Catalysis Today 176 (2011) 3–6

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Photocatalytic purification of indoor air from nitrogen oxide contaminants on modified TiO_2-based catalysts

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ARTICLE INFO

Article history:
Received 31 August 2010
Received in revised form 18 July 2011
Accepted 9 August 2011
Available online 16 September 2011

Keywords:
Air pollution
Photocatalysis
NO_x removal
TiO_2 dispersion
TiO_2 modification
Photocatalytic activity

ABSTRACT

The efficiencies of TiO_2-based bulk and supported catalysts in the NO_x ($NO + NO_2$) removal from flowing $NO–O_2–N_2$ mixture under UV irradiation are quantitatively assessed by measuring the outlet NO and NO_2 concentrations as a function of irradiation time. It is found that specific photocatalytic activity of TiO_2 in this process can be considerably enhanced by dispersing TiO_2 over high-surface alumina or by incorporating into TiO_2 alkaline additives (BaO, urea). Effect of platinum doping is dependent on the Pt oxidation state. The mechanism of NO photooxidation on TiO_2 and the role of OH radicals and O_2^- species in it are discussed.

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1. Introduction

Effective removal of highly hazardous nitrogen oxides ($NO_x = NO + NO_2$) from polluted indoor air can be successfully accomplished applying photocatalysis. Upon UV irradiation of TiO_2 in a flow of air polluted with NO, NO_2 is formed which partly remains adsorbed on the surface and further is oxidized to NO_3^- [1–4]. Both adsorbed products block the catalyst active sites. As a result, initially high photocatalytic activity of TiO_2 gradually decreases with time and finally a steady-state regime is reached in which the outlet NO_x concentration is close to the inlet one. The lifetime of the photocatalyst is controlled by a number of variables, such as initial NO concentration, TiO_2 active surface, flow rate, humidity of the polluted air, light intensity and its spectral composition, etc. Because of the photocatalyst poisoning by the reaction products, it is not possible to accomplish a long-term continuous photocatalytic conversion of NO in a plug flow reactor system without catalyst regeneration. However, the catalyst lifetime can be considerably increased when mechanical mixtures of TiO_2 with adsorbents and basic oxides are used capable of absorbing large amounts of the catalyst poisons produced by the photoreaction [5–7]. In this work a series of modified TiO_2-based bulk and supported photocatalysts for NO_x removal from indoor air was prepared and tested and the factors that may affect activity, selectivity and stability of the catalysts were considered.

2. Experimental part

Commercial TiO_2 Degussa P-25 ($S = 55\,m^2/g$) and TiO_2/Al_2O_3 samples prepared by the sol–gel method with different TiO_2 loading (50, 23 and 10 wt.% of TiO_2) were used as photocatalysts. Modified TiO_2 Degussa P-25 samples were prepared by the incipient wetness procedure using $Ba(NO_3)_2$, $CO(NH_2)_2$ and $[Pt(NH_3)_4]Cl_2$ aqueous solutions as modifiers.

The photocatalytic NO oxidation was performed at atmospheric pressure and 20 °C in a flow ($V = 440\,mL\,min^{-1}$) of 50 ppm NO–7 vol.% $O_2–N_2$ (balance) taken as a model of polluted air upon irradiation by two compact 26 W black light lamps (Camelion, LH26-30). The light intensity was measured with a Photex UVA radiometer and a set of color filters in the range of 320–390 nm. The light intensity distribution was as follows: 3.5% at 420–390 nm; 19.5% at 390–370 nm; 47% at 370–350 nm; 25.6% at 350–320 nm; 5% at 320–290 nm. NO and NO_2 concentrations at the outlet were measured with a chemiluminescent gas analyzer (Eco Physics) or with an IR gas analyzer (Gasmet).

3. Results and discussion

Fig. 1 demonstrate typical dependence of NO, and NO_x concentrations vs irradiation time for the initial Degussa P25 catalyst. As

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doi:10.1016/j.cattod.2011.08.005

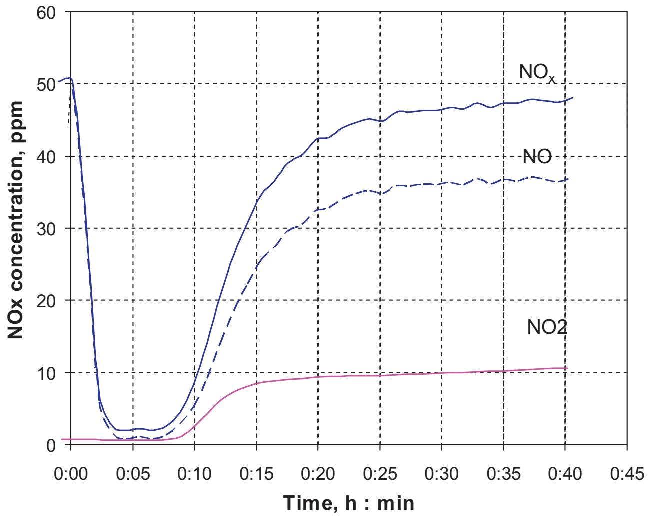


Fig. 1. Outlet NO, NO_2, and NO_x concentrations vs UV irradiation time of Degussa P-25 TiO_2.

a first approximation, the plot of Fig. 1 can be divided into three reaction stages.

