

Study on Mg/Fe Mixed Oxides Derived from Hydrotalcite as De-SO_x Catalyst

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Abstract: A novel class of desulfurization agent derived from hydrotalcite has been developed and its activity for SO_x uptake have been investigated. The results showed that the Mg/Fe mixed oxide having high SO_x uptake ability at a broad reaction temperature (*e.g.* 673K ~ 973K). The Mg/Fe ratio of the mixed oxide strongly affect the desulfurization role of the material and it can be used repeatedly without much loss of SO_x uptake ability.

Keywords: Hydrotalcite, mixed oxide, sulfur dioxide, De-SO_x.

The emissions of sulfur oxides from the combustion of coal are a serious environmental problem. At present, non-regenerative desulfurization processes based on limestone are widely used in many industrial situations¹. But such processes result in the formation of large amount of solid waste, which is also difficult to handle. Therefore, it is important to develop new desulfurization agents for cleanup SO₂. In order to control emissions of SO₂, various new technologies have been reported. Among them, regenerative processes are preferable option². Supported copper adsorbents have been extensively studied³⁻⁶. Sulfur dioxide reacts with oxygen on supported CuO and converts to copper sulfate which is regenerated easily by dilute hydrogen or methane. The presence of copper species accelerates the adsorption rate of SO₂ because they act as not only the oxidative catalysts of SO₂, but also as the adsorption active centers of SO₃. But some drawbacks exist in related to the low sulfur uptake capacity. It seems that the same active center for catalysis and adsorption of SO₂ is the main cause of low De-SO_x capacity, because the supported copper amount is usually lower (~10%). We developed a new class of magnesium-iron oxide derived from hydrotalcite, in which the Mg²⁺ acts as the absorber for SO₃ while the Fe³⁺ catalyzes the SO₂ to SO₃.

Hydrotalcite belongs to a class of anionic clays, in which divalent cations within brucite-like layers are replaced by trivalent cations. It possesses some particular properties such as high ion exchange capacity, excellent adsorption capacity *etc*⁷⁻⁸. The calcination of hydrotalcite-like compounds at high temperature leads to the collapse of the lamellar structure and formation of oxide species. Hydrotalcite derived oxides are used as antacids, ion exchangers, absorbers, catalysts and catalyst supports because of

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their high surface area, phase purity, basic surface properties, and structural stability. In recent years, it is reported that hydrotalcite-like materials are potential applicants for treatment of waste gas and water⁹⁻¹⁰. In this letter, we report that mixed magnesium-iron oxide derived from hydrotalcite, is very active for SO₂ removal from flue gas.

Experimental

Five hydrotalcite-like materials with different Mg/Fe ratio (2/1, 2.5/1, 3/1, 3.5/1 and 4/1, respectively) were prepared by co-precipitation method. The preparation process includes the following steps: slowly titration of aqueous solution of Fe(NO₃)₃·9H₂O and Mg(NO₃)₂·6H₂O to an aqueous solution of NaOH and Na₂CO₃ controlled at pH 10.0 at 328K. After washing and drying, the hydrotalcites were calcinated at 973K for 4 h, then the mixed Mg/Fe oxides were obtained. The evaluation test for SO₂ removal and regeneration of sulfated materials were performed on a microthermalgravimetric apparatus. The typical flue gas for De-SO_x experiments composes of 1.0%SO₂, 5.0%O₂ and N₂ for balance. The typical gas for regeneration experiments composes of 10%H₂ and 90%N₂. Detail operation procedures and conditions were described elsewhere¹².

XRD characterization indicates that the obtained five samples all had typical structure of hydrotalcite. After calcination, the diffraction pattern of hydrotalcite disappeared completely and the phases of MgO and spinel MgFe₂O₄ were detected.

Results and Discussion

The SO₂ uptake reaction on calcinated Mg/Fe (3/1) oxide catalyst were investigated under temperatures ranging from 473K to 1073K. The results are shown in **Table 1**. It can be seen therein the catalyst shows excellent activity at temperature ranges from 673K to 973K, and 773K is more suitable for uptake of SO₂. At temperature lower than 673K, the catalyst shows relatively lower activity because the iron species can not catalyze SO₂ at low temperature. At temperature higher than 973K, the activity also decreases gradually, it may be due to the decomposition of sulfated species and desorption from the solid phase. Comparing to that of Mg/Al spinel catalyst, which shows highest sulfur capacity at about 973K¹¹, the optimum De-SO_x temperature range on Mg/Fe catalyst is relatively lower. The results indicate that this catalyst is effective in quite wide temperature windows (*e.g.* 673K~973K) for SO₂ removal. This advantage enables the catalyst to use for SO₂ removal at different cases.

