

The preparation of Mg–Al spinels through the method of using templates

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Abstract A series of MgO-rich MgAl₂O₄ samples were prepared by co-precipitation in the presence of CTAB, Triton X-100, and glucose or a combination of CTAB and glucose, which act as templates. The effects of different types and amounts of single template, as well as adding order of the mixed templates, on the specific surface area and particle size were investigated by BET and XRD analyses. The addition of the single template can lead to the increase of the specific surface area, wherein the samples using glucose as templates own the maximum specific surface area of 198 m²/g; as for the use of mixed templates, results revealed that adding CTAB first, followed by the addition of glucose, is better, giving a surface area of 223 m²/g.

Keywords MgO-rich MgAl₂O₄ · Co-precipitation · Templates

Introduction

Magnesium–aluminum spinel (MgAl₂O₄), with attractive combination of the properties of good hydrothermal stability, high resistance against sintering, small coefficient of thermal expansion, and great mechanical strength and hardness as well as processing both acid and basic active sites, is widely applied as catalysts or catalyst supports [1]. MgAl₂O₄ can obtain different surface area and pore

distribution via various preparation methods. Among these methods, co-precipitation, sol–gel method, hydrothermal synthesis method, and supercritical drying techniques are often used [2, 3]. Compared with other methods, the co-precipitation method has great advantages in operating process, uniformity, and purity of products. MgAl₂O₄ prepared from co-precipitation shows a relatively large surface area or small particle and less diffusion limitations for reactants and products during the catalytic reaction [4, 5]. Generally, co-precipitation involves two processes: condensation and coagulation. During the condensation period, the formation of the sub-micron colloidal particles occurs, then a further growth of those sub-micron particles takes place and gradually coagulates into three-dimensional net framework structures, and at last gelatin without fluidity is formed. After the necessary subsequent treatment processes, MgAl₂O₄ powder can be further obtained.

Recently, due to the high capacity of SO₂ pick-up of MgAl₂O₄, there has been a growing interest in the application of it as a sulfur transfer catalyst in FCC for controlling SO_x emission. However, the surface area of the existing spinel tends to be no more than 100 m²/g [4–7], which is far from enough, specifically at 700 °C. As a result, when applied in catalysis, the small surface area does not facilitate the diffusion of oxides and reducibility of the catalysts [8, 9]. Wang et al. [10] prepared a series of De-SO_x catalysts by the co-precipitation method using MgNO₃ and NaAlO₂ as precursors. By evaluating their structural properties and the De-SO_x activity as well as reducibility, they concluded that those materials owning big surface area show an exceptional catalytic activity. But the price of NaAlO₂ is so high that it cannot be used widely. At the present time, the researchers have increased the surface area of spinel by adding surfactants during the preparation [1]. For example, Ashad et al. had synthesized

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the spinel magnesium aluminate nanopowders of 182.12 m²/g using 8-hydroxyquinoline (HQ) and tetraethyl ammonium hydroxide (TEAOH) [11]. The sample CuMgAlCe mixed oxides were prepared by a modified co-precipitation–calcination method using CTAB as a surfactant template. The sample had the highest specific surface area of 142.2 m²/g and also presented the best SO₂ adsorption rate and capacity [12]. But there was still a lack of further research in the literature regarding the influence of multi-surfactants and their combination on the properties of spinel.

This paper focuses on the preparation of MgAl₂O₄ with large surface area by adding multi-surfactants or some kind of organic substance during co-precipitation to explore the effects of different types and amounts as well as their different combinations of additives on the structures of Magnesium–aluminum spinel.

Experimental

Sample preparation

Magnesium–aluminum spinel was prepared using the co-precipitation method with Mg(NO₃)₂·5H₂O and Al(NO₃)₃·9H₂O as precursors and ammonia solution of appropriate concentration as a precipitating agent. First, a given amount of Mg(NO₃)₂·5H₂O and Al(NO₃)₃·9H₂O were dissolved into the deionized water weighted in advance, under stirring to obtain the clear solution. Then, some surfactant in definite proportion was added to the above solution to obtain a homogeneous system. Finally, the ammonia solution was added dropwise until the pH value of the formed slurry was controlled at about 9. The resulting slurry was further stirred for another 2 h and subsequently sealed into a flask and then heated at 80 °C to reflux for 24 h. After this step, the mixture was cooled to room temperature. It was then centrifuged and washed several times with the deionized water to collect the solid product; the obtained samples were dried at 110 °C and calcined at 700 °C in air for 2 h. Finally, the product was ground to get the fine materials with 80–120 mesh.

