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Photocatalytic reduction of NO with ethanol on Au/TiO_2

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ABSTRACT

The effect of illumination on the surface interaction and the reaction between NO + C_2H_5OH was investigated on Au/TiO_2 catalyst. By means of Fourier transform infrared spectroscopy, the formation of absorption bands at ~2180 and ~2210 cm^{-1} was observed. The first was attributed to the NCO species locating on Au particles, and the second one to NCO residing on the TiO_2 support. While the thermal reaction between NO and C_2H_5OH on Au/TiO_2 catalyst occurred with measurable rate only at and above 473–523 K, illumination of the system induced the reaction even at room temperature. A fraction of NO was converted into N_2O, another one to N_2. At the same time, the photo-induced decomposition of C_2H_5OH also occurred yielding CH_3CHO, H_2, CO, and CH_4. Interestingly, the presence of NO significantly slowed down the rate of the decomposition of C_2H_5OH. Separate studies revealed that all the products formed in the decomposition of C_2H_5OH reacted with NO. A mechanism for the photocatalytic reduction of NO with C_2H_5OH is proposed taking into account the effects of the products of C_2H_5OH photolysis. Incorporation of N into TiO_2, which significantly lowered its band gap, appreciably enhanced the reduction of NO, which occurred even in visible light.

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1. Introduction

In the last decades, extensive research has been performed on photocatalytic reactions mainly using TiO_2 as catalyst or support [1–4]. Our laboratory was mainly concerned with the production of hydrogen at room temperature by the photocatalytic decomposition of HCOOH, alcohols, and ethers [5–10]. Illumination of TiO_2-supported Pt metals and Au particles proved to be very active catalysts for the generation of hydrogen in the above-mentioned reactions. In the case of HCOOH, even pure hydrogen free of CO was achieved [5]. Relatively, few works have been devoted to the photo-induced reduction of NO pollutant [11–13]. In the case of Rh/TiO_2, we reported first time that the illumination of the system with full arc of a Hg lamp markedly accelerated the reaction between NO and CO, and promoted the formation of NCO even at 200 K [11]. Later Che et al. [12] reported that the photoassisted reduction of NO by CO can occur on pure TiO_2 even upon visible light irradiation at room temperature. The increased use of oxygenated organic compounds, particularly ethanol, as fuel or additives for automotive vehicles initiated a great deal of study of the reaction between NO and ethanol. It was found that ethanol is very effective for NO_x reduction over supported Ag catalysts [14–31].

The primary objective of the present work was to examine the effect of illumination on the NO + C_2H_5OH reaction over Au nanoparticles deposited on TiO_2 catalyst, which was found to be an active catalyst for the generation of hydrogen in the thermal [32–34] and photocatalytic reactions [1–10]. Attention is paid to the detection of surface intermediate formed in the photoreaction. An attempt will be also made to perform the reaction in the visible light by reducing the band gap of TiO_2 by N-doping.

2. Experimental

2.1. Materials and preparation of the catalysts

In most of the measurements, we used 1% Au/TiO_2 catalyst, which was purchased from STREM Chem. Inc. It is marked by "Auro." This catalyst has been used in most of the experiments. Supported Au catalysts were also prepared by a deposition–precipitation method using TiO_2 (Hombikat UV 100; pure anatase) [32]. For the preparation of N-doped TiO_2, we applied the description of Xu et al. [35]. Titanium tetrachloride was used as a precursor. After several steps, the NH_3-treated TiO_2 slurry was vacuum dried at 353 K for 12 h, followed by calcination at 723 K in flowing air for 3 h. This sample is noted with "SX." The sizes of the Au nanoparticles were determined with a transmission electron microscope. We obtained the following values: 1.5–2.0 nm for

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1% Au/TiO_2 (Auro), and 10–15 nm for 1% Au/TiO_2 (Hombikat). For photocatalytic measurements, the sample (70–80 mg) was sprayed onto the outer side of the inner tube from aqueous suspension. The surface of the catalyst film was 168 cm^2. The catalysts were oxidized at 573 K and reduced at 573 K for 60 min in situ. For IR studies, the dried samples were pressed in self-supporting wafers (30 × 10 mm; ~10 mg/cm^2).

2.2. Methods

For infrared (IR) studies, a mobile IR cell housed in a metal chamber was used. The IR cell can be evacuated to 10^{-5} Torr using a turbomolecular pumping system. The samples were illuminated by the full arc of a Hg lamp (LPS-220, PTI) outside the IR sample compartment. After illumination, the IR cell was moved to its regular position in the IR beam. Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wave number accuracy of ±4 cm^{-1}. All the spectra presented in this study are difference spectra.

