Study on Preparation and Properties of ZrO_2/Sepiolite composite

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Abstract. Sepiolite as catalyst carrier material, now commonly used in low temperature, for high temperature applications was very rare. ZrO_2/sepiolite precursor was prepared by Chemical precipitation method, catalyst coating material was prepared at 600˚C, the samples were aged at 1000˚C. The powders with and without aging were characterized by means of BET (BET surface area), TG, XRD and SEM. The effect of acidification time on sepiolite surface area and the influences of Lanthanum adding, mass ratio of ZrO2 and sepiolite on the composite properties were studied. The results indicate that after acidification 18h sepiolite surface area up to 148.12 $m^2 \cdot g^{-1}$. When added 6 Wt.% La, mass ratio of ZrO_2 and sepiolite was 3:2, ZrO_2/ sepiolite catalyst coating composite surface area is maximum, reach to 95.7553 $m^2 \cdot g^{-1}$, with the 1000 ˚C aging, the specific surface area still up to 55.7553 $m^2 \cdot g^{-1}$, besides, it has good thermal stability. Compared with the specific surface area of sepiolite with high temperature treatment, this catalyst carrier coating composite improved significantly.

Introduction

In the technology of automobile exhaust purifying catalyst, specific surface area of active carrier coating materials on the catalyst is one of the key influence for catalytic properties[1]. In addition, the operating temperature of automotive catalytic converters generally range 250˚C ~950˚C[2], so catalyst coating material should remain a large specific surface area under high temperature. Thus, research and development a new coating material which is stability at high temperature and has large surface area is important for improving the catalytic efficiency.

Sepiolite is a natural clay mineral, its main ingredient is silicon, magnesium salt. The ideal formula is $[Si_{12}Mg_8O_{30}(OH)_4](H_2O) \cdot 48H_2O$[3]. Sepiolite usually forms compact irregular fine-fibre aggregates with high porosity, so it is porous with a high specific surface area, a unique pore structure and a high capacity for ion exchange. Because of its specific chemical composition, pore structure and strength, sepiolite has attracted considerable attention from the catalytic industry. Its heat stability are too low for high temperature environment[4,5]. In the metal-oxide ceramics, zirconium oxide has high temperature stability, low thermal conductivity and heat insulation performance, has broad application prospect in high temperature situation. The attempts of applying sepiolite with zirconium oxide to obtain a catalyst carrier coating composite. Testing specific surface area of ZrO_2/Sepiolite composite after high temperature aged, and analysis its microstructure and composition[6,7].

Experimental

Materials. Sepiolite was purchased from the Hunan, the chemical composition was analysed by X Ray Fluorescence (XRF): SiO_2 65.03, MgO 24.76, Al_2O_3 3.45, Fe_2O_3 0.83, CaO 0.78 (weight%). The specific surface area was 99.92 $m^2 \cdot g^{-1}$.

Sepiolite acid treatment. Acidification can further increase sepiolite surface area[8]. Sepiolite and Hydrochloric acid (HCl) were mixed at a 1:10 solid-liquid ratio , and the concentration of HCl was 1mol/L, kept at temperature75˚Cfor different time, then washed, filtered and dried at 110˚C to produce samples which were acid modified.

Preparation of ZrO_2/Sepiolite Composites. $ZrOCl_2 \cdot 8H_2O$ and $La(NO_3)_3 \cdot 6H_2O$ was dissolved in ethanol-water mixture, 0.5 wt.% polyethyleneglycol (PEG) was added as dispersant, volume ratio of ethanol and water was 2:1. Then added acid modified sepiolite into the mixture, stirred at room temperature for 0.5h. Mixture was adjusted by NH_4OH to pH=10, continued strong stirring for 0.5h, aged at room temperature for 2h. Precipitated sepiolite–$Zr(OH)_4$ was washed with distilled water until chloride ions were absent, then washed with absolute ethyl alcohol. The sediment was dried at 110 °C, calcined at 600 °C and1000°C for 1h to get fresh and aged samples.

