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RESEARCH ARTICLE

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Study on preparation of $S_2O_8^{2-}/Fe_2O_3$–SiO_2 solid acid and its catalytic activity

Abstract The precursors of Fe_2O_3-SiO_2 mixed oxides prepared through co-precipitation method were modified by microwave hydrothermal treatment for the first time. $S_2O_8^{2-}/Fe_2O_3$-SiO_2 solid acids were formed after being impregnated by $(NH_4)_2S_2O_8$ solution and calcined at high temperature. The samples were characterized by XRD, TEM, N_2 adsorption/desorption methods. It was found that the presence of SiO_2 obviously retarded the formation and growth of Fe_2O_3 crystals. Catalyst with appropriate specific surface area and narrow pore size distribution was obtained. The catalytic activities of the solid acids were evaluated by esterification of acetic acid and butanol and the results were compared with those catalysts prepared at normal conditions. The results showed that catalytic activity was extensively improved by microwave hydrothermal treatment.

Keywords solid acid, microwave hydrothermal treatment, co-precipitation, modification, esterification

1 Introduction

Nowadays, chemical industries are facing challenges to reduce the use of environmentally hazardous chemicals. Replacement of liquid acids by solid acids is now considered an essential to the design of a cleaner process for better protection of the environment. SO_4^{2-}/Fe_2O_3 is a commonly used solid acid but the catalytic activity is low. It was reported that SO_4^{2-}/ZrO_2 [1] or SO_4^{2-}/TiO_2 [2] were solid superacids but they would sinter easily and their catalytic activities were decreased by temperature effects. To prevent ZrO_2 or TiO_2 from sintering, supporting them on a stable oxide such as silica and preparing SO_4^{2-}/ZrO_2-SiO_2 [3–5], SO_4^{2-}/TiO_2-SiO_2 [6,7] solid acids was an effective method to enhance their catalytic activities. Therefore, SO_4^{2-}/Fe_2O_3-SiO_2 solid acids have also received great interest in recent years [8]. Fe_2O_3-SiO_2 mixed oxides were conventionally prepared by sol-gel or co-precipitation method and it was found that the homogeneity of mixed oxides would greatly affect its textual, structural, and catalytic properties [5]. If Fe_2O_3-SiO_2 mixed oxides were prepared by sol-gel method [9], the distribution of each component was homogeneous, but the preparation condition should be controlled strictly, and the synthesis period is long. In contrast, if the mixed oxides were prepared by co-precipitation method, the procedure was simple but because hydroxides of different elements generally did not precipitate at the same pH value, molecular homogeneity was difficult to achieve.

In order to enhance the catalytic activity of solid acid with a simple method, Pan and co-workers modified the precursors by autoclave hydrothermal treatment [10]. With the development of science and technology, the application of microwave gradually expanded to the chemistry field. This technique has been used for the rapid synthesis of numerous oxides [11,12], hydroxylated phases [13], and so on [14,15]. It offers many distinct advantages over conventional autoclave heating [14]. Therefore, the precursors preparation from co-precipitation method were modified by microwave hydrothermal treatment, and because $S_2O_8^{2-}$ had a greater promoting effect than SO_4^{2-} [16], so $S_2O_8^{2-}/Fe_2O_3$-SiO_2 solid acids were prepared. The experiment results showed that the solid acid had higher catalytic activity, and to the best of our knowledge this method has not been reported up to now.

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2 Experimental

2.1 Materials, apparatus and characterization

All chemicals were analytical grade reagents used as received.

Fe $(NO_3)_3$ and Na_2SiO_3 were respectively dissolved in distilled water to form 1 M stock solution and filtered before use. The others were used without further purification.

Microwave hydrothermal treatments were performed using WHL 07S-2 laboratorial microwave oven (Sanle Microwave Technology Development Corp., Ltd., Nanjing, China) operating at 2.45 GHz. The microwave generator used was a continuous wave system with a power of up to 700 W. A refluxing system was connected with the microwave oven, and carried out in the ambient air.

Crystal structures were characterized by X-ray powder diffraction (XRD) method (Bruker D8 ADVANCE diffractometer, 40 kV/30 mA) using Cu $K_{\alpha 1}$ radiation with wavelength λ = 0.15406 nm. The morphology of the sample was observed using H-800 transmission electron microscope (TEM) operating at accelerating voltage of 175 kV. The specific surface area (BET method) and pore size distribution (BJH method) were determined from the N_2 adsorption/desorption isotherms obtained at 77 K using N_2 as adsorbate on an ASAP 2010 N Micromeritics apparatus.