On the first ("initial") stage, just after the start of irradiation, the outlet NO_x concentration falls down rather rapidly to a minimum value and remains at this minimum level for a certain time. The concentration of gaseous NO_2 is very low and stays nearly constant. According to the data obtained by aqueous ionic chromatography [2], considerable amounts of $NO_2{}^-$ ions are present at this stage in the water washouts of the irradiated TiO_2, i.e., NO is predominantly oxidized to HNO_2 (ads).

On the next, "transient" stage, NO_2 appears in the gas phase and its concentration gradually increases with time, i.e., a deeper oxidation of HNO_2 (ads) to NO_2 takes place as well as further oxidation of NO_2 to HNO_3. In parallel, the outlet NO concentration is growing. Finally, on the third "steady-state" stage, a stationary state is achieved in which NO_x (ss) is nearly equal to the inlet NO concentration indicating that no NO_x removal from polluted air actually occurs. Moreover, taking into account that NO_2 produced and evolved into the air flow is 4–5 times more harmful than NO, one can conclude that the toxicity of the "purified" air is even higher than that of the incoming polluted air.

The ionic chromatography analysis has revealed the predominance of $NO_3{}^-$ ions in the washouts from TiO_2 at this stage [2]. The $NO_3{}^-$ concentration does not change with irradiation time indicating that most NO is oxidized to NO_2, whereas HNO_3 remains on the surface and blocks the active sites. Note that in the steady-state regime, the outlet NO concentration is markedly smaller than the inlet one. Thus, the NO photooxidation goes on and an equilibrium is established in which the rate of NO_2 formation is equal to its desorption rate.

After the photoreaction is completed, the initial TiO_2 activity can be restored by removing the products upon heating the catalyst in air flow at 650–773 K.

Thus, the general scheme of NO photooxidation can be presented as the following sequence of reactions (Scheme 1). As is seen, the nitrogen oxidation state is gradually increasing from two in NO to five in HNO_3.

The mechanism of NO photooxidation on TiO_2 was discussed earlier [2,4,8–10]. It is generally accepted the key role of OH radicals formed upon the capture of photogenerated in TiO_2 holes by surface hydroxyls or adsorbed water molecules:

$$TiO_2 \overset{h\nu}{\rightleftharpoons} h^+ + e^- \tag{1}$$

$$OH^- + h^+ \rightleftharpoons {}^\bullet OH \tag{2}$$

$$H_2O + h^+ \rightleftharpoons {}^\bullet OH + H^+ \tag{3}$$

where h^+ and $e^-$are hole and electron centers, respectively.

The NO oxidation to HNO_3 proceeds via the sequence of reactions as shown in Scheme 1.

Most likely the electron centers $e^-$are captured by electron accepting oxygen molecules to yield $O_2{}^-$. Further possible transformations of $O_2{}^-$ are not considered in the above cited reports. However, it is quite evident that these species have to participate in the photocatalytic process. Otherwise, it would not be possible to accomplish the catalytic cycle. In [8] we suggested that $O_2{}^-$ can directly oxidize NO to nitrates which were identified by IR and by ionic chromatography:

$$NO + O_2^- \rightleftharpoons NO_3^- \tag{4}$$

Another possibility is the interaction of $O_2{}^-$ with protons to form HO_2 radicals followed by the reaction with NO to yield HNO_3:

$$O_2^- + H^+ \rightleftharpoons HO_2{}^\bullet \tag{5}$$

$$NO + HO_2{}^\bullet \rightleftharpoons HNO_3 \tag{6}$$

Furthermore, NO can be oxidized by O^-species (equivalent to an h^+ hole center) to give rise to $NO_2{}^-$:

$$O^- + NO \rightleftarrows NO_2^- \tag{7}$$

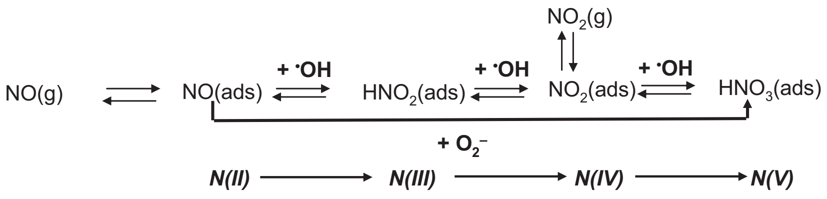
This reaction was earlier proposed on the basis of IR data on the NO photoadsorption on TiO_2 [11].

