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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 °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

1. Experimental

Two bulk Cu-Ce-O catalysts, $\text{Cu}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$ and $\text{Cu}_{0.15}[\text{Ce}(\text{La})]_{0.85}\text{O}_x$, were chosen for kinetics studies in this quarter. The catalysts were prepared by coprecipitating aqueous solutions of copper and cerium nitrates by ammonium carbonate. The precipitates were washed with de-ionized water, dried at 110 °C, and calcined for 4 h at 650 °C in air. The resulting solid materials are crushed and sieved. Particles of 60 to 200 μm size were saved for kinetics experiments. The average pore size and total BET surface areas of these two catalysts as measured by N_2 adsorption/desorption are around 200 Å and 30 m^2/g , respectively. Kinetic measurements were conducted on a fixed bed microreactor of 6mm I.D. and under near atmospheric pressure. SO_2 conversion was controlled by catalyst loading and gas flowrate. The catalyst loading varied from 6 mg to 300 mg, while the flowrate varied from 100 to 400 sccm. Experiments confirmed that inter- and intra-particle mass transfer under the present conditions were eliminated. Blank test also showed that SO_2 conversion in the absence of catalyst was less than 2% at temperatures below 650 °C. The small amounts of catalyst were usually diluted by quartz particles, resulting in a packed height about 5mm. Reaction temperature was monitored and controlled by quartz tube-sheathed K-type thermocouple that was placed on the top of the catalyst bed. The kinetic measurements were carried out under steady-state reaction conditions. Generally, no apparent activation decline within 30 min was considered as a steady state. Such steady state was easily achieved at high reaction temperatures. At low temperatures, a longer time about a few hours was needed to reach a steady state when the reaction conditions were changed. Contact time, τ , sulfur yield, X-sulfur, and $[\text{CO}]/[\text{SO}_2]$ ratio are defined by following equations in this work:

$$\tau = 60W_{\text{cat}}/F_t \quad (1)$$

$$Y_{\text{-sulfur}} = [\text{Sulfur}]/[\text{SO}_2]_{\text{inlet}} \quad (2)$$

$$R_{\text{co}} = [\text{CO}]_{\text{inlet}}/[\text{SO}_2]_{\text{inlet}} \quad (3)$$

where W is catalyst weight in gram, F_t is the total gas flowrate in sccm, $[\text{Sulfur}]$ is the elemental sulfur content in the reactor effluent gas calculated from materials balance, $[\text{CO}]_{\text{inlet}}$ is the CO content in the feed gas, and $[\text{SO}_2]_{\text{inlet}}$ is the SO_2 content in the feed gas.

2. Results

2.1 Kinetics of SO_2 Reduction by CO over $\text{Cu}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$ Catalyst

Variations of SO_2 conversion with contact time at different R_{co} ratio under 1 % SO_2 concentration are shown in Figures 1-3. These curves look like a typical autocatalytic process showing an induction stage, rapid rising stage, and saturated stage. The experimental data were best fitted by the following empirical equation:

$$X_{\text{SO}_2} = \frac{\gamma \cdot A \cdot (\exp(B \cdot \tau) - 1)}{1 + A \cdot \exp(B \cdot \tau)} \quad (4)$$

where A and B are two adjustable parameters and γ is a constant which is equal to 1 when stoichiometric or excess CO is used and 0.78 when R_{co} ratio is 1.56. The kinetic Equation 4 can be written in a differential form:

$$-\frac{dy}{dt} = \frac{B}{1+A} y(A+1-y) \quad (5)$$

where $y = [\text{SO}_2]/[\text{SO}_2]_{\text{inlet}}$. The second term in Equation 5, $A+1-y$, is related to the active surface sites available to sustain the reaction and such active sites are decreased by the presence of SO_2 . At the inlet, $y=1$, $A+1-y$ equals to A . Therefore, parameter A represents the intrinsic catalyst active sites.

Values of parameter A and B obtained by these regressions are listed in Table 1. We can see that B is very small number increasing steeply with temperature but not relating to Rco ratio, while B number is a function of Rco ratio. The Arrhenius plots of parameters A and B are plotted in Figures 4 and 5a. The plot for parameter A yielded an activation energy of 166 kJ/mol. But, both pre-exponential factor, a-B, and activation energy, Ea-B, are a strong function of Rco, which implies over simplification of reaction kinetics by Equation 5. The high activation energy of parameter A suggests that intrinsic active sites are probably generated by thermal process, such as decomposition of surface sulfates and desorption of surface oxygen. The details of such discussion will be presented in the final report.

Table 1. Values of parameters A and B in Equation 3 or 4.

T(°C)	A	B		
		Rco=1.56	Rco=2	Rco=2.5
470	0.0055	65.9	86.2	95.6
510	0.0106	95.7	111	140
560	0.0802	110	211	591
610	0.416	314	575	1530

Variations of sulfur yield with contact time and Rco ratio are illustrated by Figure 6 for 560 °C reaction temperature. Complete conversion of SO₂ to elemental sulfur was realized at Rco=1.6, while about 95% selectivity to elemental sulfur was maintained at all contact times at Rco=2. For Rco=2.5, sulfur yield was stabilized at 75 to 80% level with SO₂ conversion above 85%, which indicates some catalyst

selectivity toward elemental sulfur, because stoichiometric product will be 50% sulfur at this Rco value. It is noticed that CO formation was always minimal at short contact times for all Rco ratios. This again confirmed that COS is unlikely a reaction intermediate. Figure 7 further shows that at all reaction temperatures, almost complete conversion of SO₂ to elemental sulfur was obtained with Rco=1.5 and 95% selectivity to elemental sulfur was achieved with Rco=2. But, with Rco=2.5, high temperatures generally favors for production of elemental sulfur.

