Research Article

Silver Modified Degussa P25 for the Photocatalytic Removal of Nitric Oxide

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A study of the photocatalytic behaviour of silver modified titanium dioxide materials for the decomposition and reduction of nitric oxide (NO) gas has been carried out. The effects of silver loading, calcination temperature, and reaction conditions have been investigated. Prepared photocatalysts were characterised using XRD, TEM, and XPS. A continuous flow reactor was used to determine the photocatalytic activity and selectivity of NO decomposition in the absence of oxygen as well as NO reduction using CO as the reducing agent, over the prepared photocatalysts. XRD and TEM analysis of the photocatalysts showed that crystalline silver nitrate particles were present on the titanium dioxide surface after calcination at temperatures of up to 200°C. The silver nitrate particles are thermally decomposed to form metallic silver clusters at higher temperatures. XPS analysis of the photocatalysts showed that for each of the temperatures used, both Ag⁺ and Ag⁰ were present and that the Ag⁰/Ag⁺ ratio increased with increasing calcination temperature. The presence of metallic silver species on the TiO₂ surface dramatically increased the selectivity for N₂ formation of both decomposition and reduction reactions. When CO was present in the reaction gas, selectivities of over 90% were observed for all the Ag-TiO₂ photocatalysts that had been calcined at temperatures above 200°C. Unfortunately these high selectivities were at the expense of photocatalytic activity, with lower NO conversion rates than those achieved over unmodified TiO₂ photocatalysts.

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1. INTRODUCTION

Escalating levels of industrial activity worldwide are associated with increasing emissions of harmful pollutants, including NO_x gases. Targets to control such emissions are currently met using traditional thermal selective catalytic reduction (SCR) but with regulations concerning these emissions becoming ever more stringent, there has been a great deal of recent interest in the use of novel photocatalytic processes to convert the NO_x into harmless N₂ gas. TiO₂ has been shown to be an effective photocatalyst for removing NO_x from the atmosphere [1], however, the primary product of this process is N₂O, which is a regulated pollutant in itself. Further modifications can be used to enhance activity and/or selectivity of the TiO₂ photocatalyst, leading to greater conversion to harmless N₂.

The addition of transition metal dopants to photocatalytic materials can have a dramatic effect on the activity and/or selectivity of certain photo-induced reactions [2–6].

In most cases the role of the dopant is thought to increase the efficiency of the photoreactions via enhanced charge separation properties of the modified photocatalyst [7] although the dopants themselves may have catalytic properties [8].

The photocatalytic decomposition of NO in the absence of oxygen over silver modified TiO₂ photocatalysts has not been previously reported in the literature. Work by Matsuoka et al. [9] showed that UV irradiation of a Ag⁺/ZSM-5 catalyst in the presence of NO results in the photocatalytic formation of N₂, N₂O, and NO₂, with N₂ being the major product. Ag/Al₂O₃ and AgCl/Al₂O₃ photocatalysts have been reported to be efficient for the photocatalytic decomposition and reduction of NO with propane [10]. For the thermal selective catalytic reduction (SCR) of NO, it has been reported that supported silver catalysts are highly selective for the formation of N₂. For example, Bera et al. [11] has reported that Ag/CeO₂ catalysts are good SCR for the reduction of NO with CO. These studies illustrate that silver species can offer

adsorption sites that are active for NO conversion with the potential to selectively form N_2 .

For both the Al_2O_3 - and ZSM-5-based systems excitation was via direct UV adsorption by the silver species, as the support materials were not semiconductor photocatalysts and therefore required the use of short wavelength UV sources. However, if silver is supported on a photocatalytically active support such as TiO_2 , then excitation of the active silver sites via charge transfer from the support could be possible, thereby offering the potential to utilise near UV light for excitation.

