INVESTIGATION OF MIXED METAL SORBENT/CATALYSTS FOR THE SIMULTANEOUS REMOVAL OF SULFUR AND NITROGEN OXIDES

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ABSTRACT

Simultaneous removal of SO_2 and NO_x using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate several shortcomings of the individual SO_2 and NO_x removal operations. The work done at PETC and the DOE-funded investigation of the investigators on the sulfation and regeneration of alumina-supported cerium oxide sorbents have shown that they can perform well at relatively high temperatures (823-900 K) as regenerable desulfurization sorbents. Survey of the recent literature shows that addition of copper oxide to ceria lowers the sulfation temperature of ceria down to 773 K, sulfated ceria-based sorbents can function as selective SCR catalysts even at elevated temperatures, SO_2 can be directly reduced to sulfur by CO on CuO-ceria catalysts, and ceria-based catalysts may have a potential for selective catalytic reduction of NO_x by methane. These observations indicate a possibility of developing a ceria-based sorbent/catalyst which can remove both SO_2 and NO_x from flue gases within a relatively wide temperature window, produce significant amounts of elemental sulfur during regeneration, and use methane for the selective catalytic reduction of NO_x.

The objective of this research is to conduct kinetic and parametric studies of the selective catalytic reduction of NO_x with NH_3 and CH_4 over alumina-supported cerium oxide and copper oxide-cerium oxide sorbent/catalysts; investigate SO_2 removal at lower temperatures by supported copper oxide-cerium oxide sorbents; and investigate the possibility of elemental sulfur production during regeneration with CO or with CH_4-air mixtures.

The sorbents consisting of cerium oxide and copper oxide impregnated on alumina have been prepared and characterized. Their sulfation performance has been investigated in a TGA setup,

studying mainly the effects of temperature, sorbent composition, metal loading and support type. As a result of the sulfation experiments, a relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide as regenerable sorbents for sulfur dioxide removal. In the 723-823 K temperature range, cerium oxide-copper oxide sorbents have specific sorbent capacities (mass of sulfur removed per unit mass of metal sorbent) and sulfation rates significantly higher than those of cerium oxide and copper oxide sorbents used alone. Best sulfation performance was exhibited by the sorbent containing 1:1 molar ratio of cerium and copper. Specific sulfur capacities decreased as the coverage of the support surface by the metal oxides approached monolayer coverage. Sorbents appeared to be resistant to cycling. No loss of sulfation capacity was observed after the third cycle.

Preliminary evaluation of these sorbents for the selective reduction of NO_x gave promising results with ammonia, but indicated low selectivity when methane was used as a reductant. In the reduction of NO with NH_3, the conversion passes through a maximum at 573 K. The catalyst containing equimolar amounts of cerium and copper is not active for NO reduction by CH_4 at low temperatures and is not selective at high temperatures.

Since propylene is known to be a more active and selective reductant for NO with other SCR catalysts, the performance of Cu-Ce catalysts for SCR of NO with propylene has been investigated. Although propylene is very active in the absence of oxygen, the NO conversions obtained in wet oxygen-containing gases was limited to about 12.5% and 10.5% for Cu8Ce2 and Cu2Ce6 catalysts, respectively, for the space velocities employed in this research (about 13,700/hour). This was due to low selectivity at high temperatures and low activity at low temperatures. In fact, the NO conversion passes through a maximum at around 730 K and 740 K for Cu8Ce2 and Cu2Ce6 catalysts, respectively. It was observed that water has a negative effect on NO conversion for Cu-Ce catalysts; NO conversion reduces from 21% in the absence of water to 12.5% in the presence of 7% water on Cu8Ce2 catalyst.

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WORK DONE

I. Experimental

During this period, the main focus was on the performance of the NO reduction studies with propylene. The same experimental conditions as given in the previous report are used. Replacement parts for the ozone generator of the NO-NO_x analyzer were received and the equipment was repaired.

II. Results and Discussion

Figures 1 and 2 present the results for the effect of oxygen to methane ratio on NO reduction on two catalysts, Cu2.5Ce7.5 and Cu7.5Ce2.5, respectively. O/M ratio on the figures designates the molar ratio of oxygen to methane. The stoichiometric ratio of O/M for the complete oxidation of methane is 2. The conclusions that may be drawn from these figures are:

1. As the oxygen to methane ratio increases, the conversion of NO reduction decreases.
2. For oxygen to methane ratios less than the stoichiometric, NO conversions start at higher temperatures.
3. For oxygen to methane ratios less than the stoichiometric, copper content is important in the behavior of activity of NO reduction. There is no bendover for the catalyst with a Cu/Ce ratio of 1/3, while there is bendover for Cu/Ce ratio of 3. This observation may be explained by the fact that copper is a good oxidizing catalyst; therefore, as the copper to cerium ratio of the catalyst increases, selectivity of NO reduction to methane oxidation decreases.

