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Catalytic Reduction of Sulfur Dioxide[1]

INTRODUCTION

Many processes have been utilized with varying degrees of success for removal of sulfur dioxide from flue gases. Quite a few more have been proposed. One type of process that would appear quite attractive is the reduction of the SO_2 to sulfur. Numerous papers and patents pertaining to this subject have appeared. Bauxite- and alumina-supported systems (*1*), in particular, have received considerable attention. A variety of reducing agents have been used, the most common of which are H_2, CH_4, and CO. Operating temperatures between 300 and 600°C are generally required and substantial amounts of H_2S thus result from reactions of the sulfur produced with hydrogen. Thermodynamic and kinetic studies of this system suggest that temperatures much lower than 400°C should be used in order to minimize the H_2S formation (*2*). In those cases where CO has been used as the reductant, COS formation often plagues the systems.

The present work was undertaken to examine the effect of using an extremely active hydrogenation catalyst to promote the reduction of SO_2 with H_2 at low enough temperatures such that H_2S formation could be minimized. Ruthenium on γ-alumina was examined and found to be quite active at temperatures as low as 150°C. These results are discussed in the work described herein.

EXPERIMENTAL

γ-Alumina ($\frac{1}{8}$-in. pellets, surface area ~100 m^2/g), 0.5% Ru/alumina ($\frac{1}{8}$-in. pellets, surface area ~100 m^2/g), 5% Ru/alumina (powder, surface area 80–100 m^2/g), and ruthenium metal were obtained from Strem Chemicals. A sample of 10% Ru/alumina ($\frac{1}{8}$-in. pellets, surface impregnated) was obtained from Englehard Industries. Mass spectral data were obtained on a CVC Products mass spectrometer. All experiments were performed under static conditions in an apparatus consisting of a 250-ml round-bottom flask equipped with a greaseless stopcock connected to a manifold (~100 ml) with inlets for SO_2, H_2, and vacuum. Pressure was monitored using a Validyne readout (0–1000 Torr).

$SO_2 + H_2$ (1:2 ratio). In a typical experiment, the 250-ml vessel was loaded with 0.9 g catalyst and activated at 400°C under vacuum for 1 hr. Upon cooling, the vessel was attached to the manifold and the system was pressurized with SO_2 and H_2 in a 1:2 ratio. The total initial pressure was varied such that maximum pressure of 750–800 Torr was not exceeded during the experiment. A preheated mantle was then placed around the bottom of the flask. Usually 30 min was required for temperature equilibration, after which pressure and temperature readings were taken every 15 min, more often for the faster rates. A typical run duration was 5–6 hr. Ignoring the pressure contribution of the H_2O and sulfur formed, which condensed onto the cooler glass surfaces, the

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pressure drop was roughly proportional to the reaction rate. A final pressure reading was made at room temperature to obtain a crude measurement of the percentage SO_2 converted to sulfur. The experimental data for various runs are given in Table 1. The rates reported are those observed during the first 3 to 4 hr of each experiment. Mass spectral analyses were performed on the residual gaseous products and no measurable amount of H_2S was found and the only products obtained were sulfur and water.

To test for poisoning in the system, a series of 12 successive runs were performed using the same conditions above (0.5% Ru/alumina, 156°C, 200 Torr SO_2, 400 Torr H_2, 6 hr). The same catalyst and vessel were used for the entire series of experiments. The vessel was cooled to room temperature after each run and then evacuated, refilled, and reheated. Due to vessel design, sulfur droplets fell onto the catalyst after substantial amounts collected on the walls of the vessel. Thus, a decline in activity was observed simply due to a sulfur coating which hindered gas contact. During the final run a pressure drop of 0.2 Torr/min was observed. The vessel was evacuated, filled with 600 Torr H_2 and heated to 400°C for 2 hr. A repeated SO_2/H_2 reduction run after this showed no change and again a pressure drop of 0.2 Torr/min was observed. Full activity was restored by reactivation of the catalyst at 400°C under vacuum for 4 hr. Elemental sulfur sublimed from the catalyst bed during this operation.