The aim of the work reported in this paper was to investigate the effect of silver species supported on Degussa P25-type TiO_2 on the photocatalytic activity and the selectivity of NO decomposition reactions, as well as NO reduction reactions in the presence of CO. The effects of photocatalyst processing parameters along with their photocatalytic behaviour under varying reaction conditions are presented.

2. EXPERIMENTAL

2.1. Preparation of Ag- TiO_2 photocatalysts

Ag- TiO_2 photocatalysts with silver loadings of 1.0 and 5.0 wt.% were prepared by drying dispersions of Degussa P25 TiO_2 from the appropriate concentration of silver nitrate solution. The appropriate amount of $AgNO_3$ (99.9% purity, Aldrich) was dissolved in acidified triply deionised water (6 cm^3 0.05 M HNO_3 in 500 cm^3 TDW). TiO_2 (0.19975 g) was then added to 500 cm^3 of the acidified $AgNO_3$ solution and stirred for 12 hours to yield a partially stabilised dispersion. Powder and glass supported powder samples were prepared by drying the dispersions at 70°C for 48 hours followed by a 2-hour calcination treatment at a predetermined temperature of 120, 200, 450, or 600°C .

2.2. Characterisation

XRD diffraction patterns were recorded using a Philips PW 3710 XPERT diffractometer, operated at 40 kV and 40 mA utilising a $Cu\ K\alpha$ radiation source ($\lambda = 0.154\text{ nm}$). Data was collected using a step size of 0.02° , over a 2θ range 20 – 80° and a dwell time per step of 16 seconds. The Scherrer equation [12] and the direct comparison method [12] were used to estimate the particle sizes and the phase composition of the samples, respectively.

TEM was carried out using a JEOL FX III microscope with an accelerating voltage of 200 keV. Sample preparation involved sonication of photocatalyst powders (5–10 mg) in propan-2-ol (10 cm^3) and evaporation of the dispersions onto 300 mesh copper coated holey carbon grids.

XPS analysis of the powder samples was carried out using a Kratos AXIS ULTRA XPS system fitted with a monochromated $Al\ K\alpha$ X-ray source and a hemispherical analyser with eight channeltrons. The source was operated at 10 mA and 15 kV. High resolution scans were run over the appropriate regions using a step size of 0.1 eV and a pass energy of 40 eV. Data was processed using the CASA XPS data analysis

software using the $Ti\ 2p_{3/2}$ photoelectron peak at 459.0 eV for charge correction. Peak fitting was undertaken using a Shirley background and Gaussian/Lorentzian contributions of 30/70. The relative surface compositions of the photocatalyst samples were calculated semiquantitatively from the relative intensities of the $Ag\ 3d_{5/2}$, $Ti\ 2p_{3/2}$, and $O\ 1s$ peaks by taking the integrated intensities of the high-resolution peaks with standard library Schofield sensitivity factors applied.

2.3. Photocatalytic reactions

The photocatalytic behaviour of the Ag- TiO_2 thin film catalysts was studied using a continuous flow style photoreactor [1]. The composition of the exhaust gas was measured using a quadrupole mass spectrometer (HAL 201 system, Hidden Analytical Ltd.) fitted with a heated rapid capillary inlet system. The reactants and possible products were constantly monitored before, during, and after illumination and their corresponding changes in measured partial pressure were used to quantify the observed photocatalytic response. UV illumination of the glass-supported photocatalyst was through a quartz window using a 400 W medium pressure mercury lamp. A water filter was used to remove the infrared radiation emitted.

For each photocatalyst studied a preoxidation treatment was performed to remove surface hydrocarbons. After the oxidative pretreatment, argon was passed through the system at $50\text{ cm}^3\text{min}^{-1}$ for 2 hours, after which time no oxygen could be detected in the exhaust.

To enable quantification of the mass spectrometry data, ^{15}NO was used as the reactant molecule. The level of isotopic substitution of ^{15}N for ^{14}N was determined by the manufacturers to be greater than 99.5%. For all of the reactions studied, the desired concentration of reactants in an argon carrier gas was passed over the photocatalyst with a total flow rate of $5.5\text{ cm}^3\text{min}^{-1}$ until steady-state conditions were attained (*ca.* 30 minutes). The lamp was then switched on and the photocatalyst illuminated for 30 minutes.

