

Photocatalytic conversion of NO_x on $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst

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Abstract

The rate of NO conversion under UV illumination was evaluated over $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ catalysts at room temperature. The $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst is highly active for the conversion of NO_x . The conversion is enhanced in the presence of O_2 and further enhanced when oxygen coexists with hydrocarbons. Diffuse reflectance spectra of $\text{AgCl}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Al}_2\text{O}_3$ show an absorption band at ~ 250 nm, and a weak and broad band at ~ 230 nm, respectively. The high photocatalytic NO_x conversion is achieved over the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst. The conversion level of NO_x is maintained above 60% over 5 h in the presence of O_2 and hydrocarbons under UV-irradiation. The absorption band at ~ 250 nm is ascribed to the band gap energy of crystallized AgCl particles on Al_2O_3 . These results suggest that high photocatalytic NO_x conversion proceeds on crystallized AgCl particles formed on Al_2O_3 . © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalytic conversion; NO_x ; $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst

1. Introduction

Application of photocatalysis has been recently studied for the NO_x reduction [1–4]. Ibusuki and Takeuchi [1] reported that dilute NO_x in ambient air is effectively removed by photocatalytic oxidation on TiO_2 . Anpo et al. [2] found that NO is decomposed to N_2 and O_2 on $\text{Cu}/\text{ZSM-5}$ under the UV irradiation in the absence of oxygen. In addition, they showed that NO is photocatalytically converted into N_2 , N_2O and NO_2 on $\text{Ag}/\text{ZSM-5}$ in the presence of oxygen [3].

Miyadera et al. found that an alumina-supported silver ($\text{Ag}/\text{Al}_2\text{O}_3$) catalyst is highly effective for the reduction of NO_x with propene [5–7] and ethanol [6–8,22,9,10]. Recently,

Aoyama et al. have found that an $\text{AgCl}/\text{Al}_2\text{O}_3$ [7,11] catalyst also exhibits high activity for the reduction of NO_x with ethanol and propene.

The present work is extended to study the NO conversion on $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ catalysts under photo-irradiation in a model gas flow containing NO, NO and O_2 or NO, O_2 , C_2H_6 and C_3H_8 . It is shown that the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst exhibits high NO_x conversion under photo-irradiation.

2. Experimental

The $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ catalysts were prepared by impregnation of $\gamma\text{-Al}_2\text{O}_3$ powders (230 m^2/g , Condea Chemie) with an

aqueous solution of silver nitrate, and aqueous solution of silver nitrate and ammonium chloride, respectively. The resulting samples were then dried at 393 K for 3 h and calcined at 873 K for 2 h in air. The Ag content in these catalysts was 2.0 wt.%. No appreciable difference in Ag or Cl content was observed between bulk AgCl/Al₂O₃ dried at 393 K and calcined at 873 K.

The NO_x conversion was evaluated using a flow-type photochemical reaction system as shown in Fig. 1. The catalyst (3 g) was packed in a reactor made of quartz and irradiated by using a 500 W Xe lamp (UXL-500D, USHIO). Irradiation area was ca. 6 cm² and light intensity was ca. 60 mW/cm² (at 365 nm). A reaction gas stream containing 10 ppm NO, 10% (or 0%) O₂, 5 ppm (or 0 ppm) C₂H₆, 5 ppm (or 0 ppm) C₃H₈ and balance N₂ was flowed at a rate of 620 cm³/min. The concentration of NO_x (NO + NO₂) in the outlet gas stream was measured with a chemiluminescence based NO/NO_x analyzer.

