

锆钇柱撑蒙脱土负载 Pd 催化剂的催化性能研究

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摘要: 合成了锆钇柱撑蒙脱土(Zr-Y-MMT)载体, 并用于丙酮、甲苯和乙酸乙酯的催化氧化。通过 XRD、TEM 及 N_2 吸附-脱附技术对 Zr-Y-MMT 载体和负载 Pd 催化剂(Pd/Zr-Y-MMT)进行了表征。XRD 结果显示, 经锆钇柱撑后蒙脱土的层间距由 1.27 nm 增大至 1.78 nm; N_2 吸附脱附结果表明, 经锆钇柱撑后, 其比表面积有了很大的增加, 由 $62 \text{ m}^2 \cdot \text{g}^{-1}$ 增大至 $395 \text{ m}^2 \cdot \text{g}^{-1}$ 。活性评价结果发现, Zr-Y-MMT 载体比 Na-MMT 有更好的催化活性, 其完全氧化丙酮、甲苯和乙酸乙酯的温度分别为 320、350 和 290。此外, 当此载体上负载 0.1wt%Pd 时, 其用于完全氧化甲苯的活性有了明显的改进。

关键词: 柱撑蒙脱土; 催化氧化; 稀土

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Catalytic Performance of Pd Catalyst Supported on Zirconium and Yttrium Pillared Montmorillonite

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Abstract: A montmorillonite support material pillared with zirconium and yttrium (Zr-Y-MMT) was prepared for catalytic oxidation of acetone, toluene and ethyl acetate. The Zr-Y-MMT support and the supported Pd catalyst (Pd/Zr-Y-MMT) were characterized by XRD, TEM and low temperature nitrogen adsorption-desorption techniques. The XRD results indicate that the interlayer spacing of the montmorillonite is increased from 1.27 nm to 1.78 nm after zirconium and yttrium cation pillaring. N_2 adsorption-desorption results show that a great increase in BET specific surface area (from 62 to $395 \text{ m}^2 \cdot \text{g}^{-1}$) is found for Na-MMT pillared with zirconium and yttrium. It is also found that Zr-Y-MMT is more active than Na-MMT for the complete oxidation of acetone, toluene and ethyl acetate, and the temperature for the said catalytic oxidation can be lowered to 320, 350 and 290, respectively. Moreover, after 0.1wt% Pd was supported on Zr-Y-MMT, the catalytic activity was obviously improved for toluene combustion.

Key words: pillared montmorillonite; catalytic oxidation; rare earth

Volatile Organic Compounds (VOCs) from industrial processes represent a serious environmental problem. Catalytic combustion is one of the most attractive ways for controlling the emission of VOCs^[1]. Noble-metal-based (e.g. Pt and Pd) catalysts show the highest

activity for the oxidation of VOCs. As most reports indicated, the catalyst supports play an important role in the improvement of catalytic activity. Usually, Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 and zeolite^[2-6] are commonly used as support for noble metal catalysts. Clays, a kind of

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natural aluminosilicates, are commercially attractive for their lower price compared to some other catalyst supports^[7]. Moreover, pillared clays have caught attention as catalysts and catalyst supports for their porosity, reactivity and thermal stability. In recent years, much research has been directed to metal oxide pillared clays. Sun Kou et al.^[8] reported that Zr-PILCs samples were quite effective in methanol conversion due to their acidity and porosity. Li and co-workers^[9] used Zr-, Ce-, and Al-pillared clays as supports in palladium catalysts for the complete oxidation of benzene and found Pd/Zr-Lap was the most active catalyst.

The addition of second cation such as rare earth element is another way to be considered. As well known that the rare earth element shows excellent oxygen storage capacity, the presence of rare earth ions either in the pillars or in the interlayer can effectively improve thermal stability and catalytic activity of the pillared clays. However, rare earth cations used in combination with Zr-pillared clays or as support have not been studied extensively^[10].

In this work, a new montmorillonite material pillared with zirconium and yttrium (Zr-Y-MMT) was prepared and characterized. Furthermore, palladium catalyst supported on this support (Pd/Zr-Y-MMT) are prepared using impregnation method and tested in the deep oxidation of acetone, toluene and ethyl acetate.