Photocatalytic decomposition reactions, in the absence of oxygen, were performed using a NO concentration of 909 ppm. Photocatalytic reduction reactions were investigated using the same conditions with the addition of 1818 ppm of CO.

3. RESULTS

3.1. X-ray diffraction

The X-ray diffractograms for 1 wt.% Ag- TiO_2 photocatalysts showed reflections due to anatase and rutile phases of TiO_2 , with no change in the ratio of these phases for calcination temperatures up to 450°C . No reflections due to any silver containing species were observed, due to the low volume concentration of such species in the sample. The composition and crystallite size for the TiO_2 phases (Table 1) were consistent with those for the unmodified TiO_2 system [1].

After calcination at 600°C for 2 hours, the relative intensity of rutile to anatase reflections increased slightly more

TABLE 1: Composition and crystallite sizes calculated from the XRD data for 1 wt.% Ag-TiO₂ photocatalysts.

Calcination temperature/°C	Percentage of rutile/vol.%	Crystallite size/nm	
		Anatase	rutile
70	23.7	27.9	62.6
120	23.2	28.5	59.7
200	22.4	28.8	65.8
450	23.5	28.1	65.0
600	31.5	32.8	79.3

than was observed for the unmodified TiO₂ photocatalyst calcined using identical conditions. Calculation of the phase composition of the TiO₂ support confirmed that there was 31.5 vol.% of rutile phase present compared to only 28 vol.% for the unmodified TiO₂ calcined at 600°C for 2 h [1].

As no silver species were detected in the X-ray diffraction patterns for the 1 wt.% Ag-TiO₂ samples, a 5 wt.% Ag-TiO₂ system was prepared and characterised to help investigate the changing nature of the silver species during thermal processing. In the X-ray diffractograms for 5 wt.% Ag-TiO₂ calcined at low temperatures (70–200°C), reflections due to silver nitrate were observed along with the reflections for anatase and rutile (Figure 1(a)). As the calcination temperature was increased from 70°C to 200°C the relative intensity of the silver nitrate reflections with respect to the TiO₂ reflections decreased. After calcination at 450°C no reflections due to any silver containing species were observed, but after calcination at 600°C, reflections assigned to metallic silver were detected (Figure 1(b)).

3.2. TEM

No silver containing particles could be resolved in TEM micrographs of the 1 wt.% Ag-P25 photocatalysts up to 450°C, as illustrated in Figure 2(a), although EDX analysis confirmed the existence of silver on the TiO₂ support. D-spacings calculated from selected area diffraction patterns confirmed only the presence of anatase and rutile TiO₂. In the micrographs of 1 wt.% Ag-TiO₂ calcined at 600°C (Figure 2(b)), small spherical particles were observed, which was confirmed by EDX analysis. The selected area diffraction patterns showed no diffractions from silver species.

3.3. XPS

As the chemical shift between Ag⁰ and Ag⁺ species is less than 1 eV and due to the range of Ag 3d peak position values reported in the literature, XPS analysis of standard silver compounds, AgNO₃, Ag₂O, and Ag foil, was undertaken. The trend observed was a decrease in the binding energies of the Ag 3d_{5/2} photoelectrons from AgNO₃ (368.9 eV) to Ag₂O (368.4 eV) and finally to Ag⁰ (368.1 eV). For both silver oxide and silver nitrate one peak fitted the data well. Two peaks were fitted to the Ag foil data, the second being due to a silver oxide layer that had formed on the metal surface. The positions and full width half maximum (FWHM) of the fitted peaks are presented in Table 2.