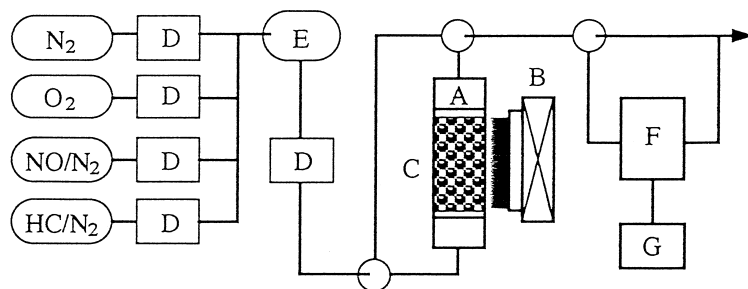
The Ag/Al₂O₃ and AgCl/Al₂O₃ catalysts were characterized by X-ray diffraction (XRD) using CuK α radiation (MPX3, MAC-Science) and ultraviolet–visible (UV–Vis) diffuse reflectance spectra using a Shimadzu UV-2400PC spectrometer before and after the NO_x reduction under photo-irradiation.

Products under photo-irradiation to the Ag/Al₂O₃ and AgCl/Al₂O₃ catalysts in the presence of NO (25 Torr) were measured by a mass spectrometer (UPM-ST-200P, ULVAC).

3. Results and discussion

Figs. 2–4 show the NO_x conversion at room temperature on the γ -Al₂O₃, Ag/Al₂O₃ and AgCl/Al₂O₃ catalysts under irradiation with a 500 W-Xe lamp. On the γ -Al₂O₃, the rate of NO_x conversion is very low in the absence of O₂ (Fig. 2a). On the other hand, reduction of NO_x occurs rapidly on the Ag/Al₂O₃ and the AgCl/Al₂O₃ catalysts (Fig. 2b and 2c). Sixty to sixty five percent of NO_x is initially converted on the AgCl/Al₂O₃ catalyst while about 10% of NO_x is converted on the Ag/Al₂O₃ catalyst. By mass spectrometric measurements it was shown that UV irradiation to the AgCl/Al₂O₃ and Ag/Al₂O₃ catalysts in the presence of NO (25 Torr) led to the formation of N₂O.

NO_x conversion over the Ag/Al₂O₃ and AgCl/Al₂O₃ catalysts is enhanced in the presence of oxygen (Fig. 3). Initial conversion of NO_x is 70–75% on AgCl/Al₂O₃. The conversion level of NO_x over Ag/Al₂O₃ and γ -Al₂O₃ is much lower than that over AgCl/Al₂O₃. It is



A: reactor, B: 500W Xe lamp, C: catalyst, D: mass flow controller
E: mixing chamber, F: NO_x analyzer, G: recorder
HC: hydrocarbon (C₂H₆ + C₃H₈)

Fig. 1. Schematic diagram of a flow-type photochemical reaction system.

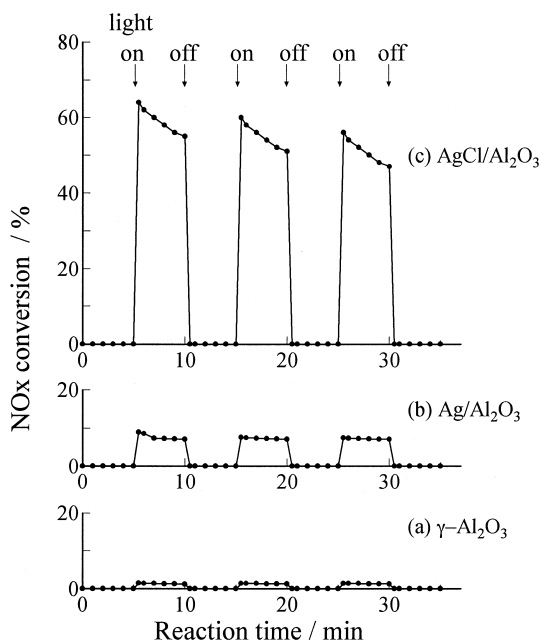


Fig. 2. Time-course of the photocatalytic NO_x conversion on the $\gamma\text{-Al}_2\text{O}_3$ (a), $\text{Ag}/\text{Al}_2\text{O}_3$ (b) and $\text{AgCl}/\text{Al}_2\text{O}_3$ (c) catalysts. Test conditions: 10 ppm NO , balance N_2 , flow rate = $620 \text{ cm}^3/\text{min}$, catalysts weight = 3.0 g.