Main chemical reaction in this experiment is:

$ZrOCl_2+2NH_4OH+(n-1)H_2O \rightarrow Zr(OH)_4 \bullet nH_2O+2NH_4Cl$

$Zr(OH)_4 \rightarrow ZrO_2+2H_2O$

Measurements and Characterization. X-ray powder diffraction (XRD) was made with Bruker D8. Specific surface area(BET) was measured using a JW-BK112 specific surface area and pore size Analyzer. Thermogravimetric analysis (TGA) was measured using a METTLER TOLEDO STARe apparatus. Measurements were performed at a heating rate of 20 ^oC/min under a nitrogen flow of 20 mL/min. Scanning electron microscopy (SEM) analyses for the morphology with a Hitachi S-4800 scanning electron microscopy.

Results and discussion

Acid pretreatment of sepiolite

Table 1 Variation of surface area against time at acid treatment

t/h	0	6	12	18	24	30	36	42	48
Surface area /m^2 g^{-1}	99.92	105.91	141.80	148.12	127.36	131.46	125.05	123.10	110.83

Table 1 shows the specific surface area of sepiolite after different acid time. Results show that after acid treatment, specific surface area of sepiolite first increases and then decreases over acid time. After acidized 18h, its specific surface area reach the maximum, is 148.115m^2g^{-1}. Besides, the crystals on surface of sepiolite are seriously corroded by HCl, so the surface roughness of sepiolite is increased, in favor of ZrO_2 compounded with sepiolite in follow-up experiments.

Study on influence of lanthana. Fig. 1 shows the XRD patterns of fresh(a) and aged(b) supports modified by lanthana with different loading contents. As can be seen from Fig. 4 (a), XRD diffraction peaks of all fresh samples have shown low diffraction intensity, and the peak Broaden. 2θ is in the range of 10 ° -70 °, Peak is the cubic phase ZrO_2. XRD diffraction peaks of La_2O_3 did not appear in fresh sample, so there is no La_2O_3 phase formation. As La added, 2θangle offset, 2θ low angle deviation is caused by lattice expansion. La^{3+} ionic radius is 1.06 Å, bigger than Zr^{4+}(0.84 Å), lattice expansion occurred description of La^{3+} doped into the lattice of ZrO_2[9]. The characteristic diffraction intensity of aged sample is enhanced, and the peak sharp, the result suggests that a serious sintering occurred.

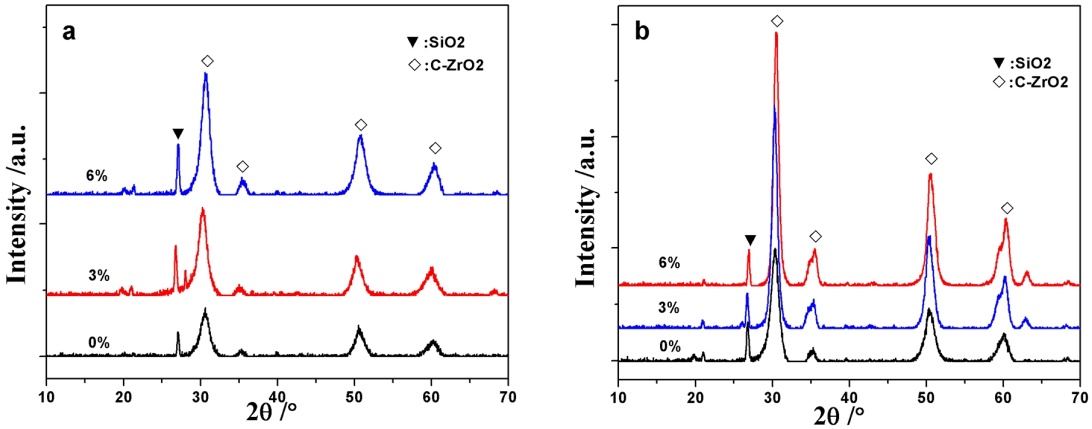

Fig. 1 XRD patterns of fresh(a) and aged(b) samples modified by lanthana with different loading contents

The BET surface area of fresh(a) and aged(b) were showed in Table 2, as for fresh , with more La added, specific surface area increases, indicated that the La will help improve the structural stability of the composite. After aging, due to effects of sintering, specific surface area decreases obviously, but La doped can help to increase surface area. After aging, surface area loss ratio of 6 Wt. % La addition sample is minimum, which is 44.57%, so this addition can make the best thermal stability.