The results of NO reduction by methane on sulfated (extent of sulfation=2%) Cu2Ce6 are presented on Figure 3. At this extent of sulfation, the effect of sulfation of the catalyst on the extent of NO reduction is not significant.

When propylene is used as a reductant, similar activity was observed for NO reduction on a catalyst with a copper to cerium ratio (by mass) of 4 and 1/3 as was presented in Figure 2 of the previous Progress Report. As in the case with methane as reductant, at 2% extent of sulfation, the effect of sulfation of the catalyst on the extent of NO reduction was not significant with propylene as the reductant.

Figures 4 and 5 present the effect of oxygen to propylene ratio on the extent of NO reduction on two catalysts, Cu8Ce2 and Cu2Ce6, respectively. These two catalysts have been selected for these experiments since copper is a good oxidizing catalyst and cerium is expected to make the copper catalyst more resistant to sulfur poisoning. O/P ratio on the figures designates the molar ratio of oxygen to propylene. The stoichiometric O/P ratio is 4.5 when propylene is used as a reductant. The O/P ratio of 18.75 corresponds to 1.5% (molar) oxygen in the reactant gases

The following conclusions are drawn from these figures:

1. As the oxygen to propylene ratio increases, the conversion of NO reduction decreases and the temperature where the catalysts become active for NO reduction increases. The second observation is opposite to what has been observed in the case of methane as the reductant.
2. In the absence of oxygen, there is no bendover in NO conversion for either of the catalysts. However, the light-off temperature for the catalyst with the higher copper to cerium ratio is lower than that with the lower Cu/Ce ratio. The bendover occurs with the O/P ratio of 18.75 due to the competition between NO reduction and propylene oxidation reactions. This behavior indicates that the activation energy of the former reaction is lower than that of the latter.
3. The light-off temperatures with propylene as the reductant are lower than those with

methane. Therefore, one can conclude that propylene activates NO at lower temperatures than methane, and thus, is a better reductant for NO reduction.

In the previous Progress Report, it was mentioned that addition of 3000 ppm SO_2 poisoned the Cu8Ce2 catalyst completely and irreversibly. The same experiment was repeated with the Cu2Ce6 catalyst: Activity was lost with the introduction of the sulfur dioxide, however, it was restored partially with oxygen at the reaction temperature, and completely with increasing temperatures. This is due to the fact that ceria is not reduced to metallic cerium easily and hence, does not form a sulfide. It is also expected to retard the reduction of copper under reducing conditions. Therefore, the sulfidation of copper will also be retarded.

A simple model was used to estimate the values of the activation energy for the NO reduction by propylene on the two catalysts employed. The assumptions used in deriving the model are that the reactor operates in the plug flow regime; the reaction kinetics is rate-limiting; and the reaction is first order with respect to NO concentration and zero order with respect to oxygen since oxygen is in large excess.

$$-r_{NO} = kC_{NO}$$

Therefore, the mole balance on NO in the reactor after integration gives:

$$k = -[U_g/(1-\varepsilon)L] \ln(1-X_{NO})$$

Where: k = reaction rate constant

U_g = superficial gas velocity, m/s

ε = porosity of the bed

L = bed height,m

X_{NO} = NO conversion

The dependence of k on temperature is expressed by using the Arrhenius relationship:

$$k = k_o \exp[-E/RT]$$

The values of the activation energy, E, from experimental NO conversion versus temperature data are as follows:

For Cu8Ce2 catalyst: E = 131 kJ/mol

For Cu2Ce6 catalyst: E = 199 kJ/mol

The performance of our catalysts were compared with the results of some work in literature. Kiel, et al (1) reported 45% NO conversion at 643 K on fresh CuO/SiO_2 catalyst with an activation energy of 68 kJ/mol and 65% NO conversion at 643 K on sulfated CuO/SiO_2 catalyst with an activation energy of 73 kJ/mol with ammonia used as reductant. Our catalysts showed similar behavior with ammonia. Our activation energies are larger with propylene used as reductant, indicating that ammonia is a more effective reductant that propylene.