2.2 Preparation of catalyst

The precursors of Fe_2O_3-SiO_2 mixed oxides were prepared as follows: (a) co-precipitation method: took certain volume of 1 M $Fe(NO_3)_3$ and Na_2SiO_3 solution simultaneously added dropwise to vigorously stirred water, and aqueous ammonia or HNO_3 solution (according to the molar ratio of Fe to Si) was added dropwise at the same time to the mixed liquid in order to keep pH values of the system ca. 9; (b) separate precipitation method: $Fe(NO_3)_3$ and Na_2SiO_3 solution were separately precipitated by aqueous ammonia or HNO_3 solution to pH values ca. 9, mixed the precipitates. The gels of the above were stirred for another 30 min then modified by different methods and the precipitates were separated by centrifugation and washed with distilled water or 0.1 M $(NH_4)_2CO_3$ solution over eight times, dried at 110°C, then grinded, impregnated in 0.75 M $(NH_4)_2S_2O_8$ solution (10 mL/g solid) while stirring. This was followed by filtration and drying at 110°C, calcined at 500 °C for 3 hours to form $S_2O_8^{2-}/Fe_2O_3$-SiO_2 solid acid.

2.3 Catalytic reaction

The esterification of acetic acid and butanol was used to evaluate the catalytic activities of the solid acids. 0.8 g catalyst, 0.2 mol acetic acid, and 0.24 mol butanol were added to a 250 mL dried three-neck flask fitted with a magnetic stirrer and a water-cooled condenser, mixed the liquid homogenously by stirring. A proper liquid was drawn off and spun, then taking 1 mL supernatant, using 0.1 M NaOH solution titrated to end point, and the volume of consumption was named V_0 mL. After reaction under reflux conditions for 3 h, the same NaOH solution was used and then titrated 1 mL supernatant and the volume of consumption was named V_1 mL. The catalytic activity was evaluated by the conversion of acetic acid: $\alpha = \frac{V_0 - V_1}{V_0} \times 100\%$.

3 Result and discussion

3.1 XRD and TEM measurements

XRD patterns of some solid acids were presented in Fig. 1.

It could be seen from Figure 1 that the solid acid without adding SiO_2 showed α-Fe_2O_3 characteristic diffraction peaks [Fig. 1(a)], however, the samples which added SiO_2 were amorphous [Fig. 1(b~d)]. Therefore, the presence of SiO_2 in Fe_2O_3-SiO_2 obviously inhibited the crystallization and growth of Fe_2O_3 and resulted in amorphous Fe_2O_3. This was in accordance with the reports that adding SiO_2 could intensively retard the crystallization of ZrO_2 or TiO_2 [3–6].

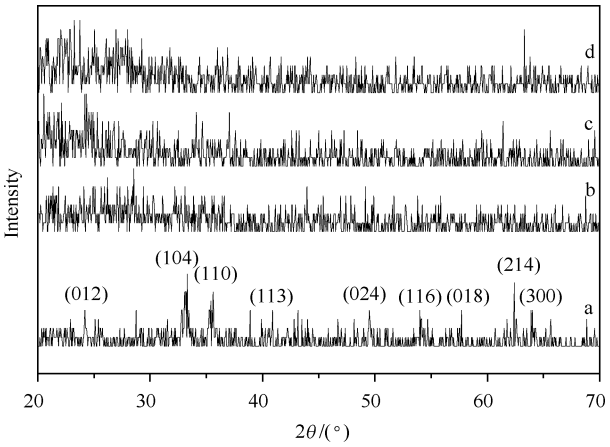

Fig. 1 XRD patterns of some solid acids
n(Fe):*n*(Si); *a*. 1:0; *b*. 1:2; *c*. 1:4; *d*. 1:6
(modified by microwave hydrothermal method for 1.5 hour, washed with 0.1 M $(NH_4)_2CO_3$ solution)

When the molar ratio of Fe:Si was fixed at 1:4, changing the precipitation method and modification method, TEM micrographs of some solid acids were shown in Fig. 2, Table 1 was the preparation conditions.

Figure 2 showed that in the solid acids obtained from un-aged [Fig. 2(a)] or separate precipitation method [Fig. 2(d)], the particle sizes were small. The precursors prepared by co-precipitation method modified by (microwave) hydrothermal treatment [Fig. 2(c,e)], their particle sizes were evidently large and agglomeration occurred in a certain degree.

