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Catalytic reduction of nitric oxide by hydrogen sulfide over γ-alumina

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The ability of H_2S to reduce NO in a fixed bed reactor using a γ-alumina catalyst was studied with the objective of generating new methods for conversion of NO to N_2. Compared to the homogenous reaction of NO with H_2S, the catalyzed reaction showed improved conversions of NO to N_2. Using a gas space velocity of 1000 h^{-1} and a feed of 1% NO and 1% H_2S in argon, it was found that the conversion of NO to N_2 was complete at 800 °C. This result compared to a 38% conversion of NO to N_2 for the homogeneous gas phase reaction at 800 °C. At temperatures below 800 °C, a short fall in the nitrogen balance was discovered when the γ-alumina was employed as a catalyst. This discrepancy was explained by conversion of NO to NH_3 and subsequent reaction of the NH_3 with any SO_2 in the system to form ammonium sulfur oxy-anion salts. This suggestion is supported by the finding that when larger amounts of H_2S were used relative to NO, more NH_3 was formed together in tandem with lower N_2 mass balances. Several reaction pathways have been proposed for the catalytic reduction of NO by H_2S.

KEY WORDS: NO; H_2S; selective catalytic reduction; gamma alumina.

1. Introduction

The oxides of nitrogen (NO_x) are emitted from many industrial processes and are considered to be major contributors to atmospheric pollution. The past three decades have brought about strict new limits on the amount of NO_x industries are allowed to release into the atmosphere due to their contribution to acid rain, trace metal leaching in soils and other detrimental effects on the environment [1]. Therefore, it is important to develop new and efficient technologies for removing NO_x from exhaust gases.

One of the most effective methods of removing NO_x from industrial exhaust gases is the selective catalytic reduction (SCR) of NO_x [2–7]. The reducing gas for the SCR process has predominantly been ammonia but hydrocarbons and hydrogen can also be used to convert NO_x to nitrogen. As all three of these reducing agents generally need to be synthesized and shipped to the facility producing NO_x, it would be beneficial to utilize a reducing agent already present in the plant producing the NO_x. One such reducing agent is H_2S which is present in abundance in most oil refineries and hydrocarbon processing plants. Instead of converting H_2S directly to sulfur as is the normal practice, it may be possible to utilize this reducing agent for deNO_x purposes. The limited studies previously reported on the use of H_2S for SCR of NO_x have shown that hydrogen sulfide can reduce NO_x to nitrogen [8,9], but, to date, deNO_x with H_2S does not appear to have been implemented commercially.

The overall reaction of NO and H_2S could occur according to the following equation, assuming that the process is conducted at temperatures at which S_2 is the major allotrope present in sulfur vapor.

$$2H_2S + 2NO \rightarrow S_2 + N_2 + 2H_2O \qquad (1)$$

In reaction 1, the H_2S reduces the NO to N_2 while also producing sulfur and H_2O, although partially reduced nitrogen containing species would be formed as intermediates and SO_2 may form by the reverse Claus reaction (see later discussion).

Two articles published by Korsh and Ivanovski describe the reduction of NO by H_2S to form H_2O, N_2 and sulfur [8,9]. With a feed gas containing 3.10% NO and 0.25% H_2S, these researchers reported 100% transformation of NO at 200 °C over NiS and CuS and 100% conversion at 150 °C over FeS. NH_3 formation was reported at higher temperatures and was explained by reaction 2.

$$NO + 5/2H_2 \rightarrow NH_3 + H_2O \qquad (2)$$

NH_3 formation using H_2S was also reported by other researchers during the SCR of NO_x, especially if SO_2 was present [10,11]. The aforementioned papers speculated that the NH_3 could also be bound up in the catalyst as is, or could react with other species in the reactor to yield ammonium salts such as ammonium sulfate and ammonium nitrate. The salt accumulation on the catalyst surface was reported at low temperatures, but no formation was observed at higher temperatures. Jung *et al.* stated that at temperatures >400 °C, conversion rates to NH_3 increased and the rate of the SCR of NO decreased [12]. The production of ammonium compounds could adversely affect the SCR

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reaction by pore filling with stable salts or adsorption of ammonium compounds onto active sites of the catalyst. Therefore, the presence of any salts needs to be determined and subsequently avoided.