Shimizu, et al(2) reported 20% NO conversion at 610 K with propylene used as reductant, with NO/P=0.5 and O_2/P=67 and dry reactant gases on a 8% CuO/alumina catalyst. Our Cu8Ce2 catalyst exhibited 21% NO conversion at 700 K under dry conditions and 12.5% NO conversion at 720 K with 7% water, with NO/P=1 and O_2/P=18.75. These are very comparable results.

Some of our catalysts were analyzed by ALCOA on XRD. Cu8Ce2 catalyst (SOR10-V) showed major chi-Al_2O_3; major CuO-type structure (tenorite); and major CeO_2. Cu5Ce5 catalyst (SOR10-II) exhibited major chi-Al_2O_3; major CeO_2; trace CuO-type structure (tenorite).

III. Additional Activities

A presentation, entitled “Selective Catalytic Reduction of NO by Hydrocarbons on Supported Copper-Oxide-Cerium Oxide Catalysts”, based on some results from this work was made at the AIChE Spring 2000 Meeting, Atlanta, GA, March 5-9, 2000.

FUTURE PLANS

It is planned:

1. to complete the experimental program;
2. to write the final report.

Errata for the October 1999 Report:

- Abstract, p.iv : space velocity is 13,500/hour instead of 46,000/hour.
- p.2, 3rd paragraph: Cu3Ce1 should be Cu1Ce3.
- Figure 1 was put in this report by mistake. It shows NO reduction data by methane (not propylene) in the absence of oxygen.
- Figure 2: Cu3Ce1 must be Cu1Ce3 in the legend of the figure.
- Figure 3: ‘dry’ must be ‘7% water’ and ‘7% water’ must be ‘dry’ in the legend of the figure.

FIGURE 1. NO Conversion by CH_4 on catalyst Cu2.5Ce7.5 in the presence of oxygen, wet

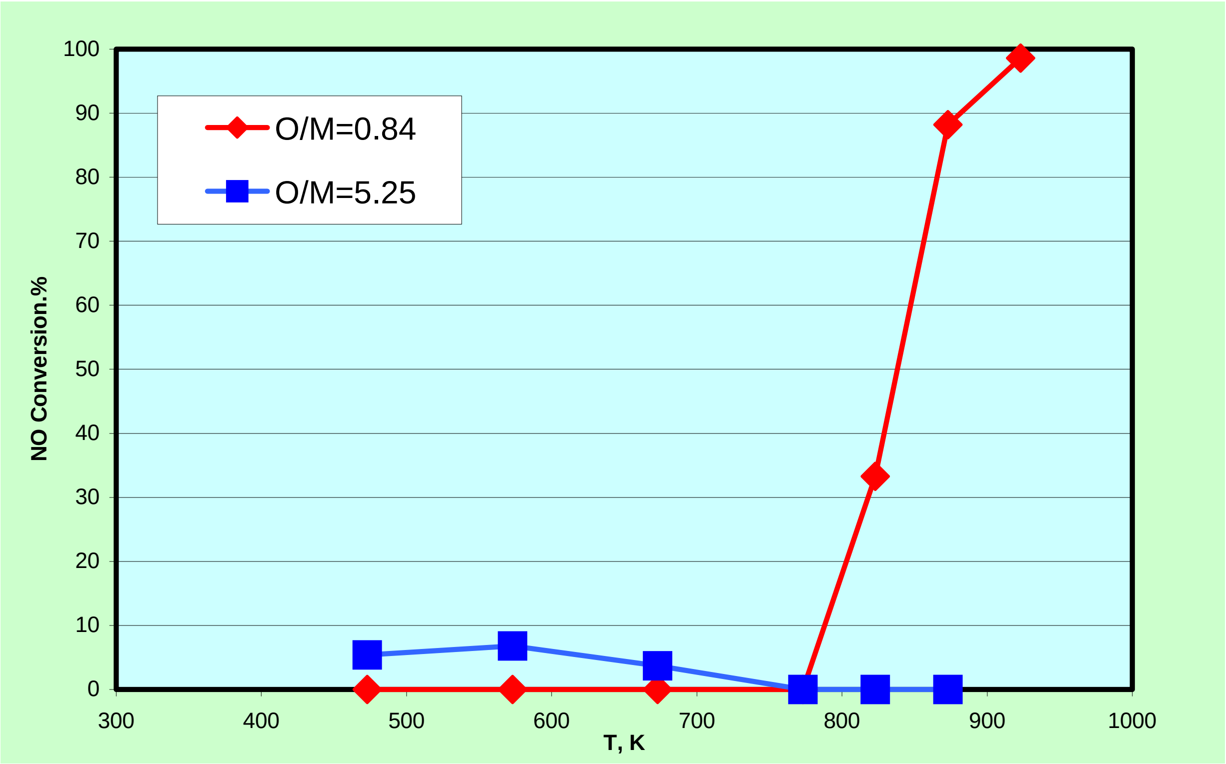

FIGURE 2. NO Conversion by CH_4 on catalyst Cu7.5Ce2.5 in the presence of oxygen, wet

