TITLE PAGE

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ABSTRACT

This study was undertaken in order to assess the potential for oxidizing NO to NO₂ in flue gas environments, with the aim of promoting the so-called fast SCR reaction. In principle this can result in improved SCR kinetics and reduced SCR catalyst volumes. Prior to commencing experimental work, a literature study was undertaken to identify candidate catalysts for screening. Selection criteria comprised (i) proven (or likely) activity for NO oxidation, (ii) low activity for SO₂ oxidation (where data were available), and (iii) inexpensive component materials. Catalysts identified included supported base metal oxides, supported and unsupported mixed metal oxides, and metal ion exchanged ZSM-5 (Fe, Co, Cu). For comparison purposes, several low loaded Pt catalysts (0.5 wt% Pt) were also included in the study.

Screening experiments were conducted using a synthetic feed gas representative of flue gas from coal-fired utility boilers: [NO] = 250 ppm, [SO₂] = 0 or 2800 ppm, [H₂O] = 7%, [CO₂] = 12%, [O₂] = 3.5%, balance = N₂; T = 275-375 °C. Studies conducted in the absence of SO₂ revealed a number of supported and unsupported metal oxides to be extremely active for NO oxidation to NO₂. These included known catalysts (Co₃O₄/SiO₂, FeMnO₃, Cr₂O₃/TiO₂), as well as a new one identified in this work, CrFeO_x/SiO₂. However, in the presence of SO₂, all the catalysts tested were found to be severely deactivated with respect to NO oxidation. Of these, Co₃O₄/SiO₂, Pt/ZSM-5 and Pt/CeO₂ showed the highest activity for NO oxidation in the presence of SO₂ (based on peak NO conversions to NO₂), although in no cases did the NO conversion exceed 7%.

Reactor studies indicate there are two components to SO₂-induced deactivation of Co₃O₄/SiO₂, corresponding to an irreversible deactivation due to sulfation of the surface of the Co₃O₄ phase, together with a reversible inhibition due to competitive adsorption of SO₂ with NO on the catalyst. In an effort to minimize the deactivating effect of SO₂ on Co₃O₄/SiO₂, two synthetic approaches were briefly examined. These consisted of (i) the incorporation of highly dispersed Co(II) ions in silica, as a non-sulfating matrix, via the sol-gel preparation of CoO-SiO₂; and (ii) the sol-gel preparation of a mixed metal oxide, CoO-Nb₂O₅-SiO₂, with the aim of exploiting the acidity of the niobium oxide to minimize SO₂ adsorption. While both catalysts showed almost no activity for NO oxidation in the absence of SO₂, when SO₂ was present low activity was observed, indicating that SO₂ acts as a promoter for NO oxidation over these materials.

The kinetics of NO oxidation over Co₃O₄/SiO₂, Pt/SiO₂ and Pt/CeO₂ were also examined. Co₃O₄/SiO₂ was found to exhibit a higher apparent activation energy for NO oxidation than the Pt catalysts, while the combined reaction order in NO and O₂ for the three catalysts was very close to one. CO₂ was found to have no effect on the kinetics of NO oxidation over these catalysts. The presence of H₂O caused a decrease in NO conversion for both Co₃O₄/SiO₂ and Pt/CeO₂ catalysts, while no effect was observed for Pt/SiO₂. The inhibiting effect of water was reversible and is attributed to competitive adsorption with the reactants.

In sum, this study has shown that a variety of base metal catalysts are very active for NO oxidation. However, all of the catalysts studied are strongly deactivated in the presence of 2800 ppm SO₂ at typical flue gas temperatures; consequently improving catalyst resistance to SO_x will be a pre-requisite if the fast SCR concept is to be applied to coal-fired flue gas conditions.

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EXECUTIVE SUMMARY

The objective of the study reported herein was to assess the potential for oxidizing NO to NO₂ in flue gas environments, with the aim of promoting the so-called fast SCR reaction. In principle this can result in improved SCR kinetics and reduced SCR catalyst volumes. Two main reactions contribute to NO_x conversion over ammonia SCR catalysts:

NO_x formed in combustion processes is typically composed of >90% NO and reaction (1) therefore dominates. In the case that equimolar amounts of NO and NO₂ are present, NO_x reduction occurs according to equation (2). This is the so-called “fast” SCR reaction. Expressed in terms of a first order rate law, the ratio of the two rate constants, $k(2)/k(1)$, is at least ten at $T > 200$ °C. This implies that the rate of NO_x conversion can be accelerated by use of an oxidation catalyst upstream of the SCR unit, so as to convert *ca.* 50% of the NO to NO₂; this, in turn, enables the SCR catalyst volume to be reduced. Specific objectives of the project were two-fold, being firstly to identify a catalyst which is selective for the oxidation of NO to NO₂ under typical flue-gas conditions while possessing minimal activity for the oxidation of SO₂, and which shows adequate stability with respect to long term operation in a flue-gas environment. Secondly, the activity and manufacturing cost of the catalyst should be such that a 25% saving in total SCR catalyst costs can be realized.

Prior to commencing experimental work, a literature study was undertaken to identify leads for the design of selective NO oxidation catalysts. Based on the outcome of this study, a number of candidate catalysts were identified for screening. Selection criteria comprised (i) proven (or likely) activity for NO oxidation, (ii) low activity for SO₂ oxidation (where data were available), and (iii) inexpensive component materials. Catalysts identified, and subsequently prepared, included (i) supported oxides of Cr, Co and Cu, (ii) Fe-Mn, Fe-Cr and Cu-Ce mixed oxides, and (iii) metal ion exchanged ZSM-5 (Fe, Co, Cu). For comparison purposes, several low loaded Pt catalysts (0.5 wt% Pt) were also included in the study.

Catalysts were prepared by means of standard procedures, including incipient wetness impregnation for the preparation of the supported metal oxide and Pt catalysts. TiO₂ and SiO₂ were employed as the support materials, chosen for their weakly sulfating nature. Mixed metal oxides were prepared using co-precipitation procedures, and zeolite catalysts by means of ion-exchange and impregnation methods. The resulting materials were characterized using elemental analysis (XRF), powder X-ray diffraction (XRD) and nitrogen physisorption (BET surface area and pore volume). Based on XRD results, it is apparent that even at the high metal loadings employed (typically 15 wt%), the titania support is able to stabilize the supported oxide phase in highly dispersed form. Use of silica as support afforded metal oxide phases with higher crystallinity due to the weaker metal oxide-support interaction.

Screening experiments were conducted using a synthetic feed gas representative of flue gas from coal-fired utility boilers: [NO] = 250 ppm, [SO₂] = 0 or 2800 ppm, [H₂O] = 7%, [CO₂] = 12%, [O₂] = 3.5%, balance = N₂; $T = 275\text{--}375$ °C. In initial studies, conducted in the absence of SO₂, a number of supported and unsupported metal oxides were found to be extremely active for NO oxidation to NO₂. These oxides include known catalysts (Co₃O₄/SiO₂, FeMnO₃, Cr₂O₃/TiO₂), as

well as a new one identified in this work, $\text{CrFeO}_x/\text{SiO}_2$. However, in the presence of SO_2 , all the catalysts tested were found to be severely deactivated with respect to NO oxidation. Of these, $\text{Co}_3\text{O}_4/\text{SiO}_2$, Pt/ZSM-5 and Pt/ CeO_2 showed the highest activity for NO oxidation in the presence of SO_2 (based on peak NO conversions to NO_2), although in no cases did the NO conversion exceed 7%.

Reactor studies suggest that there are two components to SO_2 -induced deactivation of $\text{Co}_3\text{O}_4/\text{SiO}_2$, corresponding to an irreversible deactivation due sulfation of the surface of the Co_3O_4 phase, together with a reversible inhibition due to competitive adsorption of SO_2 with NO on the catalyst. In an effort to minimize the deactivating effect of SO_2 on $\text{Co}_3\text{O}_4/\text{SiO}_2$, two synthetic approaches were briefly examined. These consisted of (i) the incorporation of highly dispersed Co(II) ions in silica, as a non-sulfating matrix, via the sol-gel preparation of CoO-SiO_2 ; and (ii) the sol-gel preparation of a mixed metal oxide of Co and Nb, $\text{CoO-Nb}_2\text{O}_5\text{-SiO}_2$, with the aim of exploiting the acidity of the niobium oxide to minimize SO_2 adsorption. While both catalysts showed essentially no activity for NO oxidation in the absence of SO_2 , when SO_2 was present low activity was observed, indicating that SO_2 acts as a promoter for NO oxidation over these materials. Although the limited scope of this project prevented further examination of this phenomenon, these results are intriguing and worthy of further study.