For the determination of band gap of solids, we applied the same procedures as described in previous papers [7]. Diffuse reflectance spectra of TiO_2 samples were obtained using an UV/Vis spectrophotometer (OCEAN OPTICS, Typ.USB 2000) equipped with a diffuse reflectance accessory. In the calculation, we used the equation $\alpha = A(h\nu - E_g)^n/h\nu$, where α is the absorption coefficient, A is a constant, $h\nu$ is the energy of light, and n is a constant depending on the nature of the electron transition. Assuming an indirect band gap ($n = 2$) for TiO_2, with α proportional to $F(R_\infty)$, the band gap energy can be obtained from the plots of $[F(R_\infty)h\nu]^{1/2}$ vs. $h\nu$, as the intercept at $[F(R_\infty)h\nu]^{1/2} = 0$ of the extrapolated linear part of the plot. For the band gap of pure TiO_2, we obtained a value of 3.02 eV, and for N-doped TiO_2 1.98 eV, which agreed very well with the previously determined values [7,9].

Photocatalytic reaction was followed in the same way as described in our previous papers [8–10]. Briefly, the photoreactor (volume: 670 ml) consists of two concentric Pyrex glass tubes fitted one into the other and a centrally positioned lamp. It is connected to a gas-mixing unit serving for the adjustment of the composition of the gas or vapor mixtures to be photolyzed in situ. The length of the concentric tubes was 250 mm. The diameter of outer tube was 70 mm, and that of the inside tube 28 mm long. The width of annulus between them was 42 mm, and that of the photocatalyst film was 89 mm. We used a 15 W germicide lamp (type GCL 307T5L/CELL, Lighttech Ltd., Hungary), which emits predominantly in the wavelength range of 250–440 nm, and its maximum intensity is at 254 nm. For the visible photocatalytic experiments, another type of lamp was used (Lighttech GCL 307T5L/GOLD) with 400–640 nm wavelength range and two maximum intensities at 453 and 545 nm. The approximate light intensities at the catalyst films are 3.9 mW/cm^2 for the germicide lamp and 2.1 mW/cm^2 for the other lamp. The incident light intensities were determined by an actionometry. The carrier gas was Ar, which was bubbled through ethanol at room temperature. Afterward, argon containing ~1.5% (167.5 μmol) ethanol and ~1.5% (167.5 μmol) NO was introduced in the reactor through an externally heated tube avoiding condensation. The amount of NO was controlled by a Pfeiffer capacitance gauge and was fed from a gas-dosing system. The gas mixture was circulated by a pump. The reaction products were analyzed with a HP 5890 gas chromatograph equipped with PORAPAK Q and PORAPAK S packed columns. The sampling loop of the GC was 500 μl. The amount of all products was related to this loop.

3. Results

3.1. FTIR studies

The primary aim of IR spectroscopic measurements is to establish the surface species formed during the photocatalytic reaction of NO + C_2H_5OH. We are particularly interested in the detection of NCO species formed in the thermal reduction of NO with C_2H_5OH over Ag/TiO_2 [17–21,23,31]. Adsorption of NO + C_2H_5OH on 1% Au/TiO_2 resulted in the production of strong absorption bands at 2952, 2906, 2879, 1381, 1125, and weaker ones at 1550, 1449 and 1073 cm^{-1}. (Fig. 1A) We obtained the same spectral features following the adsorption of pure C_2H_5OH on Au/TiO_2 [9]. Illumination in the presence of NO + C_2H_5OH gas mixture caused a slight attenuation of the high frequency bands, the slow development of a new band at 1635 cm^{-1}, and the strengthening of vibration at 1550 cm^{-1}. The presence of adsorbed NO is indicated by an absorption feature at 1755 cm^{-1}, which underwent a slow attenuation on the effect of illumination. After prolonged illumination, weak absorption features were developed at ~2185 and ~2150 cm^{-1}, which were not eliminated by degassing. Similar measurements were performed with the main products of the photocatalytic decomposition of C_2H_5OH. Exposing Au/TiO_2 to NO + CH_3CHO gas mixture yielded several spectral features due to CH_3CHO adsorption. On the effect of illumination, all absorption bands underwent slow attenuation. New absorption bands appeared at ~2180 and ~2206 cm^{-1} at the beginning of photolysis, which grew with the time of irradiation. Spectra are presented in Fig. 1B. Illumination of NO + CO gas mixture on Au/TiO_2 at 300 K also produced absorption bands at ~2180 and ~2210 cm^{-1} (Fig. 1C). In contrast, irradiation of NO + CH_4 gas mixture yielded no new spectral features.

3.2. Photocatalytic reduction of NO with C_2H_5OH

In the photocatalytic reaction between NO + C_2H_5OH on Au/TiO_2, most of the NO was converted into N_2, and a less amount to N_2O. Minor amount of acetonitrile was also formed. The extent of the decomposition of NO was about 53% in 210 min. For comparison, similar measurements were carried out on TiO_2 used for the preparation of Au/TiO_2. From the data presented in Fig. 2, it appears clearly that deposition of Au onto TiO_2 markedly enhances the extent of the photocatalytic reaction. When pure NO was illuminated on Au/TiO_2, N_2 and N_2O were produced almost in the same quantity (Fig. 3A). The extent of NO decomposed was one-third as that measured in the presence of C_2H_5OH. Some experiments were carried out on Au deposited on TiO_2 (Hombikat). This catalyst exhibited much less photoactivity than Au/TiO_2 (Auro) did, which is attributed to the much larger Au particles. This is in harmony with our previous results [7–9] and also with the finding of Bowker et al. [36], namely that Au in nanosize is an active photocatalyst in the photoreforming of alcohols.