1 Experimental

1.1 Catalyst Preparation

The starting material for the pillaring procedures was Na-type montmorillonite (Neimenggu, China) obtained by exchanging with $1\text{ mol} \cdot \text{L}^{-1}$ NaCl solution and followed by washing and centrifuging until free of chlorides (referred to as Na-MMT)^[11]. Zirconyl chloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) (Shanghai, China, C.P.) and yttrium nitrate ($\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (Shanghai, China, A.R.) were used as source of zirconium and yttrium ion for the preparation of Zr-Y mixed cation pillared clays. The solution of the pillaring agent with Zr/Y molar ratio of 5/1 was prepared by adding suitable amount of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ to $1\text{ mol} \cdot \text{L}^{-1}$ Zr solution. The resulting solution

was heated at $80\sim 90^\circ\text{C}$ under consecutive stirring for 2 h and then aged for 4 h at the same temperature. The pillaring solution was gradually added to the 1wt% clay aqueous suspension under stirring conditions at a ratio of 10 mmol Zr per gram of clay at $60\sim 70^\circ\text{C}$. The mixture was kept under a continuous stirring for 2 h and aged for 4 h at the same temperature and then centrifuged, washed with distilled water until free from chloride ions. At last, the sample was dried at 110°C and calcined for 2 h at 500°C . The obtained material is denoted as Zr-Y-MMT.

The supported Pd catalyst was prepared by wet impregnation method with an aqueous of H_2PdCl_4 as metal precursors. At last, after reduction with hydrazine hydrate, the samples were dried at 110°C and calcined at 500°C for 1 h. For the obtained catalyst, the palladium content on Zr-Y-MMT support was 0.1wt%.

1.2 Characterization

Low angle XRD patterns were recorded on a Rigaku D/max-BX power diffractometer using Nifiltered monochromatized Cu K α ($\lambda=0.15418\text{ nm}$) radiation. The voltage and current applied to the X-ray tube were 40 kV and 25 mA, respectively. The intensity data were collected over 2θ range of $0.5^\circ\sim 30^\circ$ for Na-MMT and Zr-Y-MMT. The transmission electron microscopy (TEM) images were taken on a JEM-200CX electron microscope analyzer and the accelerating voltage was 160 kV. The surface areas of the samples were determined by N_2 adsorption isotherms at 77 K with the BET method, using a Coulter OMNISORP-100 apparatus. Prior to adsorption measurements, the samples were degassed under vacuum for 1 h at 200°C .

1.3 Catalytic activity tests

Model reactions of the complete combustion of acetone, toluene and ethyl acetate were carried out in a tubular fixed-bed quartz glass micro-reactor (WFS-3010, China). The concentration of acetone, toluene and ethyl acetate in air is $1\,700\sim 2\,500\text{ mg} \cdot \text{L}^{-1}$, $1\,000\sim 1\,600\text{ mg} \cdot \text{L}^{-1}$ and $1\,100\sim 1\,700\text{ mg} \cdot \text{L}^{-1}$, respectively, and the space velocity (S.V.) was $10\,000\text{ h}^{-1}$. The catalyst (60~80 mesh ($250\sim 177\text{ }\mu\text{m}$), 0.3 mL) was loaded in the quartz reactor, with quartz wool packed at both ends of the catalyst bed. A thermocouple was placed inside the

reactor in the centre of the catalyst bed to monitor the reaction temperature. The catalysts were directly exposed to reaction gas as the reactor temperature stabilized without any pretreatment. The analysis of reactor effluent was performed on a GC-8A chromatograph using FID mode and The analysis of reactor effluent was performed on a GC-8A chromatograph with a FID detector. The GC column was 3 mm \times 0.3 μ m \times 3 m stainless steel tubing packed with OV101. The analysis conditions were as follows: the temperatures of injector, detector and column chamber were 180, 180 and 140 $^{\circ}$ C, respectively. The flow rate of carrier gas (N_2) was 20 $cm^3 \cdot min^{-1}$.

2 Results and discussion

2.1 XRD

The XRD patterns of the Na-MMT and the Zr-Y mixed cation pillared montmorillonite calcined at 500 $^{\circ}$ C are presented in Fig.1. As shown in Fig.1, the d_{001} reflection for the basal spacing was found to increase from 1.27 nm in the sample of Na-MMT to 1.78 nm in Zr-Y-MMT sample. These results suggest that the Zr-Y mixed cation has intercalated into the layers of Na-MMT during the preparation process. On the other hand, it can be found that the basal spacing is shifted to lower angle and becomes broader and weaker on the Zr-Y-MMT sample. On the sample of Pd/Zr-Y-MMT (as shown in the wide-angle XRD pattern), the characteristic peaks of PdO can not be detected. This is probably related to two reasons: one is caused by PdO particles highly dispersed on the Zr-Y-MMT support^[12] and the other is due to part of PdO particles gotten into the Zr-Y-MMT support.