In parallel with the catalyst sulfation studies, the kinetics of NO oxidation over $\text{Co}_3\text{O}_4/\text{SiO}_2$, Pt/ SiO_2 and Pt/ CeO_2 were examined in an effort to gain an understanding of the mechanism of NO oxidation over these different catalyst types. $\text{Co}_3\text{O}_4/\text{SiO}_2$ was found to exhibit a higher apparent activation energy for NO oxidation than the Pt catalysts, while the combined reaction order in NO and O_2 for the three catalysts was very close to one. CO_2 was found to have no effect on the kinetics of NO oxidation over these catalysts. The presence of H_2O caused a decrease in NO conversion for both $\text{Co}_3\text{O}_4/\text{SiO}_2$ and Pt/ CeO_2 catalysts, while no effect was observed for Pt/ SiO_2 . The inhibiting effect of water was reversible and is attributed to competitive adsorption with the reactants.

In sum, this study has shown that a variety of base metal catalysts are very active for NO oxidation. However, all of the catalysts studied are strongly deactivated in the presence of 2800 ppm SO_2 at typical flue gas temperatures; consequently improving catalyst resistance to SO_x will be a pre-requisite if the fast SCR concept is to be applied to coal-fired flue gas conditions.

REPORT NARRATIVE

1. Introduction

Since its introduction in Japan in the 1970s, Selective Catalytic Reduction (SCR) using ammonia has widely gained acceptance as the most effective and technologically proven method for deep NO_x removal from flue-gas. Current SCR technology generally employs extruded monolithic catalysts, containing V₂O₅, WO₃ (or MoO₃) and TiO₂, for which the temperature range of operation lies between *ca.* 260 and 500 °C [1]. It can be anticipated that in the future progressively more stringent emissions legislation will necessitate increased use of SCR on a range of NO_x sources, including coal-fired boilers. For this reason there is a need to decrease the costs of SCR technology.

The objective of the study reported herein was to assess the potential for oxidizing NO to NO₂ in flue gas environments, with the aim of promoting the so-called fast SCR reaction. In principle this can result in improved SCR kinetics and reduced SCR catalyst volumes. The concept can be understood by consideration of the two main reactions that contribute to NO_x conversion over ammonia SCR catalysts [2,3]:

NO_x formed in combustion processes is typically composed of >90% NO and reaction (1) therefore dominates. In the case that equimolar amounts of NO and NO₂ are present, NO_x reduction occurs according to equation (2). This is the so-called “fast” SCR reaction. Expressed in terms of a first order rate law, the ratio of the two rate constants, $k(2)/k(1)$, is at least ten at $T > 200$ °C [2]. This implies that the rate of NO_x conversion can be accelerated by use of an oxidation catalyst upstream of the SCR unit, so as to convert *ca.* 50% of the NO to NO₂; this, in turn, enables the SCR catalyst volume to be reduced. Studies with diesel engine exhaust have shown that by promoting the fast SCR reaction in this manner, SCR catalyst volumes can effectively be halved, while maintaining a given NO_x conversion level (at typical diesel engine operating temperatures) [4]. Additionally, the use of an oxidation catalyst extends the useful range of operation of monolithic vanadia-based SCR catalysts to temperatures as low as *ca.* 220 °C (for low sulfur applications) [5]. At temperatures above 350 °C the positive effect of NO₂ on the SCR reaction rate largely disappears [2].

Given that NO oxidation catalysts typically operate at high space velocities, and hence relatively low catalyst volumes are required, the use of an oxidation catalyst represents an opportunity to significantly reduce overall catalyst volumes, and in turn the capital cost of the SCR system. For example, in mobile applications the oxidation catalyst volume is typically set at ~0.3 that of the SCR catalyst, which is itself set at ~0.5 that of the volume required when no oxidation catalyst is used [4]. Assuming that the oxidation catalyst is not more than 50% more expensive to manufacture than the SCR catalyst, the combined oxidation/SCR catalyst system shows a cost saving relative to the SCR-only system of at least 27.5%.

As an alternative to reducing the SCR catalyst volume, the superior SCR kinetics obtained through use of an oxidation catalyst provides an opportunity to reduce the operating temperature of the SCR system (at fixed SCR catalyst volume), this being typically set at around 650-700 °F (~340-370 °C) [6]. This enables increased heat recovery from the flue-gas upstream of the SCR system. Alternatively, in configurations where the SCR system is placed downstream of an electrostatic precipitator, decreased fuel costs will be incurred during the flue-gas re-heat. In all cases the operating temperature of the SCR unit must be set at a minimum of ~270 °C (520 °F) in order to prevent the deposition of ammonium (bi)sulfate on the SCR catalyst [7].

Based on the foregoing, the use of an oxidation catalyst appears to represent a promising option for reducing SCR capital and operating costs. However, any strategy for reducing the cost of SCR technology must take into account the fact that flue-gas can constitute a harsh environment for catalysts, especially when originating from coal-fired power plants. Assuming a coal sulfur content of 2.5 wt%, SO_x is present in the flue-gas at a concentration of around 6.0 lb/BTU (~2800 ppm), of which ~99% is SO_2 and ~1% SO_3 [8]. For a boiler equipped with low- NO_x burners, NO_x is produced at a concentration of typically 0.35-0.45 lb/BTU (~225-300 ppm) [6]. Other components are water (~7 %), O_2 (~3.5%), CO_2 (~12%), dust, As and Hg in trace amounts and nitrogen (balance). The main challenge in applying this concept to coal-fired boilers lies in the required selectivity of the catalyst for NO oxidation, as opposed to oxidation of SO_2 to SO_3 , as well as the need for adequate resistance to poisoning by SO_x and trace contaminants such as Hg and As. Formation of SO_3 over the oxidation catalyst must be kept to a minimum (as for the SCR catalyst) in order to avoid problems associated with corrosion downstream of the SCR system.

For mobile applications, high activity platinum-based diesel oxidation catalysts are employed for NO oxidation [4,5]. However, such catalysts are unsuitable for applications in which high SO_2 concentrations are present due to their considerable activity for SO_2 oxidation. On this basis two main options are apparent: base metal oxide catalysts and low-loaded precious metal catalysts incorporating an agent for suppression of SO_2 oxidation activity. In this report we describe the results of a study designed to assess the potential of NO oxidation catalysts of this type for flue gas applications.

2. Experimental Methods

2.1. Catalyst preparation

Supported catalysts were prepared using commercial supports, SiO_2 (Davison Catalysts) and TiO_2 (Alfa Aesar). Additionally, a ceria support was used, prepared by precipitation in the presence of urea [9]. Cr_2O_3 , Co_3O_4 , CuO , and mixed Fe-Mn and Fe-Cr oxides were supported by means of incipient wetness impregnation using aqueous solutions of the corresponding nitrates. The target metal loading was generally 15-20 wt%. This figure was chosen based on reports [10,11] that NO conversion over $\text{Cr}_2\text{O}_3/\text{TiO}_2$ and $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalysts increases with metal loading up to the maximum loading of 20 wt% metal studied. Supported MoO_3 and Nb_2O_5 catalysts were prepared by wet impregnation using ammonium heptamolybdate and ammonium niobium(V) oxalate, respectively. Supported Pt catalysts were prepared by incipient wetness impregnation using aqueous $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$, the Pt loading being 0.5 wt%. A V_2O_5 -doped

Pt/SiO₂ catalyst was prepared by impregnating calcined Pt/SiO₂ with VO(OⁱPr)₃ dissolved in dry *iso*-propanol. In all cases the impregnated catalysts were dried on a rotary evaporator at 60 °C and then calcined in air for 4 h in a muffle furnace (ramp = 15 °C/min). The final calcination temperature was 500 °C for the silica and ceria catalysts, and 450 °C for the titania catalysts.

Unsupported FeMnO₃ mixed oxide was prepared by co-precipitation according to a literature procedure [12], as was CuO-CeO₂ [13]. CoO-Nb₂O₅-SiO₂ was prepared using a sol-gel method [14], employing Co(NO₃)₂·6H₂O, Nb(OEt)₅ and Si(OEt)₄ as precursors. Sol-gel CoO-SiO₂ was similarly prepared but with omission of the niobium compound. In all cases the mixed oxides were calcined for 4 h at 500 °C.

Fe-ZSM-5 (Fe/Al = 0.75) was prepared according to a solid state ion exchange procedure [15] using FeCl₂ and a commercial ZSM-5 in the ammonium ion form (CBV 3024E from Zeolyst, Si/Al = 30). Co-ZSM-5 and Cu-ZSM-5 were prepared by wet impregnation using the protonic form of the zeolite and the corresponding metal acetates. After drying on a rotary evaporator, the zeolite was calcined in air at 550 °C for 3 h. Pt-ZSM-5 was prepared by ion exchange of NH₄-ZSM-5 (CBV 3024E) with aqueous Pt(NH₃)₄(NO₃)₂ (room temperature, 20 h) and was calcined at 550 °C for 5 h.