Table 2 The BET surface area of fresh(a) and aged(b) supports modified by lanthana with different loading contents

Sample	0 Wt.%	3 Wt.%	6 Wt. %
Fresh/m^2g^{-1}	85.57	89.87	93.75
Aged/m^2g^{-1}	34.06	46.90	51.97
Loss ratio	60.19%	47.81%	44.57%

Study on ZrO_2/sepiolite mass ratio. Used acidified sepiolite, $ZrOCl_2 \cdot 8H_2O$ as zirconium source and ammonia as the precipitating agent, 6 wt. % added, ZrO_2/sepiolite composites were prepared by Chemical precipitation method. The samples were characterized by means of BET, TG, XRD and SEM.

BET results analysis. Table 3 shows the BET results of samples with different ZrO_2/sepiolite mass ratio before and after aging. Aging or not, added ZrO_2 in acid-modified sepiolite to form composites, surface area of ZrO_2/sepiolite composites increase. The results suggest that adding ZrO_2 could dramatically improve the thermal stability of composite, which is coincided with TGA. With the increase of ZrO_2, surface area of composites increase, but with further increase of ZrO_2, surface area of composite decrease. Beside, after aging, surface area of the samples fell-off, sintering reunion was occurred, a result supported by the SEM. When the mass ratio of ZrO_2 and sepiolite is 2:1, its specific surface area reach to the maximum and the loss ratio is the minimum.

Table 3 The BET surface area of samples with different ZrO_2/sepiolite mass ratio before and after aging

Sample	acid-sepiolite	1:2	2:2	3:2	4:2
Fresh/m^2g^{-1}	56.98	79.76	84.57	95.75	84.53
Aged/m^2g^{-1}	9.45	14.68	34.57	55.76	32.58
Loss ratio	83.43%	81.60%	59.12%	41.76%	64.26%

TGA results analysis. TGA analysis is employed to study the thermal stability of the ZrO_2/sepiolite samples upon heating. TGA curves, which were recorded simultaneously with a heating rate of 20˚C/min, are shown in Fig. 2. TGA curves of acid-sepiolite given in Fig. 2 suggest that weight loss during heating, while during 350-600°C, the weight loss fast. TGA curves of ZrO_2/sepiolite given in Fig. 2 suggest that with adding ZrO_2, quality almost no loss during heating, and too much ZrO_2 added, has little effect on thermal stability. It illustrates that ZrO_2/sepiolite composite has good thermal stability.

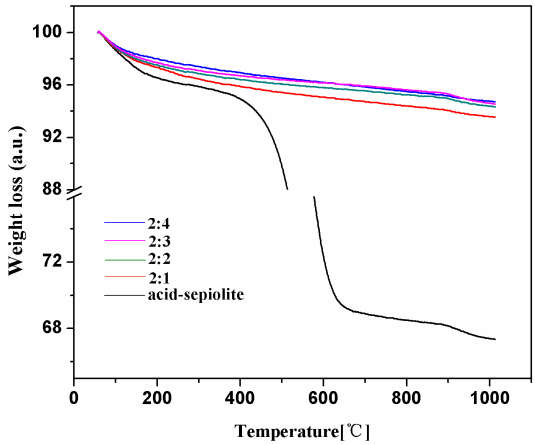

Fig . 2 TGA curves for the different mass ratio of ZrO_2/sepiolite samples

Phase analysis. X-ray diffraction patterns for fresh and aged samples were analysed, The results are shown in Fig. 3. Fig. 3(a) and (b) shows that the most characteristic peaks of acid-sepiolite was SiO_2, in composite materials, with the increase of ZrO_2, characteristic diffraction peak intensity of SiO_2

decrease, characteristic peaks of ZrO_2 appears gradually and to strengthen. The results show that ZrO_2 successfully compound with acid-sepiolite. The generated ZrO_2 are cubic both with the heat treatment of 600˚Cand1000˚C. ZrO_2 in the composite which prepared by this method is much smaller than the average particle size of zirconia stable critical dimensions (30nm)[10], cubic energy below the monoclinic phase, so ZrO_2 particles in composite are cubic phase. After 600˚C treatment, the characteristic diffraction intensity of ZrO_2 is low, and the peak Broaden, Grain size is smaller. After 1000˚C treatment, the characteristic diffraction intensity of ZrO_2 is enhanced, and the peak sharp. The results show that crystallization of ZrO_2 is low at 600˚C,crystal structure is not very complete, when After 1000˚C treatment, sintering reunion was occurred.