Characterization

X-ray diffraction (XRD) of the materials was carried out on an X'pert Pro diffractometer system using Cu K α radiation ($\lambda = 0.154$ nm, where λ is the radiation wavelength) at 40 kV and 40 mA, running from 5 to 75°.

The specific surface area, pore volume, and pore size distribution of materials were obtained from isotherm data of the nitrogen adsorption–desorption isotherms at 77 K measured on Quadrasorb SI analyzer (Quantachrome). The

surface area, pore distribution, the mesoporous area, and pore volume were calculated by Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH), and *t* plot methods. Note that the materials should be degassed at 300 °C before test.

Catalytic test

The sample MgAl₂O₄ was impregnated with cerium and used for reaction testing on TG–DTA of Beijing Bo Yuan Precision Technology Development Co. Ltd. The experiment process is as follows: First, the sample was heated from room temperature to 700 °C using the temperature-programmed under nitrogen with a heating rate of 10 °C/min. Second, the sample was heated in the mixture of SO₂ and N₂ with SO₂ concentrations of 1 % for 80 min at 700 °C.

Results and discussion

Preparation of MgAl₂O₄ using single template

The addition of some surfactants or organic substances as templates during co-precipitation is an effective way to obtain MgAl₂O₄ with exceptionally large surface area. The surfactants can be classified as anionic, cationic, and non-ionic. The present work investigated the effects of different types of templates on the surface area of MgAl₂O₄ using CTAB (cetyltrimethylammonium bromide, a common cationic surfactant), Triton X-100 (a nonionic surfactant), and glucose, respectively.

Different types of surfactants

Samples M-CTAB-0.3, M-CTAB-0.9, and M-CTAB-1.2, which, respectively, corresponded to the molar ratios of Al/Mg/CTAB of 2/2/0.3, 2/2/0.9, and 2/2/1.2, were prepared by co-precipitation using magnesium and aluminum nitrates as precursors, concentrated ammonia solution as a precipitating agent, and CTAB as templates. Similarly, samples M-TritonX-0.3, M-TritonX-0.9, and M-TritonX-1.2 were distinguished by the molar ratios of Al/Mg/Triton X-100 of 2/2/0.3, 2/2/0.9, and 2/2/1.2, respectively.

Figure 1a illustrates the XRD patterns of the samples prepared with the addition of different amounts of CTAB. The XRD patterns of these samples exhibit characteristic reflections of MgO-rich MgAl₂O₄. Samples prepared without any addition of templates show the very sharp characteristic peaks of both MgO and MgAl₂O₄. Adding a small amount of CTAB (samples M-CTAB-0.3) can broaden the peaks of MgO and MgAl₂O₄, implying the reduction of their crystalline sizes. However, the further increase in CTAB addition (samples M-CTAB-0.9) causes the increase of the height of the characteristic peaks of