Fig. 2 depicts the plots of the outlet NO concentration vs UV irradiation time for some of the studied modified TiO_2-based catalysts. The general appearance of all the curves is similar, but they considerably differ in the minimum NO_x concentration attained soon after the onset of irradiation and in the time required to reach the steady-state regime.

The efficiencies of the TiO_2-based photocatalysts in the removal of nitrogen oxides from the O_2–N_2 flow have been quantitatively assessed by calculating the total amount of NO_x trapped by the photocatalysts for 2 h of UV illumination by integrating corresponding kinetic curves. Specific photoadsorption capacities (SPC) per 1 g of the catalysts are summarized in Table 1.

The following conclusions can be drawn from these data.

(1) SPCs of 50 and 23% TiO_2 dispersed on Al_2O_3 exceed that of original bulk TiO_2 Degussa by a factor of 5.3 and 3.0, respectively, at approximately equal inlet NO concentration of 48–55 ppm. Note a very low NO_2/NO ratio for 23% TiO_2/Al_2O_3 catalyst. Thus,



Scheme 1.

Table 1
Specific photoadsorption capacity to NO_x of the TiO_2-based photocatalysts.

	Photocatalyst	Inlet NO concentration in ppm	Specific photoadsorption capacity in μmol (NO_x) (gCat)$^{-1}$	NO_2/NO at steady state
	TiO_2 Degussa P25	55	60	0.25
		35 (H_2O)[a]	104	1.00
Dispersed TiO_2	50% TiO_2/Al_2O_3	48	320	0.11
	23% TiO_2/Al_2O_3	48	205	~0.01
	10% TiO_2/Al_2O_3	50	No activity	
Modified bulk TiO_2	5% BaO/TiO_2	50	121	0.35
	0.5%Pt/5%BaO/TiO_2	55	194	5.09
	5% $(NH_2)_2CO/TiO_2$	50	190	0.27
	0.5% Pt/TiO_2 (ox)	50	110	4.49
	0.5% Pt/TiO_2 (red)	50	44	0.20

[a] Humidified gaseous mixture.

dispersion of TiO_2 on alumina results in a substantial enhancement of the catalyst capacity compared to bulk TiO_2, apparently because much larger amounts of NO_2 formed by the photoreaction can be strongly trapped by the support and more TiO_2 active sites are available for the reactions. As 10% TiO_2/Al_2O_3 is not active, one may assume that the presence of a TiO_2 surface phase is a necessary prerequisite for the photoinduced reaction.

(2) Humidification of the initial gaseous mixture favors the removal of NO_x on the bulk TiO_2 by a factor of 1.7. This effect may be associated with the enhancement of reaction (3) to generate more OH radicals as well as with a more efficient removal of NO_2 and HNO_3 from the TiO_2 surface by wet gas flow thus liberating active sites necessary for photocatalysis.

(3) Modification of the TiO_2 surface with BaO and urea results in the increase of SPC by a factor of 2.0 and 3.2, respectively. The promoting effect is supposed to be associated with basic properties of the modifiers which efficiently neutralize NO_2 and HNO_3 produced by NO oxidation. Similar approach was used earlier by Ichiura et al. [12]. They used additives of basic oxides (CaO, MgO) or $CaCO_3$ to composite sheets (pulp slurry plus TiO_2) to increase the efficiency of the photocatalytic NO_x removal. Considerable positive effect is found also for $Pt/BaO/TiO_2$ catalyst.

(4) The behavior of the Pt-doped TiO_2 depends on the pretreatment conditions. Following calcinations in air at 500 °C, the SPC of Pt/TiO_2 approximately doubles compared to that of the initial TiO_2, and the NO_2/NO ratio considerably increases. This effect may be associated with intensive NO oxidation on ionic Pt which was detected by FTIR of CO adsorbed on the calcinated catalysts [13]. In contrast, following reduction of Pt/TiO_2 in H_2 at 200 C, the SPC drops below the value of unmodified TiO_2 without a marked change in the NO_2/NO ratio. One may suggest that this inhibiting effect is related to the capture of electronic centers generated upon UV irradiation in TiO_2 by metal platinum particles. As a result, the chain of transformations shown in Scheme 1 slows down.