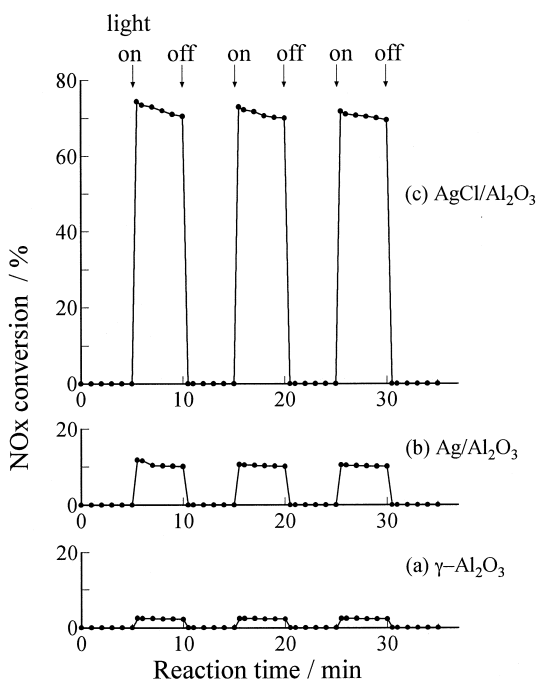


Fig. 3. Time-course of the photocatalytic NO_x conversion on the $\gamma\text{-Al}_2\text{O}_3$ (a), $\text{Ag}/\text{Al}_2\text{O}_3$ (b) and $\text{AgCl}/\text{Al}_2\text{O}_3$ (c) catalysts. Test conditions: 10 ppm NO , 10% O_2 , balance N_2 , flow rate = $620 \text{ cm}^3/\text{min}$, catalysts weight = 3.0 g.

to be noted that the NO_x conversion is further enhanced in the presence of hydrocarbons along with oxygen on the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst (Fig. 4). The conversion reaches 75–78% over $\text{AgCl}/\text{Al}_2\text{O}_3$, while that over $\text{Ag}/\text{Al}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$ is 11% or 3%. It was found that more than 10 mol of NO is converted for 1 mol of AgCl in the long time experiments. Thus, it is suggested that NO is photocatalytically converted on the $\text{AgCl}/\text{Al}_2\text{O}_3$.

Fig. 5 shows the UV–Vis diffuse reflectance spectra of the $\gamma\text{-Al}_2\text{O}_3$, $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ catalysts calcined at 873 K in air. The $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst exhibits a broad and weak absorption band at $\sim 230 \text{ nm}$ followed by a shoulder at $\sim 300 \text{ nm}$ and the spectra are different from those of $\gamma\text{-Al}_2\text{O}_3$. On the other hand, an intense absorption band appears at $\sim 250 \text{ nm}$ for the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst calcined at 873 K.

Fig. 6 shows the XRD spectra of the $\gamma\text{-Al}_2\text{O}_3$, $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{AgCl}/\text{Al}_2\text{O}_3$ catalysts calcined

