MODIFIED PEROVSKITES, $La_{1-x}Mg_xMO_3$, - EXCELLENT De-SOx AGENTS.

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INTRODUCTION

The De-SO_x catalyst, cerium containing mixed spinel materials, $Ce/MgO \cdot MgAl_{2-x}M_xO_4$ M=Fe, V, Cr, Mn etc) has been effective for the SO_x and NO_x removal from the emission of the fluid catalytic cracking (FCC) regenerator [1,2]. Another type of mixed metal oxides structurally analogous to the naturally occurring mineral perovskite ($CaTiO_3$) have for decades formed the testing and breeding ground for ideas in solid state chemistry. The properties of perovskites that are important in catalysis are primarily the stability of mixed valence states of Co, Mn, Ti, etc., the stabilization of unusual oxidation states, and in particular, the mobility of oxygen ions.

For the automotive application, encouraging results were obtained with manganite and cobaltate perovskites in the oxidation of CO and the reduction of NO. The sensitivity of these particular perovskites to deactivation by SO_2 dampened the initial enthusiasm for their application in automotive exhaust catalysis. Since then, the deactivation mechanism has been understood, the SO_2 resistant catalysts such as $La_{0.6}Sr_{0.4}Co_{1-x}M_xO_3$ has been found [3]. IR spectroscopy indicates that SO_2 absorbed on B sites ions in perovskite, AB_3, deactivate the catalyst by blocking the surface sites that are necessary for CO absorption and lattice oxygen replenishment. The poisoning is due to the stable sulfate formation on B sites with SO_3 formed by oxidation of SO_2 in O_2 [4]. This prompted us to look into application of these types of mixed oxides materials for SO_x removal from the emission of FCC regenerator.

EXPERIMENTAL

Catalyst preparation - over recent years specialized catalyst preparation techniques such as freeze-drying and various types of sol-gel process have been used to produce oxides in a fine partiuclate form. In particular the amorphous citrate process [5] and chemical vapor deposition technique [6] have been shown to be effective because of the high yields of uniformly dispersed mixed oxides with high surface area. However, the modified perovskites studied in this work were prepared by the coprecipitation method for simplicity. The preparation of modified perovskites is described using $La_{0.5}Mg_{0.2}CoO_3$ as an example. The catalyst was precipitated from the aqueous nitrate solutions of La, Mg, and Co with n-butylamine according to the procedure discussed in a previous paper [7]. These nitrates of La, Mg, and Co were dissolved in the minimum amount of water. The pH of aqueous solution of La, Mg, and Co were 0.50, 4.75, and 0.76, respectively. These three metal nitrate solutions were mixed with agitation, and the n-butylamine was added dropwise to produce a coprecipitate over an hour. A spectacular color change and an exothermicity were observed. After amine addition was complete, the slurry pH was 9.46, and the pH of the mother liquor was 9.64. The final slurry was extremely viscous and required vigorous stirring. The slurry was filtered, a water wash followed by an ethanol wash to remove final trace of n-butylamine. The resulting cake was allowed to dry in air and further dried in a vacuum oven at 100°C for 12 hours. The dried cake was a crumbly multi-colored solid. The solid was a uniform color after grinding to 40 minus mesh. The 40 minus mesh grind size was fluidized while cartying out calcination at 732°C for 3 hours. The empirical formular of the final dark-brown product was $La_{0.5}Mg_{0.2}CoO_3$.

The SO_x pickup half cycle - Absorption of SO_3 on the catalyst was measured on an Omni Thermal Analysis System which employs a model 35000 Data Reduction system and a rebuilt Du pont 951 Thermogravimetric Analyzer (TGA). The TGA analyzer was equipped with a special reaction cell to allow the use of corrosive gases (i.e. SO_2) without affecting the delicate balance mechanism. The following test procedure was followed: 1) Approximately 8 mg of catalyst was placed on a quartz pan on the TGA balance. 2) The reaction cell was connected to gas lines and exhaust line. Purged with nitrogen at a flow rate of 200 cc/min throughout an entire run to sweep reacting gases away from balance and out exhaust line. 3) Nitrogen was passed at 100 cc/min while sample was heated at 25°/min to 732°C. 4) After the reactor temperature stabilized at 732°C, the N_2 gas was shut off and the gas blend containing 1.5% SO_2 and 5.9% O_2 in N_2 was introduced over the sample at 100 cc/min. 5) Maintained a weight gain for 15 min while the data point was taken every 10 seconds. 6) At the end of 15 min, the reactor was allowed to cool down, shut off the SO_2 blend gas and switched to air (100 cc/min) for 5 min. When the reactor was cooled to 500°C, air was switched to N_2. It was assumed that a net weight gain was attributed to the SO_3 uptake, and % sulfur was calculated from the net weight gain.