γ-Al_2O_3 is a widely used catalyst for much of the research carried out on the SCR of NO_x using NH_3 because of its high surface area and thermal stability [13,14]. γ-Al_2O_3 is often used as a support, but it has been suggested that it is also responsible for certain steps of the SCR reaction [15]. The conclusions drawn from calculations made by Sohlberg *et al.* [16] suggest that reaction of the alumina surface with H_2O can result in oxide sites with hydrogen species migrating into the bulk lattice. Overall, it was calculated that γ-Al_2O_3 units can release three hydrogen atoms and take in one aluminum atom from the surface to satisfy valence requirements on reaction with H_2O. These calculations indicate that γ-Al_2O_3 should possess both oxidizing and reducing sites that could contribute to the catalytic pathways for NO_x conversion to N_2. Thus alumina, without any additional active species derived from transition metal promoters may be an effective catalyst for NO_x conversion.

In this work, an investigation of the catalytic reduction of NO with H_2S over γ-Al_2O_3 has been undertaken by studying the rates of formation of products at various temperatures and ratios of NO:H_2S with the aim of gaining a better understanding of this reaction.

2. Experimental

The γ-Al_2O_3 used in this study was provided by Saint-Gobain Norpro Corporation in the form of extruded cylindrical pellets with a diameter of approximately 1 mm and an average length of 7 mm. The reactor consisted of a quartz tube with an internal diameter of 1.05 cm. The catalyst bed was 30 cm long and was held in place with quartz wool plugs and was pretreated at 300 °C for 30 min under an argon flow (200 mL min^{-1}). The surface area of the catalyst was determined using N_2 adsorption (BET method) on an Advanced Scientific Designs Inc. model RXM-100 surface characterization system. The specific surface area was 225 m^2/g.

All experiments were carried out under continuous flow of reactant gases at atmospheric pressure with a gas hourly space velocity (GHSV) of 1000 h^{-1} (calculated at 1 atmosphere and 25 °C). Typically, the feed gas consisted of 1 mole% NO and 1 mole% H_2S with a balance of argon, though the ratio of NO to H_2S was varied in some tests. Argon was chosen as a balance gas to facilitate the measurement of N_2 in the products. Data were collected over a temperature range 200–800 °C and measurements were made in triplicate at each temperature after stabilization of the reactor system at each condition for at least 1 h.

A single-zone tube furnace (Lindberg/Blue 1500 °C model) with temperature controller was employed for the experimentation. The temperatures of the reactions were measured independently of the furnace setting by using a thermocouple placed in the center of the catalyst bed.

Reactant gases were delivered through calibrated mass flow controllers. Downstream of the catalyst bed, two paths were available for the product gas mixture. The main route, which was used during reactor stabilization, allowed the gases to flow through a heated condenser (140 °C) to condense sulfur and then through chemical traps to remove all toxic gases. Following the sulfur trap, a 2.4 meter fixed path multi-pass gas cell (obtained from International Crystal Laboratories Ltd.) was set up in the flow path. The purpose of the cell was to analyze the product gases for the oxides of nitrogen by Fourier Transform Infrared Spectroscopy (FTIR) on an ATI Mattson Genesis Series spectrometer. The other path for the effluent gases consisted of a smaller diameter quartz tube which was positioned at the end of the catalyst bed and which by-passed the sulfur trap. The narrow tube was used to withdraw a sample of the product stream using a Masterflex Microprocessor Pump Drive in order to sample and determine all gaseous products other than sulfur, H_2O and NO_x. At the end of the tube, samples of product gas were extracted with a syringe through a small P_2O_5 filter to remove H_2O, sulfur and NO_x. These samples were analyzed by a SRI 8610C GC fitted with a molecular sieve and U-Plot columns and a TCD for measuring N_2, SO_2 and H_2S. The purpose of the P_2O_5 filter was to remove sulfur and H_2O in order to prevent the possible reaction of H_2S with SO_2 in condensed water that could form as the gases cooled to ambient temperature in the sampling system.

