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SELECTIVE CATALYTIC REDUCTION OF SULFUR DIOXIDE TO ELEMENTAL SULFUR

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ABSTRACT

Elemental sulfur recovery from SO_2 -containing gas stream is highly attractive as it produces a salable product and no waste to dispose of. However, commercially available schemes are complex and involve multi-stage reactors, such as , most notably in the Resox (reduction of SO_2 with coke) and Claus plant(reaction of SO_2 with H_2S over catalyst). This project will investigate a cerium oxide catalyst for the single stage selective reduction of SO_2 to elemental sulfur by a reductant, such as carbon monoxide. Cerium oxide has been identified in recent work at MIT as a superior catalyst for SO_2 reduction by CO to elemental sulfur because its high activity and high selectivity to sulfur over COS over a wide temperature range(400-650 $^{\circ}\text{C}$). The detailed kinetic and parametric studies of SO_2 reduction planned in this work over various CeO_2 -formulations will provide the necessary basis for development of a very simplified process, namely that of a single-stage elemental sulfur recovery scheme from variable concentration gas streams, The potential cost- and energy-efficiency benefits from this approach can not be overstated. A first apparent application is treatment of a regenerator off-gases in power plants using regenerative flue gas desulfurization. Such a simple catalytic converter may offer the long-sought "Claus-alternative" for coal-fired power plant applications.

Progress Summary

Doped CeO₂ Catalyst

1 at % La₂O₃ doped CeO₂. In previous study, we reported that catalytic activity of CeO₂ can be enhanced by introducing dopant ions into its crystal structure. Among three tri-valent dopants tested (Y, Sc, La), 1 at% La₂O₃-doped CeO₂, CeO₂(La) (Table I), was identified as the best one. The effect of contact time on elemental sulfur yield with the CeO₂(La) catalyst is shown in Figure 1. Changing the contact time did not change the product selectivity. More than 95% elemental sulfur yield was always achieved under complete SO₂ conversion. The sulfur yield curve fell off at a lower temperature when a longer contact time was used. However, the fall-off temperature was no longer affected above a value of 0.02 g·s/cc(STP) contact time. The sulfur yield-temperature curve fell off at about 500 °C at this or longer contact times. Thus, the temperature of 500 °C appears to be related to an intrinsic property of this catalyst. According to Yao and Yao's studies(1), the surface capping oxygen of ceria is reduced by hydrogen only when the temperature reaches about 500 °C. Therefore, in our studies when the reaction temperature is below 500 °C, CO may not be able to keep the catalyst surface in a reduced state which is, presumably, the active state for this reaction.

Effect of La₂O₃ Dopant Concentration and MgO Dopant. In this quarter, the effect of La₂O₃ dopant content and di-valent dopant on the catalytic performance were examined. These catalysts were prepared with the amorphous citric acid method as before and its

properties are listed in Table I. The test results are shown in Figure 2. Increasing the dopant concentration of La_2O_3 from 1 to 35 at % did not change the catalyst performance. On the other hand, incorporation of 5% MgO into the 1% La_2O_3 -doped ceria greatly decreased the catalytic activity. The fall-off temperature over $\text{CeO}_2(5\text{Mg}+\text{La})$ catalyst is about 50°C higher than that on the $\text{CeO}_2(\text{La})$. XRD analysis revealed the existence of only ceria crystal phase in these oxide compounds. According to Butler et al's calculation(2), the vacancy association energy in MgO -doped ceria is 1.23 eV, much higher than that in the La_2O_3 -doped ceria, 0.26 eV, as shown in Table II. This strong association stabilized the oxygen vacancy and thus capped outside oxygen on the $\text{CeO}_2(5\text{Mg}+\text{La})$ catalyst surface. Higher temperature would be needed to remove the more strongly bonded surface capped oxygen to maintain the reduction/oxidation cycle.

For the same contact time, $0.02 \text{ s}\cdot\text{g}/\text{cc}(\text{STP})$, the fall-off temperature over the $\text{CeO}_2(\text{La})$ catalyst shown in Figure 1 is about 50°C lower than that in Figure 2. The feed gas used in the studies shown in Figure 2 was contaminated by a small amount of water vapor(400 ppm). This indicated that the catalyst may be poisoned by water vapor.

All catalysts studied here were pre-reduced in-situ by 10% CO/He at 600°C . After activation, the reacting gases were introduced and the reaction temperature was raised to about 650°C . When a steady-state reaction was reached, the temperature was lowered in steps of about 50°C until the reaction was quenched.

Light-off behavior on Lanthanide Oxide Catalysts

In this test, we started with the fresh catalyst without any pretreatment by a reducing agent and raised the reaction temperature from 500 to 700 °C in a 50 °C-step, holding at each temperature for half an hour. The test results are shown in Figure 3. The reaction was lighted-off at the same temperature (around 650 °C) over all the rare earth oxide catalysts tested except for CeO₂(Sc). The light-off temperatures on the La₂O₃ doped ceria catalysts were independent of dopant content and the amount of catalyst used. The reaction did not light-off on the CeO₂(Sc) catalyst even at temperature as high as 690 °C. Figure 3 also shows the effect of water vapor on the CeO₂(La) catalyst. When 3% H₂O was added into the feed gas, the sulfur yield decreased from 96% for dry gas to 53 % due to the formation of H₂S. In comparison with the dry gas case, the fall-off temperature increased from 500 to 570 °C due to the poisoning effect of H₂O. Compared to CeO₂(La) catalyst, La₂O₃ and PrO₂ catalysts need longer activation times though Figure 3 shows similar light-off temperatures. In addition, the La₂O₃ and PrO₂ more favor the formation of oxysulfides in the reacting environment than the CeO₂(La).