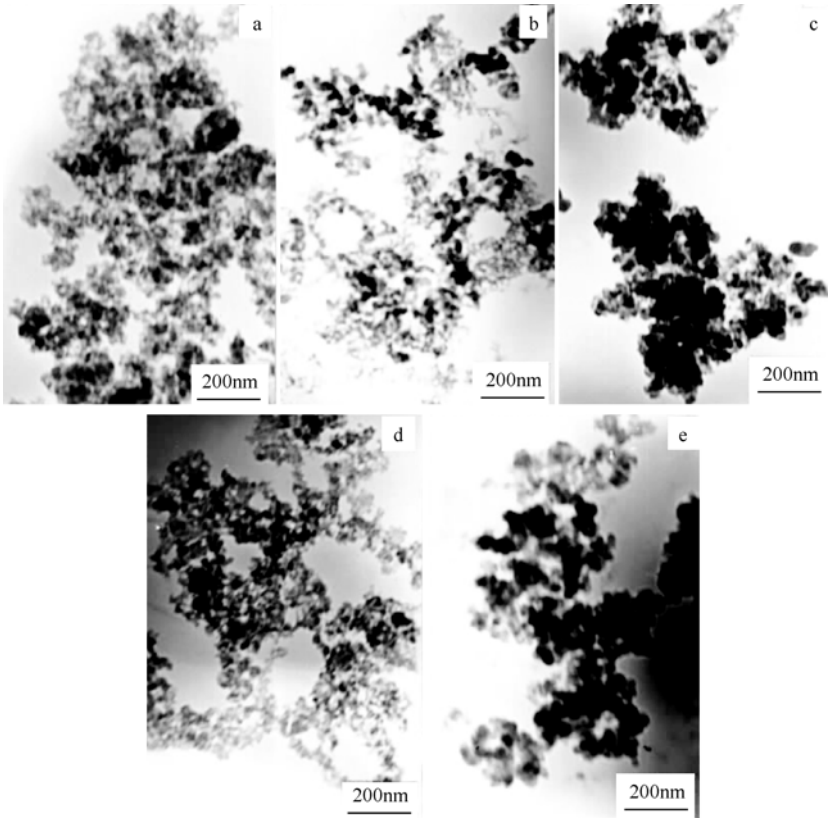

Fig. 2 TEM micrographs of some solid acids

Table 1 Preparation conditions of some solid acids

Sample	Precipitation method	Modification method	Treatment time/h
a	Co- precipitation	-	0
b	Co- precipitation	70 °C water bath	2
c	Co- precipitation	150 °C hydrothermal treatment	1
d	Separate precipitation	250 W microwave hydrothermal	1.5
e	Co- precipitation	250 W microwave hydrothermal	1.5

3.2 Specific surface area and average pore size measurement

Under the conditions found in Table 1, BET specific surface areas and average pore sizes of solid acids are reported in Table 2. N_2 adsorption/desorption isotherms of some samples are shown in Fig. 3. The isotherms corresponded to type Ⅱ, indicating the materials have the structure of open-ended pore channels [8] and this structure of catalysts was favorable for the diffusion of molecules of reactants and products. It could be seen from Fig. 3(a,d) that the hysteresis loops of adsorption/desorption isotherms separated at low p/p_o, according to the Kelvin equation, there were the existence of micropores, but Table 2 shows that their average pore sizes were much larger than that of the sample(e), so larger pores were existent. In other words, their pore size distributions were broad; in contrast, Fig. 3(e) shows that sample (e) had narrow pore size distribution.

It could be found from the data of Table 2 that for the precursors prepared by co-precipitation method modified by (microwave) hydrothermal methods, the specific surface areas and average pore sizes of the obtained solid acids were significantly decreased. The probable reason is that the precursors through (microwave) hydrothermal treatment, $Fe(OH)_3$ gel could partially dissolve and deposit (also deposit on the pore wall surface), so micropores disappeared, macropores decreased, and mesopores increased, therefore, the specific surface areas and average pore sizes decreased.

Compared with Table 2 (d, e), it could be found that the specific surface area and average pore diameter of the sample (d) was remarkably larger than that of the sample (e). The reason is that maybe under separate precipitation method, in the precursors, $Fe(OH)_3$ mixed with silicon gel was more heterogeneous, although treated at the same microwave hydrothermal conditions, the quantity of dissolution and deposition of $Fe(OH)_3$ was less than that of the co-precipitation method, so the specific surface area and average pore diameter were larger.

