元素负载到合成的 ETS-10 上. 通过 X 射线粉末衍射、N₂ 吸附-脱附、²⁹Si 魔角旋转核磁共振、紫外漫反射光谱、X 射线荧光光谱等表征手段对负载前后的 ETS-10 进行了表征. 以有机染料甲基橙为底物, 考察了负载各种稀土及氢氟酸腐蚀对 ETS-10 的光催化活性的影响. 结果表明, 四种稀土元素的引入均可有效提高 ETS-10 的光催化活性. 反应活性提高的程度与稀土元素负载量有关. 对 ETS-10 同时进行氢氟酸腐蚀和稀土元素的负载, 可以将 ETS-10 的光催化活性提高近一倍, 与锐钛矿相 TiO₂ 相当, 但前者更易分离.

关键词: 钛硅沸石; 微孔钛硅分子筛 (ETS-10); 稀土; 光催化反应; 甲基橙

中图分类号: O643 **文献标识码:** A

收稿日期: 2011-07-21. 接受日期: 2011-09-26.

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基金来源: 国家重点基础研究发展计划 (973 计划, 2009CB623506); 国家高技术研究发展计划 (863 计划, 2009AA033701); 上海市优秀学科带头人计划 (10XD1400300); 上海市重点学科建设项目 (B108).

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Preparation and Photocatalytic Activity of Lanthanide Loaded Microporous Titanosilicate ETS-10 Catalysts

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Abstract: The three dimensional microporous titanosilicate, ETS-10, was synthesized by a hydrothermal synthesis route using TiCl₄ and a sodium silicate aqueous solution as starting materials. Lanthanide (La, Ce, Pr, Nd) loaded ETS-10 catalysts were prepared by the impregnation method. The catalysts were characterized by X-ray diffraction, ²⁹Si magic angle spinning NMR, UV-Vis diffuse reflectance spectroscopy, N₂ adsorption-desorption measurement, and X-Ray fluorescence spectroscopy. The degradation of methyl orange under near-UV light was used to investigate the photocatalytic activity of the catalysts in aqueous suspensions. The lanthanide loaded ETS-10 catalysts exhibit higher activity than the unmodified ETS-10. The combination of loading lanthanide and increasing the surface defects of ETS-10 by a HF treatment gave an enhancement of the photocatalytic activity, which became comparable with that of anatase TiO₂.

Key words: microporous titanosilicate; Engelhard titanosilicate material number 10 (ETS-10); lanthanide; photocatalysis; methyl orange

Received 21 July 2011. Accepted 26 September 2011.

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This work was supported by the National Basic Research Program of China (973 Program, 2009CB623506), the National High Technology Research and Development Program of China (863 Program, 2009AA033701), the Program of Shanghai Subject Chief Scientist (10XD1400300), and the Shanghai Leading Academic Discipline Project (B108).

English edition available online at Elsevier ScienceDirect (<http://www.sciencedirect.com/science/journal/18722067>).

TiO₂ is well known as the most active and efficient solid photocatalyst for the degradation of organic compounds in aqueous solution under mild conditions [1,2]. However, the post-treatment needed for the removal of the catalyst requires a costly liquid-solid separation because of the formation of milky dispersions formed after the mixing of the catalyst with the substrate during the photoirradiation, which greatly restricts its application [3]. Much work has been done to improve the mechanical property and photocatalytic activity of TiO₂ by loading with transition metal or rare earth metal oxides [4–11].