2.2. Catalyst characterization

Surface area and pore volume measurements were performed according to the BET method by nitrogen adsorption at -196 °C using a Micromeritics Tri-Star system. Catalyst samples were outgassed overnight at 160 °C under vacuum prior to the measurements. The chemical composition of the catalysts was determined by X-ray fluorescence spectroscopy (XRF). X-ray powder diffraction (XRD) measurements were performed on a Phillips X'Pert diffractometer using Cu K α radiation (λ = 1.54157 Å), with a step size of 0.02°. High resolution transmission electron microscopy (HRTEM) measurements were carried out with a JEOL 2010 FastEM field emission electron microscope operated at an accelerating voltage of 200 kV. The point-to-point resolution of the electron beam was 0.3 nm. Pt dispersion measurements were performed by hydrogen chemisorption using a Zeton-Altamira AMI-200 unit which employs a thermal conductivity detector (TCD). Samples were pre-treated with flowing H₂+Ar at 573 K for 1 h and then allowed to cool under flowing H₂ to 373 K. Dispersion calculations were based on the assumption of a 1:1 H:Pt stoichiometric ratio and a spherical particle morphology.

2.3. Catalyst screening

Catalyst performance was evaluated under steady state conditions using a stainless steel reactor with an internal diameter of 15.9 mm. Catalysts were tested as a 0.55-1.0 mm sieve fraction diluted with glass beads. The feed gas contained 250 ppm NO, 0 or 2800 ppm SO₂ (as indicated), 3.5% O₂, 12% CO₂, 7% H₂O and N₂ as the balance. Water was added to the feed by means of a syringe pump (ISCO Model500D) via a steam generator and heated gas lines maintained at 140 °C. The total gas flow rate was 1667 cm³ min⁻¹ and the standard amount of sample was 3.0 g (W/F = 0.03 g h dm⁻³, where W is the weight of the catalyst and F is the total flow rate over the catalyst, equivalent to a GHSV of approximately 20,000 h⁻¹). The reactor was contained in a vertical tubular furnace (Lindberg/Blue M). A K-type thermocouple was situated in a thermocouple well directly in the middle of the catalyst bed for temperature measurement. Prior to measurements, the temperature (± 3 °C) was raised to the reaction temperature (Omega

ramp and soak programmable temperature controller) and allowed to equilibrate. Measurements were performed at intervals of 25 °C in the range 275-400 °C. Under these conditions the level of NO conversion is not only determined by the intrinsic chemical kinetics but is also subject to both physical (mass transport) and thermodynamic limitations. Nonetheless, use of the above experimental conditions provides an indicator of likely catalyst performance in a typical flue-gas environment.

NO and NO₂ concentrations were determined continuously using an Eco Physics CLD 700 EL chemiluminescence NO_x analyzer. SO₂ was determined on-line using a Rosemont non-dispersive IR analyzer. Catalyst activity was evaluated in terms of NO conversion using the equation:

NO conversion to NO₂ = $([\text{NO}_2]/([\text{NO}] + [\text{NO}_2]) \times 100\%$,
 where [NO] and [NO₂] are the concentrations measured at the reactor exit.

Equilibrium NO₂ concentrations were calculated using CHEMCAD (Chemstations, Inc.), based on the gas mixture used for the catalyst screening experiments.

2.4. Kinetic studies

Kinetic measurements were performed using a stainless steel reactor with an internal diameter of 10 mm. Other features of the reactor set-up were broadly as described above. Catalysts were tested as an undiluted 106-180 µm sieve fraction. Glass beads were placed upstream of the catalyst to ensure adequate mixing and uniformity of the gas flow. Typically 0.150 g of catalyst was used, the total gas flow being 1667 cm³ min⁻¹. The reactor was operated in a differential manner by restricting the NO conversion to no more than 15%. Prior to performing the kinetic measurements, a series of experiments using different amounts of catalyst were performed in order to check that NO conversion was subject to chemical control only. NO conversion to NO₂ was found to be proportional to the catalyst loading (when the catalyst loading was no more than 0.200 g), consistent with the absence of mass transfer limitations. At the end of each kinetic run, the conditions of the first data point were duplicated to check for possible catalyst deactivation. For the determination of apparent activation energies, the temperature was varied in a non-sequential manner in order to avoid systematic errors. Similarly, when testing the effect of gas composition on the rate, the concentration of the species of interest was varied non-sequentially, while the concentrations of the other species were kept constant.

3. Results and Discussion

3.1. Selection of catalysts for screening in NO oxidation

Prior to commencing experimental work, a literature study was undertaken to identify leads for the design of selective NO oxidation catalysts. Pertinent literature from 1984 onwards is summarized in Tables 1-3 (it should be noted that the last reference in Table 2 contains a summary of the literature prior to 1984). As shown in Table 1, Pt-catalyzed NO oxidation has been the subject of considerable attention in recent years, principally due to the key role that NO oxidation over Pt plays in NO_x storage catalysts and catalyzed diesel particulate filters. Base

metal catalyst have also been studied, for which a division can be made into supported and bulk metal oxides on the one hand (Table 2), and metal ion-exchanged zeolites on the other (Table 3). There are also many reports of NO oxidation catalyzed by activated carbons, although the propensity of carbon to undergo gasification in the presence of NO₂/O₂ renders it unsuitable for flue-gas applications in the temperature range of interest.

Some of the first studies employing base metal catalysts were reported by Japanese workers in the 1970s [16-20]. Mn and Co oxides, either unsupported or supported on alumina, were found to be particularly active in NO oxidation. In many studies the presence SO₂ and H₂O was found to suppress the oxidation rate. Karlsson and Rosenberg [21] studied NO oxidation under simulated flue gas conditions (including 2400-2800 ppm SO₂) and found that a variety of supported and unsupported oxides were active, the best performance being shown by CoO/Al₂O₃, NiO/Al₂O₃, and a physical mixture of Fe₂O₃ + MnO + ZnO. These catalysts afforded NO conversions of over 50% at low temperatures (93 °C) and space velocities (1500 h⁻¹), although after 15 h on stream some evidence of deactivation was apparent. Other studies have generally reported data for feeds in which SO₂ and water were not present. Shiba and co-workers [22] studied Cr₂O₃ and CuO supported on titania and found that both catalysts were active for NO conversion in the 200-500 °C range. Luo and Li [23] studied a series of metal oxides supported on silica-alumina and reported the order of catalyst activity as: Cr > Fe > Co > Mn > Cu. Fe-Mn mixed oxides were also reported to be active, the optimum molar Fe:Mn ratio being 10:1. Fe-Mn mixed oxides were also studied extensively by Yang and co-workers [12,24]. Mixed oxides of Fe-Mn-Ti (1:1:1), as well as Fe-Mn (1:1) supported on TiO₂, were found to be highly active catalysts. Lu *et al.* [11] investigated the properties of metal oxides supported on alumina, titania and silica in NO oxidation. On γ-Al₂O₃, activity followed the order Mn > Cr > Co > Cu > Ni ≥ Fe > Zn, while on TiO₂ oxides of Cr and Mn were found to be the most active. NO oxidation on silica-supported metal oxides followed the order Co > Mn > Cr.

While studies employing zeolite-based catalysts are less numerous than those concerning supported metal oxides, a number of promising systems have nonetheless been reported. In their study performed using a simulated flue gas, Karlsson and Rosenberg [21] found that Cu-exchanged 13X molecular sieves was an active catalyst at temperatures in the range 260-371 °C (500-700 °F), albeit at relatively low GHSV (1500 h⁻¹). In contrast, Arai *et al.* [20] found that SO₂ caused strong deactivation of metal ion-exchanged zeolites, including those containing Cu, Cr, Fe and Co. Fe-exchanges zeolites are reported to be particularly active in NO oxidation [25,26], although both Fe-ferrierite and Fe-ZSM-5 are strongly deactivated in the presence of SO₂ [25]. Co-ZSM-5 [27,28] and Pt-ZSM-5 [29] are also reported to be very active for NO oxidation in the absence of SO₂.

Based on the literature study, a number of candidate catalysts were identified for screening. Selection criteria comprised (i) proven (or likely) activity for NO oxidation, (ii) low activity for SO₂ oxidation (where data were available), and (iii) inexpensive component materials. Catalysts selected, and subsequently prepared, included supported oxides of Cr, Co, and Cu, and Fe-Mn mixed oxides. Additionally, Mo, Nb and Fe-Cr oxides supported on silica were also prepared, as well as an unsupported Cu-Ce mixed oxide. These oxides are of interest given that their properties in NO oxidation have yet to be described; further, it was anticipated that oxides of Mo and Nb, being acidic in nature, should be less susceptible to the effects of poisoning by sulfur

oxides than more basic oxides. Platinum, dispersed on silica, titania and ceria, was also selected for screening: although supported Pt possesses unacceptably high activity for the oxidation of SO_2 , it represents a useful reference against which the activity of base metal catalysts can be assessed. Further, it is known that addition of vanadia to supported Pt catalysts greatly suppresses SO_2 oxidation [30], while CO and hydrocarbon oxidation activity is suppressed to a much lesser degree; data pertaining to the effect on NO oxidation activity appear to be lacking.