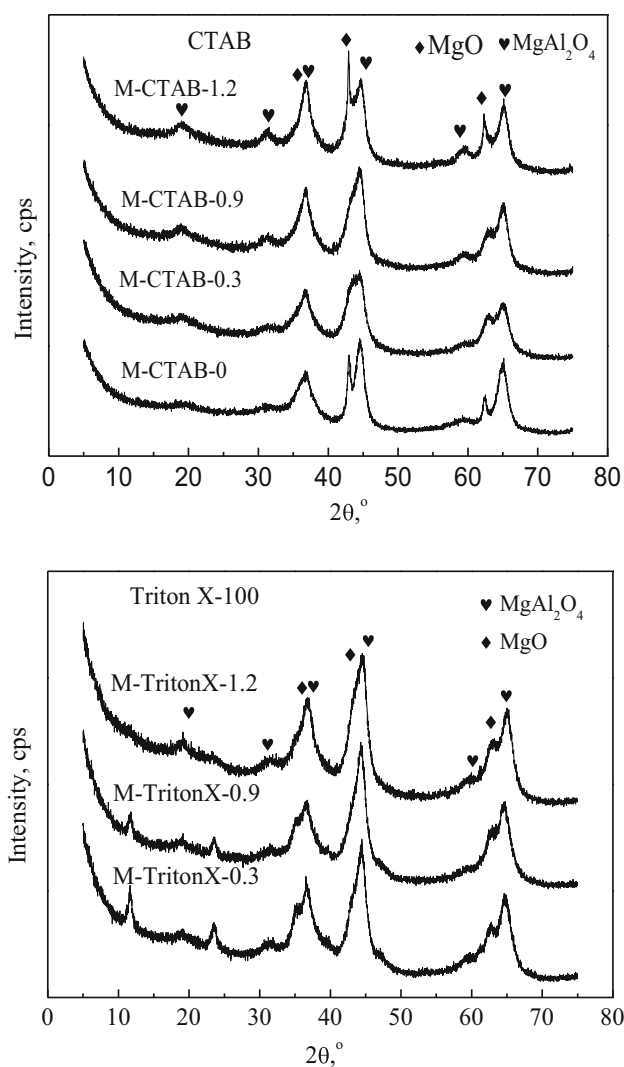


Fig. 1 XRD of MgO-rich MgAl_2O_4 prepared using different templates: **a** CTAB and **b** Triton X-100

MgAl_2O_4 which means that their particle sizes increase. For samples M-CTAB-1.2, the addition of CTAB in the corresponding quantity causes a big jump of the characteristic peak height of MgO. These results suggest that the excessive addition of CTAB cannot facilitate the interaction of MgO and Al_2O_3 to form MgAl_2O_4 , but leads to the rise of MgO crystalline phase in quantity. At the lower CTAB concentration, with their hydrophilic group toward the water phase and hydrophobic group toward the air, the surfactants surround the gel particles to form precipitated aggregates. With the increase of the CTAB content to the “saturation point,” surfactants tend to aggregate due to their hydrophobic interactions, which prevent the components of the gel, i.e. MgO and Al_2O_3 , from interacting.

Table 1 presents the surface area of prepared MgO– MgAl_2O_4 . From Table 1, the prepared materials with different CTAB concentrations show different surface areas

Table 1 The surface area of MgO-rich MgAl_2O_4 prepared using different templates

Sample	Surface area (m^2/g)	Volume (cm^3/g)	Mean diameter (nm)
M-0	107.06	0.25	8.24
M-CTAB-0.3	181.04	0.78	17.30
M-CTAB-0.9	169.24	0.73	17.20
M-CTAB-1.2	150.52	0.99	26.30
M-TritonX-0.3	166.01	0.61	14.72
M-TritonX-0.9	162.00	0.67	17.90
M-TritonX-1.2	168.00	0.52	12.48

and pore structure. It can be seen that the addition of CTAB has a significant influence on the specific surface area and the highest specific surface area is $181 \text{ m}^2/\text{g}$ for sample M-CTAB-0.3 which is higher than the value of $142 \text{ m}^2/\text{g}$ reported in [12]. However, further increase in CTAB amount leads to the reduction of surface area and the increase of pore size gradually, which is similar to the properties of CuMgAlCe oxides [12] and hydrotalcite-like sulfur transfer catalysts reported in other papers [13]. For one thing, the addition of CTAB can change the co-precipitates’ particle size during the formation of the materials; for another, excessive CTAB can precipitate from the solution, adsorb on the surface of precursor, and promote particle agglomeration. Furthermore, the more heat and gas from CTAB decomposition could destroy the pore walls and then increase the pore size, which led to a decrease in specific surface area.

As shown in Fig. 1b, the XRD patterns also display the characteristic reflections of MgO-rich MgAl_2O_4 prepared with different amounts of Triton X-100. It can be seen that the addition of Triton-X can also broaden the characteristic peaks of MgAl_2O_4 , but the effect is not obvious and the change only occurs at $2\theta = 35^\circ$. Based on the surface area of the prepared materials, the involvement of Triton X-100 can increase the surface area of the prepared samples but is not obvious. The results are not consistent with the previous research which found that the materials prepared in the presence of nonionic surfactants own large surface area and perfect thermal stability [14]. The different surfactants are directionally adsorbed on different planes, and this affects the surface free energies of crystals and the crystal plane growth rate, which results in the modification of the particle size and morphology [15]. Based on the results above, the addition of Triton-X or CTAB can produce different effects on the experimental results. Namely, the types of surfactants can influence the gel properties, resulting in the changes of relative crystallinity and surface area of materials, so the appropriate type of surfactants should be chosen as desired.