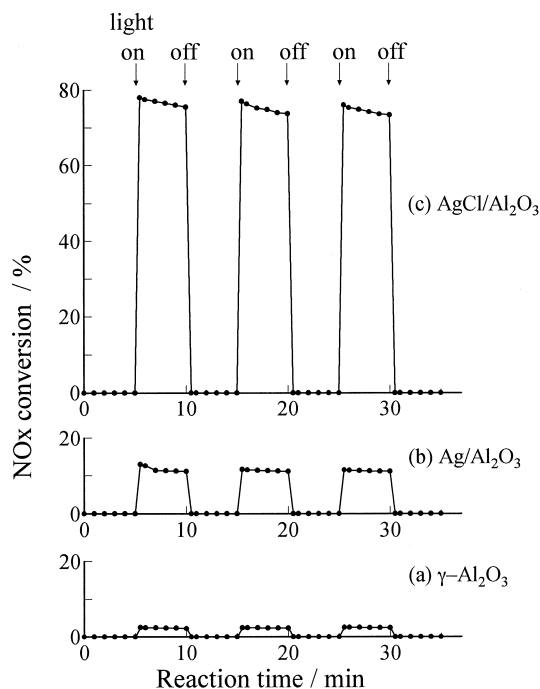


Fig. 4. Time-course of the photocatalytic NO_x conversion on the $\gamma\text{-Al}_2\text{O}_3$ (a), $\text{Ag}/\text{Al}_2\text{O}_3$ (b) and $\text{AgCl}/\text{Al}_2\text{O}_3$ (c) catalysts. Test conditions: 10 ppm NO , 10% O_2 , 5 ppm C_2H_6 , 5 ppm C_3H_8 , balance N_2 , flow rate = $620 \text{ cm}^3/\text{min}$, catalysts weight = 3.0 g.

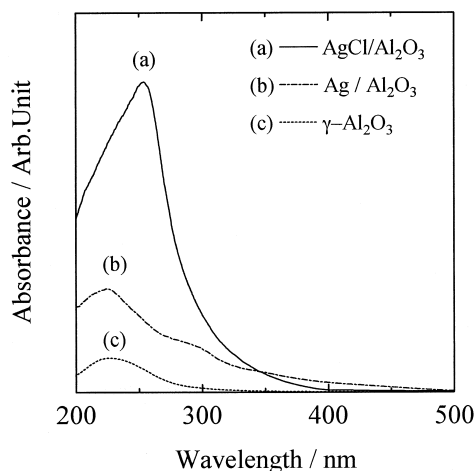


Fig. 5. UV-Vis diffuse reflectance spectra from the γ - Al_2O_3 (a), $\text{Ag}/\text{Al}_2\text{O}_3$ (b) and $\text{AgCl}/\text{Al}_2\text{O}_3$ catalysts (c) calcined at 873 K in air.

at 873 K in air. No XRD peaks attributable to crystallized silver metal or silver compounds are seen in the spectra of the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst. We previously reported [7] that oxidation of the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst at 873 K induced an interac-

tion between Ag and Al_2O_3 , resulting in the growth of the disordered silver oxide particles on Al_2O_3 . Thus, the broad and weak absorption band at ~ 230 nm in Fig. 5b is attributable to the silver oxides on Al_2O_3 . The shoulder band at ~ 300 nm is ascribed to the Ag^0 atoms reported by Ozin and Huber [12]. On the other hand, distinct XRD peaks attributable to crystallized AgCl are observed for the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst calcined at 873 K.

The present $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst calcined at 873 K in air showed high NO_x conversion under UV irradiation. The absorption band observed at ~ 250 nm in the UV-Vis diffuse reflectance spectra of $\text{AgCl}/\text{Al}_2\text{O}_3$ is attributed to the band gap energy of crystallized AgCl particles [13–15] on Al_2O_3 . Thus, it is suggested that crystallized AgCl particles on Al_2O_3 play an important role in the high NO_x conversion on $\text{AgCl}/\text{Al}_2\text{O}_3$ under UV irradiation. The $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst calcined at 773 K in air showed low NO_x conversion under UV irradiation compared with that calcined at 873 K in air. By XRD measurements, it was shown that calcination of

