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SIMULTANEOUS REMOVAL OF NO_x AND SO_x FROM FLUE GAS BY USE OF MOLTEN HYDROGENSULFATES AS REACTION MEDIA

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The simultaneous removal of NO_x and SO_x by reaction with ammonia from flue gas was found to be attained at temperature ranging from 150 to 200°C in molten salts of hydrogensulfates dissolving V_2O_5. The addition of transition metal sulfates such as $Ti(SO_4)_2$, $Zr(SO_4)_2$ or $CuSO_4$ led to a marked increase in the SO_x removal.

Solid catalyzed gas phase reduction of nitrogen oxides with ammonia has been considered to be the most promising process for the removal of NO_x in flue gases emitted from staitionary sources such as boiler and furnace.[1-5] However, in the case of flue gases containing SO_2 the latter pollutants are not removed in the method and hence another equipment is required for removing them. It is desirable as second generation for the flue gas cleaning techniques that NO_x and SO_x are simultaneously removed in the same reactor and that the reactions proceed in the temperature range from 100 to 200°C. The authors have performed the simultaneous removal of NO_x and SO_x by use of low-melting molten salts as reaction media taking into considerations the following three facts.

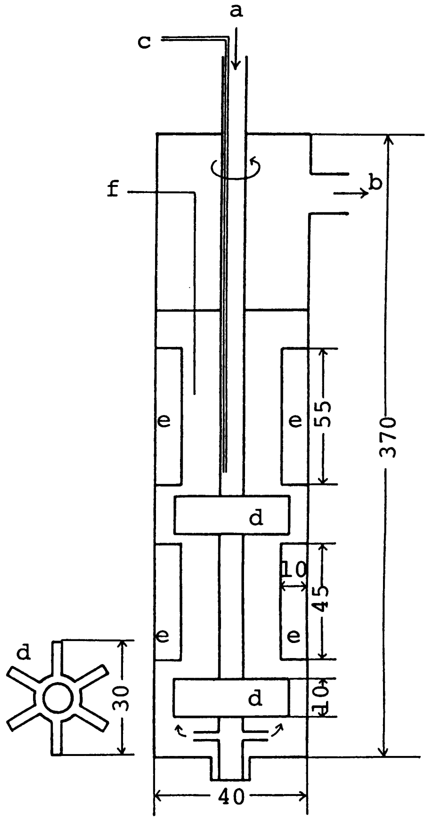
1) Supported vanadium oxide catalysts show high activities for the reduction of NO with ammonia even when they are covered with several tenth percent by weight of ammonium hydrogensulfate.[6,7]
2) A equimolar mixture of ammonium hydrogensulfate and sodium hydrogensulfate keeps a low viscosity liquid state in the temperature range 100-200°C.
3) Various metal sulfates and oxides are highly soluble in the molten salt above mentioned.

It is expected in this reaction system that NO is reduced to N_2, while SO_2 is fixed as SO_4^{2-} in the reaction media, as shown in the following equations.

$$NO + NH_3 + 1/4\ O_2 \longrightarrow N_2 + 3/2\ H_2O \qquad (1)$$

$$SO_2 + 1/2\ O_2 + NH_3 + H_2O \longrightarrow NH_4HSO_4 \qquad (2)$$

In the above equations, O_2 is from excess air added to fuel for complete combustion. In the present work, it has been found that V_2O_5 shows a high catalytic activity for the removal of both NO_x and SO_x and the addition of various transition metal sulfates leads to a marked increase in the removal of SO_x. The details are described here.



a: Gas inlet, b: Gas outlet, c: Ammonia water, d: Stirrer, e: Baffle, f: Thermocouple

Fig. 1. Stirred vessele and impeller

All chemicals used in this experiment for reaction media and catalysts were reagent grade. Catalyst consisting of V_2O_5-NH_4Br-TiO_2-SiO_2 was prepared by a conventional impregnating method as described previously.[8)] A continuous flow type reaction apparatus was employed at atmospheric pressure. Fig. 1 shows the reactor which is an agitated bubble type one equipped with two stirrers. Reaction conditions adopted were as follows: amount of molten salt, 3.2 mol (250 ml); catalyst concentration, 5 wt%; gas flow rate, 1000 ml/min; inlet gas composition, 300 ppm of NO, 400 ppm of SO_2, 450 ppm of NH_3, 5% O_2, 10% H_2O in N_2; stirring speed, 1200 rpm. Nitrogen monoxide and sulfur dioxide were analyzed by a chemiluminescence NO/NO_x meter and a controlled potential electrolysis SO_2 meter, respectively.