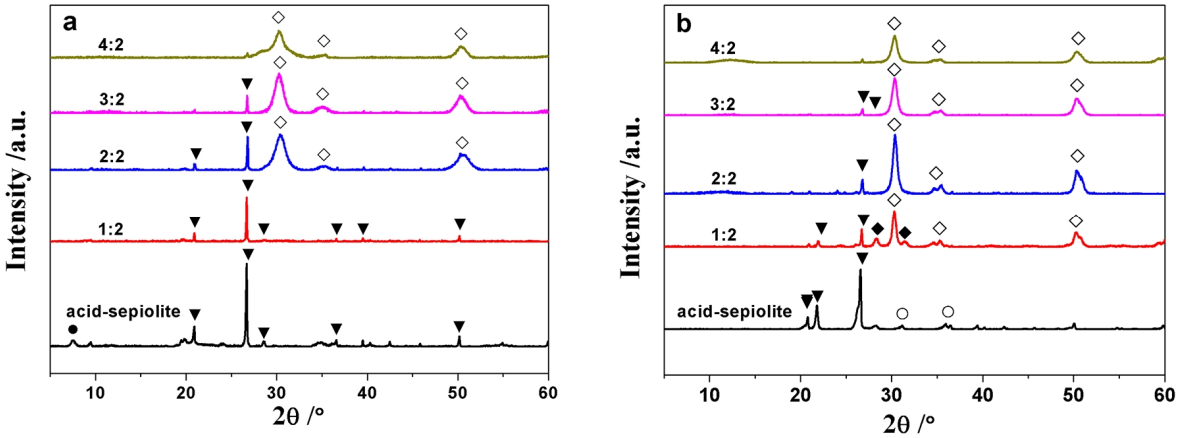

Fig.3 XRD patterns of different mass ratio of $Zr0_2$/sepiolite calcined at600˚C(a)and1000˚C(b)
(●:Sepiolite ▼:SiO_2 ○:enstatite □:C-ZrO_2)

Morphology analysis. Fig. 4 shows an SEM photomicrograph of surface of the acid-sepiolite samples. In Fig. 4 (a) SEM micrograph of the acid-sepiolite sample is shown. Sepiolites are distributed as fibre aggregates and individual fibres[11]. Large fracture holes and cracks in between the fibrous and fine granular structure can be observed. In Fig. 4 (b), after 1000˚C heat treatment, serious sintering occurred, typical fibrous structure bonded crunch, flake, block structure appeared, surface fracture holes reduced .

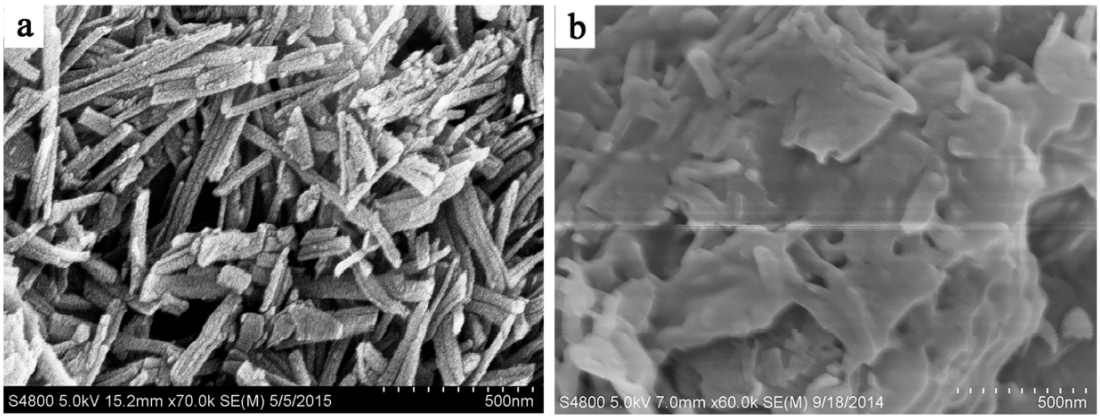

Fig.4 SEM images of the acidulated sepiolite at room temperature(a) and sintered at 1000˚C(b)

Fig.5 shows an SEM photomicrograph of surface of the ZrO_2/sepiolite samples sintered at1000˚C.