The H_2 reduction half cycle - The sulfated sample resulting from the SO_x pick-up half cycle was reduced with H_2. 1) The sulfated sample was heated to 677°C (in some cases 677 – 732°C) under the N_2 flow of 100 cc/min at a rate of 25°C/min. 2) After the

temperature was stabilized, N_2 is shut off and H_2 was admitted at a rate of 100 cc/min. A weight loss was monitored for 10 min (data points were taken every 2 seconds). 3) At the end of 10 min., the oven was shut off, H_2 was shut off and then N_2 was admitted at 100 cc/min. A catalyst cycle was complete by conducting the SO_x pick-up half cycle and then the H_2 reduction half cycle in sequence. The catalyst stability was determined by the prolonged catalyst cycle tests.

RESULTS AND DISCUSSTIONS

The oxidative SO_x pick-up half cycle - A series of modified perovskite type mixed oxides, $La_{1-x}Mg_xMO_3$, where M=Mn, Co, Cu, Fe were prepared by the coprecipitation procedure. The evaluation of the calcined materials was conducted according to the procedure described in the experimental section. A feed consisting of 1.5% SO_2, 5.9% O_2 and the balance N_2 passed over the catalyst on a pan in the cell of du pont 951 Thermogravimetric Analyzer for 15 min at 732°C. The typical results for manganite, cobaltate, ferrate and cuprate are compared in Figure 1.

H_2 reduction half cycle - The sulfated manganite such as $MgMnO_3$ and $La_{0.2}Mg_{0.8}MnO_3$ and modified cobaltate such as $La_{0.8}Mg_{0.2}CoO_3$ and $La_{0.5}Mg_{0.5}CoO_3$ in the SO_x pick-up half cycle was subjected to the H_2 reduction half cycle. After the catalyst blend in a FCC equilibrium catalyst was sulfated in the SO_x pick-up half cycle, the sulfated system was flushed with nitrogen, brought back to 677°C, reduced in flowing H_2 for 5 minutes, flushed with N_2, and then retested for the SO_x pick-up reaction. The catalytic cycle, SO_x pick-up half cycle followed by H_2 reduction half cycle, was repeated with these catalysts. The weight change (mg) occurred in each half cycle was presented along with calculated S% on the catalyst in Table 1, and plotted in Figure 2. Among these catalyst, $La_{0.8}Mg_{0.2}CoO_3$ appears to be the most stable and promising one.

It has been well known that perovskites are able to exchange oxygen quite easily as the oxidation state of the metals changes due to oxidation or reduction. Reller and colleagues [8] have shown the following conversion: $CaMn^{+4}O_3 \rightleftharpoons CaMn^{+2}O_2 + H_2O$ under H_2 at 500-600°C. It is thus difficult to measure the reduction capability of a sulfated perovskites by TGA. The reaction we want to observe is: $M\text{-}O\text{-}SO_3 + H_2 \rightarrow M\text{-}O + H_2 + SO_2$, where the weight loss is solely due to the loss of SO_3. But the abstraction of labile oxygens from the perovskite lattice complicates the interpretation of the weight loss observed. This phenomenon has been observed in reductions of the sulfated peroskites. The final weight after reduction is lower than the initial weight of the sample (before sulfation) in our own work as well. Any pickups occurred subsequent to the reduction will not only indicate the weight gain of SO_3 but also the replacement of any oxygen missing from the lattice. Because the TGA indicates only weight losses and gains, one must report to final testing of the perovskite catalysts in a cyclic unit where actual pick-up of SO_2 after the sulfate reduction step can be monitored. This will indicate whether or not sulfur is being removed by the reduction or picked up on the catalyst.

Non-oxidative SO_x pick-up chemistry

The same modified cobaltate, manganite, and ferrate were also subjected to non-oxidative SO_x uptake in a feed containing 1600 ppm SO_2 in N_2 by varying the reaction temperatures. The results shown in Table 2 indicate that some of the samples were excellent for SO_x uptake. Catalyst D, $La_{0.8}Mg_{0.2}CoO_3$, exhibited the highest activity in the non-oxidative system among the catalysts studied. Figure 3 is a plot of non-oxidative SO_x pick-up as a function of temperature. Main reactions occurring in the non-oxidative system are believed to be disproportionation of metal sulfite, MSO_3, into sulfate and sulfide [9], and direct reduction of SO_2 to elemental sulfur by the reducing agent such as CO [10]. These results suggest that modified perovskites can be used either in oxygen rich or in oxygen starved FCC regeneration mode.