The effect of glucose as template

Samples M-Glu-0.3, M-Glu-0.9, and M-Glu-1.2 are prepared according to the corresponding molar ratios of Mg/Al/glucose of 2/2/0.3, 2/2/0.9, and 2/2/1.2, where M stands for MgO-rich MgAl₂O₄.

Figure 2 illustrates the XRD patterns of the prepared materials with the addition of different amounts of glucose as templates. It can be seen that the amount of glucose added during the preparation can also change the height and width of the characteristic peaks of materials. In our work, with the addition of glucose, diffraction peaks at $2\theta = 40\text{--}45^\circ$ of both MgO and MgAl₂O₄ show large peak width, so that there is some obvious overlap between them. Unlike CTAB, whose excessive addition can increase the content of the MgO crystalline phase, the addition of glucose has some effect on the relative crystallinity and particle size of the prepared materials and simultaneously inhibits the formation of the MgO phase.

Table 2 presents the surface area of MgO-rich MgAl₂O₄ prepared with glucose as templates. Compared with materials without the addition of any templates, adding

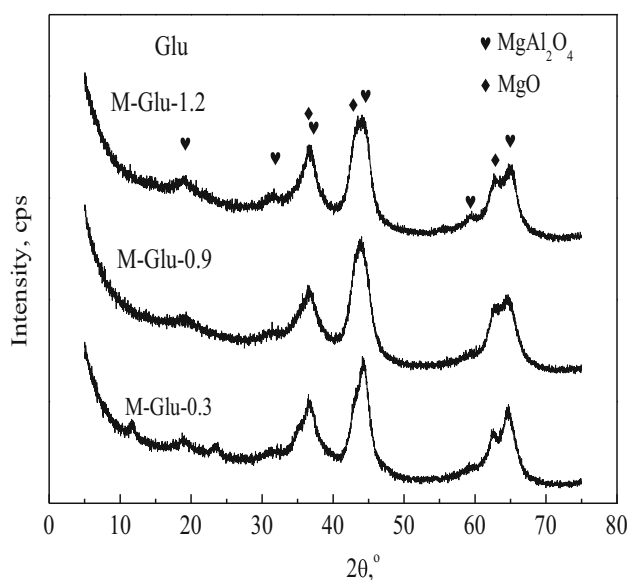


Fig. 2 XRD of MgO-rich MgAl₂O₄ prepared by using glucose

Table 2 The surface area of MgO-rich MgAl₂O₄ prepared by using glucose

Sample	Surface area (m ² /g)	Volume (cm ³ /g)	Mean diameter (nm)
M-0	107.06	0.25	8.24
M-Glu-0.3	198.00	0.43	8.71
M-Glu-0.9	175.25	0.47	10.80
M-Glu-1.2	164.89	0.44	10.70

glucose during preparation can help materials increase surface area obviously, with a maximum of 198 m²/g for sample M-Glu-0.3. An appropriate amount of Glucose can distribute evenly on the surface of precipitated MgAl₂O₄. Thus, during calcination, those hydrocarbons inhibit the particles growing larger and finally materials with large surface area can be obtained. Nevertheless, excessive addition of glucose can lead to the formation of unevenly distributed aggregates of glucose molecules, which can bring out the aggregates of particles of spinel, and results in the reduction of the surface area.

The combination of glucose and CTAB as templates

In fact, both the single templates and mixed templates can be employed during the co-precipitation to synthesize MgO-rich MgAl₂O₄. Various templates have their advantages and disadvantages, and recently there is a growing interest in the application of mixed templates. The mixed templates can be either a combination of two kinds of surfactants, such as a mixture of cationic–cationic, cationic–anionic, or cationic–nonionic surfactants et al. or a combination of surfactants and its additives. The common additives include polar and non-polar solvents or some mixed organics.

From the above discussion, CTAB and glucose can increase the surface area of spinel obviously, so in the paper a thorough investigation was made to study the effects of dosage of their mixtures and their adding order on the materials' structural properties during the co-precipitation.

The mixed templates are composed of CTAB and glucose with a molar ratio of 1/1. The three samples with the addition of different amounts of the above-mixed templates were prepared to study the effects of dosage. They were prepared, respectively, corresponding to the molar ratios of Mg/Al/T of 2/2/0.3, 2/2/0.9, and 2/2/1.2, where T represents the mixed templates. During the preparation, CTAB was added first and then followed by glucose. Additionally, another sample with a molar ratio of Mg/Al/T of 2/2/1.2 was prepared with the reverse adding order of these two templates.