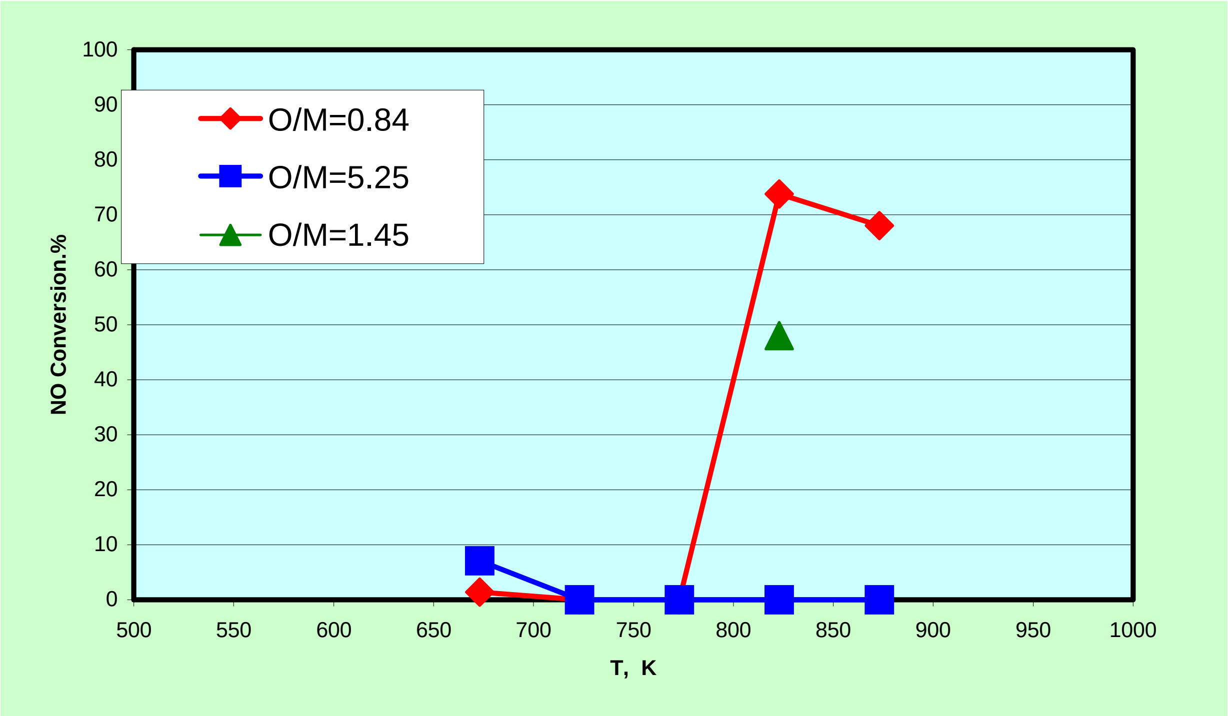

FIGURE 3. NO Conversion by CH_4 on sulfated catalyst Cu2Ce6 in the presence of oxygen, wet, (O_2/CH_4=5.25)