ETS-10 is a microporous titanasilicate with the stoichiometry of (Na,K)₂Si₅TiO₁₃. It was first synthesized by Kuznicki in 1989 [12]. The framework of ETS-10 contains two sets of Ti–O–Ti chains composed of corner-sharing TiO₆ octahedra in orthogonal directions. The Ti–O–Ti chains are embedded into corner-sharing SiO₄ tetrahedral units through bridging oxygen atoms to form the pore structures with large 12-membered rings (0.76 nm × 0.49 nm) [13]. The framework of ETS-10 is negatively charged and balanced by cations such as Na⁺ and K⁺ [14]. ETS-10 has been studied as the catalyst for the gas phase oxidative dehydrogenation of cyclohexanol and cycloaddition of propylene oxide with carbon dioxide to propylene carbonate [15–17]. The most attractive property of ETS-10 is its shape-selective photocatalysis [18] of large organic molecules although the activity of ETS-10 is lower than that of TiO₂. However, the controllable introduction of surface defects by a dilute solution of HF [19] and the loading of transition metal on ETS-10 [20] have proved effective for the enhancement of photocatalytic activity. Lanthanide loaded anatase titania catalysts showed a good photocatalytic performance due to increased adsorption of the substrate on the catalysts [21–23]. Photocatalysis by lanthanide loaded ETS-10 has not been reported yet.

ETS-10 has been synthesized by employing a range of organic templates [24–28]. Subsequently, some improved template-free methods using TiO₂ and TiCl₄ as titanium sources in the presence of fluoride ions were published [29,30]. Rocha et al. [31] reported the synthesis of ETS-10 using TiO₂ and TiCl₃ without a template or fluoride ions and Lv et al. [32] showed that commercial Degussa TiO₂ P25 is a better titanium source when crystalline seeds of ETS-10 were necessary for a high quality product. However, a simple and effective approach to prepare ETS-10 is desirable.

Here, ETS-10 was synthesized by a simply hydrothermal method using sodium silicate aqueous solution and TiCl₄ in the absence of any organic template, fluoride ions or ETS-10 seeds. Lanthanide loaded ETS-10 catalysts were prepared by the impregnation method. The heterogeneous photocatalytic degradation of methyl orange in an aqueous medium was carried out. The influences of the loaded lan-

thanides, loading amount, and catalyst surface defects on photocatalytic activity were investigated.

1 Experimental

1.1 Preparation of ETS-10

ETS-10 was synthesized using a method similar to a reported procedure [31] but using titanium tetrachloride as the titanium source instead of titanium dioxide or titanium trichloride. NaOH (6.43 g) and KOH (4.20 g) were dissolved in 10.0 g water in a polyethylene beaker. Then 32.03 g of sodium silicate aqueous solution (containing 7.2 wt% Na₂O and 25.7 wt% SiO₂) was added. TiCl₄ (4.75 g) was added slowly into 10.0 g of H₂O under vigorous stirring, and then the solution was added dropwise into the sodium silicate solution under stirring. The pH value of the mixture was kept at 10.4–10.5 with concentrated hydrochloric acid. The resulting gel with the molar ratio of 4.7 Na₂O:1.5 K₂O:TiO₂:5.5 SiO₂:92 H₂O was transferred into a Teflon-lined autoclave for crystallization at 230 °C for 36 h. The products were filtered, washed with water, and dried at 100 °C.

1.2 Preparation of lanthanide loaded ETS-10 before and after HF treatment

Lanthanide loading was performed by the impregnation method. ETS-10 (3.0 g) was stirred in 20 ml water and 10 ml of Ln(NO₃)₃ (0.020 mol/L, Ln = La, Ce, Pr, and Nd) solution was added into the suspension. After stirring for 2 h, the pH of the mixture was adjusted with NaOH (1 mol/L) to *ca.* 11 and the resulting solid was filtered, washed with water, and heated at 100 °C for 12 h. The samples were denoted Ln-ETS-10.

The HF treatment of ETS-10 was carried out using the procedure of Valente et al. [16]. ETS-10 (1.0 g) was stirred in 5 ml of HF (2 wt%) for a few seconds, then the catalyst was quickly washed with water, filtered, and dried at 110 °C. The product was denoted as HF-ETS-10. The HF treated ETS-10 was loaded with different amounts of La and Ce (denoted La-HF-ETS-10 and Ce-HF-ETS-10, respectively) by the same impregnation method as above.