FIGURE 1: (a) Powder XRD diffractograms for 5 wt.% Ag-TiO₂ photocatalysts calcined at 70°C (A), 120°C (B), 200°C (C), 450°C (D), and 600°C (E). (b) Enlarged section of (a) showing metallic silver diffractions. Reflections due to anatase, rutile, silver nitrate, and silver are indicated by the symbols *, †, ♦, and ♣, respectively.

FIGURE 2: TEM micrographs and their corresponding selected area electron diffraction patterns for 1 wt.% Ag-TiO₂ calcined at (a) 450°C and (b) 600°C.

For the 1 wt.% and 5 wt.% Ag-TiO₂ photocatalysts the high-resolution scans of the Ag 3d_{5/2} peaks were broadened indicating that they were the sum of multiple peaks. Fitted data, peak positions, and FWHM for the 1 wt.% Ag-TiO₂

FIGURE 3: Fitted high-resolution XPS spectra of the Ag 3d_{5/2} peaks for 1 wt.% Ag-TiO₂ photocatalysts calcined at (a) 70°C, (b) 200°C, (c) 450°C, and (d) 600°C.

TABLE 2: Ag 3d_{5/2} photoelectron peak positions and FWHM for standard silver compounds. Values in brackets are for the oxide layer detected on the silver foil.

Compound	Ag 3d _{5/2}	
	BE/eV	FWHM/eV
Silver nitrate	368.9	1.12
Silver oxide	368.4	1.15
Silver foil	368.1	0.65
	(368.2)	(1.48)

system are given in Figure 3 and Table 3, respectively. Using the data obtained from the silver standards, the fitted peaks were assigned to Ag⁺ and Ag⁰ species, respectively. As the calcination temperature was increased from 70°C to 600°C the relative intensity of the Ag⁺ to Ag⁰ decreased for both the 1 wt.% Ag-TiO₂ and the 5 wt.% Ag-TiO₂ systems, as shown in Table 4. For all of the calcination temperatures the percentage of Ag⁰ was higher for the 5 wt.% Ag-TiO₂ system.

3.4. Photocatalytic reactions

As can be seen from Figure 4, increasing the silver concentration dramatically increased the selectivity for N₂ formation, especially when CO was present in the reaction gas. Selectivities as high as 90% and 100% were observed when silver loadings of 1 and 5 wt.% were used, respectively. However, these high selectivities were achieved at the expense of activity, as the NO conversions rate decreased with increasing silver concentration.

The range of calcination temperatures used in these studies produced dramatic changes in photocatalytic behaviour, as shown in Table 5. For low calcination temperatures (70–200°C) the NO conversion rate remained largely unaltered, but calcination at 450°C and above resulted in a significant reduction in the NO conversion. Similar trends were observed for both the NO decomposition and reduction reactions.

Rates of formation of N₂ and N₂O in the decomposition and reduction reactions over Ag-P25 photocatalysts were

FIGURE 4: Rate of NO conversion and selectivity for N₂ formation over Ag-TiO₂ photocatalysts with varying silver concentrations under both decomposition and reduction conditions.

TABLE 3: Table of Ag 3d_{5/2} peak positions and FWHM for 1 wt.% Ag-TiO₂ photocatalysts at various calcination temperatures.

Calcination temperature/°C	BE/eV		FWHM/eV	
	Ag ⁰	Ag ⁺	Ag ⁰	Ag ⁺
70	368.0	368.3	0.64	1.38
120	368.0	368.4	0.61	1.30
200	368.0	368.3	0.61	1.30
450	367.9	368.3	0.61	1.29
600	367.9	368.3	0.67	1.30

TABLE 4: XPS data showing ratio of silver species for 1 wt.% Ag-TiO₂ and 5 wt.% Ag-TiO₂ photocatalysts at various calcination temperatures.

