Influence of the pore structure of Ce/MgAl hydrotalcite-derived mixed oxides on its SO_x pick-up capacity

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The sulfur-transfer catalyst is widely used to remove the sulfur oxides (SO_x) from the flue gas in the fluid catalytic cracking (FCC) units. This paper reports the influence of the pore structure of the Ce/MgAl hydrotalcite-derived mixed oxides on its SO_x pick-up capacity. The Ce/MgAl hydrotalcites precursors were synthesized by the separate nucleation and aging steps (SNAS), and then were calcined in air at 800°C to prepare the Ce/MgAl mixed oxides. And in our preparations, the pore structures of the Ce/MgAl mixed oxides were controlled by modifying the aging time of the hydrotalcites precursors. It is found that with the aging time of 4 to 6 h produced the largest pore volume (the largest total pore volume and the least pore less than 10 nm) and resulted in the largest SO_x pick-up capacity.

hydrotalcite, fuel, pore structure, sulfur-transfer catalyst, FCC

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The fluid catalytic cracking (FCC) process, a petroleum refining process applied commercially on a very large scale, is one of the major sources of SO_x emission. In order to meet the increasing stringent environmental regulations, most refineries used the sulfur-transfer catalysts in their FCC units [1–5].

So far, Ce/MgAl hydrotalcite-derived mixed oxides system has been the most popular one for the sulfur-transfer catalyst in the FCC processing. Yet previous studies in this field have mainly focused on the respective and/or synergistic role of their chemical composition [3,6–12] as well as the preparation processes. For example, we reported the preparation of Ce/MgAl hydrotalcite-derived mixed oxides prepared by impregnation, conventional coprecipitation and SNAS (separate nucleation and aging steps) approaches and following by their properties studies. It was confirmed that sample prepared via the SNAS method possessed both the highest rate and the largest capacity during the SO_x pick-up

process [13]. However, the catalyst's pore structure, which is actually one important factor in controlling the catalyst's performance in SO_x pick up capacity, have not been studied carefully.

In this work, the SNAS method was applied in the synthesis of the Ce/MgAl hydrotalcites precursors, followed by the aging process with different time. And finally the mixed oxides were gotten by calcination. Both the precursors and the catalysts were characterized carefully and the relationship between the SO_x pick-up capacity of the catalysts and their pore size distributions was studied.

1 Experimental

1.1 Preparation of Ce/MgAl hydrotalcite-derived mixed oxides by SNAS method

Ce/MgAl hydrotalcite precursorss were synthesized by coprecipitation using separate nucleation and aging steps (SNAS) in our laboratory [14]. Then, the precursors were

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calcined in air at 800°C for 2 h to obtain the Ce/MgAl hydrotalcite-derived mixed oxides. The final catalysts were denoted SMAC-0, SMAC-1, SMAC-2, SMAC-4, SMAC-6, SMAC-8, SMAC-24, respectively, to represent their different aging time.

1.2 Characterizations

The XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu K α radiation ($\lambda=0.154056$ nm) at 40 kV, 30 mA. The specific surface area, pore volume, and pore size were measured by nitrogen adsorption at 77 K on an Autosorb-1 apparatus. Elemental analyses of the metal contents were performed by atomic emission spectroscopy with a Shimadzu ICPS-7500 instrument.

1.3 SO_x oxidation and adsorption evaluation

A PC-controlled home made HCT-1 thermogravimetric instrument with an accuracy of 0.01 mg was used to detect the weight change of the sample during the measurements of SO_x oxidation and adsorption performance. A small amount of sample (10–20 mg) was placed on a crucible and an inert gas, e.g. N₂, was introduced into the test chamber. The sample was heated to 732°C and then was switched to a 70 mL/min stream of 6% (v/v) O₂, 2% (v/v) SO₂ and balance N₂ for some time, simulating the FCC regenerator atmosphere. Finally, the system was flushed with N₂ and the sample was cooled down to room temperature.

The SO_x oxidation and adsorption capacity for the sample was calculated based on dry basis, as the following equation:

$$\text{SOAC} = (W_2 - W_1)/W_1,$$

where SOAC is SO_x oxidation and adsorption capacity (g/g), W_1 is the weight of fresh sample on dry basis (g), W_2 is the weight of sample after reaction (g).