NH_3 measurements were carried out by passing the entire product stream through a fritted gas bubbler containing 0.01 M HCl for a measured amount of time. An aliquot of the solution was then analyzed by an ion chromatograph (IC). The IC system consisted of a Waters Model 510 Pump, a Waters 431 Conductivity detector and a Hamilton PRP-X200 cation exchange column. Data processing was carried out with a Varian CDS 401 data station. The IC pump was set to a flow rate of 2.0 mL/min using an eluent of 4 mM nitric acid in 30% methanol. Samples of the γ-Al_2O_3 were also collected after running the system for a known amount of time. NH_3 that had collected on the catalyst was analyzed by grinding the catalyst sample, extracting any NH_3 or into 10 mL of a 0.01 M HCl solution and measuring the ammonium content by IC. Adding this result to the amount of NH_3 collected in the gas bubbler gave a good approximation of the total NH_3 produced by the system at any given condition.

Instrumental and analytical errors were calculated and are shown as error bars in the following figures. The analytical procedures gave an error of a maximum of ± 5%, with the FTIR determinations showing the largest errors (5%) and IC the least (1%). GC results were found to be in the ± 3% range.

It should be noted that any reported sulfur and H_2O quantities were calculated from mass balance equations of sulfur and hydrogen respectively. This method was utilized due to the difficulty of precise measurements of both products since they are trapped during gas sampling.

3. Results and discussion

Initial investigations on the reduction of NO to N_2 with H_2S examined the homogeneous NO reduction with H_2S in the gas phase without catalyst. The use of γ -Al_2O_3 as a catalyst was then examined under the same conditions for comparison. To investigate the underlying principle behind ammonia production, similar experiments were run at 400 °C and 800 °C with the ratio of NO:H_2S ranging from 2:1 to 1:2.

3.1. *Effect of temperature on conversion of NO to N_2 with H_2S*

The homogenous reaction of NO with H_2S was initially studied using an empty quartz tube reactor. Examination of the data for the non-catalyzed reaction of NO with H_2S (figure 1) showed that appreciable conversion (ca. 10%) of NO to N_2 occurred when a temperature of 500 °C was reached and a conversion of 38% was observed at the maximum temperature (800 °C) used in this study. The nitrogen balance observed throughout all reaction temperatures was near or at 100% and the reaction appeared to obey the constraint of equation (1). Small amounts of the by-products SO_2 and N_2O were observed at temperatures greater than 500 °C and these materials reached a maximum concentration of ≤500ppm and ≤200ppm, respectively, at 800 °C.

The results of the corresponding catalyzed reaction of 1 mole% NO and 1 mole% H_2S in a balance of argon over γ -Al_2O_3 are displayed in table 1. These data show that complete conversion of NO was achieved at 500 °C for the catalyzed reaction compared to only ca. 10% conversion for the un-catalyzed reaction at 500 °C.

Figure 1 displays a full comparison of the % conversion of NO to N_2 for the non-catalyzed and catalyzed reactions over the entire temperature range of the study. It can be seen that at a temperature of 600 °C the conversion of NO to N_2 was 93% for the catalyzed reaction versus 15% for the non-catalyzed reaction, showing the significant role that γ -Al_2O_3 plays as a catalyst in promoting the conversion of NO to N_2. Prior to performing any experiments with both NO and H_2S over the γ -Al_2O_3 catalyst, an experiment was performed by passing 1% NO in argon over the catalyst. This reference experiment showed no conversion of the NO indicating that H_2S was responsible for the NO reduction and that γ-alumina was not contributing to the reaction by itself.