$SO_2 + H_2$ (variable ratio). Under the standard conditions described above, 0.5% Ru/alumina was examined at 156°C with varying SO_2/H_2 ratios for 5½ hr reaction times. These data are presented in Table 2. No H_2S was observed in the products even under large excess of H_2.

$SO_2 + CH_4$; $SO_2 + CO$. Under the standard reaction conditions the reaction of SO_2 and CH_4 was examined (5% Ru/alumina, 152°C, 200 Torr SO_2, 400 Torr CH_4, 4 hr). No reaction was observed either by pressure drop or by mass spectral analysis.

Similarly, the reaction of SO_2 and CO (5% Ru/alumina, 200°C, 200 Torr SO_2, 400 Torr CO, 5½ hrs) failed to yield appreciable pressure drop and only a trace of products (CO_2) was observed in the mass spectrum of the remaining gases.

$NO + H_2$; $NO + SO_2 + H_2$. The standard reaction conditions were used to examine the reaction of NO and H_2 (5% Ru/alumina, 156°C, 51 Torr NO, 551 Torr H_2, 5½ hrs). At the end of the reaction, mass spectral analysis revealed that all of the NO had been consumed and N_2 and H_2O were the only products observed. In

TABLE 1

SO_2 (Torr)	H_2 (Torr)	Temp (°C)	Catalyst	Pressure drop (Torr/min)	Turnover $\left(\frac{\text{mmoles } SO_2}{\text{mmoles Ru} \cdot \text{hr}}\right)$
200	400	156	0.5% Ru/Al_2O_3	~0.5	~3
200	400	200	0.5% Ru/Al_2O_3	~1.1	~6.5
160	320	250	0.5% Ru/Al_2O_3	~3	~18
160	320	300	0.5% Ru/Al_2O_3	~10–12	~65
160	320	300	γ-Al_2O_3	~0.2–0.3	~1.5[a]
200	400	156	5% Ru/Al_2O_3	~4–5	~3
200	400	156	10% Ru/Al_2O_3	<0.05	—
200	400	156	Ru metal (99.95%)	No reaction	—

[a] Turnover expressed as mmoles SO_2/hr.

TABLE 2

SO_2 (Torr)	H_2 (Torr)	SO_2 converted to sulfur (%)
50	550	>90
100	500	~31
200	400	~20
400	200	~3

Note. 0.5% Ru/Al_2O_3, 156°C, $5\frac{1}{2}$ hr.

the initial stages of the reaction a pressure drop of ~1 Torr/min was observed (not compensated for N_2 produced).

A similar experiment was performed using a mixture of NO, SO_2, and H_2 (5% Ru/alumina, 156°C, 500 Torr NO, 200 Torr SO_2, 400 Torr H_2, $5\frac{1}{2}$ hrs). Mass spectral analysis of the volatile products showed NO, SO_2, N_2, H_2O, and a trace of N_2O, in addition to elemental sulfur coating the walls of the vessel. A pressure drop of 2–3 Torr/min was observed (not compensated for N_2 produced).

RESULTS AND DISCUSSION

The reactions described in the experimental section and the corresponding results depicted in Tables 1 and 2 were obtained in a static system with natural convection as the only means of contacting the gases with the catalyst. These conditions are by no means the optimum ones for this type of reaction, so the extreme activity observed for ruthenium/alumina is indeed quite remarkable. This reactivity can be calibrated somewhat by comparison to the reactivity of γ-alumina under the same conditions. The 0.5% Ru/Al_2O_3 shows good reactivity at 156°C (0.5 Torr/min, turnover = 3 mmoles SO_2/mmoles Ru · hr), while γ-alumina is essentially unreactive at this temperature. At temperatures where γ-alumina has appreciable activity (300°C, 0.2–0.3 Torr/min), 0.5% Ru/Al_2O_3 is almost too reactive to get anything but an estimate of the rate (300°C, 10–12 Torr/min). The 5% Ru/Al_2O_3 (4–5 Torr/min, turnover = 3 mmoles SO_2/mmoles Ru · hr) gave a reduction rate ~10 times faster than the 0.5% Ru/Al_2O_3. Since the rate increased proportionally to the ruthenium percentage, 10% Ru/Al_2O_3 and ruthenium metal were tested. The surface impregnated 10% Ru/Al_2O_3 catalyst showed only slight activity, while ruthenium metal had no activity as a catalyst for the reduction of SO_2 with H_2. Surface area differences for these latter two catalysts limit the accuracy of these comparisons, especially for the ruthenium metal.