2.2 Kinetics of SO₂ Reduction by CO over Cu_{0.15}[Ce(La)]_{0.85}O_x Catalyst

Figure 8 shows light-off curves the Cu_{0.15}[Ce(La)]_{0.85}O_x catalyst under various reaction conditions. The light-off occurred at the temperature range from 440 to 470 °C irrespective to SO₂ % concentration and contact times. This confirmed that the light-off temperature was determined by the intrinsic kinetics property of the catalyst and not a thermal effect. Pre-reduction of the catalyst by CO showed the lowest light-off temperatures. The activation profiles in Figure 9 illustrated that reduced catalyst surface facilitated the light-off. The nano-Cu_{0.15}Ce_{0.85}O_x catalyst prepared by the inert gas phase deposition is of non-stoichiometry as opposed to the coprecipitated catalyst. Further information about nano catalyst will be given in the final report. Figure 9 clearly shows that activation becomes more rapidly on a reduced catalyst than an un-treated catalyst.

Reaction kinetics over the Cu_{0.15}[Ce(La)]_{0.85}O_x catalyst was investigated by varying SO₂ concentration with Rco being fixed at 2. Under such gas composition, selectivity to sulfur was always about 95 % same as the result obtained with Cu_{0.02}[Ce(La)]_{0.98}O_x catalyst. Therefore, only SO₂ conversion is reported. Variations of SO₂ conversion with contact time and inlet SO₂ concentration are shown in Figures 10a-d. Various kinetic equations were evaluated to regress the experimental data. The data can be well fitted with Equation 5 as in the case of the

$\text{Cu}_{0.02}[\text{Ce}(\text{La})]_{0.98}\text{O}_x$ catalyst. But, a simple first order equation gives a reasonably good fitting.

$$-\frac{dP_{\text{CO}}}{2dt} = -\frac{dP_{\text{SO}_2}}{dt} = 2k \cdot P_{\text{CO}} \quad (6)$$

$$P_{\text{SO}_2} = 2P_{\text{CO}} \quad (7)$$

The curves in Figures 10a-d show that experimental data do not converged to zero point naturally and there is an induction time. The reaction constant is in the range of 32 to 257 /s, indicating very fast reaction process, while the induction time is a small number from 6.5 to 0 ms. The reaction constant, k , and the induction time, t_{ind} , are plotted Figure 11 in the form of Arrhenius equation. Resulting activation energy is 83 kJ/mol which is comparable to the activation energy for CO oxidation by oxygen given in the previous report. The activation energy for the induction time is -78.6 kJ/mol. The reciprocal form of the induction time is proportional to the dead catalyst volume. Therefore, the dead volume decreased with temperature. In-situ observations found that a shallow layer of catalyst on the top facing entrance reacting gas stream is different from the other part of the catalyst bed in the color. Possibly, the top layer was in an oxidized state. Further information about catalyst structure and surface compositions will be discussed in the final report. As a result, the plot of the calculated SO_2 conversion from the simple first order equation versus the experimental data in Figure 12 shows that the first order model is a good approximation and the data scattering mostly resulted from experimental error.

Differential reactor measurements found that the kinetic equation is more generally represented by a following power order equation:

$$\text{Rate}_{\text{CO}_2} = k \frac{P_{\text{CO}}^n}{P_{\text{SO}_2}^m} \quad (8)$$

The reaction order in P_{CO} varies from 1.5 to 2.2, while the order to P_{SO_2} varies from 0.8 to 1.5. This kinetic form clearly indicates the inhibition effect of SO_2 on the reaction. While the SO_2 inhibition effect was counteracted by the high order of P_{CO} . More detail results will be discussed in the final report.

Figure 1. Variation of SO₂ conversion with contact time at [CO]/[SO₂]=0.78.

Figure 2. Variation of SO₂ conversion with contact time at [CO]/[SO₂]=2.

Figure 3. Variation of SO₂ conversion with contact time at [CO]/[SO₂]=2.5.

Figure 4. Arrhenius Plot of Parameter A.

Figure 5a. Arrhenius Plot of Parameter B.

Figure 5b. Correlations of Arrhenius constants for parameter B with $[CO]/[SO_2]$ ratio.

Figure 6. Effects of contact time and [CO]/[SO₂] ratio on sulfur yield at 560 C.

Figure 7. Effect of $[CO]/[SO_2]$ ratio and reaction temperature on product distribution under a constant contact time of $0.09 \text{ s}^*g/cc$.

Figure 8. Effect of experimental conditions on light-off temperature of $\text{Cu}_{0.15}[\text{Ce}(\text{La})]_{0.85}\text{O}_x$ catalyst.

* pre-reduced by 2% CO for 1 h at 400 C.

Figure 9. Activation profile of 15 at% Cu-containing Cu-Ce-O catalysts in the reacting gas mixture.

Figure 10a. Variation of SO₂ conversion over Cu_{0.15}[Ce(La)]_{0.85}O_x catalyst with contact time at 440 C with [CO]/[SO₂]=2.

Figure 10b. Variation of SO₂ conversion over Cu_{0.15}[Ce(La)]_{0.85}O_x catalyst with contact time at 470 C with [CO]/[SO₂]=2.

Figure 10c. Variation of SO₂ conversion over Cu_{0.15}[Ce(La)]_{0.85}O_x catalyst with contact time at 510 C with [CO]/SO₂=2.

Figure 10d. Variation of SO₂ conversion over Cu_{0.15}[Ce(La)_{0.85}O_x catalyst with contact time at 560 C with [CO]/SO₂=2.

Figure 11. Arrhenius plots of reaction constant and induction time.

Figure 12. Plot of calculated conversion versus experimental data.