A plausible reaction sequence for the conversion of NO and H_2S over γ -Al_2O_3 is shown by the series of equations (3–6). Thus, H_2S and NO can react to produce two surface adsorbed species, $HS_{(ads)}$ and $NOH_{(ads)}$ on the surface of the alumina. The HS species could then decompose to produce H_2 and sulfur as shown in reaction 4, and the NOH species could react to produce N_2O and H_2O (reaction 5). H_2 was detected in small amounts at temperatures above 400 °C and its minimal occurrence is likely due to a rapid reaction

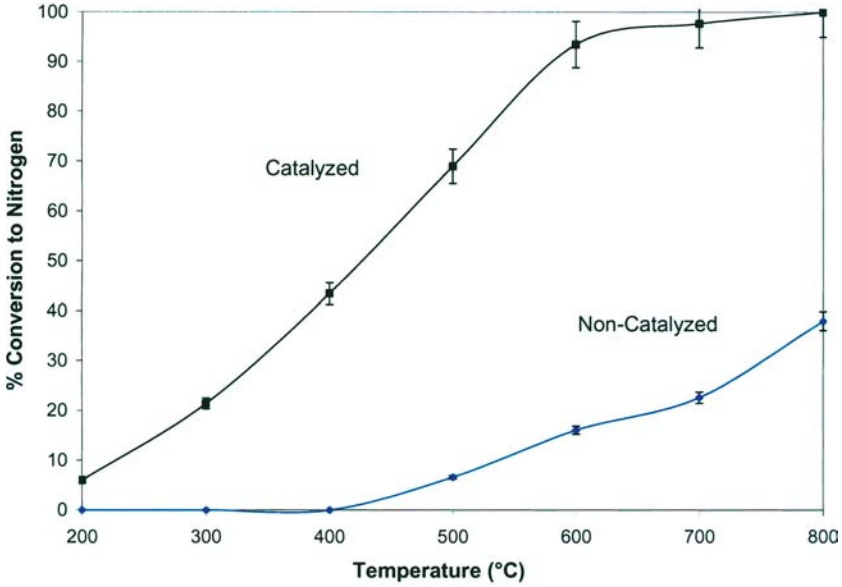

Figure 1. Comparison of the % conversions of NO to N_2 for non-catalyzed and catalyzed experiments.

Table 1
Results of 1:1 H_2S:NO reaction over γ -Al_2O_3

T (°C)		Ar	H_2S	N_2	NO	N_2O	NO_2	H_2	SO_2	% Conversion to N2	N_2 Mass %Balance
	Feed	98	1		1						
200	Exp.		0.05	0.03	0.75	0.02	0.01	0	0	6.0	84.4
300	Exp.		0.00	0.11	0.38	0.02	0.00	0	0.07	21.4	64.2
400	Exp.		0.05	0.22	0.01	0.05	0.00	0	0.04	43.4	53.9
500	Exp.		0.08	0.35	0.00	0.01	0.00	.003	0.08	69.0	70.6
600	Exp.		0.12	0.47	0.00	0.00	0.00	.004	0.05	94.0	93.5
700	Exp.		0.16	0.49	0.00	0.00	0.00	.015	0.05	97.7	97.7
800	Exp.		0.23	0.50	0.00	0.00	0.00	.035	0.04	100.0	100.0

Amounts expressed as moles of product per 100 moles of reactants.

between H_2 and NO to form N_2 and H_2O [17–19]. N_2O, which was detected at lower temperatures, disappeared on increasing the temperature due to either decomposition over the catalyst (reaction 7) or direct reaction with H_2S (reaction 8). This reaction pathway should not be construed as the mechanistic pathway for the reaction of H_2S with NO but it does explain the major and minor products observed (table 1) for the temperature range investigated in this study.

$$H_2S + NO \rightarrow HS_{(ads)} + NOH_{(ads)} \quad (3)$$

$$2HS_{(ads)} \rightarrow H_2 + S_2 \quad (4)$$

$$2NOH_{(ads)} \rightarrow N_2O + H_2O \quad (5)$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \quad (6)$$

$$N_2O \rightarrow N_2 + 1/2O_2 \quad (7)$$

$$N_2O + H_2S \rightarrow N_2 + H_2O + 1/2S_2 \quad (8)$$

An interesting feature of the data in table 1 is the increase in residual H_2S as the temperature was increased from 300 to 800 °C. This trend can be explained by the Claus equilibrium (reaction 9), a process that is readily catalyzed over alumina.