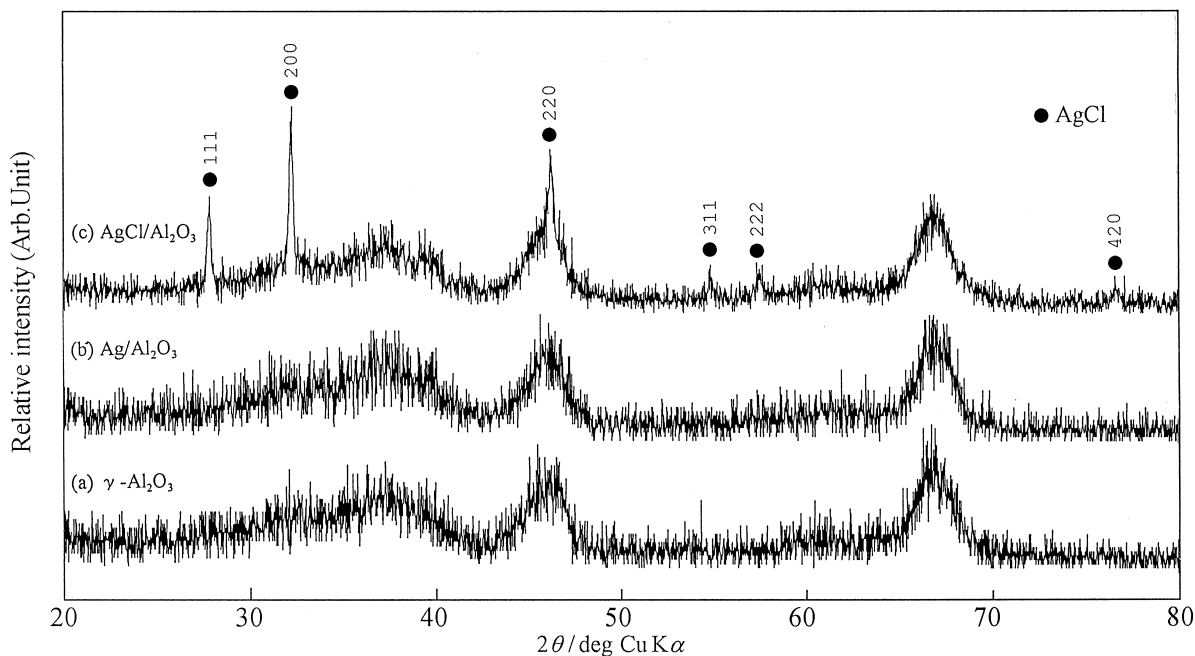


Fig. 6. X-ray diffraction spectra from the γ - Al_2O_3 (a), $\text{Ag}/\text{Al}_2\text{O}_3$ (b) and $\text{AgCl}/\text{Al}_2\text{O}_3$ (c) catalysts calcined at 873 K in air.

the catalyst below 773 K results in the formation of large crystallized AgCl particles on Al_2O_3 [16]. In contrast, calcination at temperatures higher than 773 K leads to the formation of highly dispersed AgCl particles [16]. The dispersion was enhanced on calcination at 873 K. Thus, high NO_x conversion under UV irradiation observed on the AgCl/ Al_2O_3 catalyst calcined at 873 K in air is ascribed to the progress of the dispersion of AgCl on Al_2O_3 .

The rate of NO_x conversion decreased gradually in the absence of O_2 with reaction time (Fig. 2). On the other hand, the presence of oxygen and hydrocarbons suppressed the lowering of the rate (Figs. 3 and 4). The conversion level of NO_x was maintained above 60% over 5 h under UV irradiation in the presence of O_2 and hydrocarbons over the AgCl/ Al_2O_3 catalyst.

Fig. 7 shows the XRD spectra of the AgCl/ Al_2O_3 catalysts observed before and after NO_x

conversion for 30 min in the presence of O_2 under photo-irradiation. The photo-irradiation results in the formation of crystallized metallic Ag particles.

Fig. 8 shows UV–Vis diffuse reflectance spectra of the AgCl/ Al_2O_3 catalysts observed before and after the photo-irradiation. An intense absorption band at ~ 210 nm and a broad and weak absorption band at $300 \sim 500$ nm appear with the intense absorption band at ~ 250 nm in UV–Vis diffuse reflectance spectra of the catalyst after the photo-irradiation. The absorption band at ~ 210 nm is attributed to the $4d^{10} \rightarrow 4d^9 5s^1$ electron transition of isolated Ag^+ ions [3,17–19] whereas that at $300 \sim 500$ nm is attributed to the Ag^0 atom, Ag_n^0 and Ag_m^{n+} clusters [12,20]. Thus, it is suggested that the photo-irradiation leads to the formation of isolated Ag^+ ions which are followed by the formation of Ag^0 atom, Ag_n^0 , and Ag_m^{n+} clusters. The lowering of photocatalytic conversion