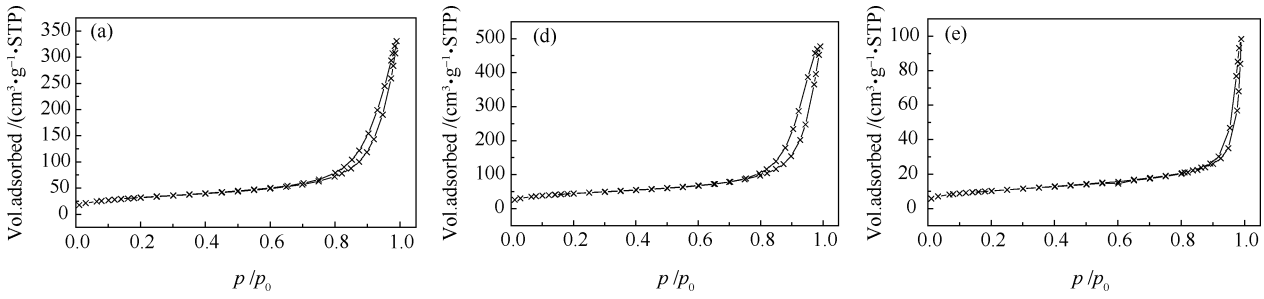

Fig. 3 N_2 adsorption/desorption isotherms of some solid acids

Table 2 BET specific surface area and average pore diameter of some solid acids

Sample	*a*	*b*	*c*	*d*	*e*
Specific surface area /($m^2 \cdot g^{-1}$)	114.5	54.3	32.1	160.4	37.1
Average pore size / nm	14.0	12.3	6.63	14.1	9.48

Table 3 Effect of catalyst composition on the catalytic activity (250 W microwave hydrothermal 1.5 h)

n (Fe):*n*(Si)	1:0	1:2	1:4	1:6	0:1	1:4*
α (HAc)/%	58.4	86.9	97.7	95.6	38.6	94.5

*Washed with water; the others were washed with 0.1 M $(NH_4)_2CO_3$ solution.

Table 4 Effect of precipitation and aging method on the catalytic activity

Sample	a	b	C	d	e
α (HAc)/%	77.3	90.4	91.1	80.1	97.7

3.3 Catalytic activities measurement

Effect of the composition of catalysts on the catalytic activities: the catalytic activities of solid acids prepared by co-precipitation under various molar ratio of Fe to Si were reported in Table 3. Table 3 shows that with adding SiO_2, the catalytic activities were greatly enhanced. Our former work [8] showed that the higher the content of SiO_2, the larger the specific surface area, the smaller the pore size of the catalyst. The sample of *n*(Fe):*n*(Si) =1:4 had appropriate specific surface area and pore size, the diffusion of molecules of reactants and products were easy, so the catalytic activity was high. Additionally, it also could be seen that washing liquid could also affect the catalyst activities. If the precipitates washed with 0.1 M $(NH_4)_2CO_3$ solution, the catalytic activity of solid acid was a little higher than washed with water. The reason is that NH_4^+ was probably easy to exchange with Na^+, and Na^+ could make the solid acid sites deactivate.

Effect of the precipitation and modification method on the catalytic activities: Under the preparation conditions of Table 1, the results of effect of precipitation and modification methods on the catalytic activities (at the most appropriate time under the appointed modification method) were reported in Table 4. The data of Table 4 showed that if the precursors was un-aged, the catalytic activity of the solid acid was much lower, though it was also prepared by co-precipitation method, the active components didn't through dissolution and deposition procedure, each component distribution was heterogeneous, so the catalytic activity was low; if the precursors aged at 70 ºC water bath or treated by autoclave hydrothermal at 150 ºC, the active components partially dissolved and deposited, and the catalytic activities would be enhanced. Particularly, if the precursors obtained by co-precipitation modified by microwave hydrothermal, it could be seen from Table 4 that the catalytic activity was very high. The reason was that under this condition, each component of the catalysts would be mixed much homogeneous through sufficient dissolution and deposition, especially because the active components could deposit in the pore walls, though the specific area and pore size decreased, mesopores increased, and the available ratio of the internal surface of the catalyst was enhanced, so the catalyst showed the highest catalytic activities: esterification for 3 hours, the conversion of acetic reached to 97.7%. If the precursors prepared by separate precipitation method, because $Fe(OH)_3$ gel couldn't be dissolved or deposited effectively, though the solid acid had the largest specific surface area, but the amounts of active components in the internal surface were fewer, the catalytic activity was low.

4 Conclusions

The precursors of mixed oxides prepared by co-precipitation method, modified by microwave hydrothermal treatment

could make the sufficient dissolution and deposition of precipitated gels, so the distribution of each component became more homogeneous, and greatly enhanced the catalytic activities of the catalysts. This is a simple and effective method to modify solid acid to enhance its activity.

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