Zeolite-based catalysts were also considered for screening. The available literature suggests that Fe-exchanged ferrierite and ZSM-5 are the most active catalysts for NO oxidation, although the relatively high price of these zeolites (particularly ferrierite) represents a significant disadvantage. Based on these considerations, a Fe-ZSM-5 catalyst was prepared, and for comparison purposes, samples of Cu-ZSM-5 and Co-ZSM-5.

3.2. Catalyst preparation and characterization

Data pertaining to catalyst characterization are summarized in Tables 4-7. For the supported simple oxides (Table 4), XRD data indicate that even at the high metal loadings employed (which are in excess of those required for monolayer coverage), the titania support is able to stabilize the supported oxide phase in highly dispersed form, the titania-based catalysts being in all cases X-ray amorphous (excepting the anatase support). Similar observations have been reported previously for supported oxides of Cr [31], Co [32] and Cu [33], and can be attributed to the strong interaction of titania with these oxides. In contrast, the weaker nature of the silica-metal oxide interaction means that use of silica as the support affords crystalline metal oxide phases in a number of cases, metal oxide crystallite sizes, calculated from line broadening using the Scherrer equation, being 8.1 nm for Co_3O_4 and 12.0 nm for Cr_2O_3 .

Comparison of the BET surface areas and pore volumes of the catalysts with those of the corresponding supports reveals significant decreases upon loading the metal oxides. Assuming that the supported metal oxides do not possess significant surface area, in many cases the decrease corresponds to that which would be expected based on a physical mix of the metal oxide and support. Table 4 shows a comparison of the measured surface areas with those calculated for a physical mix. In some instances, e.g., $\text{Co}_3\text{O}_4/\text{TiO}_2$, the decrease in measured surface area is significant, implying that a degree of pore filling of the support occurs. This was also found to be the case for the supported mixed metal oxide catalysts in some cases (see Table 5). All of the latter were found to be X-ray amorphous, in contrast to the unsupported oxides, FeMnO_3 and CuO-CeO_2 , which were crystalline materials. For the latter material, the X-ray diffractogram contained reflections due to ceria only, implying that the CuO phase was highly dispersed.

Table 6 summarizes the physical data collected for the zeolite catalysts prepared in this work. In all cases the zeolite was the only crystalline phase observed by XRD, i.e., bulk oxides of Fe, Co or Cu were not detected. Finally, Table 7 collects data for the Pt catalysts prepared. For the Pt/ CeO_2 sample TEM micrographs (not shown) indicated that the platinum was highly dispersed, Pt particles with diameters in the range 2 – 3 nm typically being observed.

3.3. Catalyst screening in NO oxidation

3.3.1. Screening experiments without added SO_2

As detailed in section 2.3, screening experiments were conducted using a synthetic feed gas representative of the flue gas from coal-fired utility boilers (both with and without SO_2). The results of the screening studies are summarized in Figures 1-5. Figures 1-4 show the percent conversion of NO to NO_2 as a function of reactor temperature for feed gas without SO_2 . Of the simple supported metal oxides tested (Figure 1), $\text{Co}_3\text{O}_4/\text{SiO}_2$ is found to be the most active catalyst. Indeed, at temperatures in the range 325-400 °C, the formation of NO_2 over $\text{Co}_3\text{O}_4/\text{SiO}_2$ is thermodynamically controlled, i.e., NO_2 formation corresponds to the equilibrium value calculated from thermodynamics. Significant support effects are observed, as exemplified by the fact that $\text{Co}_3\text{O}_4/\text{SiO}_2$ is considerably more active for NO oxidation than $\text{Co}_3\text{O}_4/\text{TiO}_2$, whereas $\text{Cr}_2\text{O}_3/\text{TiO}_2$ is more active than $\text{Cr}_2\text{O}_3/\text{SiO}_2$. These results are broadly in line with the literature: Lu and co-workers [11] reported NO oxidation on silica-supported metal oxides followed the order $\text{Co} > \text{Mn} > \text{Cr}$, while we find the order to be $\text{Co} > \text{Cr} \cong \text{Mn}$. Similarly, the same study reported the order $\text{Mn} > \text{Cr} > \text{Cu} > \text{Co}$ for NO oxidation over the titania-supported oxides at 300 °C, while our results show the order $\text{Cr} > \text{Cu} > \text{Co}$ at this temperature.

As shown in Figure 2, of the supported and unsupported mixed oxide catalysts tested, unsupported FeMnO_3 shows the highest activity for NO oxidation, followed by $\text{FeCrO}_x/\text{SiO}_2$ and $\text{FeMnO}_x/\text{TiO}_2$. The high oxidation activity of the Fe-Mn mixed oxide catalysts is in agreement with studies reported by Yang and co-workers [12,24]. The use of titania as support is found to afford more active Fe-Mn catalysts than silica, while the 1:1 mixed oxide is clearly superior to the 10:1 material. CuO-CeO_2 also shows good NO oxidation activity.

Results for the zeolite catalysts are presented in Figure 3. In agreement with the work of Iwamoto *et al.* [29], Pt-ZSM-5 is indicated to be an extremely active catalyst. Co-ZSM-5 and Cu-ZSM-5 also show significant activity, while the Fe-ZSM-5 sample is somewhat less active. This contrasts with results obtained by Cant and co-workers, who found Fe-ZSM-5 to be more active than the Co- and Cu-exchanged zeolite [26]. This apparent discrepancy may be due to the synthesis method employed: although we attempted to employ the same solid state synthesis procedure used by Cant *et al.* [25], a number of the steps involved are difficult to reproduce exactly, e.g., the intensity of the ball milling process.

Results for the Pt-containing catalysts are shown in Figure 4. The lower activities of the Pt catalysts, as compared to the most active base metal oxide catalysts, can be attributed to the low Pt loading used (~0.5 wt%, excepting the Pt/SiO_2 catalyst for which the loading was 0.26 wt%). For comparison purposes the data for Pt-ZSM-5 are included in the figure, from which it is apparent that ZSM-5 affords a more active catalyst as compared to the use of CeO_2 and TiO_2 as support. In agreement with the literature [35], Pt supported on silica was found to be significantly more active than Pt on titania. Also presented in Figure 4 are data for a Pt/SiO_2 catalyst which had been impregnated with vanadia. From these results it is clear that the addition of vanadia significantly impairs the activity of the Pt for NO oxidation.

3.3.2. Screening experiments with added SO_2

With the exception of $\text{Nb}_2\text{O}_5/\text{SiO}_2$ and $\text{MoO}_3/\text{SiO}_2$, upon addition of SO_2 to the feed all of the

catalysts tested exhibit a sharp decline in activity for NO oxidation. Figure 5 summarizes the NO conversion data for the most active catalysts (catalysts not shown afforded a maximum NO conversion to NO₂ of not more than 3%). Of these, Co₃O₄/SiO₂, Pt/ZSM-5 and Pt/CeO₂ show the highest activity for NO oxidation in the presence of SO₂ (based on peak NO conversions to NO₂), although in no cases does the NO conversion exceed 7%. In the case of Nb₂O₅/SiO₂ and MoO₃/SiO₂, SO₂ acts as a slight promoter for NO oxidation. In the absence of SO₂, NO oxidation over these catalysts does not exceed 2%, whereas in the presence of SO₂ peak conversions to NO₂ are in the order of 3-4%. The absence of sulfur-inhibition/deactivation effects observed with the supported Nb and Mo oxides reflects their high acidity and inability to form stable sulfates. Baseline NO conversion, measured in the absence of catalyst, did not exceed 1.3% with or without SO₂ present.

In an effort to minimize the deactivating effect of SO₂ on Co₃O₄/SiO₂, two synthetic approaches were briefly examined. These consisted of (i) the incorporation of highly dispersed Co(II) ions in silica, as a non-sulfating matrix, via the sol-gel preparation of CoO-SiO₂; and (ii) the sol-gel preparation of a mixed oxide of Co and Nb, CoO-Nb₂O₅-SiO₂, with the aim of exploiting the acidity of the niobium oxide to minimize SO₂ adsorption. As shown in Figure 5, both catalysts show slight activity for NO oxidation in the presence of SO₂, however, conversion levels are generally lower than for the impregnated Co₃O₄/SiO₂ catalyst. Of note is the finding that in the absence of SO₂, these catalysts show essentially no activity for NO oxidation: NO conversion was found to be equivalent to that obtained in the absence of catalyst. Clearly, as for Nb₂O₅/SiO₂ and MoO₃/SiO₂, SO₂ acts as a promoter for NO oxidation over these materials. Although the limited scope of this project prevented further examination of this phenomenon, these results are intriguing and worthy of further study. Further, given the lower Co loadings of the sol-gel catalysts relative to the impregnated Co₃O₄/SiO₂ catalyst (6.3 wt% and 8.8 wt% for the sol-gel catalysts CoO-SiO₂ and CoO-Nb₂O₅-SiO₂, respectively), there may exist scope for improving the performance of the sol-gel catalysts by increasing their Co content.