In parallel with the catalytic reduction of NO, the photocatalytic decomposition of C_2H_5OH also occurred. From the data presented in Fig. 3B and C, it appears that NO markedly lowers the extent of the decomposition of C_2H_5OH. The conversion of C_2H_5OH decreased from ~100% to ~25% in a given time. From the comparison of various products stemmed from C_2H_5OH in the two cases, we obtained that the largest reduction occurred in the amount of H_2 formed. Related data are shown in Table 1. Further studies revealed that even a small amount of NO ($NO/C_2H_5OH/ = 0.1$) exerted a well-observable inhibiting effect on the photocatalytic decomposition of ethanol (Fig. 4).

In order to establish the effect of illumination on the reduction of NO with C_2H_5OH, some measurements were performed at dif-

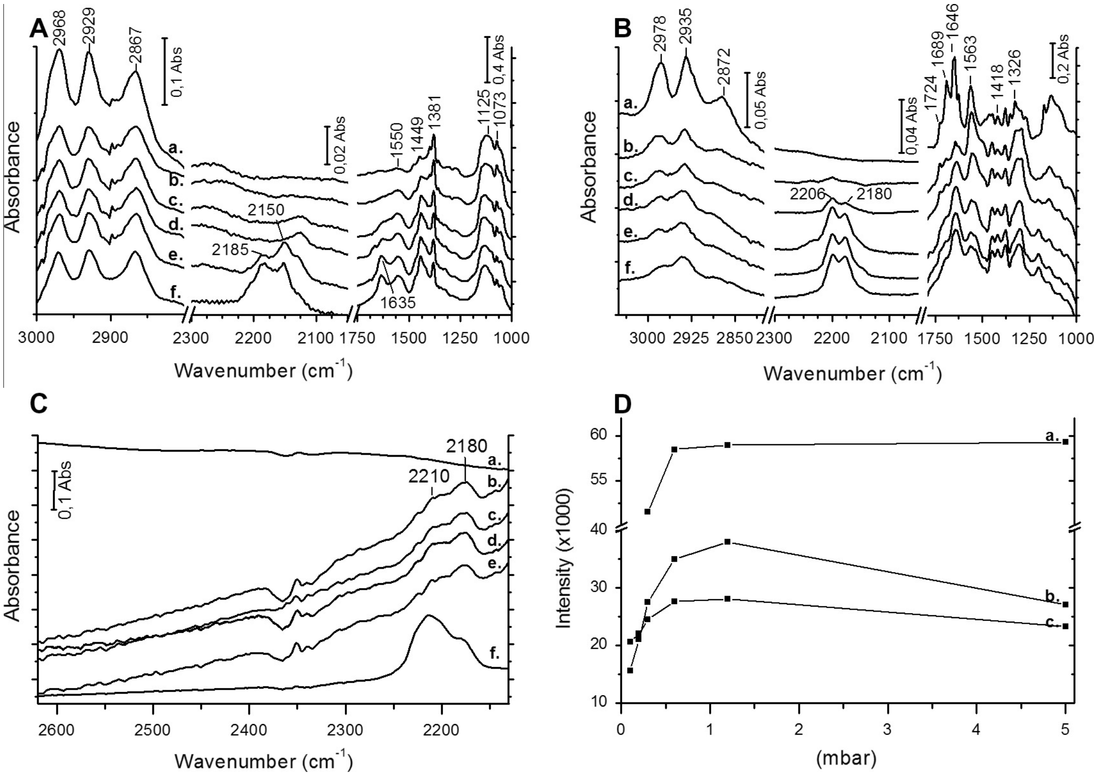

Fig. 1. Effects of illumination on the FTIR spectra of 1% Au/TiO_2 in the presence of NO + C_2H_5OH (A); NO + CH_3CHO (B); NO + CO (C). Effect of the amount of NO on the development of C_2H_5O band at 2968 cm^{-1} (a), pure C_2H_5OH (b), NO:C_2H_5OH 1:10 (c), NO:C_2H_5OH ~ 1:1 (D).