Calcination temperature/°C	Percentage of Ag ⁰ species present	
	1 wt.% Ag-P25	5 wt.% Ag-P25
70	4.2	7.8
120	5.7	10.8
200	9.5	25.9
450	15.8	29.6
600	33.6	63.8

used to quantify and compare the effect of calcination temperature on selectivity for N₂ formation (Table 5). For both reaction types the selectivity of the reactions for N₂ formation increased with increasing calcination temperature, with significantly higher selectivities being observed when CO was present in the reaction gas. A 100% conversion to N₂ was observed under reduction conditions for the catalysts that had been calcined at 450°C and 600°C.

4. DISCUSSION

4.1. Characterisation

The decreasing X-ray diffraction intensities of the silver nitrate reflections with increasing calcination temperature (Figure 1) for the 5 wt.% Ag-TiO₂ photocatalysts indicated that the silver nitrate was thermally decomposed. Although no diffractions due to any silver species were detected in the sample calcined at 450°C, the silver species were not removed from the TiO₂ surface as metallic silver reflections were present in the X-ray diffractogram from the sample calcined at 600°C. Therefore, at 450°C, it is thought that the silver was present as either Ag⁰ or Ag⁺ species (or both) but the particle sizes were too small to be detected using X-ray diffraction. Increasing the calcination temperature to 600°C induced the growth of the silver particles and hence they became visible in the X-ray diffraction pattern. Although no silver species were detected in the XRD analysis of the 1 wt.% Ag-TiO₂ photocatalysts it can reasonably be expected that a similar thermal decomposition of silver nitrate and subsequent formation of metallic silver particles also occurred on samples with lower silver loadings.

TEM coupled with EDX analysis of the 1 wt.% Ag-P25 photocatalysts calcined between 70°C and 450°C confirmed the presence of silver species evenly distributed over the TiO₂ surface, but no silver containing particles were resolved, adding further evidence to the above hypothesis that after calcination at 450°C the silver species present (either Ag⁰ or Ag⁺) were nanocrystalline (i.e., <1 nm in diameter). Based on the X-ray analysis of the 5 wt.% Ag-P25 photocatalyst calcined at 600°C, it is thought that the small spherical particles observed in the micrographs of 1 wt.% Ag-P25 sample calcined at 600°C were metallic silver. It was not possible to confirm this by selected area diffraction due to the particle size of the silver species being significantly smaller than the selected areas resulting in a volume concentration of silver relative to the titanium dioxide support material that was below the detection limit.

The XPS analysis of the standard silver compounds showed that binding energies of the Ag 3d_{5/2} photoelectrons in AgNO₃, Ag₂O, and Ag metal were 368.9 eV, 368.4 eV, and 368.1 eV, respectively. The increased FWHM of the Ag 3d_{5/2} photoelectrons peaks for Ag₂O and AgNO₃ compared to the metallic Ag sample is expected due to a number of factors including charging of the nonmetallic materials, the degree of crystallinity, and the number of different silver sites in the structure [13]. The two fitted components for the metallic silver standard at 368.1 eV and 368.2 eV were assigned to photoelectrons from metallic silver and a silver oxide overlayer, respectively. The reason for the variation of the peak position and FWHM of the peak arising from the oxide layer compared to standard Ag₂O studied was most likely to be because it was a less well-ordered oxide that formed on the metal surface.

Considering the evidence from the X-ray analysis, the Ag 3d_{5/2} peak at 368.3 eV, observed for the 1 wt.% Ag-TiO₂ system calcined at temperatures up to 200°C, was assigned to the photoelectrons emitted from AgNO₃ species. The second

TABLE 5: Rate of NO conversion and selectivity for N₂ formation for 1 wt.% Ag-TiO₂ photocatalysts at various calcination temperatures under decomposition and reduction conditions.