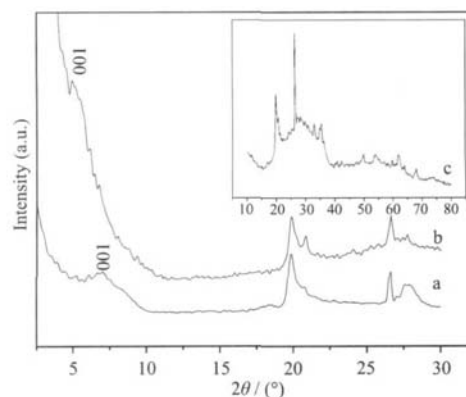


Fig.1 XRD patterns of (a) Na-MMT; (b) Zr-Y-MMT; (c) Pd/Zr-Y-MMT

2.2 TEM

Fig.2 gives the TEM images of Na-MMT, Zr-Y-MMT and Pd/Zr-Y-MMT. It can be seen clearly that Na-MMT is comprised of many parallel silicate layers with about 1.2 nm interlayer spacing (Fig.2a). After pillared with Zr-Y mixed cation, the interlayer spacing of Na-MMT is increased. The interlayer spacing of Zr-Y-MMT is changed from 1.2 nm to 1.5~2.0 nm (Fig.2b). This gives direct evidence that the zirconium, yttrium ions have intercalated into the layer of Na-MMT. This observation is in good agreement with the XRD result. However, the TEM image of Pd/Zr-Y-MMT sample (Fig. 2c) is quite different from those of Na-MMT, Zr-Y-MMT samples. The palladium particles were dispersed on the surface of Zr-Y-MMT support, and the average size of Pd particle is about 12 nm. This suggests that the Zr-Y-MMT support is favorable to the dispersion of palladium particles. We think that the highly dispersed palladium species on a Zr-Y-modified MMT is responsible for the high and stable activity for the total oxidation of acetone, toluene and ethyl acetate.

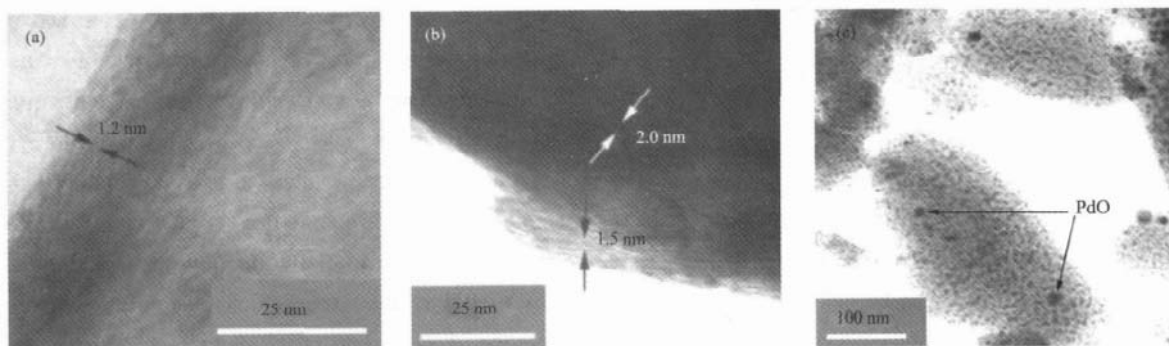


Fig.2 TEM photographs of (a) Na-MMT; (b) Zr-Y-MMT; (c) Pd/Zr-Y-MMT

2.3 BET surface area

Fig.3 shows the BET specific surface areas of Na-MMT, Zr-Y-MMT and 0.1%Pd/Zr-Y-MMT samples. As expected, there is a notable increase of the specific surface area on the sample of Zr-Y-MMT compared with Na-MMT sample. The surface area of Zr-Y-MMT is $395 \text{ m}^2 \cdot \text{g}^{-1}$, more than six times larger than that of Na-MMT ($62 \text{ m}^2 \cdot \text{g}^{-1}$). Besides, a decrease is observed in the specific surface area on 0.1%Pd/Zr-Y-MMT sample, which is possibly due to the fact that some particles of Pd are impregnated onto the Zr-Y-MMT and block up some of pores of the catalyst^[13].

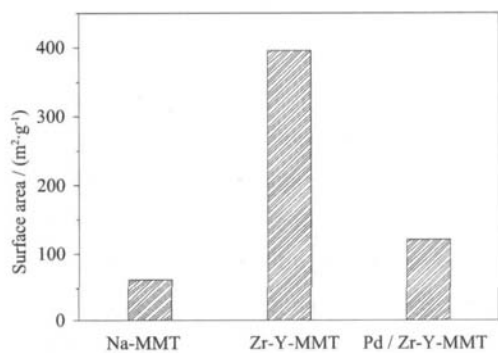


Fig.3 BET surface area of Na-MMT, Zr-Y-MMT and Pd/Zr-Y-MMT

2.4 Catalytic activity tests

The catalytic activities for acetone, toluene and ethyl acetate complete oxidation over the samples of Na-MMT, Zr-Y-MMT, Pd/Na-MMT and Pd/Zr-Y-MMT were also investigated. As shown in Fig.4~6, the catalytic activity of Na-MMT is quite low and the total oxidation temperature for acetone, ethyl acetate requires a temperature as high as 490 and 420. The $T_{80}(T_{80}$