Anatase TiO₂ was prepared with the method described by Zhang et al. [33].

1.3 Characterization

X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-IIA X-ray diffractometer using Cu K_α radiation with a voltage of 30 kV and a current of 20 mA. ²⁹Si magic-angle spinning (MAS) NMR spectra were obtained at

59.6 MHz with a 60° pulse and a 120 s recycle delay on a Bruker Avance DSX-300 spectrometer spun at 4 kHz. Tetramethylsilane was used as an external standard. The average pore size, pore volume, and BET specific surface area were determined by N₂ adsorption-desorption measurement at -196 °C on a Micromeritics Tristar 3000 analyzer. Elemental analysis was performed using a Bruker S4 Explorer X-ray fluorescence spectrometer. UV-Vis diffuse reflectance spectra (DRS) in the region of 190–900 nm were recorded on a JASCO UV550 spectrophotometer.

1.4 Photocatalytic activity

The photocatalytic degradation of an aqueous solution of methyl orange (MO) under near-UV light was employed to characterize the photoactivity of the catalysts. A GGY 125-W medium pressure mercury lamp in conjunction with a quartz water jacket was used as the light source. Irradiation was carried out with light of $\lambda > 365$ nm. The jacket was inserted into a magnetically stirred sample solution with an optical path length of *ca.* 2 cm. Cooling water was circulated through the jacket to keep the sample solution at room temperature during the photoirradiation.

In a typical run for the photocatalytic degradation of MO, 0.14 g of catalyst was dispersed in 140 ml of aqueous solution containing 1×10^{-4} mol/L of MO. This was stirred in the dark for 2 h to achieve the adsorption-desorption equilibrium. Then the suspension was aerated with air (200 ml/min) and irradiated with near-UV light. Aliquots (4 ml) were taken out at fixed time intervals and centrifuged to remove the ETS-10 particles for monitoring the degradation of MO by an Agilent-8453 UV-visible absorption spectrometer.

2 Results and discussion

2.1 Characterization of the catalysts

Figure 1 shows the XRD patterns of ETS-10, Ln-ETS-10,

Fig. 1. XRD patterns of ETS-10 (1), La-ETS-10 (2), Ce-ETS-10 (3), Pr-ETS-10 (4), Nd-ETS-10 (5), HF-ETS-10 (6), and La-HF-ETS-10 (7).

HF-ETS-10, and La-HF-ETS-10 in the 2θ range of 5°–40°. The ETS-10 sample gave XRD patterns similar to those reported previously [13]. The pattern revealed that ETS-10 can be simply prepared by using TiCl₄ as the titanium source as in the present work without an organic template, fluoride ions, or ETS-10 crystalline seeds. As shown in Fig. 1(2)–(5), the XRD patterns of the rare earth metal loaded ETS-10 samples were almost the same as the parent ETS-10. No peak from the lanthanides was observed, suggesting the fine dispersion of the lanthanide species in ETS-10.

The XRD patterns of the HF-modified ETS-10 and typical lanthanide loaded HF-treated ETS-10 samples showed no obvious difference when compared with that of the parent ETS-10, which indicates that the crystalline structure of ETS-10 was preserved after the HF treatment and further lanthanide loading, in spite of the dissolution of small portions of SiO₄ units in the framework by the dilute HF solution.

Figure 2 shows the ²⁹Si MAS NMR spectra of ETS-10, Ce-ETS-10, and HF-ETS-10. ETS-10 showed four peaks with chemical shifts at -94.1, -95.8, -96.4, and -103.3. The

Fig. 2. ²⁹Si MAS NMR spectra of ETS-10 (a), Ce-ETS-10 (b), and HF-ETS-10 (c).

resonances at -94.1 , -95.8 , and -96.4 can be assigned to $\text{Si}(3\text{Si}, 1\text{Ti})$ and the resonance at -103.3 to $\text{Si}(4\text{Si}, 0\text{Ti})$ [13]. No significant difference was observed with the Ce loaded sample, which suggested that the framework structure of ETS-10 was not affected by the loading of lanthanides. The other lanthanide loaded ETS-10 samples gave the same spectra. However, a significant line broadening was observed with the HF modified ETS-10, indicating a change in the local structural environment of Si sites after the treatment with HF, which cannot be seen with XRD [34].

