CHEMISTRY LETTERS, pp. 721-724, 1983.

SIMULTANEOUS REMOVAL OF NO_x AND SO_x FROM FLUE GAS. EFFECTS OF MOLTEN SALT REACTION MEDIA

Tsutomu SHIKADA,* Takamasa OBA, Kaoru FUJIMOTO, and Hiro-o TOMINAGA

Department of Synthetic Chemistry, Faculty of Engineering,

The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Among the several combinations of hydrogensulfate salts tested, a molten salt of $NaHSO_4/LiHSO_4$ was shown to be most effective as a reaction medium for the simultaneous removal of NO_x and SO_x from flue gas catalyzed by V_2O_5. ESR study revealed that V_2O_5 dissolved in the molten salt was partly reduced, during the reaction, to V^{4+} suggesting a redox cycle of vanadium constituted an essential part of the catalysis.

It has been already reported that the simultaneous removal of NO_x and SO_x from flue gas proceeds in a molten salt of $NH_4HSO_4/NaHSO_4$ system containing dissolved V_2O_5 in the temperature range of 150 to 200°C.[1] Addition of various transition metal sulfates has been also found to promote the removal of SO_2 markedly. In the present work, the influence of molten salts as the reaction media on the simultaneous remorval of NO_x and SO_x was investigated. It was found that the molten salts containing lithium compounds were particularly effective for the removal of NO. The change in oxidation state of vanadium in liquid phase was also studied.

Experimental apparatus and procedures, conditions of reaction, and analytical methods of NO and SO_2 were similar to those described in the preceding paper.[1] Melting points of various reaction media were measured with a differential thermal analyzer. ESR spectra of the reaction media, both before and after the reaction, were recorded at room temperature using an ESR spectrometer (X-band, 100 kHz/s). The concentrations of V^{4+} in the liquid media were obtained from two-stage integral values of the ESR signals using an analogue-type integrator.

Table 1 shows the extent of NO and SO_2 removal in several molten

hydrogensulfate mixtures (with various melting points) containing dissolved V_2O_5 catalyst. In $NH_4HSO_4/NaHSO_4$ solution, the simultaneous removal of NO and SO_2 proceeded in the temperature range of 130 to 190°C as already reported.[1] It was suggested that SO_2 was oxidized and reacted with NH_3 and H_2O to form NH_4HSO_4 which was held in the reaction medium while NO was reduced by NH_3 to form N_2. When $KHSO_4$ was used insted of $NaHSO_4$, NO conversion decreased and SO_2 conversion increased markedly. The potassium salt in the reaction media seems to increase the catalytic activity of V_2O_5 for the oxidation of SO_2 as in the case where K_2SO_4 is used as a promoter for SO_2 oxidation catalyzed by V_2O_5.[2] However, the melting point of the salt including $KHSO_4$ was high as shown in Table 1 although the mixture of the salt and V_2O_5 used for the reaction showed a liquid state at 160°C. Therefore, the salt is unsuitable as the medium for the present purpose. When $LiHSO_4$ was used in place of $NaHSO_4$, NO conversion increased markedly while the conversion of SO_2 remained almost unchanged. Using the molten salt composed of $NaHSO_4$ and $LiHSO_4$, higher NO conversion, 71%, was obtained. In addition, a slight increase of SO_2 conversion was observed. The molten salt of $NaHSO_4/LiHSO_4$ system has a melting point of 112°C which is well favored for the reaction media. Thus, high conversions of NO were obtained by use of the reaction media containing $LiHSO_4$. Similar action of lithium salts has been observed in the case of the reduction of NO with ammonia on supported V_2O_5 catalysts,[3] although the role of lithium salts for reaction of NO was not clear.

Table 1 Effect of reaction media

Medium (Molar ratio 1/1)	Melting point of medium (°C)	Conversion (%) NO	Conversion (%) SO_2
$NH_4HSO_4/NaHSO_4$	104	22.4	33.0
$NH_4HSO_4/KHSO_4$	172	11.7	51.2
$NH_4HSO_4/LiHSO_4$	92	59.3	34.1
$NaHSO_4/LiHSO_4$	112	71.1	46.4

Gas composition : NO 300 ppm, SO_2 400 ppm, NH_3 450 ppm, O_2 5 vol%, H_2O 10 vol%, N_2 balance

Catalyst : V_2O_5 (5 wt%)

Temperature : 160°C

It has been reported that the addition of transition metal sulfates to the

reaction media of $NH_4HSO_4/NaHSO_4$ increases markedly the catalytic activity of V_2O_5 for SO_2 removal.[1] The $NaHSO_4/LiHSO_4$ media containing various transition metal sulfates were studied in order to increase the SO_2 removal. The results are shown in Table 2. While the addition of $CuSO_4$ or $Ti(SO_4)_2$ brought about an increase of SO_2 conversion, that of $Zr(SO_4)_2$ accelerated NO conversion.