From the XRD patterns of MgO-rich MgAl₂O₄ shown in Fig. 3, the appropriate addition of mixed templates can broaden the characteristic peaks of both MgO and MgAl₂O₄ obviously, and as a result they overlap with each other and cannot be distinguished, which is similar to the results of using single templates. However, when added excessively, the characteristic peak strength of MgAl₂O₄ is enhanced and the crystal grows more completely without the formation of the additional MgO crystalline phase, which is quite different from that of CTAB. Therefore, it can be concluded that the mixtures of CTAB and Glucose can facilitate the interaction of MgO and Al₂O₃ to form MgAl₂O₄ spinel.

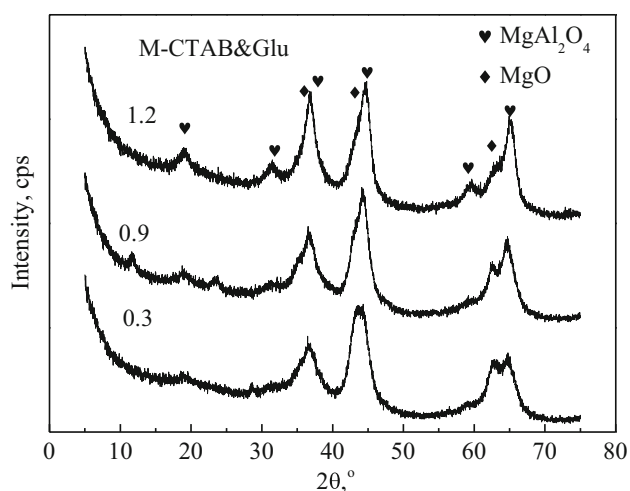


Fig. 3 XRD of MgO-rich MgAl_2O_4 prepared by using mixed templates

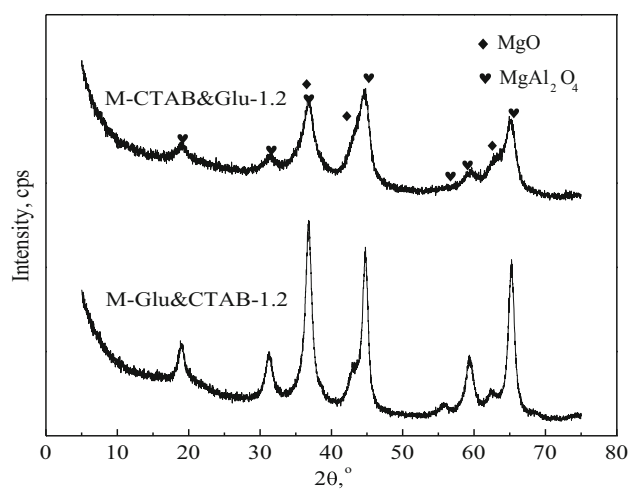


Fig. 4 XRD of MgO-rich MgAl_2O_4 prepared through changing design order of composite template

Table 3 The surface area of MgO-rich MgAl_2O_4 prepared by using composite template

Sample	Surface area (m^2/g)	Volume (cm^3/g)	Mean diameter (nm)
M-CTAB&Glu-0.3	223.60	0.57	10.36
M-CTAB&Glu-0.9	203.60	0.58	11.14
M-CTAB&Glu-1.2	188.42	1.06	22.60
M-Glu&CTAB-1.2	132.73	0.86	25.90

The surface areas of the prepared samples are presented in Table 3. We can see that in the presence of the mixed templates with the appropriate addition, the samples with much larger surface area ($>200 \text{ m}^2/\text{g}$) can be obtained, which is obviously higher than that of samples prepared with single templates. On the basis of the results, it is deduced that there are some synergistic effects between these two templates, which can promote the formation of MgAl_2O_4 with much larger surface area.