XRF analysis was carried out to determine the amount of loaded lanthanides. The molar ratio of the unmodified ETS-10 was $\text{Na}:\text{K}:\text{Si}:\text{Ti} = 1.83:0.32:4.93:1.00$, which is consistent with the stoichiometry of ETS-10, $(\text{Na},\text{K})_2\text{Si}_5\text{TiO}_{13}$. The contents of the loaded lanthanide were in the range of 0.9 wt%–1.0 wt% (Table 1).

The BET specific surface area and pore volume of ETS-10, HF-ETS-10, and lanthanide loaded ETS-10 from N_2 sorption experiments are listed in Table 1. The surface area increased slightly after the modification by HF and decreased slightly after lanthanide loading, indicating the maintenance of the porous structure during the loading of lanthanides and HF modification.

Table 1 Content of lanthanide, BET specific surface area, and pore volume of different samples

Sample	Lanthanide content (wt%)	Surface area (m^2/g)	Pore volume (cm^3/g)	Percentage of adsorbed MO ^a (%)
ETS-10	—	357	0.172	4.1
La-ETS-10	0.92	348	0.171	8.1
Ce-ETS-10	0.97	346	0.167	8.3
Pr-ETS-10	0.95	348	0.170	8.1
Nd-ETS-10	0.90	345	0.169	8.0
HF-ETS-10	—	365	0.180	5.9
La-HF-ETS-10	0.94	354	0.178	8.1

^aBased on the calculation of $(1 - c_0/c_{\text{initial}}) \times 100\%$, where c_{initial} denoted the initial concentration of MO (1×10^{-4} mol/L) and c_0 denoted the concentration of MO in suspension after 2 h of stirring in dark.

The UV-Vis DRS spectra of ETS-10 and Ln-ETS-10 are shown in Fig. 3. The main absorption band of ETS-10 is at 300 nm, which was assigned to the ligand-to-metal charge transfer bands in the Ti–O–Ti chains [35]. The spectra of lanthanide loaded ETS-10 samples showed slight red shifts, which was possibly due to the change of the band gap between the f electrons of lanthanide and the conduction or valence bands of ETS-10. This was also observed in the lanthanide loaded TiO_2 samples [10]. The band gap values of these catalysts are summarized in Table 2. The extension of the absorption band to the visible region meant the possibility of exciting lanthanide loaded ETS-10 by longer wavelength irradiation [10].

Fig. 3. UV-Vis diffuse reflectance spectra for ETS-10 (1), La-ETS-10 (2), Ce-ETS-10 (3), Pr-ETS-10 (4), and Nd-ETS-10 (5).

Table 2 Rate constants for the photocatalytic degradation of methyl orange over the different ETS-10 catalysts

Catalyst	k^a/h^{-1}	Band gap (eV)
Anatase TiO_2	0.946	3.20
ETS-10	0.476	4.15
La-ETS-10	0.652	3.97
Ce-ETS-10	0.680	3.93
Pr-ETS-10	0.550	4.02
Nd-ETS-10	0.601	3.98
HF-ETS-10	0.705	4.15
La-HF-ETS-10	0.907	3.97

^aThe first order rate constant.

2.2 Photocatalysis

After stirring of the aqueous suspension of MO with the catalyst in the dark for 2 h, the adsorption equilibrium of MO on the catalyst was achieved. The amount of adsorbed MO was estimated by comparing the concentration of MO in the suspension before and after the addition of the catalyst (Table 1). For lanthanide loaded and HF modified ETS-10 catalysts, in particular the former catalysts, the amounts of adsorbed MO on the catalyst showed an obvious increase.