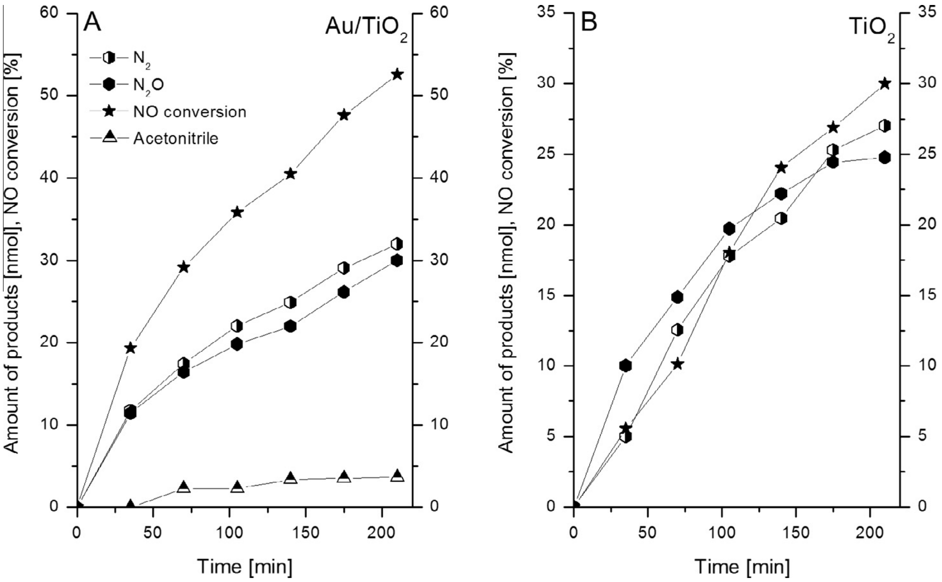

Fig. 2. Formation of N-containing products in the photocatalytic reduction of NO by C_2H_5OH over 1% Au/TiO_2 (A) and TiO_2 (B) samples. NO:C_2H_5OH ~ 1:1.

ferent temperatures without illumination. For reliable comparison, these experiments were carried out in the photoreactor on the same Au/TiO_2 film used for the photostudies. No appreciable reaction was observed at 373–423 K. The formation of products appeared first at 473 K, and the conversion of NO was about ~8% in 60 min. At 573 K, this value was 19%. Note that the presence of NO only slightly affected the thermal decomposition of ethanol.

3.3. Photocatalytic reduction of NO with other compounds

As all the products of the photocatalytic decomposition of ethanol exhibit reductive properties, in the next experimental series we examined their influence on the photocatalytic reduction of NO. Results are presented in Fig. 5. It appears that all the products promoted the photocatalytic reduction of NO. Acetaldehyde exerted the largest effect followed by CO, H_2, and CH_4. While in

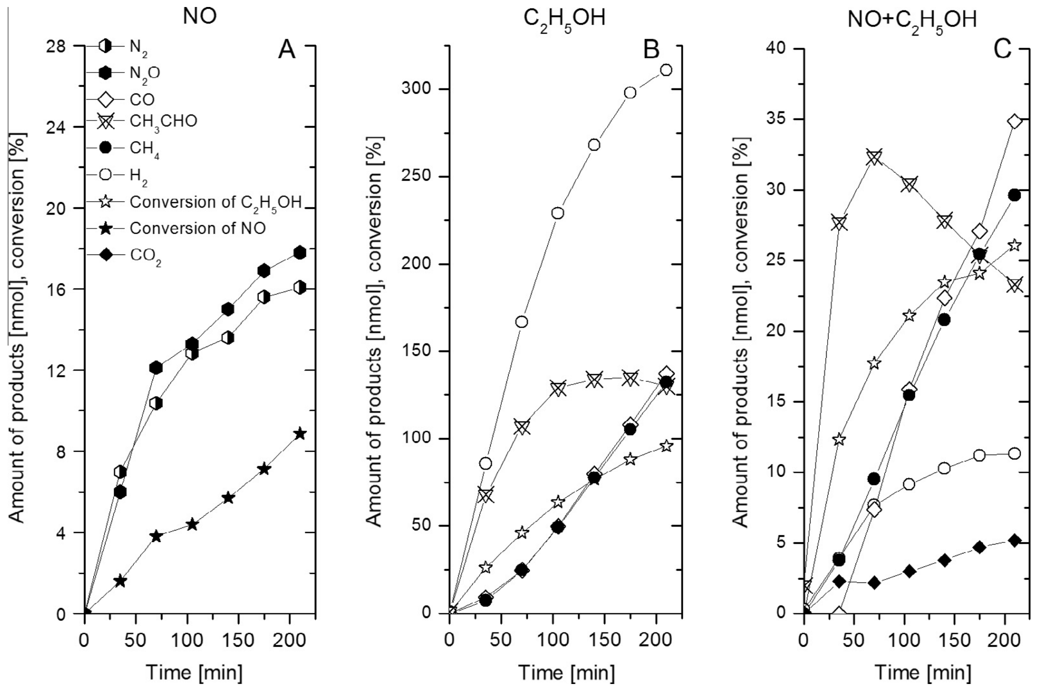

Fig. 3. Products of the illumination formed in the decomposition of pure NO (A), pure C_2H_5OH (B), and C_2H_5OH in the presence of NO; NO:C_2H_5OH ~ 1:1 (C).