The above results, particularly for the supported and unsupported Fe-Mn mixed oxides, contrast with reports in the literature suggesting the relatively sulfur-tolerant nature of these and related NO oxidation catalysts. For example, Karlsson and Rosenberg [21] found that a physical mixture of Fe₂O₃, MnO and ZnO oxides showed roughly 70% NO oxidation at 200 °F (93 °C) in the presence of 2600-2800 ppm SO₂, although after 15 h on stream some evidence of catalyst deactivation was apparent. Huang and Yang [12] reported that Fe-Mn-Ti mixed oxides show 14% NO oxidation in the presence of 200 ppm SO₂ (at 25 °C and a GHSV of 6,000 h⁻¹). The apparent discrepancy with the results obtained in the present study can most likely be ascribed to differences in the experimental conditions used. In Karlsson and Rosenberg's work a space velocity of 1500 h⁻¹ was used, as opposed to the value of 20,000 h⁻¹ employed in this work; at the higher GHSV deactivation effects can be observed at a much earlier stage. Further, at the reaction temperature of 93 °C used in the Karlsson and Rosenberg study, SO₂ oxidation to SO₃ should be negligible, with the consequence that relatively weakly bound sulfite species would be formed on the catalyst via SO₂ adsorption, as opposed to more strongly adsorbed sulfate; the latter would be expected to irreversibly block sites for NO adsorption (as discussed below). Indeed, at higher temperatures (≥260 °C) NO conversion was found to be negligible [21]. Similar reasoning can be used to explain Huang and Yang's results, given the reaction temperature of 25 °C employed.

3.4. Catalyst deactivation studies

Figure 6 shows the effect of SO_2 addition on NO conversion catalyzed by $\text{FeCrO}_x/\text{SiO}_2$ at 350 °C, the resulting plot of NO conversion versus time on stream being rather typical of the metal oxide catalysts tested. Addition of SO_2 to the feed causes an immediate drop in NO oxidation activity, attributable to the competition of SO_x with NO and/or O_2 for adsorption sites on the catalyst. Rapid sulfation of the catalyst surface is indicated, as evidenced by the very low initial concentration of SO_2 detected at the reactor outlet (although this is likely due in part to some degree of oxidation of SO_2 to SO_3 over the catalyst, the presence of which is not detected by the NDIR SO_2 analyzer). At approximately 4 minutes after the introduction of SO_2 , the level of NO conversion assumes a more constant value, although a further, gradual decline occurs until a steady state value is obtained at approximately 40 minutes on stream. This slow decline in activity is attributed to progressive sulfation of the supported metal oxide. Of note is the observation of a small surge in NO_x measured at the reactor outlet at times between 3 and 5 minutes on stream. Although small (e.g., NO_x out = 255 ppm versus NO_x in of 245 ppm), this surge is consistent with the release of stored NO_x from the catalyst due to displacement by SO_3 (stored as sulfate). The irreversible blocking of NO_x storage sites upon exposure to SO_2 , as a consequence of sulfate formation, has been extensively documented for NO_x adsorber catalysts [36]. In the case of the CuO-CeO_2 catalyst this effect is more pronounced (see Figure 7): addition of SO_2 to the feed results in release of NO_x from the catalyst such that the peak outlet NO_x concentration exceeds the inlet concentration by a factor of about two. This result reflects the high NO_x adsorption capacity of ceria; indeed, ceria is frequently used as a component of NO_x storage catalysts.

Given the promising performance of the $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalyst when fresh, the nature of the deactivation induced by SO_2 was examined in a series of experiments which are summarized in Figure 8. Exposure of the fresh catalyst to 2800 ppm SO_2 resulted in a decrease in activity, maximum NO conversion falling to a value of 6% (at 350 °C). Upon replacing the SO_2 in the feed with additional nitrogen (so as to maintain a constant flow rate), the catalyst activity recovered somewhat (after equilibration at 350 °C) to reach a maximum value of 32% (obtained at 400 °C). Re-exposure of the catalyst to the SO_2 -containing feed again suppressed the NO oxidation activity to the original low level, while removing it from the feed again resulted in partial restoration of the oxidation activity, the NO conversion reaching 29% at 400 °C. These results suggest that there are two components to SO_2 -induced deactivation of $\text{Co}_3\text{O}_4/\text{SiO}_2$. The first corresponds to an irreversible deactivation due a chemical or physical change in the catalyst brought about by exposure to SO_2 . Based on the results of a post mortem analysis (see below), sulfation of the surface of the Co_3O_4 phase is indicated as being responsible for this deactivation. The second component corresponds to a deactivation of the catalyst which occurs only when SO_2 is present in the feed (and can thus be regarded as reversible). Logically, this can be accounted for by the competitive adsorption of SO_2 with NO on the catalyst.

Table 8 summarizes the results of post mortem analyses performed on a number of the spent catalysts. During screening the catalysts had been exposed to a total of approximately 0.01 moles of SO_2 , equivalent to 0.64 g SO_2 per 3 g catalyst charge. In the case of silica-supported Cr_2O_3 and Co_3O_4 , relatively low sulfur contents were found (0.24 and 1.5 wt%, respectively), suggesting that only the surface of the supported metal oxides were sulfated. Consistent with

this, the BET surface areas of the catalysts were virtually unchanged, while bulk metal sulfates could not be detected by XRD. Interestingly, in both cases the crystallite size of the metal oxide phase (calculated using the Scherrer equation) was observed to have increased, suggesting that surface sulfation of the metal oxide may have induced sintering.

For the titania- and silica-supported FeMnO_x catalysts, measured sulfur concentrations were relatively high (4.7 and 3.49 wt%, respectively), and although XRD showed the Fe-Mn phase to be amorphous in both cases, a significant decrease in BET surface area was observed for the titania catalyst (and to a lesser extent its silica analog). These findings suggest a more extensive degree of sulfation of the supported mixed metal oxide phase than for the Cr_2O_3 and Co_3O_4 catalysts. Surface sulfation of the titania support is also indicated, given the higher sulfur concentration in the titania catalyst relative to its silica analog, and greatly reduced BET surface area.

The spent unsupported FeMnO_3 catalyst was also examined. A significant loss in surface was noted (from $64.7 \text{ m}^2/\text{g}$ to $10.5 \text{ m}^2/\text{g}$), while powder XRD revealed the sample to be largely amorphous, with weak reflections attributed to $\text{Mn}(\text{SO}_4)_3$ and Fe_2O_3 . This suggests that a degree of segregation of the mixed oxide may have occurred, possibly as a consequence of sulfation. The sulfur content of 11.35 wt% was consistent with extensive sulfation of the catalyst surface, while the corresponding S:(Fe+Mn) mole ratio of 0.38:1 was close to the value of 0.37:1 found for its silica-supported analog.

3.5. Kinetic studies

Although several reports have recently appeared concerning the kinetics and mechanism of NO oxidation over Pt catalysts, and in particular Pt/ Al_2O_3 [37-40], there have been no reports concerning base metal catalysts such as $\text{Co}_3\text{O}_4/\text{SiO}_2$. This fact, coupled with the desire to elucidate the mechanism of NO oxidation (as a possible means to assist catalyst optimization), prompted us to study the kinetics of NO oxidation over $\text{Co}_3\text{O}_4/\text{SiO}_2$. Two Pt catalysts were also included in this study: Pt/ SiO_2 , which is reported by several authors [35,40] to be the most active Pt catalyst for this reaction, and Pt/ CeO_2 , which is of interest due to its activity in the presence of SO_2 (Figure 5). The physical properties of the catalysts are collected in Table 9. Note that for the $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalyst, a cobalt loading of only 4.7 wt% was used. This relatively low loading was chosen in order to limit the NO conversion under the conditions employed to values of less than 15%.

The kinetic study was initially performed in the absence of H_2O , CO_2 and SO_2 , keeping the concentrations of NO and O_2 the same as for the screening experiments. Figure 9a shows the temperature dependence of the NO oxidation rate for the three catalysts in the range 220-380 °C, the rate being defined as moles of NO reacted per hour per gram of catalyst. From these plots the apparent activation energies (E_a) were determined to be 70.9 kJ/mol for $\text{Co}_3\text{O}_4/\text{SiO}_2$, 40.6 kJ/mol for Pt/ SiO_2 and 31.4 kJ/mol for Pt/ CeO_2 (Table 10). The activation energy determined for Pt/ SiO_2 is similar to the value of 39 kJ/mol reported for Pt/ Al_2O_3 [37], but lower than that (57.7 kJ/mol) reported for Pt/ SiO_2 by Marques *et al.* [34].