Mechanistic Consideration

Based on previous and present results, we have postulated a following redox reaction mechanism.

The reaction is initiated by the catalyst surface reduction by CO. As one oxygen vacancy is created by a CO₂ release, the SO₂ donates its oxygen to that vacancy to form a SO group. The SO could be mobile on the surface until it finds another vacancy to donate its oxygen or a vacancy may migrate to a neighboring site to accept its oxygen. High oxygen mobility in the catalyst lattice will facilitate the oxygen transfer from one site to another on the surface or from the bulk to the surface. However, the oxygen vacancy can be taken up by other molecules existing in the reacting gas phase, such as H₂O and O₂. The more strongly these impurity oxygen atoms attach to the vacancy, the more severe a poisoning effect they will bring about. Thus, the creation of oxygen vacancies on the surface is a key step.

Incorporation of dopant ions into ceria lattice enhances the oxygen vacancy concentration and mobility. But, the vacancies created by the dopant on a fresh catalyst surface are always capped by the oxygen atoms from ambient oxygen or water. Therefore, the capping oxygen has to be removed to activate the catalyst. The oxygen vacancy and the dopant ion are associated pairs by a certain energy. The stronger this association, the lower the vacancy energy state is and the more strongly the vacancy is capped by an outside oxygen. In other words, the strong association increases the difficulty of removing the capping oxygen. Table II indicates that the association energy increases with dopant content. Therefore, increasing the dopant concentration does not necessarily enhance the catalytic activity as illustrated by Figure 2.

Transition Metal-Promoted Ceria catalysts

The transition metal-contained ceria catalysts prepared and tested in this work are tabulated in Table I. 0.5M transition metal nitrate solutions were used for the impregnation, while the hydrogen hexachloroplatinate(IV) hydrate solution of 10 mg Pt/cc was used for the Pt/CeO₂. The CeO₂ support, of particle sizes from 35 to 100 mesh, about 1.0 cc void/g and 22m²/g specific surface area, was made by means of the decomposition of cerium acetate at 750 °C for three hours. The impregnated CeO₂ was dried at room temperature for one day, calcined at 600 °C for four hours, and reduced by 10% CO/He at 310 °C before use. The reaction light-off curves on the impregnated catalysts are plotted in Figure 4. The light-off temperatures were 500 °C for the Cu/CeO₂ and Ni/CeO₂, 550 °C for the Pt/CeO₂, and 600 °C for the Co/CeO₂ and Mn/CeO₂ systems. These light-off temperatures are lower than those on the bare rare earth oxides shown in Figure 3. Among those metal/ceria catalysts tested, only the Cr/CeO₂ catalyst had a light-off temperature higher than 605 °C.

The fall-off behavior and water vapor effect on the metal/ceria catalysts are shown in Figure 5. Compared to Figure 4, some of the catalysts extended their fall-off temperatures below 500 °C and some did not. The water vapor has less poisoning effect on the impregnated catalysts (except for the Cr/CeO₂) than on the bulk ceria catalysts. But, the water vapor still promoted the production of H₂S. In the presence of 2% H₂O, about 70% sulfur yield was realized on the Ni/CeO₂, Cu/CeO₂ and Co/CeO₂ catalysts over the tested temperature range of 500 to 550 °C. The Cu/ceria was chosen for further studies because of its overall superior performance.

Figure 6 shows the long-term test results with the Cu/CeO₂ catalyst. No visible deactivation was observed during a 25-hour test at 510 °C in the presence of water. The COS formation was negligible in this case. But, the production of H₂S consumed more reductant(CO) that there was not sufficient reductant left for the reduction of inlet SO₂. However, about 75% sulfur yield was still obtained with the two times contact time used in the previous study(Figure 5).

Metal Oxide Composite Catalysts

The bulk Cu-Ce-O composite catalysts were prepared by coprecipitation method as following: copper nitrate and cerium nitrate were dissolved in de-ionized water; ammonium carbonate solution was dropwise added to this mixture solution at 75 °C with vigorously stirring; the precipitate was filtered and washed twice with 75 °C - deionized water; resulting precipitate cake was dried at 100 °C for one day and then calcined in the furnace in flowing air at 600 °C for four hours; particles of 35 to 100 mesh size were used for tests. Three Cu-Ce-O composite catalysts and one Cu-Zr-O were prepared in this way(Table I). The test results are plotted in Figure 7. All three Cu_xCe_{1-x}O_{2-x} catalysts tested showed excellent performance. The Cu_{0.15}Ce_{0.85}O_{1.85} appears to be the best one. It gave more than 90% sulfur yield for the dry gas and more than 70% sulfur yield in the presence of 2% water at the temperature as low as 450 °C. More testing proved that this catalyst system is superior to any catalysts reported so far in this field in terms of the activity and selectivity as well as tolerance to impurity.