Table 1
Changes in the amount of products formed in the photolysis of C_2H_5OH in the absence and presence of NO.

Products (nmol)	At 100% conversion of C_2H_5OH obtained (nmol)	At 26% conversion of C_2H_5OH calculated[a] (nmol)	Found in the presence of NO (nmol)	Decrease in %
CH_3CHO	130.4	33.9	23.3	31.2
H_2	311.1	80.8	11.3	86.0
CO	137.3	35.7	34.8	2.5
CH_4	132.4	34.4	29.6	13.9

[a] In this calculation we took into account the less amount of C_2H_5OH added to NO.

the NO + CH_3CHO reaction N_2O was the main N-containing compound in the presence of CO, the amount of N_2 exceeded that of N_2O. From the comparison of the photocatalytic decomposition of CH_3CHO in the absence and in the presence of NO, we did not experience the inhibiting effect of NO as observed in the case of C_2H_5OH. This is demonstrated by the results presented in Fig. 6.

3.4. Photocatalytic studies in visible light

It is well known that the decrease in the band gap of TiO_2 by N-doping makes possible several photocatalytic reactions to proceed in the visible light [1–10]. In the following experiments, the reduction of NO with C_2H_5OH is investigated over Au deposited on N-doped TiO_2. Note that for these studies we used different TiO_2 samples prepared by the description of Xu et al. [35]. Fig. 7 depicts the results obtained on Au deposited on pure and N-modified TiO_2 (SX) in UV and in visible light. It appears clearly that incorporation of N into TiO_2 markedly enhances the photoactivity of Au/TiO_2 in UV, and what is more important is it makes possible the occurrence of the photocatalytic reaction in the visible light, too. This is reflected in the conversion of NO and in the amounts of the products formed.

4. Discussion

4.1. IR studies

Adsorption of NO + C_2H_5OH gas mixture on Au/TiO_2 gave practically identical absorption bands as obtained by the adsorption of C_2H_5OH alone on the same catalyst [9]. Following the previous interpretation [9,19], the appearance of 2968 and 2867 cm^{-1} can be attributed to the asymmetric and symmetric stretches of ethoxy, C_2H_5O, formed in the dissociation of C_2H_5OH. The 1125 and 1073 cm^{-1} bands are assigned to the ν(OC) vibration of the same adsorbed species. Illumination led to slight attenuation of these bands, and the slow development of absorption at 1550 and 1635 cm^{-1} assigned to the vibration of formate and acetate [9,19]. New spectral features were developed at the later phase of the irradiation at ~2185 and ~2150 cm^{-1}. In the case of photolysis of NO + CH_3CHO on Au/TiO_2, two absorption bands appeared in this frequency range, at 2180 and 2260 cm^{-1} (Fig. 1B). These peaks also formed the following illumination of NO + CO gas mixture (Fig. 1C). Taking into account the results of extensive IR spectroscopic studies concerning the NO + CO catalytic reaction on different supported metals [37–41], and the adsorption of HNCO on TiO_2, Au/TiO_2, and Au(111) surfaces [42–44], the band at ~2180 cm^{-1} is ascribed to the vibration of NCO species bonded to Au particles, and the other one at 2206 cm^{-1} to the NCO attached to TiO_2. The absorption feature at 2150 cm^{-1} very likely belongs to adsorbed CN group. As regards the formation of NCO and CO_2, the obvious explanation is that CO formed in the photocatalytic processes enters reaction with activated NO according to the following reaction sequence:

$$NO_{(a)} + CO_{(g)} = N_{(a)} + CO_{2(a)} \tag{1}$$

$$N_{(a)} + CO_{(g)} = NCO_{(g)} \tag{2}$$

Considering the low reactivity of NCO group both on Au and TiO_2 [43,44], we do not consider that it could function as a real surface intermediate in the photocatalytic reduction of NO by C_2H_5OH at 300 K.