The change in the oxidation state of vanadium in the reaction liquid, both before and after the reaction, was investigated by use of an ESR spectrometry. The ESR spectra are shown in Fig. 1. A powder of V_2O_5 exhibited an unsymmetrical absorption line. The molten salt gave, before reaction, an ESR spectrum due to V^{4+} with ambiguous splitting of the hfs. The sample, after 2 h of experimental use at 160°C, exhibited the spectrum with well-resolved hfs which is characteristic of solution.[4] It is apparent from the results that V_2O_5 was soluble in the media during the reaction. The percentages of V^{4+} to the total of vanadium in the reaction liquid were, given in Fig. 1, 6.4 and 39.2%, respectively, indicating that V^{5+} was reduced to V^{4+} during the reaction. The catalysis of V_2O_5 for the present reactions is supposedly correlated with the redox mechanism which is similar to that of supported V_2O_5 for the reduction of NO with ammonia.[5]

Table 2 Effect of sulfate additives

Additive (1 wt%)	Conversion (%) NO	SO_2
-	71.7	46.4
$Zr(SO_4)_2$	81.8	44.2
$CuSO_4$	68.4	61.5
$Ti(SO_4)_2$	74.1	52.2

Medium : $NaHSO_4/LiHSO_4$ (1/1 molar ratio)
Catalyst : V_2O_5 (5 wt%)
Temperature : 160°C

In conclusion, a molten salt of $NaHSO_4/LiHSO_4$ system was found most effective as the reaction medium for the catalytic removal by V_2O_5 of both NO_x and SO_x in the presence of ammonia and oxygen.

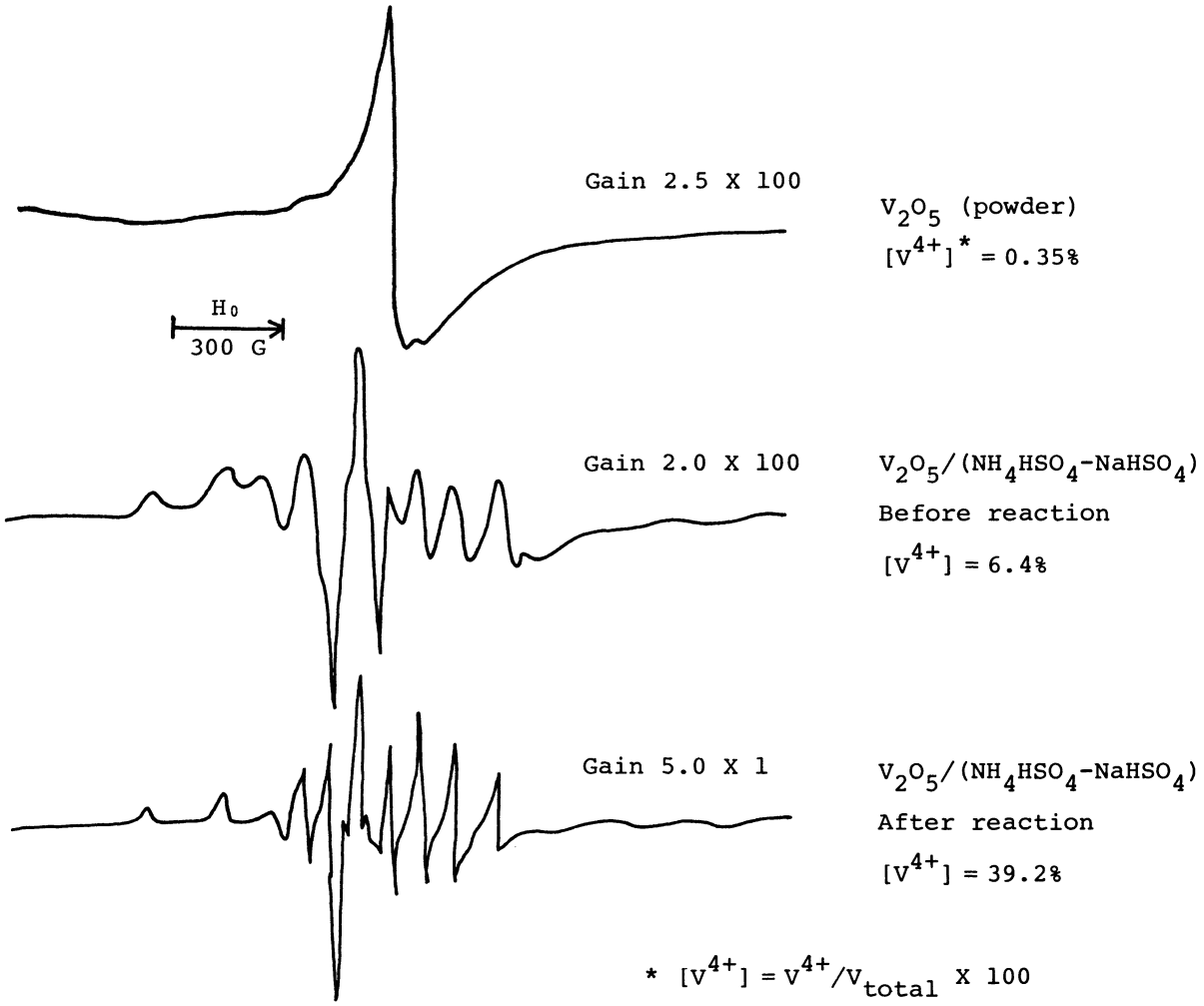

Fig. 1 ESR spectra of V_2O_5 and molten salts containing V_2O_5 before and after reaction

References

1) T. Shikada, T. Oba, K. Fujimoto, and H. Tominaga, Chem. Lett., 1983, 511.

2) J.K. Dixon and J.E. Longfield, "Catalysis VII," ed by P.H. Emmett, Reinhold Pub. Corp., New York (1960), p.322.

3) T. Shikada and K. Fujimoto, Chem. Lett., 1983, 77.

4) K. Ishizu, "Jitsuyo ESR Nyumon," Kodansha, Tokyo (1981).

5) T. Shikada, H. Ogawa, K. Fujimoto, and H. Tominaga, Nippon Kagaku Kaishi, 1983, 141.

(Received February 28, 1983)