The CuZrO_3 catalyst showed comparable activity and selectivity to the Cu-Ce-O catalysts. Smaller particle size and more weight was used for the CuZrO_3 catalyst test, because this catalyst has high bulk density (5.0 g/cc) and small micropores. Thus, the pore-diffusion became the rate-determined step in this case.

Conclusion and Future Work

Transition metal modified ceria catalysts showed high activity and selectivity, and resistance to the impurity gases. Detailed studies of this catalyst system is planned in next quarter.

Literature Cited

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2. Butler, V.; Catlow, C.R.A.; Fender, B.E.F.; Harding, J.H. *Solid State Ionics* **1983**, *8*, pp109-113.
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Table I. Catalysts Tested in This Study

No.	Catalyst	Composition ^d	Surface Area (m ² /g)	
			fresh ^e	used ^f
<u>Lanthanide Oxides^a</u>				
1.	CeO ₂ (La)	1 at % La ₂ O ₃	34.0	19.5
2.	CeO ₂ (6La)	6 at% La ₂ O ₃	32.6	22.8
3.	CeO ₂ (20La)	20 at %La ₂ O ₃	37.5	19.4
4.	CeO ₂ (35La)	35 at %La ₂ O ₃	28.8	17.2
5.	CeO ₂ (5Mg+La)	1 at % La ₂ O ₃ + 5 at % MgO	30.2	22.4
6.	La ₂ O ₃		19.0	18.4
7.	PrO ₂		7.2	5.5
<u>Impregnated Ceria^b</u>				
8.	Cu/CeO ₂	-	21.4	15.7
9.	Ni/CeO ₂	-	22.7	-
10.	Cr/CeO ₂	-	16.3	11.1
11.	Co/CeO ₂	-	22.5	16.5
12.	Mn/CeO ₂	-	20.8	-
13.	Pt/CeO ₂ ^{b*}	-	22.9	20.6
<u>Composite^c</u>				
14.	Cu _{0.05} Ce _{0.95} O _{1.95}		65.8	29.0
15.	Cu _{0.15} Ce _{0.85} O _{1.85}		42.0	26.4
16.	Cu _{0.2} Ce _{0.8} O _{1.8}		39.2	10.4
17.	Cu _{0.5} Ce _{0.5} O _{1.5}		51.6	20.0
18.	Cu _{0.5} Zr _{0.5} O _{1.5}		58.5	-

^aCatalysts were prepared with the amorphous citric acid method.

^bCeO₂ support was impregnated with 0.5 M metal nitrate solution and estimated metal content is about 8 atomic percent.

^{b*}CeO₂ was impregnated with 10 mg Pt/cc hydrogen hexachloroplatinate(IV) hydrate solution.

^cCatalysts were prepared with the coprecipitation method.

^d"at %" denotes the corresponding metal atomic percentage.

^eMeasured before use.

^fMeasured after about 6-hour reaction time on-stream.

Table II. Association Enthalpy h_A and Conductivity for Solid Solutions of Different Dopants in CeO_2

Dopant	Ionic radius (Å)	$h_A(\text{ev})^a$		$\sigma(\text{ohm-cm})^{-1}$ 1% D_2O_3 at 400 °C
		1% D_2O_3	6% D_2O_3	
La^{3+}	1.18	0.14/0.26 ^b	0.18	3.27×10^{-4}
Gd^{3+}	1.06	0.12/0.17 ^b	0.16	5.3×10^{-4}
Y^{3+}	1.01	0.21/0.38 ^b	0.26	3.27×10^{-4}
Sc^{3+}	0.87	0.67/0.62 ^b	-	4.43×10^{-7}
Mg^{2+}	0.89	1.23 ^b	-	-
Ca^{2+}	1.12	1.12 ^b	-	-

^a h_A related to σ by $T\sigma \propto \exp(-(h_A + h_m)/RT)$.

^bdata calculated by Butler et al.(2).

(other data from Gerhart-Anderson and Nowick(3)).

Figure 1. Effects of Contact Time on Reaction Conversion and Selectivity on CeO₂(La) Catalyst.

Figure 2. Effect of La₂O₃ Dopant Content and MgO Dopant on Catalytic Performance.

Figure 3. Light-off Behavior of SO₂ and CO Reaction over the Rare Earth Oxides Catalysts

Figure 4. Light-Off Behavior of the CeO₂ Catalysts Impregnated by 0.5M Transition Metal Nitrate Solution

Figure 5. Fall-off Behavior of the Impregnated CeO₂ Catalysts and Water Vapor Effect on Sulfur Yield
(* Activated by reduction with 10% CO/He at 600°C)

Figure 6. Long-term Test of . . Cu/CeO₂

Figure 7. Effects of Catalyst Composition on Its Activity and Selectivity
(all catalysts were prepared with coprecipitation method)

* +100 mesh particles were used, while 35-100 mesh used for others

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