As detailed in the literature [37], the rate of NO oxidation expressed in a power rate form may be written as:

$$r = k_f[\text{NO}]^a[\text{O}_2]^b[\text{NO}_2]^c(1-\beta), \text{ where } \beta = [\text{NO}_2]/K[\text{NO}][\text{O}_2]^{1/2}.$$

k_f is the forward rate constant, a , b and c are the forward rate orders, K is the equilibrium constant and the term β takes account of the reverse reaction. In the kinetic measurements the reaction was performed far from equilibrium ($\beta < 0.25$) and so the term $1-\beta$ approximates to one. The presence of NO_2 in the above rate expression reflects the inhibiting effect of NO_2 on the NO oxidation rate, which can be attributed to the strong adsorption of NO_2 on catalyst surfaces (both oxidic [35] and metallic [37]). However, given that NO_2 was not present in the feed, and given the low NO conversion levels studied, the NO_2 term can be discounted to a first approximation.

To determine the reaction orders in NO and O_2 , their concentrations were independently varied over the ranges 100-500 ppm and 1-10 %, respectively. Figure 9b shows the effect of NO and O_2 concentration on the NO oxidation rate over $\text{Co}_3\text{O}_4/\text{SiO}_2$ at 260 °C. The reaction orders in NO and O_2 were determined to be, respectively, 0.5 and 0.4. In the case of Pt/SiO_2 , the reaction orders in NO and O_2 were found to be 0.46 and 0.52, respectively, while those determined for Pt/CeO_2 were 0.55 and 0.36 (Table 10). These reaction orders are similar to those reported by Marques *et al.* [34] for Pt/SiO_2 and Pt/CeZrO_2 at 217 °C and 308 °C, respectively.

The effect of H_2O and CO_2 on the kinetics of NO oxidation were also investigated for the three catalysts. Addition of CO_2 to the feed was found to have no effect on the rate of NO oxidation for all three catalysts. However, the addition of H_2O led to a decline in NO conversion over both $\text{Co}_3\text{O}_4/\text{SiO}_2$ and Pt/CeO_2 , as shown in Table 11, while the activity of Pt/SiO_2 remained unchanged. The resulting kinetic data are collected in Table 9. Upon addition of H_2O to the feed, the apparent activation energy decreased from 72.6 to 51.2 kJ/mol for $\text{Co}_3\text{O}_4/\text{SiO}_2$, while in contrast, that measured for Pt/CeO_2 increased (from 31.4 to 36.9 kJ/mol). It should be noted that the activity of both $\text{Co}_3\text{O}_4/\text{SiO}_2$ and Pt/CeO_2 could be fully recovered by stopping the addition of H_2O to the feed. From this it follows that the inhibiting effect of H_2O on NO oxidation is most likely a consequence of the competitive adsorption of H_2O with the reactants on the catalyst surface.

Given that in the screening experiments all the catalysts showed a pronounced decline in NO conversion after exposure to SO_2 , the effect of SO_2 on the kinetics of NO oxidation was studied. Before performing the kinetic measurements, each catalyst was exposed to a mixture containing NO, O_2 and 100 ppm SO_2 at 300 °C ($\text{Co}_3\text{O}_4/\text{SiO}_2$) or 280 °C (Pt/SiO_2 and Pt/CeO_2). SO_2 addition was ceased after the NO conversion had dropped to a specified value (~75% of the original value measured at 300° C), after which the catalyst was allowed to equilibrate in the NO + O_2 mixture at 400 °C until the NO conversion attained a constant value. In the case of $\text{Co}_3\text{O}_4/\text{SiO}_2$, no recovery of the activity was observed even after a prolonged hold at 400 °C. In contrast, Pt/CeO_2 recovered 50% of its activity after regeneration at this temperature, and Pt/SiO_2 recovered *ca.* 85% of its activity. Subsequently, kinetic measurements were performed on the sulfated/regenerated catalysts (in the absence of H_2O and CO_2). As shown in Table 10, the sulfated catalysts showed lower apparent activation energies as compared to the non-sulfated ones, while the reaction orders in NO and O_2 were only slightly changed. The physical

properties of both the as-prepared and sulfated catalysts are listed in Table 9. $\text{Co}_3\text{O}_4/\text{SiO}_2$ and Pt/SiO_2 exhibited almost no changes in BET surface area and pore volume after sulfation, although hydrogen chemisorption showed a decrease in the Pt dispersion (from 79.5% to 35.8%), indicative of sintering. Pt particle sintering has previously been reported for $\text{Pt}/\text{Al}_2\text{O}_3$ oxidation catalysts exposed to sulfur [41]. In contrast, the spent Pt/CeO_2 catalyst showed a pronounced decrease in BET surface area and an increase in the average pore radius, consistent with sulfation of the ceria [42]. Sulfation of the ceria support is confirmed by the measured sulfur content of 1.7 wt% in the spent catalyst, as compared to a sulfur content of 0.15 wt% determined for the Pt/SiO_2 catalyst after exposure to SO_2 .

4. Conclusions

A number of base metal oxide and Pt-based catalysts were found to be extremely active for NO oxidation to NO_2 in the absence of SO_2 . These oxides included known catalysts ($\text{Co}_3\text{O}_4/\text{SiO}_2$, FeMnO_3 , $\text{Cr}_2\text{O}_3/\text{TiO}_2$), as well as a new one identified in this work, $\text{CrFeO}_x/\text{SiO}_2$. Kinetic studies revealed that $\text{Co}_3\text{O}_4/\text{SiO}_2$ exhibits a higher apparent activation energy for NO oxidation than Pt-based catalysts such as Pt/SiO_2 and Pt/CeO_2 , while the combined reaction order in NO and O_2 for the three catalysts is very close to one. CO_2 was found to have no effect on the kinetics of NO oxidation over these catalysts. The presence of H_2O caused a decrease in NO conversion for both $\text{Co}_3\text{O}_4/\text{SiO}_2$ and Pt/CeO_2 catalysts, while no effect was observed for Pt/SiO_2 . The inhibiting effect of water was reversible and is attributed to competitive adsorption with the reactants.

In the presence of 2800 ppm SO_2 , all the catalysts tested were found to be severely deactivated with respect to NO oxidation. $\text{Co}_3\text{O}_4/\text{SiO}_2$, $\text{Pt}/\text{ZSM-5}$ and Pt/CeO_2 showed the highest activity for NO oxidation in the presence of SO_2 (based on peak NO conversions to NO_2), although in no cases did the NO conversion exceed 7%. Reactor studies suggest that there are two components to SO_2 -induced deactivation of $\text{Co}_3\text{O}_4/\text{SiO}_2$, corresponding to an irreversible deactivation due to sulfation of the surface of the Co_3O_4 phase, together with a reversible inhibition due to competitive adsorption of SO_2 with NO on the catalyst. Of note is the finding that catalysts which are acidic in nature, such as a sol-gel $\text{CoO-Nb}_2\text{O}_5\text{-SiO}_2$ mixed oxide and Nb_2O_5 supported on SiO_2 , while showing essentially no activity for NO oxidation in the absence of SO_2 , are found to possess low oxidation activity when SO_2 was present. SO_2 therefore acts as a promoter for NO oxidation over these materials. Although the limited scope of this project prevented further examination of this phenomenon, this result appears worthy of further study.

In sum, this study has shown that a variety of base metal catalysts are very active for NO oxidation. However, all of the catalysts studied are strongly deactivated in the presence of 2800 ppm SO_2 at typical flue gas temperatures; consequently improving catalyst resistance to SO_x will be a pre-requisite if the fast SCR concept is to be applied to coal-fired flue gas conditions.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
BTU	British Thermal Unit
GHSV	Gas Hourly Space Velocity
SCR	Selective Catalytic Reduction
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

APPENDICES

Tables 1-11.

Figures 1-10.

Table 1. Summary of literature concerning catalytic oxidation of nitric oxide: supported precious metal catalysts