$$3/8S_8 + 2H_2O + \text{HEAT} \leftrightarrow 2H_2S + SO_2 \quad (9)$$

3.2. *Nitrogen mass balance*

One further notable feature of the current and previous research on the SCR of NO_x with H_2S is the low nitrogen mass balance obtained under some of the conditions (see table 1). The discrepancies are particularly notable at lower temperatures where the conversion of NO to N_2 was somewhat less that 100%. Thus, as shown in table 1, the alumina catalyzed conversion of NO was 25% at 200 °C reaching 100% at temperatures at 500 °C but the mass balance to N_2 was always $<100\%$ until the reaction temperature of at least 500 °C was employed. As no significant quantities of other gaseous nitrogen species were detected in the product gas mixture, a possible explanation for the low nitrogen mass balance could be the formation of NH_3 and ammonium salts that remain trapped on the catalyst. [20, 21]. Indeed, ion chromatographic analysis (see Experimental Section) of solutions obtained by trapping the total gaseous product and from washing of the catalyst with aqueous HCl showed that NH_3 was present in both extracts. However, the amount of NH_3 present either on the catalyst or in the gas products at higher (800 °C) temperatures was found to be negligible suggesting that all ammonium salts are decomposed at this temperature.

Anion analysis for the materials extracted from the catalysts used at reaction temperatures below 800 °C showed the presence of sulfate and thiosulfate. Based on previous work, these observations are not unexpected since it has been demonstrated [22] that oxide sites on the alumina surface can oxidize H_2S to these sulfur-oxyanions. Thus, the retention of NH_3 as ammonium species on the catalyst will be partly dependent on the stability and adsorption or bonding of the sulfate and thiosulfate to the surface. Most probably, such species are completely desorbed from the surface at 800 °C as N-mass balances are quantitative at this temperature, within experimental error.

3.3. *Effect of variable NO:H_2S ratio at 400 °C*

In an effort to understand the loss of nitrogen reflected in the mass balance analysis, a series of experiments was conducted at 400 °C where the ratio of NO to H_2S was varied from 1:2 to 2:1. The results of these experiments at 400 °C (figure 2) provided a rationale for the role of NH_3 formation in explaining the poor N_2 balance in that as the ratio of NO:H_2S was decreased, the conversion of NO to N_2 decreased from 62% at 2:1 NO:H_2S to 14% at 1:2 NO:H_2S together with a poorer nitrogen balance at the lower ratio. A probable explanation for the poor nitrogen balance is therefore that the increase of H_2S in relation to NO provides a more reducing system that subsequently causes the reduction of NO to NH_3 via the simplified