The molten salt composed of 50 mol% of NH_4HSO_4 and 50 mol% of $NaHSO_4$ was employed as reaction media. The melting point of the salt was 104°C and the viscosity was 45 cP at 190°C. In cases of reaction in a solution, the catalysis by the solvent itself or adsorption of NO_x and SO_x to the solvent is not negligible. Details of the effect of reaction media will be reported in a subsequent paper. It may be concluded that the reaction medium is virtually inactive in the removal of NO while SO_2 is absorbed in the medium to some extent. Sulfur dioxide seems to be absorbed in an unstable form, probably as ammonium sulfite in the absence of catalyst.

Table 1 Catalytic activities of various compounds

Catalyst	Conversion (%)	
	NO	SO_2
V_2O_5-NH_4Br-TiO_2-SiO_2	4.7	32.5
NH_4VO_3	6.1	31.1
V_2O_5	22.4	33.0
$Ti(SO_4)_2$	0	32.6
$CuSO_4$	0	13.1

Medium : $NH_4HSO_4/NaHSO_4$ (1/1 molar ratio)
Catalyst concentration : 5 wt%
Temperature : 160°C

Table 1 shows the catalytic activities of various compounds added into the molten salt on the removal of NO and SO_2. V_2O NH_4Br-TiO_2-SiO_2 catalyst, which has been shown to be highly active at temperatures as low as 150°C for the reduction of NO with ammonia by the present authors,$^{8)}$ was powdered to sizes smaller than 100 mesh and dispersed in the reaction media. All other compounds which were added to the reaction media were soluble in the media. From the results shown in Table 1, V_2O_5 showed a high activity for the removal of NO while all compounds tested, except $CuSO_4$, showed about the same activities for removal of SO_2. Sulfur dioxide is removed by reaction media alone (22.5% conversion of SO_2 at 160°C) and hence the effect of addition of catalyst does not seem to be so much large. However, SO_2 is trapped as more stable form,$^{9)}$ probably as ammonium hydrogensulfate in the presence of catalyst as described above. On the other hand, it is confirmed by the experiment using relatively high concentrations (2-3%) of NO, NH_3 and O_2 balanced He that NO is

Table 2 Effect of sulfate additives

Additive 1. (1wt%)	Additive 2. (1wt%)	Conversion (%)	
		NO	SO_2
-	-	40.0	27.8
$Ti(SO_4)_2$	-	48.1	45.3
$Zr(SO_4)_2$	-	45.3	52.9
$CuSO_4$	-	40.0	59.9
$Ti(SO_4)_2$	$CuSO_4$	42.0	70.0
$Ti(SO_4)_2$	$Zr(SO_4)_2$	34.4	44.0

Medium : $NH_4HSO_4/NaHSO_4$ (1/1 molar ratio)
Catalyst : V_2O_5 (5 wt%)
Temperature : 190°C

reduced by NH_3 to N_2 (Eq. 1).[9] Thus, V_2O_5 was found to be effective as the catalyst for the simultaneous removal of NO and SO_2.

The addition of various transition metal sulfates has been tried in order to increase the conversions of NO and SO_2. The experiments were carried out in the media containing 5% by weight of V_2O_5 and 1% by weight of $Ti(SO_4)_2$, $Zr(SO_4)_2$ or $CuSO_4$ The results are given in Table 2. The addition of the sulfates promoted the removal of SO_2 by about two times in SO_2 conversion. The simultaneous addition of two kinds of sulfates was not so much effective. On the other hand, the addition of these sulfates was scarcely effective for the enhancement of NO removal.

In summary, the simultaneous removal of NO and SO_2 was achieved at relatively high levels in the molten salts of NH_4HSO_4/$NaHSO_4$ system containing dissolved V_2O_5. The addition of various transition metal sulfates enhanced markedly the removal of SO_2.

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