Year	Catalysts studied	Comment	Authors	Reference
2005	Pt/Al ₂ O ₃	Rate equation derived. Inhibition by NO ₂ studied	S.S. Mulla, N. Chen, W.N. Delgass, W.S. Epling, F.H. Ribeiro	<i>Catal. Lett.</i> , 100 , 267-270
2005	Pt/Al ₂ O ₃	Kinetic model derived	M. Crocoll, S. Kureti, W. Westweiler	<i>J. Catal.</i> , 229 , 480-489
2005	Pt on various supports (SiO ₂ , Al ₂ O ₃ , Al ₂ O ₃ -SiO ₂ , ZrO ₂ , TiO ₂ , CeO ₂ , YSZ)	Silica is best support. Activity increases with decreasing Pt dispersion	S. Benard, L. Retailleau, F. Gaillard, P. Vernoux, A. Giroir-Fendler	<i>Appl. Catal.B</i> , 55 , 11-21
2004	Pt/SiO ₂ , Pt/CeZrO ₂	Rate equation derived. Reaction mechanisms proposed	R. Marques, P. Darcy, P. Da Costa, H. Mellottée, J.-M. Trichard, G. Djéga-Mariadassou	<i>J. Mol. Catal. A</i> , 221 , 127-136
2004	Pt/Al ₂ O ₃	Kinetic model derived	M. Crocoll, W. Weisweiler	<i>Chem. Ing. Technik</i> , 76 , 1490-1494
2004	Pt/Al ₂ O ₃	Limited conversion data given	J. Li, J. Hao, L. Fu, T. Zhu, Z. Liu, X. Cui	<i>Appl. Catal. A</i> , 265 , 43-52.
2004	Pt/SiO ₂	Parametric study	J. Després, M. Elsener, M. Koebel, O. Kröcher, B. Schnyder, A. Wokaun	<i>Appl. Catal. B</i> , 50 , 73-82
2003	Pt/SiO ₂	Limited conversion data given	D.C. Chambers, N.W. Cant	<i>Appl. Catal. B</i> , 41 , 61-70
2002	Pt/Al ₂ O ₃ , Pt/BaO/Al ₂ O ₃	Influence of Pt dispersion studied, as well as catalyst deactivation	L. Olsson, E. Fridell	<i>J. Catal.</i> , 210 , 340-353
2002	Pt/Al ₂ O ₃	Conversion data given	S. Kikuyama, I. Matsukuma, R. Kikuchi, K. Saskia, K. Eguchi	<i>Appl. Catal. A</i> , 226 , 23-30
2001	Pt/Al ₂ O ₃ , Pt/BaO/Al ₂ O ₃	Kinetic study	L. Olsson, H. Persson, E. Fridell, M. Skoglundh, B. Andersson	<i>J. Phys. Chem.</i> , 105 , 6895-6906
1999	Pt/Al ₂ O ₃	Kinetic study	L. Olsson, B. Westerberg, H. Persson, E. Fridell, M. Skoglundh, B. Andersson	<i>J. Phys. Chem. B</i> , 103 , 10433-10439
1996	Pt on SiO ₂ , Al ₂ O ₃ , ZrO ₂	Pt/SiO ₂ >Pt/Al ₂ O ₃ >Pt/ZrO ₂ (same order as for SO ₂ oxidation). For silica, large Pt particles more active than small particles	E. Xue, K. Seshan, J.R.H. Ross	<i>Appl. Catal. B</i> , 11 , 65-79

Table 2. Summary of literature concerning catalytic oxidation of nitric oxide: metal oxide catalysts

Year	Catalysts studied	Comment	Authors	Reference
2003	10%Fe-10%Mn/TiO ₂ , 10%Mn/TiO ₂ (via impregnation)	10%Fe-10%Mn/TiO ₂ > 10%Mn/TiO ₂ ; Fe-Mn/TiO ₂ resistant to 100 ppm SO ₂ at 150 °C	G. Qi, R.T. Yang	<i>Appl. Catal. B</i> , 44 , 217-225
2003	Alumina	Effect of SO ₂ on NO oxidation over alumina	P. Li, G.Z. Lu, X.G. Zhao, W.D. Xiao	<i>Cui hua xue bao</i> , 24 (9), 681-686 (in Chinese)
2002	Ni/alumina	Effect of SO ₂ on NO oxidation studied	Y. Zhao, P. Li, G. Lu, X. Zhao, W. Lu, W. Xiao	<i>Huan jing ke xue xue bao</i> , 22 (2), 188-193 (in Chinese)
2002	Cu/TiO ₂	Catalyst optimized, kinetic study performed	J.-C. Lou, C.-M. Hung, J.-J. Wang	<i>Zhongguo Huanjing Gongcheng Xuekan</i> , 12 , 353-361 (in Chinese)
2001	Mixed oxides of Mn-Fe w/ one of Ti, Zr, Ce, Ni, Co, Cu added	Fe-Mn-Ti and Fe-Mn-Zr best	H.Y. Huang, R.T. Yang	<i>Langmuir</i> , 17 , 4997-5003
2001	Perovskites: La _{0.8} A _{0.2} MnO ₃ (A = Sr, Ba, K, Cs)	Conversion data given	F.-C. Buciuman, E. Joubert, J.-C. Menezes, J. Barbier	<i>Appl. Catal. B</i> , 35 , 149-156
2000	Mn, Cr, Co, Cu, Ni, Fe, Zn oxides on alumina; Pt/alumina; Mn, Cr, Cu, Ni, Co oxides on titania; Pt/titania; Co, Mn, Cr oxides on silica	Alumina: Mn > Cr > Co > Cu > Ni > Fe > Zn Titania: Mn > Cr > Cu > Ni > Co Silica: Co > Mn > Cr	W. Lu, X. Zhao, H. Wang, W. Xiao	<i>Cui hua xue bao</i> , 21 (5), 423-427 (in Chinese)
2000	Co/alumina	Effect of SO ₂ on NO oxidation studied	X. Zhang, H. Wang, W. Xiao, J. Wang	<i>Cui hua xue bao</i> , 21 (3), 239-242 (in Chinese)
1997	Co, Cu, Fe, Cr, Ni, Mn, Ti, V, Zn, W oxides; Fe-Mn, Co-Cu-Fe, Fe-Cu-Co-Cr mixed oxides	Cr oxide and Fe-Mn (10:1) mixed oxide show highest activity. Single oxides: Cr > Fe > Co > Mn > Cu (ASA as support)	L. Luo, S. Li	<i>Huanjing Gongchen</i> , 15 (4), 30-33 (in Chinese)
1997	MnO ₂ /TiO ₂	Japanese patent	N. Imada, Y. Kato	JP 09155190 (in Japanese)
1996	Cr/TiO ₂ , Cu/TiO ₂	Cr ≥ Cu; for Cr, activity follows loading: 20 > 10 > 4 > 1 wt%	K. Shiba, H. Hinode, M. Wakihara	<i>React. Kinet. Catal. Lett.</i> , 58 , 133-137
1984	Various supported metal oxides, physical mixtures of oxides, zeolite X exchanged with Cu ²⁺ , Fe ²⁺ , Cr ³⁺ ; Also contains review of earlier work	>500 F: Cu ²⁺ -X, Pt/alumina > others <500 F: Fe ₂ O ₃ /MnO/ZnO > Ni/alumina ~ Co/alumina ~ Fe/MoO ₃ -Al ₂ O ₃ , V ~ MoO ₃ -Al ₂ O ₃ ~ Bi/MoO ₃ -Al ₂ O ₃	H.T. Karlsson, H.S. Rosenberg	<i>Ind. Eng. Chem. Process Des. Dev.</i> , 23 , 808-814

Table 3. Summary of literature concerning catalytic oxidation of nitric oxide: zeolite-based catalysts

Year	Catalysts studied	Comment	Authors	Reference
2002	Metal ion-exchanged zeolite Y	Effect of SO ₂ on NO oxidation studied	Z. Chen, A. Yu, W. Rao	<i>Henan Huagong</i> , 3 , 13-15 (in Chinese)
2002	Fe-mordenite	Conversion data given (activity rather low)	R.Q. Long, R.T. Yang	<i>J. Catal.</i> , 207 , 274-285
2002	Pd, Co supported on H-ZSM-5	Moderate activity, loading dependent	F. Bustamante, F. Cordoba, M. Yates, C. Montes de Correa	<i>Appl. Catal. A</i> , 234 , 127-136
2000	Cu-ZSM-5, Pt/SiO ₂ , Co-ZSM-5, Fe-ZSM-5, Fe-FER	Fe-FER>>Fe-ZSM-5>rest	N.W. Cant, I.O.Y. Liu	<i>Catal. Today</i> , 63 , 133-146
2000	Fe-ZSM-5, Fe-FER	Fe-FER>Fe-ZSM-5; both catalysts strongly inhibited by SO ₂	R. Giles, N.W. Cant, M. Kögel, T. Turek, D.L. Trimm	<i>Appl. Catal. B</i> , 25 , L75-L81
2000	Pt-ZSM-5	Japanese patent	M. Iwamoto, K. Kawanabe	JP 2000084364
2000	Noble metals/zeolite	Japanese patent	T. Kamioka, T. Kurokawa	JP 2000225323
1998	Co/H-ZSM-5, H-ZSM-5, Co/H-USY, H-USY	Co/H-ZSM-5 >> H-ZSM-5 >> Co/H-USY = H-USY	J.-Y. Yan, H.H. Kung, W.H.M. Sachtler, M.C. Kung	<i>J. Catal.</i> , 175 , 294-301
1998	H-mordenite	Kinetic study	J.G.M. Brandin, L.H. Andersson, C.U.I. Odenbrand	<i>Acta. Chem. Scand.</i> , 44 , 784-788
1997	Pt-ZSM-5	Conversion data given (high activity)	M. Iwamoto, A.M. Hernandez, T. Zengyo	<i>Chem. Commun.</i> 1997, 37-38