An important consideration in SO_2 reduction experiments where sulfur is generated, is catalyst poisoning. A series of repeated runs using 0.5% Ru/Al_2O_3 showed a slow decrease in reaction rate. This decrease in rate, we feel, is a consequence of our static system which allowed sulfur to drop back onto the catalyst and perhaps hinder gas contact. This hypothesis is not inconsistent with the return of 100% of the activity for this catalyst by simply heating under vacuum and subliming off sulfur. It is interesting to note that heating the catalyst at 400°C with hydrogen did not restore the activity. While these data do not preclude loss of activity by sulfide formation, it might be expected that a surface sulfide would react with H_2 to yield H_2S at 400°C and some return of activity to the catalyst would be expected.

The data presented in Table 2 indicate that the stoichiometry of the reactants (SO_2 and H_2) need not be controlled precisely. Clearly some excess H_2 is desirable but an acceptable rate is observed when stoichiometric amounts of SO_2 and H_2 are available. Because of the low temperature of operation (156°C), the reaction of sulfur with excess H_2 to yield H_2S, does not occur to a measurable extent even where a large excess of H_2 is available and >90% of the SO_2 has been consumed. Both characteristics would be particularly advantageous should such a system be applied directly to the removal of SO_2 from flue gases.

A number of other potentially reactive species are present in flue gases in addition to SO_2. Thus a variety of experiments were performed to test the effects of such species as NO, CO, and CH_4 on the reaction under study. The reduction of NO with H_2 has been examined extensively and Ru/Al_2O_3 not only catalyzes the reaction but promotes N_2 formation (*3*). For comparison this reduction was examined under our experimental conditions using 5% Ru/Al_2O_3 and then a mixture of NO, SO_2, and H_2 was examined. Reduction of both NO and SO_2 was observed to occur with a total pressure drop of 2–3 Torr/min. The products obtained were N_2, S_8, H_2O, and a trace of N_2O, in addition to unreacted NO and SO_2.

The reaction of CO and SO_2 has also been studied quite extensively over a variety of catalysts (*4*). Under our conditions even at 200°C, no appreciable reaction of CO with SO_2 was observed over 5% Ru/Al_2O_3. Since Ru/Al_2O_3 catalyzes the conversion of CO and H_2 to hydrocarbons (Fischer–Tropsch reactions) at moderate temperatures, the mixture of CO, SO_2, and H_2 was not examined. Methane, however, is a major product of this Fischer–Tropsch chemistry, so the reaction of CH_4 with SO_2 was studied. Again numerous such studies over a variety of catalysts have been reported (*1*, *5*). But at 152°C under our experimental conditions, no reaction of CH_4 with SO_2 was observed over 5% Ru/Al_2O_3 catalyst. These data suggest then that NO, CO, and CH_4 will not hinder the reduction of SO_2 with H_2 over Ru/Al_2O_3 under our experimental conditions. The Fischer–Tropsch reaction of CO and H_2, however, does present one complication that might arise should this catalyst be used directly in the reduction of SO_2 with H_2 in flue gas streams. The increased H_2 consumption would probably necessitate the removal of the CO from the NO and SO_2 prior to the reduction step with H_2.

In summary, Ru/Al_2O_3 has been found to be quite active as a catalyst for the reduction of SO_2 with H_2 to sulfur and H_2O, at temperatures low enough that H_2S formation is not a problem. The stoichiometry of reactants does not have to be precisely controlled. Poisoning of the catalyst has not proved to be a problem. Nitric oxide reduction occurs readily under the same conditions with no apparent complication arising from the simultaneous reduction of both NO and SO_2. These data would thus suggest that this catalyst should be examined for possible direct application to desulfurization of flue gases.

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