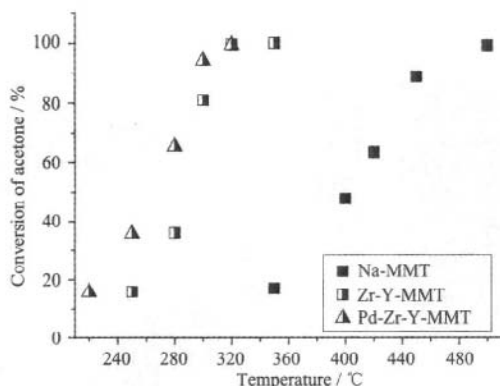


Fig.4 Light-off curves for acetone combustion over Na-MMT, Zr-Y-MMT and Pd/Zr-Y-MMT

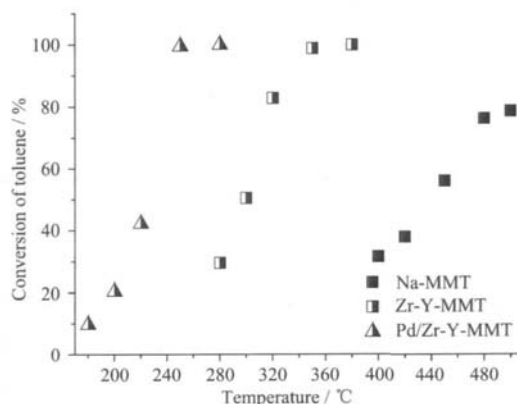


Fig.5 Light-off curves for toluene combustion over Na-MMT, Zr-Y-MMT and Pd/Zr-Y-MMT

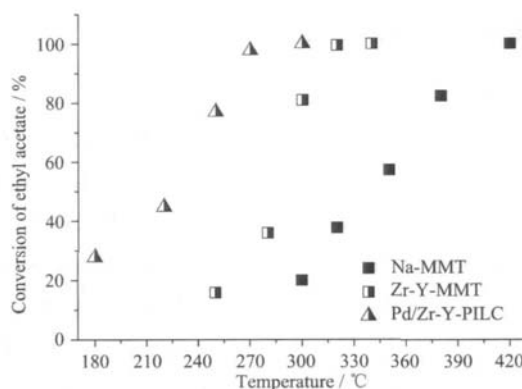


Fig.6 Light-off curves for ethyl acetate combustion over Na-MMT, Zr-Y-MMT and Pd/Zr-Y-MMT

denotes that temperature at which toluene conversion reaches 80%) for toluene is 550. However, the activity of Zr-Y mixed cation pillared montmorillonite is obviously improved, and the corresponding complete oxidation temperature for acetone, toluene and ethyl acetate is 320, 350 and 290, respectively. Apparently, the complete oxidation temperatures for the three compounds on Zr-Y-MMT are much lower than those on Na-MMT, indicating that Zr-Y mixed cation pillaring can improve the activity of Na-MMT effectively. This is consistent with the results reported by Craciun and Labaki^[14,15].

Meanwhile, the catalytic activity for the complete oxidation of three compounds is significantly improved by the presence of palladium oxides. On the Pd/Na-MMT catalyst, the temperature of complete oxidation for acetone, toluene and ethyl acetate are 320, 280 and 330. And the Pd/Zr-Y-MMT catalyst shows

higher catalytic activity than Pd/Na-MMT in toluene and ethyl acetate. Typically, the temperature for complete oxidation of toluene and ethyl acetate are lowered to 250 °C and 270 °C, respectively. It suggests that the support of Zr-Y-MMT has efficiency for active species and is suitable for supporting Pd catalysts.

3 Conclusions

A Zr-Y-MMT support and catalyst Pd/Zr-Y-MMT were prepared and characterized by XRD, TEM and low temperature nitrogen adsorption and desorption. It is found that due to the process by zirconium and yttrium pillaring, the interlayer spacing of montmorillonite is increased and the surface area is greatly improved, which leads to well dispersion of palladium particles on the Zr-Y-MMT support. Through catalytic activity tests, it can be found that the catalytic activity of Zr-Y-MMT sample is much higher than that of Na-MMT. The results of supported palladium catalysts suggest that Zr-Y-MMT is a promising support for catalytic oxidation of acetone, toluene and ethyl acetate.

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