CONCLUSIONS

A series of modified perovskites, $La_{1-x}Mg_xMO_3$, where M=Co, Mn, Cu, Fe, x=0-1, was found to be effective for removing SO_x from the emission of the fluid catalytic cracking regenerator. Typical modified perovskite samples such as $La_{0.2}Mg_{0.8}MnO_3$, $La_{0.8}Mg_{0.2}CoO_3$, $La_{0.5}Mg_{0.5}CoO_3$, and $La_{0.8}Mg_{0.2}FeO_3$ were prepared by the coprecipitation method. These materials were evaluated for the SO_x removal activity in the two types of feed streams containing 1.5% SO_2 in N_2 with or without 5.9% oxygen. These samples exhibited a remarkable SOx absorption activity in both streams. The catalyst stability of $La_{0.8}Mg_{0.2}CoO_3$ was demonstrated with the catalyst cycle test in an automated laboratory reactor. It is encouraging to find that these materials are also very active under the non-oxidative stream. This suggests that these materials can be used either in the oxygen rich or in oxygen starved FCC regeneration modes.

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Table 1

The catalytic cycle test, SO_x pick-up half cycle and sulfate reduction half cycle
Catalyst: A:$MgMnO_3$, B:$La_{0.2}Mg_{0.8}MnO_3$, C:$La_{0.5}Mg_{0.5}CoO_3$. D:$La_{0.8}Mg_{0.2}CoO3$,
Surface area. m^2/g: C:22, D:1

	S pick-up, mg				S removed, mg				S% on catalyst			
Catalyst	A	B	C	D	A	B	C	D	A	B	C	D
# of cycle												
1	49	46	46	35	34	18	29	13	13.0	12.4	12.4	10.2
2	33	14	32	17	26	13	31	17	13.4	12.2	13.5	11.5
3	23	9	30	14	23	9.6	30	12	12.8	11.4	13.5	10.9
4	18	7	26	15	19	8.6	27	13	11.8	10.8	12.8	11.4
5	16	8	24	14	20	8.3	-	-	11.2	10.7	12.2	11.2
6	18				18				10.7			

Table 2

The SO_x pick-up test in a non-oxidative system
2% blend of catalysts in an FCC equilibrium catalyst
Catalyst D: $La_{0.8}Mg_{0.2}$ CoO_3, E:$La_{0.2}Mg_{0.2}MnO_3$, F:$La_{0.8}Mg_{0.2}FeO_3$

Catalyst	% SO_x picked up					Activity	
Temp. °F	500	800	1000	1200	1350	1200	1350
D	12	16	31	63		28	
E					52		22
F					36		14

Fig. 1. Comparison of oxidative SOx pick-up results - S% vs time

La.5Mg.5MO3, M = Mn, Co, Fe, Cu

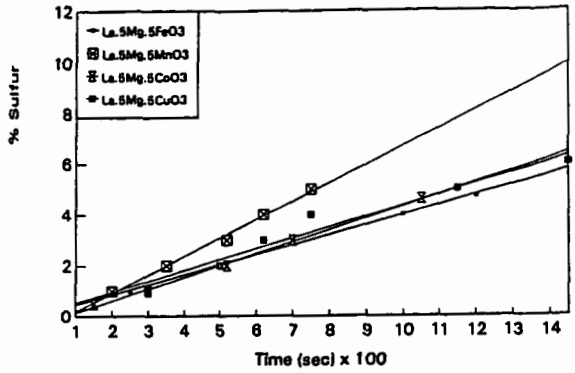


Fig. 2. The stability study of modified perovskites - SOx activity vs catalyst cyle
Repeating a catalyst cycle, SOx pickup half cycle followed by H2 reduction half cycle

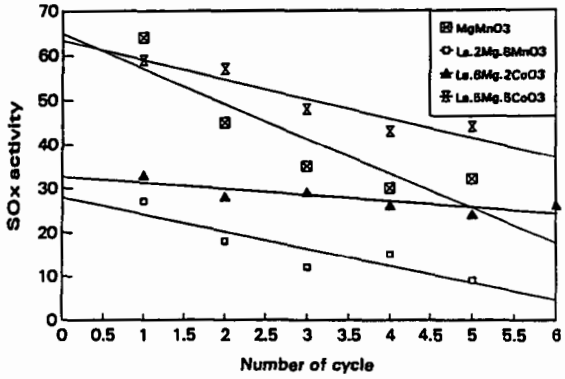
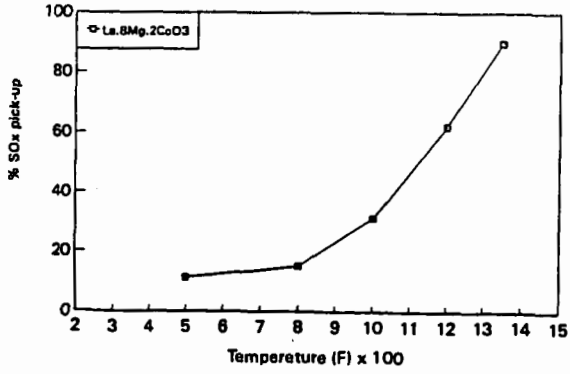


Fig. 3. Non-oxidative SOx pick-up of modified perovskite

SOx pick-up vs temperature, 1600 ppm SO2 in N2