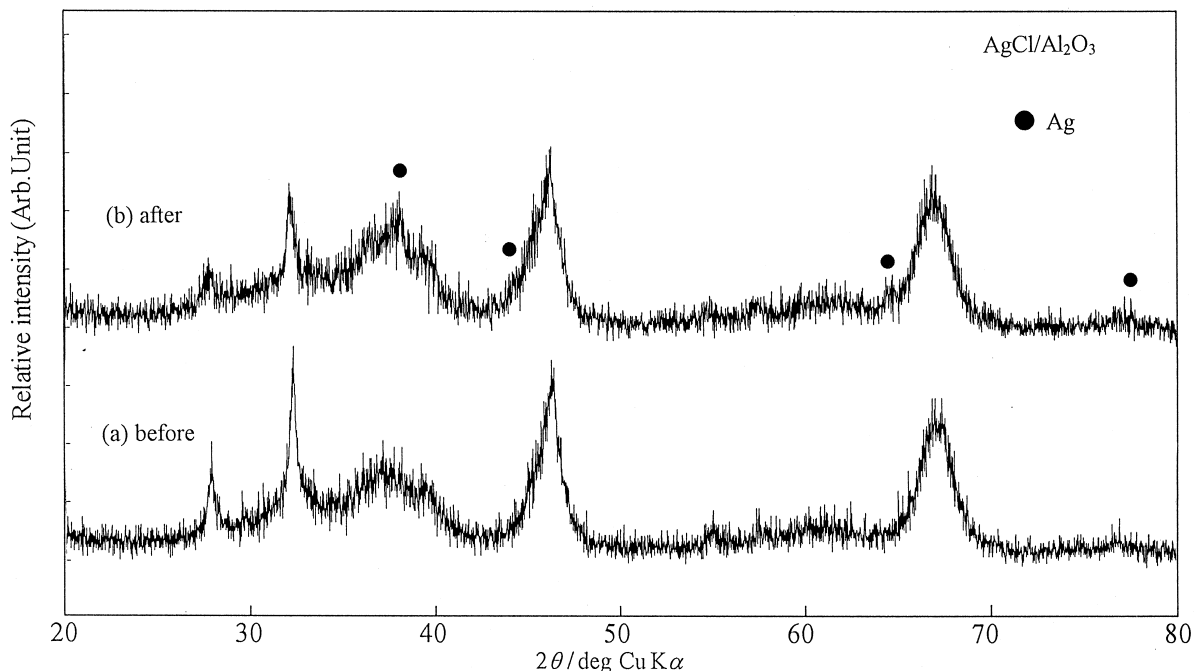


Fig. 7. X-ray diffraction spectra from the AgCl/ Al_2O_3 catalyst observed before (a) and after (b) photocatalytic NO_x conversion for 30 min. (●) XRD peaks from metallic silver.

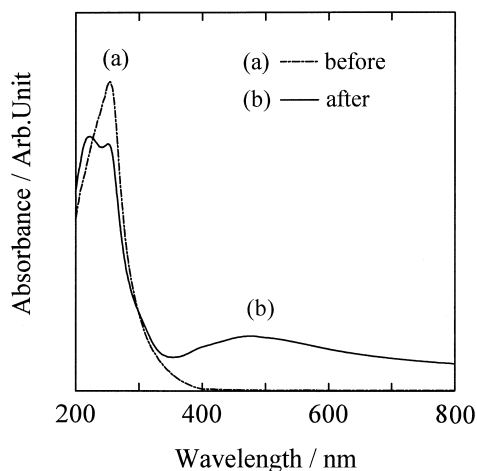


Fig. 8. UV-Vis diffuse reflectance spectra from the AgCl/Al₂O₃ catalyst observed before (a) and after (b) photocatalytic NO_x conversion in the presence of O₂ for 30 min.

of NO on the AgCl/Al₂O₃ catalyst UV-irradiated is ascribed to the formation of Ag⁰ atom, Ag_n⁰, and Ag_mⁿ⁺ clusters.