Figure 4 displays the XRD patterns of M-CTAB&Glu-1.2 and M-Glu&CTAB-1.2. For sample M-Glu&CTAB-1.2, with glucose added first, the very sharp characteristic peaks at $2\theta = 20^\circ, 32^\circ, 45^\circ, 60^\circ,$ and 65° associated with the MgAl_2O_4 crystalline phase were observed, indicating that they have relatively regular shape and large MgAl_2O_4 crystalline sizes. Changing the adding order broadens the characteristic peaks of sample M-CTAB&Glu-1.2 and reduces the peak height. In addition, the diffraction peaks at $2\theta = 60^\circ$ corresponding to the MgAl_2O_4 crystalline phase are relatively weak. It indicates the reduction of the MgAl_2O_4 crystalline size. From the results, the adding order of the components of the mixed templates can influence their synergistic effects and change the particle sizes of the samples.

Different adding order is also an important factor influencing the surface areas and pore size distribution of

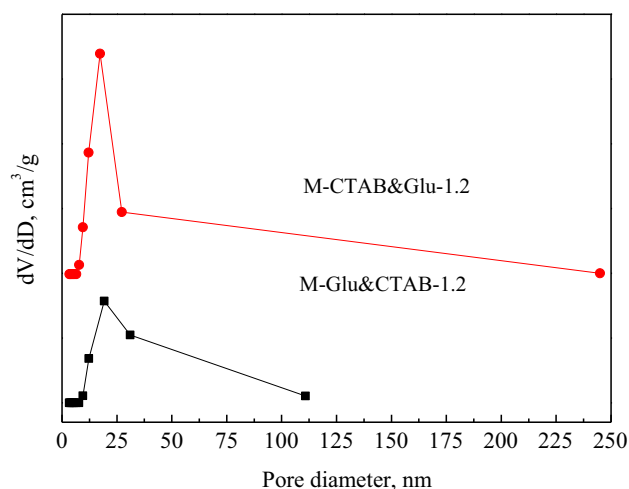


Fig. 5 The pore size distribution of MgO-rich MgAl_2O_4 prepared through changing design order of composite template

the samples. Table 3 demonstrates that the surface area of sample M-CTAB&Glu-1.2 is larger than that of sample M-Glu&CTAB-1.2, and the mean diameter is smaller and pore size distribution is centralized. CTAB plays a predominant role in increasing the surface areas of MgO-rich MgAl_2O_4 . With CTAB added first, CTAB molecules can disperse well in the gel system and cannot be disturbed by the following addition of glucose. This facilitates the formation of MgO-rich MgAl_2O_4 . However, changing the adding order makes glucose distributing orderly in the system preferentially to CTAB, and the disordered distribution of CTAB in the solution weakens the plate-like structure order of materials. In that case, the reduction of surface area and the broadening of pore size distribution of prepared MgO-rich MgAl_2O_4 cannot be avoided.

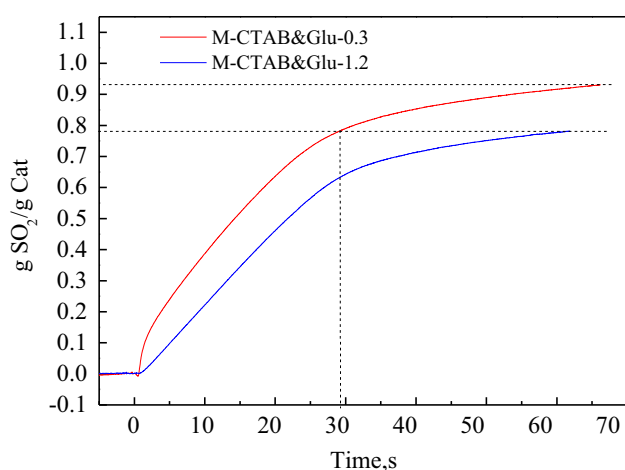


Fig. 6 SO₂ adsorption curve of samples

Catalytic test

In order to achieve suitable SO_x adsorption in short time, SO₂ transfer additives used in FCC units must have high adsorption rates. Figure 6 presents that both samples exhibit the higher absorption capacity as reaction time goes on. The largest absorption capacity increased from 0.79 to 0.93 gSO₂/g Cat, while specific surface area increased from 223 to 188 m²/g (Fig. 5), which proves that higher specific surface is in favor of increasing the largest absorption capacity of SO₂ transfer.