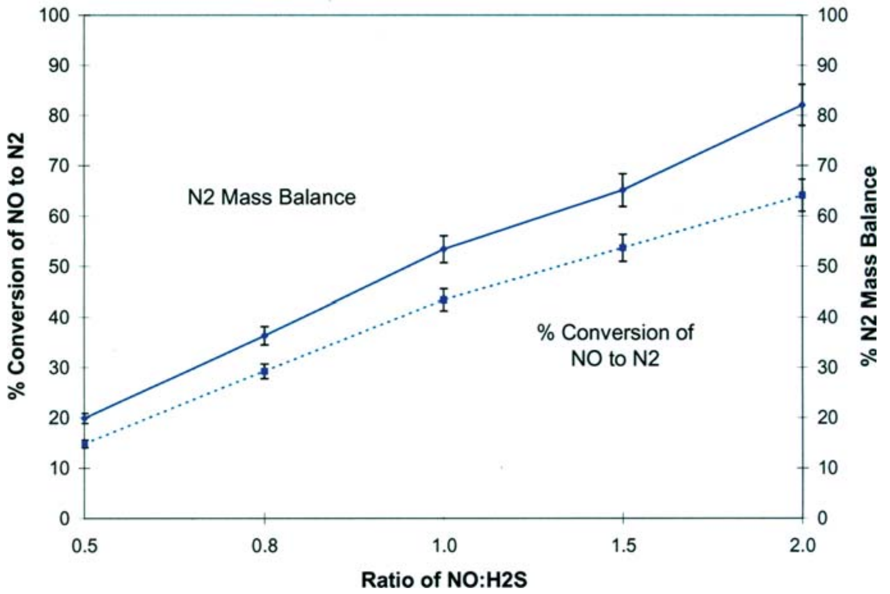

Figure 2. Variation of % conversion of NO to N_2 and N_2 mass balance with changing ratio of NO to H_2S at 400 °C.

reaction 8. This over-reduction reaction is similar to NH_3 formation reported in the case of the SCR of NO with other reducing agents [13, 18, 23,24]. In this work, this explanation is supported by the observation that greater quantities of NH_3 were found in the experiments with the higher amounts of H_2S in relation to NO.

Another possible route to NH_3 could be through the H_2 produced by reaction 4, followed by reduction of NO to NH_3 via reaction 2. However, it should be noted that even when the NH_3 quantities are taken into account (determined to be 350 ppm NH_3 per 100 moles of reactants at 400 °C), there is still a large deficiency in the nitrogen balance at 400 °C. Probably, not all of the ammonium salts formed on the catalyst can be removed by the aqueous HCl washing procedure.

$$2NO + 5H_2S \rightarrow 2NH_3 + 2H_2O + 5/8S_8 \qquad (8)$$

3.4. *Effect of varied NO:H$_2$S ratio at 800 °C*

In contrast, the results of similar ratio experiments at 800 °C were found to greatly improve the nitrogen mass balance overall (100% at 2:1 NO:H_2S and 87% at 1:2 NO:H_2S). A number of postulates can be put forward to account for this observation including thermal dissociation of ammonium salts on the catalyst surface, catalytic oxidation of NH_3 *via* lattice oxygen ions (from dissociated NO) at the higher temperatures with conversion of NH_3 to N_2 and H_2O (equation 9) and reaction NH_3 with SO_2. Indeed, this reaction is known to proceed rapidly over γ-alumina at temperatures greater than 600 °C (reaction 10) [25]. The well documented SCR of NO_x with ammonia [2,7, 20], shown as the simplified reaction 11, may also have occurred once more favorable temperatures were achieved.

$$2NH_3 + 3O_{(\text{adsorbed on catalyst})} \rightarrow N_2 + 3H_2O \qquad (9)$$

$$4NH_3 + 3SO_2 \rightarrow 2N_2 + 6H_2O + 3/2S_2 \qquad (10)$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \qquad (11)$$

Since NH_3 formation seems to be significant only at lower temperatures, then either the SCR of NO_x with H_2S should be run at higher temperatures or in the presence of some additive to avoid NH_3 build up. In theory O_2 might serve this role as it may be possible to promote oxidation of NH_3 in the presence of a strong oxidizing agent such as O_2. Future studies will investigate the conversion of NO according to the following equation.

$$2NO + 4H_2S + O_2 \rightarrow 2S_2 + 4H_2O + N_2 \qquad (12)$$

4. Conclusion

The use of H_2S as a reducing agent could provide an efficient way of reducing NO_x to N_2 in an oil and gas setting where H_2S is available in abundance. While gas phase homogenous reaction between H_2S and NO was not entirely effective, it was found that with the introduction of γ -Al_2O_3 as a catalyst, NO conversion to N_2 increased greatly and reached 100% at 800 °C. Increased levels of H_2S relative to NO were found to lead to the production of NH_3 and subsequently ammonium salts, resulting in low nitrogen balances. At higher temperatures this phenomenon was not observed likely due to ammonium salt decomposition and/or NH_3 oxidation which can occur at temperatures above 600 °C. Overall, the reduction of NO with H_2S could prove to be a viable and efficient way to deal with NO_x exhaust in industrial systems.

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