2 Results and discussion

2.1 Structural characterization

The powder XRD patterns for the hydrotalcite-precursors and the final mixed oxides were shown in Figure 1(A) and (B), respectively. It was found from Figure 1(A) that the characteristic reflections of hydrotalcite with a series of (00 l) peaks were exhibited for all hydrotalcite precursors. In addition, it is further confirmed that their intensities increased with the aging time, while their FWHM values became smaller, which means that with the aging time, these particles became larger. So the sum of several peak areas of (006), (110) and (113) were used to calculate the relative crystallinity as shown in Table 1. The relative crystallinity reaches maximum when the aging time reaches 6 h, and then decrease slightly with the aging time. Though their intensities kept increasing, their FWHM values decreased and resulted in the maximum with aging time of 6 h. Meanwhile, the lattice parameters of a and c did not change with the loading of CeO₂, which indicated that (as can be

Figure 1 XRD patterns of Ce/MgAl hydrotalcite precursors (A) and the mixed oxides thereof (B). (a)–(g) SMAC aged for 0, 1, 2, 4, 6, 8, 24 h, respectively. *, one or more of Ce(OH)₃ (PDF 22-0542), Ce(CO₃)(OH) (PDF 52-0352) and Ce₂(CO₃)₂(OH)₂ (PDF 46-0369); Δ , CeO₂; #, MgO.

Table 1 Unit cell parameters of the Ce/MgAl hydrotalcite precursors with varied aging time

Sample	<i>a</i> (nm)	<i>c</i> (nm)	Relative crystallinity (%)
SMAC-0	0.305	2.29	32.9
SMAC-1	0.305	2.29	59.1
SMAC-2	0.305	2.29	76.9
SMAC-4	0.306	2.30	89.9
SMAC-6	0.306	2.30	100
SMAC-8	0.306	2.30	94.9
SMAC-24	0.305	2.29	85.8

seen from Table 1) the loading of CeO₂ did not change the structure of the intra- and/or inter-layers.

Figure 1(B) showed that the lamellar structure of hydrotalcite collapsed for all the samples after calcined at 800°C for 2 h. Yet the existence of CeO₂ and MgO were confirmed according to the diffraction peaks of (111), (200), (220), (311), (222), and (400) corresponding to a pure fluorite CeO₂ phase (PDF 81-0792) and the diffraction peaks of (200) and (220) corresponding to a cubic MgO phase (PDF 89-4248). Moreover, the characteristic peaks of a poorly crystallized Mg₂O₄ spinel phase ($2\theta \sim 36^\circ$) was also observed for all samples. The particle size of CeO₂ is estimated by means of Debye-Scherrer formula based on the diffraction peaks (111). As shown in Table 2, the first 2 h played predominant effect in the growth of CeO₂ particles, yet after 2 h, the particles seemed to stopped growing and the sizes were kept around 17–19 nm.

The chemical compositions analysis Using ICP showed that Mg/Al=3.16 and CeO₂ wt.%=7.2%, which matched well with the feed compositions, and further indicating that the metallic cations are incorporated at the expected levels.

The N₂ adsorption/desorption isotherms studies (Figure 2(a)) on the catalysts indicated that the aging time really resulted different isotherms types. SMAC-0 and SMAC-1 presented the H1 hysteresis loops and others presented the H3 hysteresis loops. It was attributed to the amorphous

Table 2 Ceria crystal size (*d*) and textural characteristics of Ce/MgAl mixed oxides

Sample	<i>d</i> (CeO ₂) (nm)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore size (nm)
SMAC-0	12.5	151.9	0.44	12.0
SMAC-1	12.4	150.9	0.63	16.8
SMAC-2	19.3	104.1	0.94	36.2
SMAC-4	17.6	96.7	1.33	55.0
SMAC-6	19.0	111.5	1.29	42.8
SMAC-8	17.0	130.5	1.25	38.4
SMAC-24	15.9	138.8	1.21	34.9

phase in the hydrotalcite precursors of SMAC-0 and SMAC-1. With the increasing of aging time, the amorphous phase disappeared gradually. And the calcination at 800°C is known to remove the interlayer water, interlayer anions and the hydroxyl groups and formed the cracks and crevice between the platelet-like crystallites, which led to the H3 type [14–17]. The specific surface areas and the pore structure analysis were shown in Tables 2 and 3. It can be seen that the precursor without aging had the largest specific surface area. While the specific surface areas decreased with the aging time and reached the minimum when the aging time is 4 h. However, the total pore volume and the average pore size increase with the increasing of aging time then decrease after reached the maximum at 4 h. Pore size distributions of the mixed oxides were measured by Barrett-Joyner-Halenda method for ranged from 2 to 200 nm (Figure 2(b)). It was illustrated that SMAC-0 and SMAC-1 presented a unimodal pore size distribution (ca. 10 nm for SMAC-0 and 10–20 nm for SMAC-1), whereas the others possessed the bimodal porous distributions. Furthermore, with the increase of the aging time, the pores less than 10 nm decreased and the minimum was reached with the aging time of 2 h.