The changes in the UV-Vis absorption spectra (Fig. 4) at the different time intervals showed the photocatalytic degradation of methyl orange over ETS-10, La-ETS-10, and La-HF-ETS-10. The absorption peak at 465 nm, corresponding to the degradation of the organic dye, gradually decreased with reaction time and finally vanished. The degradation curves of MO followed pseudo-first order kinetics and the degradation rate of MO was calculated using the formula $-\ln(c/c_0) = kt$, where t is the reaction time, k stands for the pseudo-first order rate constant, c_0 is the concentration of MO in the suspension after 2 h of stirring in the dark, and c is the concentration of MO at time t . In the plots of $-\ln(c/c_0)$ vs. t , the value of the slope equals the first order

Fig. 4. UV-Vis absorption spectra of methyl orange catalyzed by ETS-10 (a), La-ETS-10 (b), and La-HF-ETS-10 (c).

rate constant (Fig. 5). All the first order reaction constants of the ETS-10 catalysts, along with that of anatase TiO_2 , are listed in Table 2.

The lanthanide loaded ETS-10 catalysts showed a higher photocatalytic activity than the unmodified ETS-10. It is known that the loading of lanthanide on TiO_2 enhances photocatalytic activity because of increased interaction between the organic functional groups and the f orbitals of the lanthanide since the unfilled f orbitals have Lewis acidity [22]. Hence, the concentration of OH generated under irradiation and organic molecules adsorbed on the semiconductor increased, which accelerated the photocatalytic degradation of the organic substrate [21–23]. It was reported that the photocatalytic mechanism of ETS-10 is similar to that of anatase TiO_2 and the catalytic active sites of ETS-10 are titanol groups linked on the external surface [18].

When ETS-10 was treated with dilute HF aqueous solution, the defects of titanol groups can be induced on the surface of ETS-10 without destroying its microporous

Fig. 5. Rate law plots of methyl orange degradation catalyzed by different ETS-10 samples under UV light irradiation.

structure [19]. The treated HF-ETS-10 has a higher density of photoactive sites on the surface, leading to a reaction rate constant 1.5 times larger than that of ETS-10. With the further loading of lanthanide on HF-ETS-10, the reaction rate constant of La-HF-ETS-10 became twice as large as that of the parent ETS-10 and was comparable with that of anatase TiO_2 . Furthermore, the removal of the modified ETS-10 catalysts after reaction was easier than that of TiO_2 .

The effects of La and Ce loading on the photocatalytic activity are shown in Fig. 6. The reaction rate constants increased with the increase of lanthanide content and reached a plateau at 1 wt%, and then decreased with the further increase of lanthanide content. The optimum loading content of lanthanide depends on the thickness of the space charge layer. When the thickness of the space charge layer is equal to the irradiation penetration depth, the separation of electron-hole pairs will be the most effective [10]. With a further increase of the lanthanide loading, the ability of the space charge region to separate electron-hole pairs will be reduced [21–23]. On the other hand, excessive loaded lan-

Fig. 6. Relationship between pseudo-first rate constant and the contents of lanthanide content.

thanide can block the production of titanol groups on ETS-10 surface under irradiation. Therefore, these two contrary effects account for the optimum loading content of lanthanide.

3 Conclusions

Microporous titanosilicate ETS-10 was hydrothermally synthesized from TiCl_4 and sodium silicate aqueous solution without using an organic template, fluoride ions or ETS-10 seeds. Red shifts in the UV-Vis range were observed from the lanthanide (La, Ce, Pr, Nd) loaded ETS-10 samples. The photocatalytic degradation of methyl orange revealed that the lanthanide loaded ETS-10 catalysts gave better activity than pure ETS-10. After the treatment of ETS-10 with dilute HF, the lanthanide loaded catalyst showed a higher activity, which was comparable with that of anatase TiO_2 .

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