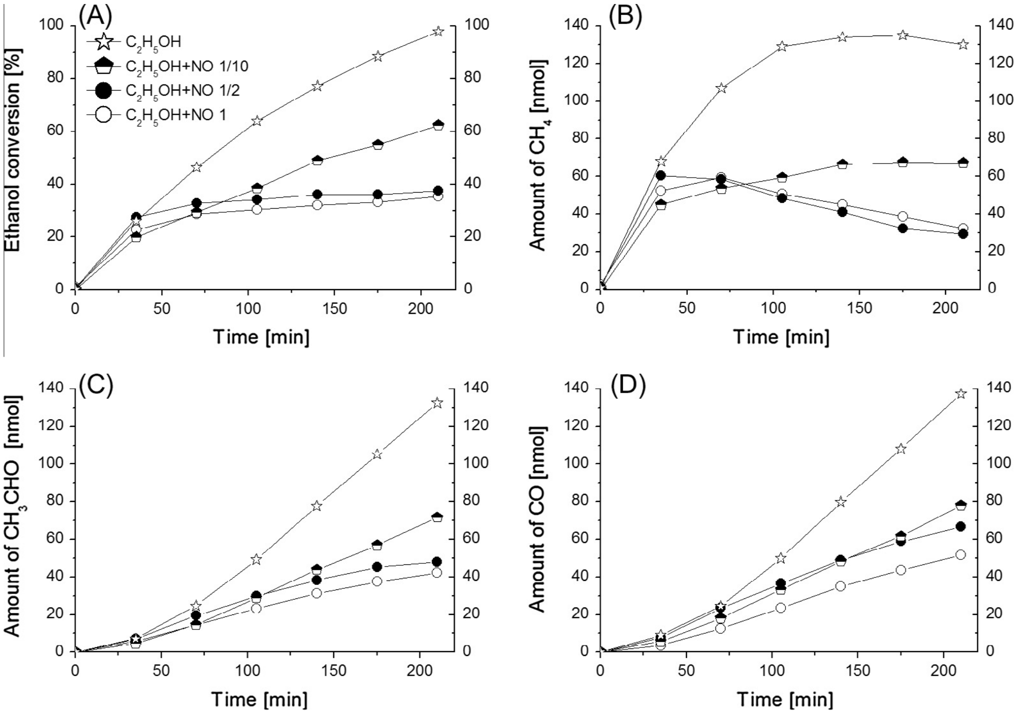

Fig. 4. Effects of the amount of NO on the photocatalytic decomposition of C_2H_5OH.

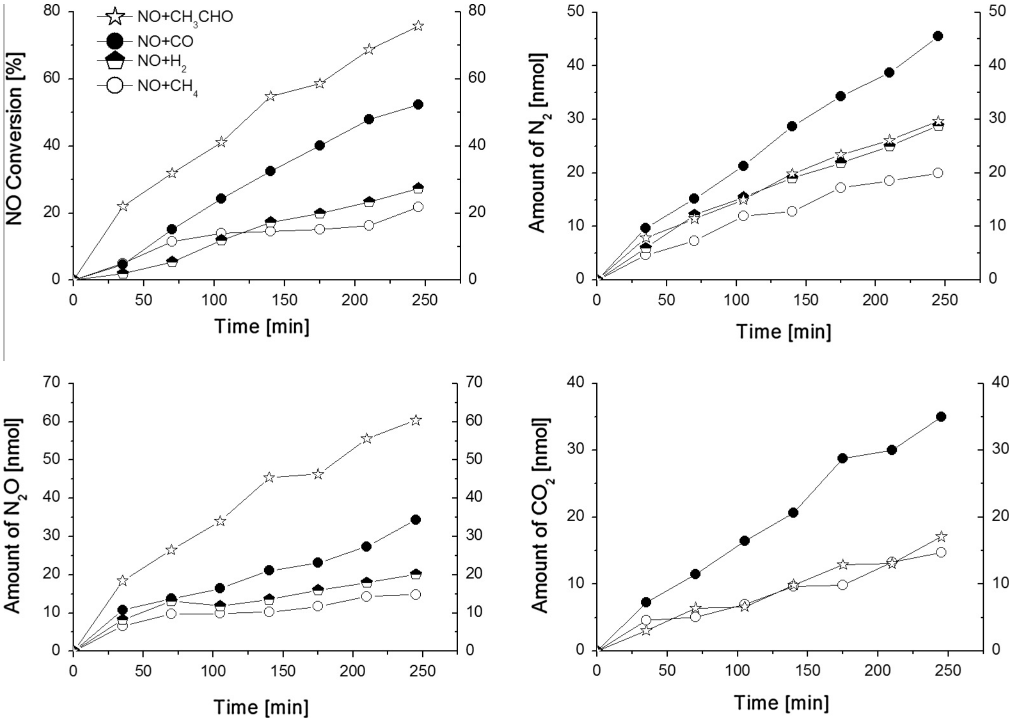

Fig. 5. Effect of illumination on the photocatalytic reaction of NO + CH_3CHO, NO + CO, NO + CH_4, and NO + H_2. It is obvious that in the latter case no CO_2 was formed.