Table 1 The influence of temperature on the SO₂ uptake on Mg/Fe (3/1) mixed oxide catalyst (SV = 500 h⁻¹; time = 4 h)

| Temp. (K) | 473 | 673 | 773 | 873 | 973 | 1073 |
|----------------------------------|------|------|------|------|------|------|
| SO ₂ uptake (g/g cat) | 0.09 | 0.57 | 1.40 | 1.31 | 0.62 | 0.24 |

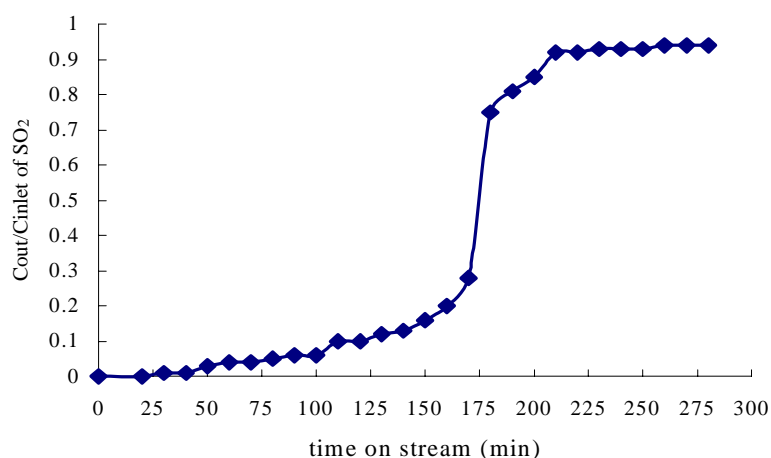
In **Table 2**, the activities of all the catalysts with different Mg/Fe ratio are compared. Although the five catalysts are all very active for the SO₂ removing, the Mg/Fe (3/1) is the best. Meanwhile, high S/Mg ratio is obtained. At 823K, The S/Mg ratio reaches 1.52. This value exceeds the stoichiometric value of pure MgSO₄ (S/Mg mole ratio is 1/1), indicating that some bridge links such as -Mg-O-SO₂-O-SO₂-O-Fe- are formed, in which sites of the iron are also served as adsorption centers. This assumption are also confirmed by the facts that in reduction process of sulfated catalyst carried out at much lower reduction temperature (at about 850K), comparing with that of pure magnesium sulfate (at about 973K), because this new agent has relative low reductive stability than magnesium sulfate¹². The high S/Mg ratio indicates that bulky active sites of Mg and Fe are utilitied, which is very different from supported catalysts. The phenomenon can be explained by two possible reasons associated with the catalyst: (1) The catalyst is fine enough that most of Mg and Fe are exposed to SO₂. (2) The diffusion resistance of SO₂ in the catalyst might be negligible, which allows the gaseous SO₂ readily to react, adsorb and immobilize into solid phase.

Table 2 Activities for SO₂ uptake over mixed oxides with different Mg/Fe ratio at 823K
(SV = 500 h⁻¹; time = 4 h)

| Mg/Fe ratio | 2/1 | 2.5/1 | 3/1 | 3.5/1 | 5/1 |
|----------------------------------|------|-------|------|-------|------|
| SO ₂ uptake (g/g cat) | 1.13 | 1.29 | 1.41 | 1.33 | 1.06 |
| S/Mg ratio | 1.22 | 1.39 | 1.52 | 1.43 | 1.14 |

We could not identify which is the main cause, but the experiments showed the catalysts prepared from hydrotalcite-like precursor seem very suitable for desulfurization process.

Figure 1 Breakthrough curve of SO₂ at 823K on the catalyst (Mg/Fe = 3/1)
(SO₂/O₂/N₂ = 1.0/5.0/94.0; SV = 1100 h⁻¹)



The breakthrough curve of SO₂ at 823K on the catalyst (Mg/Fe = 3/1) was shown in **Figure 1**. SO₂ concentration in the output stream from the bed was recorded from the start of the run until it reached the inlet concentration. The result is in agreement with the above microthermalgravimetric experiments. The steep slope shows the process for SO₂ removal proceeds with high adsorption rate, indicating the catalyst exhibits not only high adsorption capacity, but also high adsorption rate.

The regeneration of sulfate catalyst at 773K is carried out and the re-adsorption of regenerated catalyst is also performed. The results are listed in **Table 3**. It is worthwhile to note the regeneration performance of the catalyst is quite well and the catalyst can be used repeatedly without much decrease of the capacity of SO₂ uptake. After five cycles of desulfurization-regeneration process, the SO₂ uptake capacity only decreased 9.2% comparing to the fresh catalyst. We observed the catalyst turns blackish after regeneration at 773K, indicating some sulfide may be formed. This phenomenon gradually diminished at elevated regeneration temperature (~873K). Despite of the minute formation of sulfide, the regeneration process can be performed at the same temperature matching with the desulfurization process. Therefore, in this report we provide an entirely new catalyst with high sulfur capacity and adsorption rate for SO_x removal from flue gas.

Table 3 Re-adsorption performance of regenerated catalyst
(Mg/Fe = 3/1; SV = 500 h⁻¹; time = 4 h; T = 773 K)

| cycles | fresh | 1 | 2 | 3 | 4 | 5 |
|----------------------------------|-------|------|------|------|------|------|
| SO ₂ uptake (g/g cat) | 1.41 | 1.35 | 1.33 | 1.34 | 1.31 | 1.28 |

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