From Fig. 5 it can be seen that, When adding a small amount of ZrO_2, composite sintered seriously, its morphology mainly is block(Fig. 5a). But with the increase of ZrO_2, particulate matter can be seen in the surface of composite, the XRD analysis shows that is the ZrO_2 particles. As can be seen from Fig. 5c, ZrO_2 particles are spherical which diameter are 10nm ~ 50nm, Particles are stacked together loosely, there are many holes between accumulation. However when ZrO_2 added further increases, a lot of ZrO2 particles are reunited and with the tendency to multilateralism, ZrO_2 particles plug the original holes of sepiolite, which make holes reduce[12](Fig. 5d). It can be seen from the above analysis, when adding a small amount of ZrO_2, ZrO_2 particles are insufficient to cover surface of sepiolite.

During high-temperature sintering, sepiolite is still exposed in high temperature environments. With the increase of ZrO_2, the spherical ZrO_2 particles gradually increase in the surface of sepiolite, the degree of compactness of ZrO_2 particles on its surface increases, high temperature resistance ZrO_2 plays a role in heat insulation. However, when the addition amount of ZrO_2 exceeds a certain limit, spherical ZrO_2 produced in abundance, it turns out the distribution on sepiolite surface is too compact, which makes composite surface porosity reduction, thus weakening the specific surface area of the composite.

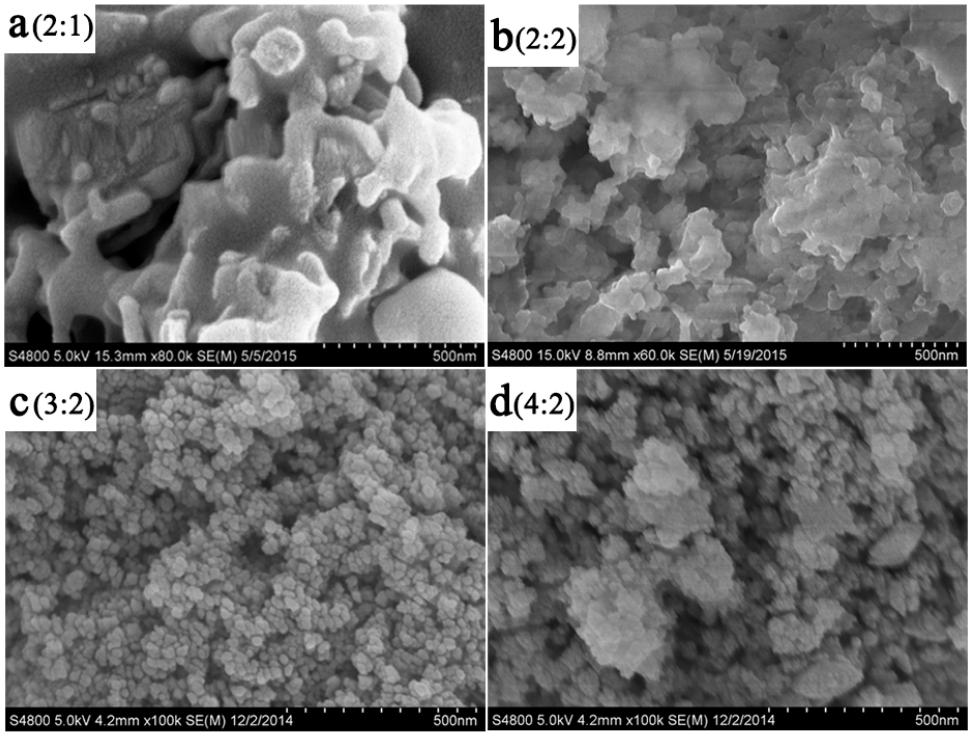

Fig.5 SEM images of different mass ratio of ZrO_2/sepiolite sintered at1000˚C

Conclusions

1. Acidification could further increase the surface area of sepiolite, after 1mol/L HCl 75 ˚C soaked 18 hours, the specific surface area was maximized.
2. Adding lanthanum benefited for improve the high temperature stability of the composite material.
3. ZrO_2/sepiolite composite material was prepared by precipitation method, when the mass ratio of ZrO_2 and acidification sepiolite was 3: 2, nanometer ZrO_2 composite particles uniformly distributed in the sepiolite surface. ZrO_2/sepiolite composite material specific surface area could reach to 95.7553 $m^2 \cdot g^{-1}$. With 1000 ˚C high temperature treatment aged , its surface area was still keep 55.7553 $m^2 \cdot g^{-1}$, and had good high temperature thermal stability, so the specific surface area could be maintained at a high temperature environment.
4. The preparation process is simple, low cost, easy to be used in the production.

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