2.2 SO_x oxidation and adsorption performance test

The test of the SO_x pick-up activity for the catalysts were tested under the conditions simulating regenerator of FCC

Table 3 Pore size distribution (*d_p*) of Ce/MgAl hydrotalcite-derived mixed oxides with various aging time

	<i>d_p</i> =2–10 nm		<i>d_p</i> =10–30 nm		<i>d_p</i> >30 nm	
	<i>V</i> (<i>d_p</i>)/ <i>V</i> (total) (%)	Pore volume (mL/g)	<i>V</i> (<i>d_p</i>)/ <i>V</i> (total) (%)	Pore volume (mL/g)	<i>V</i> (<i>d_p</i>)/ <i>V</i> (total) (%)	Pore volume (mL/g)
SMAC-0	28.769	0.127	65.275	0.287	5.956	0.026
SMAC-1	3.857	0.024	84.122	0.530	12.021	0.076
SMAC-2	0.367	0.003	17.489	0.164	82.144	0.772
SMAC-4	2.162	0.029	16.751	0.223	81.088	1.078
SMAC-6	4.713	0.061	15.813	0.204	79.474	1.025
SMAC-8	5.950	0.074	14.734	0.184	79.316	0.991
SMAC-24	5.097	0.062	14.023	0.170	80.880	0.979

Figure 2 N₂ adsorption/desorption isotherms (a) and pore size distribution (b) for Ce/MgAl hydrotalcite-derived mixed oxides with varied aging time.

Figure 3 SO_x oxidation and adsorption performance of Ce/MgAl hydrotalcite-derived mixed oxides with varied aging time. (a) The relation between SO_x pick-up rate of samples and reaction time; (b) the relation between maximum SO_x pick-up capacity of samples and aging time.

unit at 732°C. As shown in Figure 3(a), the initial SO_x pick-up rates were similar for all the samples, although the crystal size of CeO₂ varied from 12 to 19 nm. The SO_x pick-up rate gradually decreased for all the samples with the time. The declines of SO_x pick-up rate for most of the samples accelerated after 70 min except for SMAC-0, which decreased dramatically after 50 min. All samples reached their maximum SO_x pick-up content after 90–110 min. Figure 3(b) showed the variation of the maximum SO_x pick-up capacity. SMAC-4 (with the aging time of 4 h) attained the largest saturated SO_x pick-up content, 1.3 g/g, which was close to the theoretical SO_x pick-up capacity, 1.32 g/g (calculated based on the assumption that only Mg atoms are available for SO_x pick-up).

By comparing the SO_x pick-up activity and pore structures of the mixed oxides, it can be concluded that the mesopores, especially for the pores less than 10 nm, limited the sulfation of the mixed oxides. It is well known that the structure of -Mg-O- fragment and MgO phase were the active sites to absorb SO₃ and transfer to sulfate in the Ce/MgAl hydrotalcite-derived mixed oxides under the condition similar as the regenerator of FCC unit [10]. During the sulfation, a solid product layer of MgSO₄ was formed on the structure of -Mg-O- fragment and MgO phase, through which SO₃ must diffuse in order to react with inner MgO.

Because the ratio between the molar volumes of MgSO₄ and MgO is 4, the volume of MgO expanded and then MgSO₄ would block up the pore channel. When all of the pores are blocked, SO₃ can not diffuse through the MgSO₄ layer and resulting in the termination of the sulfation process. It can be deduced that the small pores with their diameters less than 10 nm, would be apt to be blocked up during the sulfation. The blockage of pores decreased the amount of available MgO. Meanwhile, the pores in the mixed oxide were resulted from the cracks and crevice between the platelet-like crystallites, so the structure of hydrotalcite precursor would have an obvious effect on the pore structure of the mixed oxide. So the average pore size of the mixed oxides should therefore increase with the increase of crystallite size of the hydrotalcite precursor. From the previous characterization of the pore structure, it was found that SMAC-4 possessed the largest total pore volume and the largest average pore size, which was in accord with the fact that SMAC-4 presents the largest maximum SO_x pick-up capacity.

3 Conclusions

The Ce/MgAl hydrotalcites precursors were synthesized by the separate nucleation and aging steps (SNAS), and then

were calcined in air at 800°C to prepare the Ce/MgAl mixed oxides for the sulfur-transfer catalyst in FCC unit. Different aging time of the hydrotalcites precursors was applied to control the pore structures of the Ce/MgAl mixed oxides. It was revealed that while the aging time of Ce/MgAl hydrotalcites precursor was 4–6 h at 100°C, the Ce/MgAl mixed oxides would possess the most reasonable pore structure (the largest total pore volume and the least pore less than 10 nm) so that the largest capacity of SO_x pick-up could be achieved. In conclusion, this work has elucidated the influence of the aging time of hydrotalcites precursor on the pore structure of the Ce/MgAl mixed oxides, and further on the SO_x pick-up capacity. We hope our findings would be shed light on the preparation and development of the sulfur-transfer catalyst in FCC units.

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