Table 4. Physical characterization of supported metal oxide catalysts

Description	XRF (wt%)	XRD (phases detected)	Measured BET SA (m²/g)	Calcd. SA for physical mix (m²/g)	Pore volume (cm³/g)
Silica support	-	-	320	-	1.15
Titania support	-	Anatase	163	-	0.411
Co ₃ O ₄ /SiO ₂	Co, 4.7	Co ₃ O ₄ , d = 2.6 nm	272	300	1.09
Co ₃ O ₄ /SiO ₂	Co, 17.3	Co ₃ O ₄ , d = 8.1 nm	227	245	0.87
Co ₃ O ₄ /TiO ₂	Co, 13.3	Amorphous	99	134	0.277
Cr ₂ O ₃ /SiO ₂	Cr, 13.5	α -Cr ₂ O ₃ , d = 12.0 nm	240	257	0.934
Cr ₂ O ₃ /TiO ₂	Cr, 13.2	Amorphous	122	132	0.301
CuO/SiO ₂	Cu, 11.8	CuO, d = 6.0 nm	209	178	0.902
CuO/TiO ₂	Cu, 16.5	CuO, d = 26.8 nm	76	97.5	0.281
Nb ₂ O ₅ /SiO ₂	Nb, 19.5	Amorphous	238	231	0.723
MoO ₃ /SiO ₂	Mo, 24.7	MoO ₃ , d = 17.7 nm	187	201	0.753
MnO _x /SiO ₂	Mn, 16.4	Mn ₂ O ₃ , d = 36.5 nm	203	189	0.885

Table 5. Physical characterization of mixed oxide catalysts

Description	XRF (wt%)	XRD (phases detected)	BET SA (m²/g)	Calcd. SA for physical mix (m²/g)	Pore volume (cm³/g)
FeCrO _x /SiO ₂	Fe, 6.2; Cr, 8.0	Amorphous	258	254	0.824
FeCrO _x /TiO ₂	Fe, 5.5; Cr, 5.4	Amorphous	121	137	0.298
FeMnO _x /SiO ₂	Fe, 7.7; Mn, 8.5	Amorphous	226	246	0.709
FeMnO _x /TiO ₂	Fe, 6.5; Mn, 7.7	Amorphous	113	130	0.255
FeMnO _x /SiO ₂	Fe, 17.5; Mn, 1.7	Amorphous	241	232	0.786
FeMnO _x /TiO ₂	Fe, 13.7; Mn, 1.7	Amorphous	97.7	127	0.237
CoO-SiO ₂	Co, 6.3	Amorphous	288	-	0.022
CoO-Nb ₂ O ₅ -SiO ₂	Co, 8.8; Nb, 7.6	Amorphous	<5	-	-
FeMnO ₃	Fe, 32.7; Mn, 33.8	FeMnO ₃ , d = 7.6 nm	64.7	-	0.345
CuO-CeO ₂	Cu, 5.6; Ce, 68.5	CeO ₂ , d = 5.6 nm	84.2	-	0.155

Table 6. Physical characterization of zeolite catalysts

Description	XRF (wt%)	BET SA (m²/g)	Total pore volume (cm³/g)	Micropore volume (cm³/g)
H-ZSM-5	-	356	0.161	0.12
Co-ZSM-5	Co, 1.24	326	0.142	0.11
Cu-ZSM-5	Cu, 2.53	309	0.133	0.103
Fe-ZSM-5	Fe, 2.0	294	0.134	0.097
Pt/ZSM-5	Pt, 0.50	332	0.135	0.104

Table 7. Physical characterization of supported platinum catalysts

Description	XRF (wt%)	BET SA (m²/g)	Pore volume (cm³/g)
Pt/SiO ₂	Pt, 0.26	310	1.247
Pt/TiO ₂	Pt, 0.49	141	0.387
Pt/CeO ₂	Pt, 0.44	71	0.233
V ₂ O ₅ -Pt/SiO ₂	Pt, 0.25; V, 4.63	252	1.074

Table 8. Analysis of spent catalysts

Catalyst	Sulfur (wt%)	S : metal mole ratio	XRD		BET surface area (m²/g)	
			Fresh	Spent	Fresh	Spent
Co ₃ O ₄ /SiO ₂	1.5	0.14 : 1	Co ₃ O ₄ , d = 8.1 nm	Co ₃ O ₄ , d = 12.8 nm	227	217
Cr ₂ O ₃ /SiO ₂	0.24	0.02 : 1	Cr ₂ O ₃ , d = 12.0 nm	Cr ₂ O ₃ , d = 26.8 nm	240	241
FeMnO _x /SiO ₂	3.49	0.37 : 1	Amorphous	Amorphous	226	189
FeMnO _x /TiO ₂	4.7	0.41 : 1	Amorphous	Amorphous	113	54
FeMnO ₃	11.35	0.38 : 1	FeMnO ₃ , d = 7.6 nm	Poorly crystalline MnSO ₄ and Fe ₂ O ₃	64.7	10.5

Table 9. Comparison of physical properties for as prepared and sulfated catalysts used in kinetic study

Catalyst	Metal (wt%)	Condition	Sulfur (wt%)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)
Co ₃ O ₄ /SiO ₂	4.7	As prepared	-	272	1.095	7.5
		After sulfation	< 0.1	274	1.088	7.4
Pt/SiO ₂ ^(*)	0.57	As prepared	-	296	1.208	7.7
		After sulfation	0.15	294	1.20	7.7
Pt/CeO ₂	0.44	As prepared	-	68.8	0.212	6.2
		After sulfation	1.70	36.3	0.18	8.9

^(*) Pt dispersion of fresh catalyst = 79.5%; Pt dispersion of sulfated catalyst = 35.8% (determined by H₂ chemisorption).

Table 10. Summary of kinetic parameters determined for NO oxidation ^(*)

Catalyst	Reaction condition	E _a (kJ/mol)	NO order	O ₂ order
Co ₃ O ₄ /SiO ₂	NO + O ₂	70.9	0.39	0.46
	NO + O ₂ + H ₂ O	51.2	0.45	0.42
	NO + O ₂ over sulfur-poisoned catalyst	49.5	0.56	0.43
Pt/SiO ₂	NO + O ₂	40.6	0.46	0.52
	NO + O ₂ over sulfur-poisoned catalyst	32.5	0.37	0.51
Pt/CeO ₂	NO + O ₂	31.4	0.55	0.36
	NO + O ₂ + H ₂ O	36.9	0.49	0.33
	NO + O ₂ over sulfur-poisoned catalyst	24.2	0.57	0.42

^(*) Feed gas: 250 ppm NO, 3.5%O₂, 3.5% H₂O where indicated, N₂ as balance; reaction orders determined at 300 °C.

Table 11. Effect of H₂O addition on NO oxidation over three different catalysts (*)

Catalyst	Temp (°C)	NO conversion (%)	
		Before adding H ₂ O	After adding H ₂ O
Co ₃ O ₄ /SiO ₂	260	13.6	4.6
Pt/SiO ₂	300	7.9	8.2
Pt/CeO ₂	260	8.7	6.8
	300	14.6	12.6

(*) Total flow rate : 1.667 L/min, 250 ppm NO, 3.5vol% O₂, 3.5 vol% H₂O, N₂ as balance.
 Catalyst loading: 0.15 g for both Co₃O₄/SiO₂ and Pt/SiO₂; 0.63 g for Pt/CeO₂.

Figure 1. NO oxidation to NO₂ catalyzed by supported metal oxides. Feed gas: 250 ppm NO, 7% H₂O, 12% CO₂, 3.5 % O₂, N₂ as balance, W/F = 0.03 g h dm⁻³.

Figure 2. NO oxidation to NO₂ catalyzed by supported and unsupported mixed metal oxides. Feed gas as for Fig. 2.

Figure 3. NO oxidation to NO₂ catalyzed by zeolite catalysts. Feed gas as for Fig. 2.

Figure 4. NO oxidation to NO₂ catalyzed by platinum catalysts. Feed gas as for Fig. 2.

Figure 5. NO oxidation to NO₂ over selected catalysts in the presence of SO₂. Feed gas as for Fig. 2 with 2800 ppm SO₂ added.

Figure 6. Effect of SO₂ addition to feed on NO oxidation over FeCrO_x/SiO₂ at 350 °C. Catalyst first stabilized in SO₂-free feed gas (as for Fig. 2); 2800 ppm SO₂ then added to feed at t = 0 min.

Figure 7. Effect of SO_2 addition to feed on measured NO, NO_2 and NO_x concentrations at reactor outlet for CuO-CeO_2 at 350°C . Catalyst first stabilized in SO_2 -free feed gas (as for Fig. 2); 2800 ppm SO_2 then added to feed at $t = 0$ min.

Figure 8. Effect of SO_2 addition to feed on NO oxidation over $\text{Co}_3\text{O}_4/\text{SiO}_2$. Catalyst equilibrated under feed gas at 350°C between each series of measurements.

Figure 9. **a:** Temperature dependence of NO oxidation rate over different catalysts. Feed: 250 ppm NO, 3.5% O₂, N₂ as balance; **b:** NO and O₂ concentration dependence of NO oxidation rate over Co₃O₄/SiO₂ at 260 °C. Feed for determination of NO order: 3.5% O₂, 100-500ppm NO, N₂ as balance; feed for determination of O₂ order: 250 ppm NO, 1-10%O₂; N₂ as balance.