4.2. Catalytic studies

The photocatalytic reaction between NO and C_2H_5OH proceeded quickly on Au/TiO_2 (Auro) catalyst at 300 K. The reaction also occurred on TiO_2 (P25) used for the preparation of Au/TiO_2 (Auro), but much more slowly (Fig. 2). This suggests that Au particles play a dominant role in the photoreaction. It is important to point out that Au/TiO_2 was found to be very effective for the photocatalytic decomposition of C_2H_5OH yielding various products of reducing properties [9,36]. We may assume that on the effects of illumination an electron generated in the photo-excitation process

$$TiO_2 + h\nu = h^+ + e^- \tag{3}$$

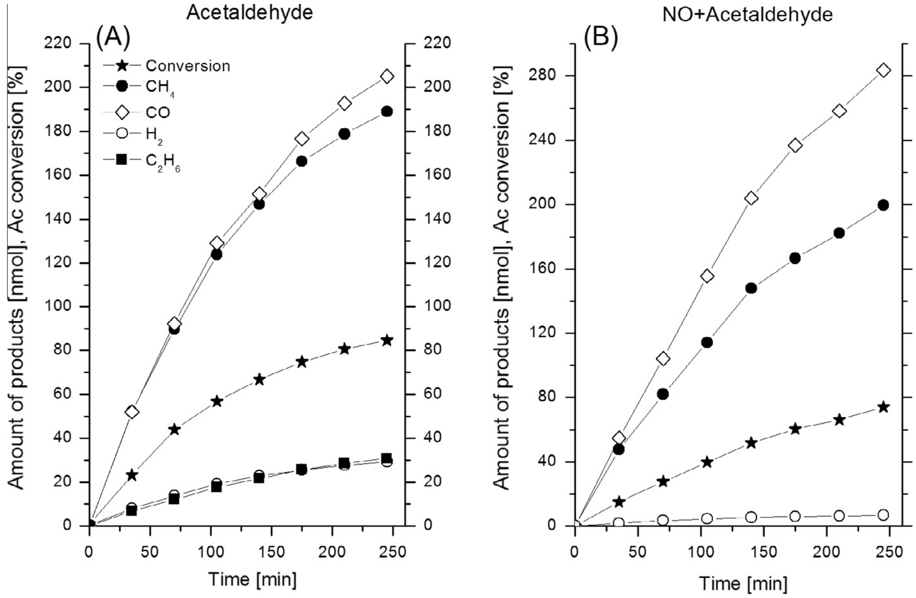

Fig. 6. Effects of NO on the photocatalytic decomposition of CH_3CHO; $NO:CH_3CHO \sim 1:1$.

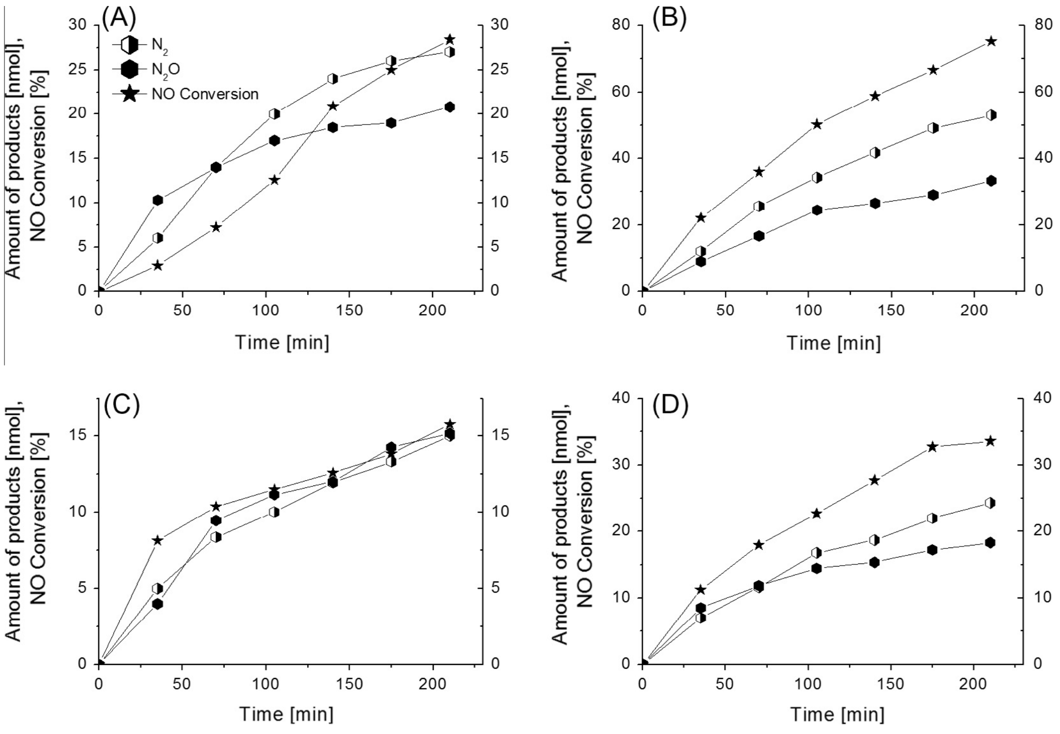

Fig. 7. Effects of N-doping of TiO_2 on the photocatalytic reaction of NO with C_2H_5OH on 1% Au/TiO_2 (SX) and $Au/TiO_2 + N$ (SX) in UV (A, B) and visible light (C, D); $NO:C_2H_5OH \sim 1:1$.