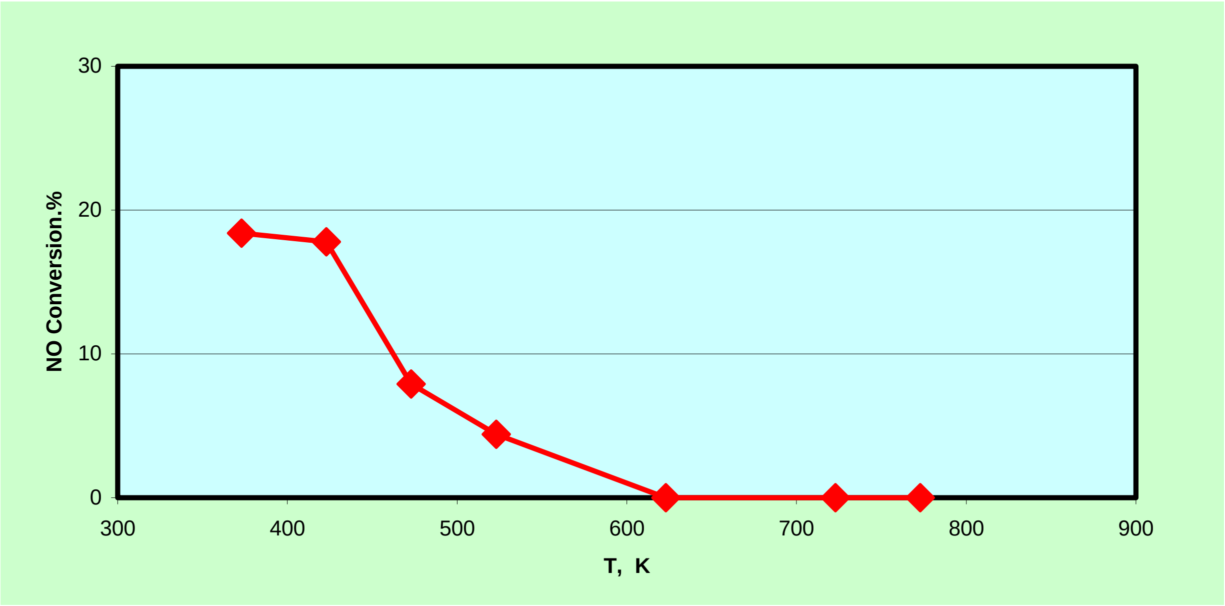

FIGURE 4. NO Conversion by C_3H_6, Cu8Ce2 catalyst, wet, NO/P=1

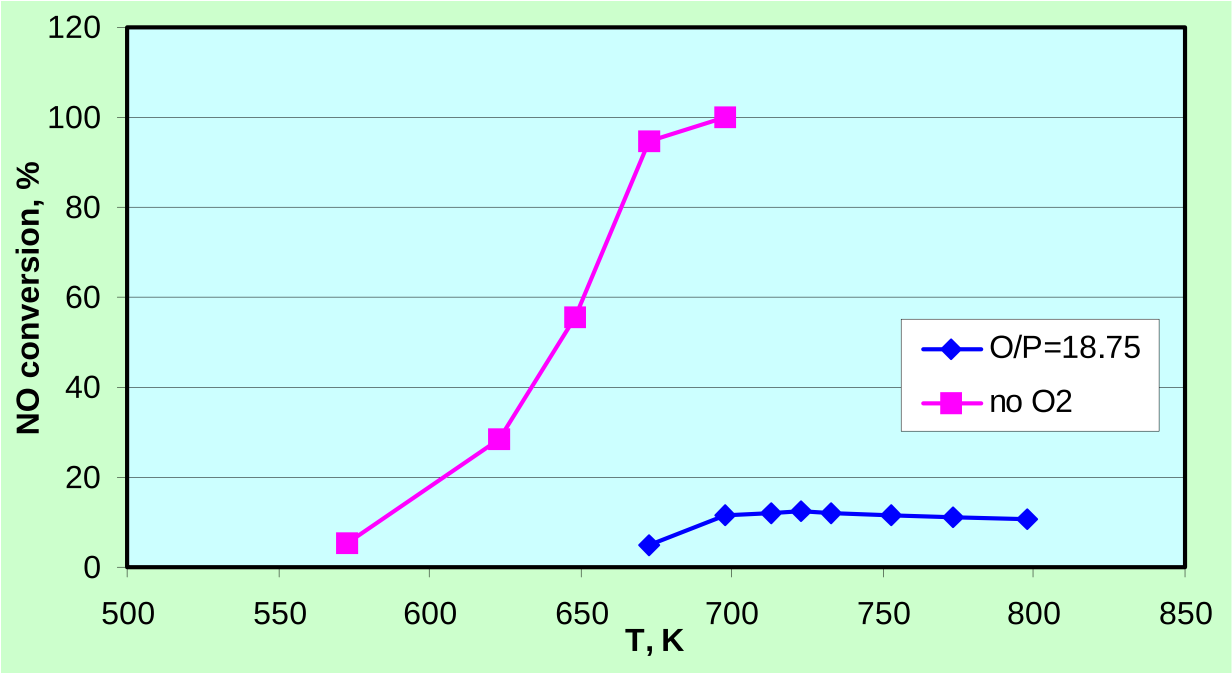

FIGURE 5. NO Conversion by C_3H_6, Cu2Ce6 catalyst, wet, NO/P=1