Calcination temperature (°C)	Rate of NO conversion ($\mu\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$)		Selectivity for N ₂ formation (%)	
	Decomposition	Reduction	Decomposition	Reduction
70	583	483	29	59
120	613	353	26	88
200	489	359	29	90
450	15	68	45	100
600	7	49	53	100

photoelectron peak was assigned to a metallic silver component. The reason for the shift observed for the nitrate peak compared to the AgNO₃ standard could be the nature of the multicomponent Ag-TiO₂ system. When two materials are in contact, equalisation of their Fermi level occurs [7], which effects the energy of the photoelectrons emitted. Another possible reason for the shift could be particle size effects. It is expected that the nanometer-sized silver nitrate clusters on the TiO₂ surface would have a different electronic structure compared to larger micron-sized crystallites found in the silver nitrate standard.

At the higher calcination temperatures of 450°C and 600°C, significant amounts of Ag⁰ were present. As the samples were calcined in air, it is expected that Ag₂O was present on the metal surface (as with the metallic silver standard), and this would contribute to Ag⁺ peaks. Due to the small difference in chemical shift observed for both types of Ag⁺ species (AgNO₃ and Ag₂O) it was not possible to deconvolute the Ag⁺ peaks. It should be noted that no change was observed in the shape of the O 1-second peak as the concentration of silver oxide present was insignificant relative to the levels of oxygen detected from TiO₂.

The percentage of Ag⁰ species present relative to Ag⁺ species was greater for the 5 wt.% Ag-P25 photocatalysts (compared to the 1 wt.% Ag-TiO₂ photocatalysts) at all the calcination temperatures investigated. An explanation of this effect is based on the mechanism of supported metal particle growth. Ag⁺ species are more likely to be reduced at Ag⁰ sites than they are on a titania surface (i.e., grain growth verses cluster nucleation) [14]. Therefore, when the TiO₂ was modified with higher loadings of silver nitrate, more Ag⁺ species are available to be reduced at the Ag⁰ sites, resulting in larger metallic silver particles.

4.2. Photocatalytic activity

The rate of NO conversion decreased with increasing calcination temperature (Table 5) which is the same trend that was previously reported for unmodified TiO₂ photocatalysts [1]. The reason for the decrease in NO conversion rate as the P25 calcination temperature increased was the removal of molecular water and hydroxyl groups from the surface of TiO₂. Surface bound OH groups act as both efficient trapping sites for photogenerated holes [5] as well as good adsorption or active sites for NO molecules [15], thus reducing

the surface density of OH groups has the effect of reducing the NO conversion rate over TiO₂ photocatalysts.

The same rationalisation of decreasing density of surface bound OH groups with increasing calcination temperature can be used to partly explain the decrease in NO conversion observed for the silver containing photocatalysts under both decomposition and reduction conditions with increasing calcination temperature. However, it was also observed that the presence of silver at the loading used in these studies had a negative effect on the NO conversion rate which became more obvious as the silver concentration was increased (Figure 4).

The interface that is formed when a photocatalyst and a metal (or metal ion) are in electrical contact can serve as an efficient trap for the photogenerated electrons, preventing the energy wasting electron-hole recombination reactions. It is also possible for a charge transfer process to occur, in which the photogenerated electron migrates to the supported species. The electron is then able to initiate a redox reaction with adsorbed molecules. Both of these processes may lead to enhanced activity of a photocatalyst. However, it is also possible that if the levels of charge transfer from the photocatalysts to the supported species become excessive, then the excess negative charge can attract the positively formed photogenerated hole, and the interface acts as a recombination centre, thus reducing the efficiency of the photocatalyst [6, 16].

The XPS analysis of the Ag-TiO₂ photocatalysts showed that for each of the silver loadings used, the relative amount of metallic silver to silver ions present increased with increasing calcination temperature, with the highest silver loading showing the greatest relative percentage of Ag⁰ at all calcination temperatures. From these observations, it is proposed that the reduction in activity of the Ag-TiO₂ photocatalysts as the silver concentration and calcination temperature increased was due to the size and number of metallic clusters formed. As the resulting metal-TiO₂ interface acts as a recombination centre for the photogenerated electrons and holes, the number of photoreactions able to proceed is reduced as the number of clusters is increased.