Figure 6 shows that the slopes of two diagram indicate that the two materials show excellent adsorption rate at about first 30 min, which is desirable since catalyst's residence time in the regenerator of FCC process is very short (about 5–30 min), as reported in [16]. Obviously, M-CTAB&Glu-0.3 also shows the highest adsorption rate in first 30 min compared with M-CTAB&Glu-1.2. The results indicate that high specific surface can increase desulfurization rate. This is because high specific surface increases the diffusion velocity and makes the dispersion of oxide better. So the catalytic behavior of the samples could be assigned to their textural properties determined by different synthetic conditions, and M-CTAB&Glu-0.3 with the beneficial structural properties could provide more chemisorption sites, which is desired for SO₂ abatement.

Conclusion

MgO-rich MgAl₂O₄ with large surface area is successfully prepared by co-precipitation with CTAB, Triton X-100 and glucose or a combination of CTAB and glucose as templates, respectively. It is found that among the prepared samples using a single template, the sample using glucose as template shows the largest area. Moreover, mixtures of glucose and CTAB bring in the further increase of surface area, wherein adding order of components is an important

factor. The addition of CTAB first followed by glucose can maximize the surface area of the prepared sample, and increase the desulfurization reaction rate.

In conclusion, during co-precipitation, types and amounts as well as combination of templates can influence crystalline phase and particle size as well as surface area. MgO-rich MgAl₂O₄ with desired surface area can be obtained by choosing effective templates with appropriate addition amount.

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References

- Shengbo L (2010) Preparation and characterization of MgAl₂O₄ spinel as catalyst support. Dalian Jiaotong University, Dalian
- Ruishuo L, Xinkui W, Limin Q et al (1995) Preparation of MgAl₂O₄ spinels and their use in cyclohexanone dimerization. *J Fuel Chem Tech* 23(2):144–148
- Ruixia J, Zaiku X, Chengfang Z et al (2003) Preparation of magnesia-alumina spinel and its application in catalytic reaction. *Ind Catal* 11(1):44–49
- Yalu M (1998) The preparation of MgAl₂O₄ powder by chemical co-precipitation method. *Inorganic Chem Ind* 30(1):5–6
- Liqun F (2013) Preparation and characterization of MgAl₂O₄ nano-powder at low temperature. *New Chem Mater* 41(8):95–97
- Khalil NM, Hassan MB, Ewais EMM et al (2010) Sintering, mechanical and refractory properties of MA spinel prepared via co-precipitation and sol-gel techniques. *J Alloy Compd* 496:600–607
- Tang C, Zhai Z, Li X et al (2015) Sustainable production of acetaldehyde from lactic acid over the magnesium aluminate spinel. *J Taiwan Inst Chem Eng* 000:1–10
- Lowell PS, Schwitzgebel K, Parsons TB et al (1971) Selection of metal oxides for removing SO₂ from flue gas. *Ind Eng Chem Process Des Dev* 10(3):384–390
- Yang W-H, Zhang Q, Li C-Y et al (2012) Studies on the regeneration mechanism of Mg–Al–Ce–Fe mixed spinel De-SO_x additives [J]. *Ind Eng Chem Res* 51:13085–13091
- Jinan W, Chenglie L, Yiyun D et al (1994) Investigation on sulfur-transfer catalyst (I): composition, structure and De-SO_x Activity of magnesium–alumina spinel. *J Phys Chem* 10(7):581–584
- Rashad MM, Zaki ZI, El-Shall H (2009) A novel approach for synthesis of nanocrystalline MgAl₂O₄ powders by co-precipitation method. *J Mater Sci* 44:2992–2998
- Kang H-T, Zhang C-Y, Lv K et al (2014) Surfactant-assisted synthesis and catalytic activity for SO_x abatement of high-surface-area CuMgAlCe mixed oxides. *Ceram Int* 40:5357–5363
- Haitao K (2012) Study of SO_x-transfer additives applied in FCC units. Shandong University, Shandong

14. Bagshaw SA, Prouzet E, Pinnavaia TJ (1995) Templating of mesoporous molecular sieves by nonionic polyethylene oxide surfactants. *Science* 269:1242–1244
15. Tan P, Gao Z, Shen C et al (2014) Ni–Mg–Al solid basic layered double oxide catalysts prepared using surfactant-assisted coprecipitation method for CO₂ reforming of CH₄. *Chin J Catal* 35:1955–1971
16. Yoo JS, Bhattacharyya AA, Radlowski CA (1991) De-SO_x catalyst: an XRD study of magnesium aluminate spinel and its solid solutions. *Ind Eng Chem Res* 30(7):1444–1448