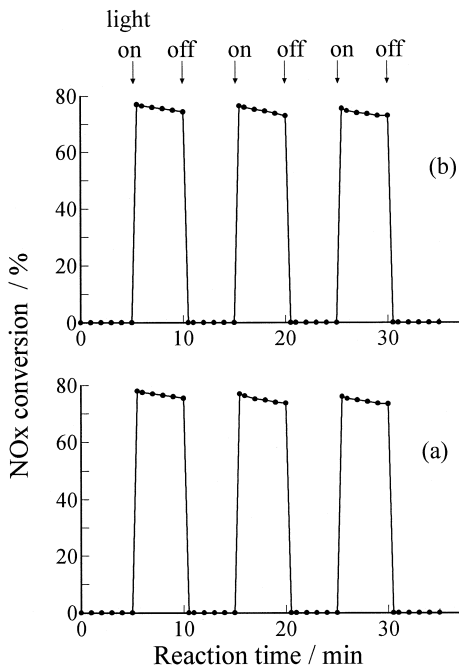


Fig. 9. Time-course of the photocatalytic NO_x conversion in the presence of O₂ on the fresh AgCl/Al₂O₃ (a) and the AgCl/Al₂O₃ calcined again at 873 K in air (b). Test conditions: 10 ppm NO, 10% O₂, 5 ppm C₂H₆, 5 ppm C₃H₈, balance N₂, flow rate = 620 cm³/min, catalysts weight = 3.0 g.

Fig. 9 compares NO_x conversion evaluated in the presence of oxygen for the fresh catalyst and the catalyst calcined again at 873 K in air after the photo-irradiated. The NO_x conversion is almost recovered to its initial one before photo-irradiation by the calcination of the irradiated catalysts at 873 K.

Fig. 10 shows UV-Vis diffuse reflectance spectra observed for the fresh catalyst and the catalyst calcined again at 873 K in air. The UV-Vis diffuse reflectance spectrum for the calcined catalyst is also almost restored to that for the fresh catalyst. These results suggest that the recovering of crystallized AgCl particles leads to the increase in the rate of NO_x conversion. Under photo-irradiation, electrons and holes are probably produced by photoactivation of the crystallized AgCl on Al₂O₃. The Ag⁰ atom, Ag_n⁰ and Ag_mⁿ⁺ clusters are formed by reaction between the created electrons and Ag⁺ ions [21]. Thus, it is suggested that the presence of oxygen suppresses the formation of Ag⁰ atom, Ag_n⁰ and Ag_mⁿ⁺ clusters, and stabilizes crystallized AgCl particles formed on Al₂O₃.

Presence of hydrocarbons enhanced the conversion of NO_x as shown in Fig. 4. Hydrocar-

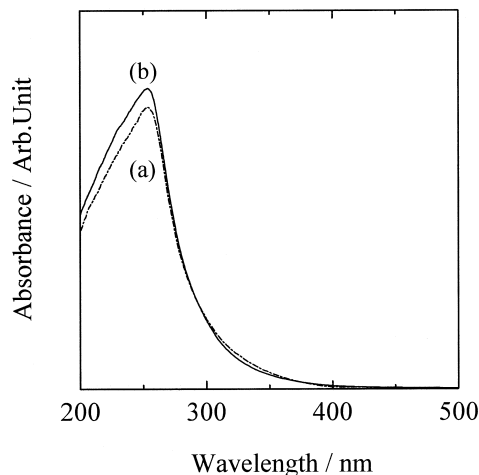


Fig. 10. UV-Vis diffuse reflectance spectra from the fresh AgCl/Al₂O₃ catalyst (a) and the AgCl/Al₂O₃ catalyst (b) calcined again at 873 K in air after photocatalytic NO_x conversion in the presence of O₂ for 30 min.

bons probably react readily with holes produced by photoactivation, suppressing the recombination of the created electron and hole. Thus, it is suggested that higher NO_x conversion in the presence of hydrocarbons is ascribed to a more efficient electron charge transfer into the π anti-bonding molecular orbital of NO.

Further studies concerning the reaction mechanism and the stability of the $\text{AgCl}/\text{Al}_2\text{O}_3$ catalyst performance are currently under way.

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