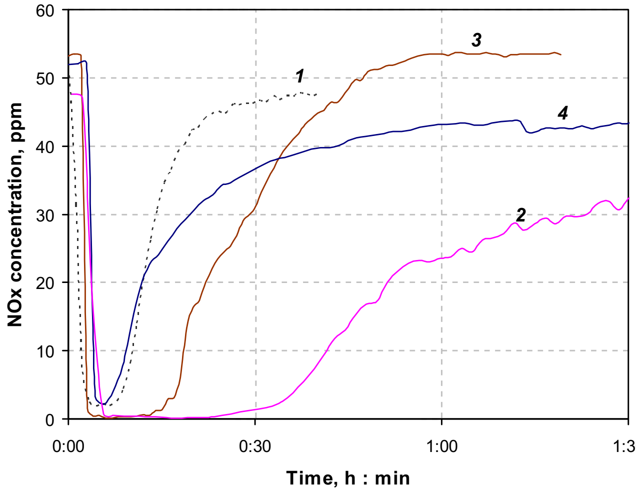


Fig. 2. Time dependence of outlet NO_x concentration upon UV irradiation of the photocatalysts. 1 – Bulk TiO_2; 2 – 50% TiO_2/Al_2O_3; 3 – BaO/TiO_2; 4 – urea/TiO_2.

Fig. 3 shows temperature-programmed desorption profiles of NO and NO_2 from Pt/TiO_2 after UV irradiation and purging the catalyst with dry nitrogen at 20 °C. A single intense NO_2 peak (T_{max} = 350 °C, I_{max} = 120 ppm) dominates for the calcined Pt/TiO_2 (Fig. 3a) which most likely arises from the decomposition of NO_3^-

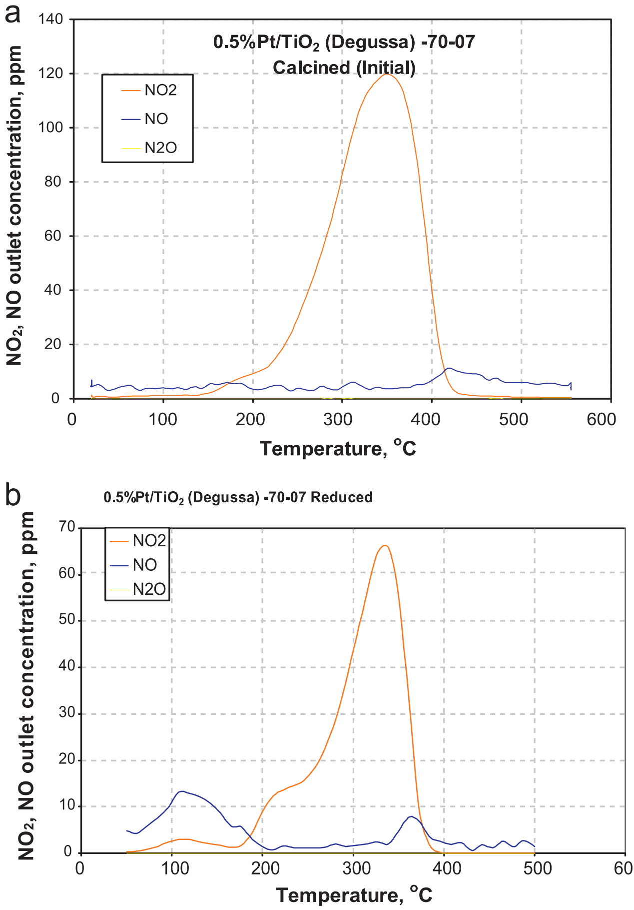


Fig. 3. TPD profiles of (a) calcined Pt/TiO_2 and (b) reduced Pt/TiO_2 after photoreaction.

and HNO_3 accumulated in the course of photooxidation. In the case of reduced Pt/TiO_2, significantly less intense NO_2 peak at the same temperature ($I_{max} = 65$ ppm) and much weaker NO desorption peaks at ~120 and ~380 °C (Fig. 3b) appear. The NO peaks probably result from the decomposition of some N-containing surface species. The thermodesorption data agree well with the above results on the effect of Pt oxidation state on the NO_2/NO ratio.

Thus, the results of this study clearly show that the photocatalytic activity of TiO_2 in the indoor air purification from oxides of nitrogen can be largely improved by simple ways: either by dispersion of TiO_2 over a high-surface alumina or by incorporation of basic additives to TiO_2. In the former case, the presence of a TiO_2 surface phase is necessary to provide fast migration of the photoinduced electrons and holes to yield OH and O_2^- which play a key role in the NO photooxidation. Incorporation of BaO and urea to TiO_2 markedly enhances the SPC of the original TiO_2 catalyst and increases its life time. The promoting action of these additives is based on their ability to neutralize acidic reaction products (NO_2, HNO_2, HNO_3) adsorbed on the surface active sites. The effect of a platinum additive is more complex and dependent on the Pt oxidation state: ionic Pt markedly enhances the SPC, whereas the presence of metal platinum particles decreases the photooxidation activity.

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