Similar effects have been observed in the studies by Chao et al. [17, 18] on the photocatalytic degradation of methylene blue over sol-gel prepared TiO₂ modified with varying amounts of silver. It was found that when a suitable amount of Ag was used, the activity of the TiO₂ photocatalysts was

effectively enhanced. For example, when a 2–4 mol.% (2.7–5.4 wt.%) Ag was used the photocatalytic activity was increased to more than that of unmodified TiO₂. However, increasing the silver concentration further reduced the photocatalytic activity, with the higher loadings resulting in activities that were lower than that for titanium dioxide alone.

4.3. Reaction selectivity

The possible surface reactions for the NO decomposition experiments and additional reactions for when CO is present are given by reactions (1)–(7) and (8)–(10), respectively. Figure 4 shows that under decomposition conditions, as the silver loading increased the selectivity for N₂ formation also increased. As discussed above, the calcination temperature and silver loading affect the nature of the silver species present. It could therefore be expected that it was the presence of a particular type of silver species that gave rise to the higher selectivity observed. From Table 5 it can be seen that the selectivity for N₂ formation was only slightly increased (compared to unmodified TiO₂) for the decomposition reactions over 1 wt.% Ag-TiO₂ photocatalysts that had been calcined at temperatures of up to 200°C. In these systems the silver was shown to be present predominantly as silver nitrate, with only small amounts of Ag⁰. Therefore, it can be concluded that silver nitrate had little or no effect on the selectivity of the NO decomposition reaction and the relative rates of the NO surface reactions were comparable to those on unmodified TiO₂ photocatalysts. When the photocatalysts were calcined at higher temperatures, the selectivity for N₂ increased. From these observations it can be inferred that metallic silver particles and clusters may enhance the number of N₂ forming NO–NO reactions (5)–(7) relative to the N₂O forming NO–NO reactions (3).

However, it was shown by XPS analysis that the surface of the silver particles and clusters was partially oxidised. It has been reported that oxidised silver species are highly selective for N₂ formation [19–21], hence it may be that it is silver oxide species that facilitate the production of N₂.

Theoretical calculations based on Ag⁺ monomers and oligomers have shown that UV initiated NO decomposition reactions forming N₂ and O₂ via metal-to-ligand charge transfer (MLCT) transitions are feasible reactions as such transitions are favoured due to the symmetry for electric dipole transitions and require low energies which are accessible by UV light sources [22]. It has also been suggested that the likelihood for photoreactions is increased for oligomeric

Ag⁺ species, which is a more realistic model of the surface for the silver clusters present on the photocatalysts reported here.

When CO was present in the reaction gas, the selectivity for N₂ formation increased with both increasing temperature and silver loading. The reaction became 100% selective for photocatalysts calcined at or above 450°C or when 5 wt.% silver was used. This again suggests that the presence of metallic silver (or silver oxide) particles promotes the rate of the N₂ forming reactions (9)–(10) relative to the rate of the N₂O forming reactions (8), thus reaction (9), below, occurs readily:

5. CONCLUSIONS

The characteristics of the photocatalytic decomposition and reduction of NO in the presence of CO have been determined for silver modified Degussa P25 TiO₂ photocatalysts, and it has been shown that both activity and selectivity of the NO photoreactions were strongly dependant on the nature of the silver species present on the TiO₂ surface.

It was found that in the presence of CO, silver modified photocatalysts were 100% selective in the conversion of NO to N₂. This is the first time that TiO₂-based photocatalysts have been demonstrated to be so highly selective for this reaction, without the use of toxic ammonia as a reducing agent. It has been proposed that metallic silver clusters with a partially oxidised surface are responsible for the high N₂ selectivities observed, however, it should be noted that the high selectivities were at the expense of photocatalytic activity as the metal clusters acted as electron-hole recombination centres, thereby reducing the number of photoreactions that were able to proceed.

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