activates the ethoxy species formed in the dissociation of C_2H_5OH

$$C_2H_5OH = C_2H_5O_{(a)} + H_{(a)} \tag{4}$$

$$C_2H_5O_{(a)} + e^- = C_2H_5O^{\delta-}_{(a)} \tag{5}$$

which is followed by its decomposition

$$C_2H_5O^{\delta-}_{(a)} = CH_3CHO^{\delta-}_{(a)} + H_{(a)} \tag{6}$$

$$2H_{(a)} = H_{2(g)} \tag{7}$$

$$CH_3CHO^{\delta-}_{(a)} = CO^{\delta-}_{(a)} + CH_{4(g)} \tag{8}$$

$$CO^{\delta-}_{(a)} + h^+ = CO(g) \tag{9}$$

However, Au/TiO_2 also induced the photocatalytic decomposition of NO giving N_2 and N_2O; the extent of the reaction was only ~9% in the measured time (Fig. 2A). This result suggests that not only the $C_2H_5O_{(a)}$, but also the NO is also activated by a photoelectron resulting in a more reactive negatively charged NO

$$NO + e^- = NO^-_{(a)} \tag{10}$$

Previous studies concerning the reactivity of NO_x, NO^{+}, and NO^{-} on solid surfaces [37–41] clearly demonstrated that the negatively charged NO is the most reactive NO form.

As regards the reduction of NO, we have to take into account that C_2H_5OH readily dissociates on Au/TiO_2 into ethoxy (C_2H_5O) species (Eq. (4)), which is stable at room temperature. Based on this observation, it is obvious to assume that the illumination initiates its decomposition into CH_3CHO. This is followed by the fast photo-induced reaction of CH_3CHO resulting in the production of CO and CH_4 (Eq. (8)). The results presented in Fig. 5 show that on the effect of illumination all the compounds react with NO yielding N_2 and N_2O. However, the photoreduction of NO with all substances including H_2 is slower than that measured with C_2H_5OH. Taking into account the changes in the products of photo-induced decomposition of C_2H_5OH in the presence of NO (Table 1), it appears that the amount of H_2 underwent a most significant decrease. Therefore, we tentatively assume that adsorbed H atoms formed in the primary dissociation of C_2H_5OH (Eq. (4)) and CH_3CHO (Eq. (6)) are the main reductive species for NO.

Alternatively, Bowker et al. [36] studying the photoreforming of biofuels came to the conclusion that it is essential for good activity to have an H at the α-position. We may also consider the role of enolic species assumed to play a dominant role in the high-temperature reduction of NO ($+O_2$) with C_2H_5OH on Ag/Al_2O_3 catalyst [18,22,24]. Absorption bands at 1633, 1416, and 1336 cm^{-1} were attributed to this species. Although from the analysis of IR spectra of $NO + C_2H_5OH$ (Fig. 1) we can trace vibrations around these wavenumbers, no changes were experienced in their intensities as a result of illumination. This finding makes it uncertain that this species could play an important role in the photocatalytic reduction of NO with C_2H_5OH on Au/TiO_2 at room temperature. Further studies are clearly needed for the refinement of the mechanism of this photocatalytic reaction.

An interesting feature of the photocatalytic reaction of $NO + C_2H_5OH$ is that while C_2H_5OH, or more precisely its products can participate in the photocatalytic reduction of NO (Fig. 4), at the same time NO inhibits the occurrence of the decomposition of ethanol (Fig. 3). As we did not experience such a feature in the case of photolysis of $NO + CH_3CHO$ mixture (Fig. 5), we assume that adsorbed NO blocks the first step, the rupture of O–H bond in C_2H_5OH, for example the formation of C_2H_5O, species (Eq. (2)). This conclusion is supported by the analysis of the IR spectra taken during the photolysis of $NO + C_2H_5OH$. The intensities of the bands at ~2968 and ~2867 cm^{-1} attributed to the formation of ethoxy species [9,19] were appreciably less compared to those registered in the absence of NO. Even very small amount of NO was sufficient to reduce the extent of the dissociation of C_2H_5OH (Fig. 4). In contrast, NO does not affect the cleavage of C–C bond in the CH_3CHO, for example its photodecomposition to CH_4 and CO (Fig. 6).

The deposition of Au onto TiO_2 greatly enhanced the photocatalytic effect of the TiO_2, which indicates that Au particles actively participate in the photocatalytic reaction. In the explanation of its promoting effect, we may assume that the C_2H_5O species formed on the Au particles or at the Au/TiO_2 interface are much more reactive than that located on TiO_2. As the other metals, Au particles may also cause a better charge carrier separation induced by illumination. As the work function of TiO_2 (~4.6 eV) is less than that of Au (5.31 eV), an electron transfer from TiO_2 to the deposited Au also occurs, which is enhanced by illumination. In harmony with this finding, the photocatalytic effect of Au/TiO_2 was also increased when the band gap of TiO_2 was lowered by N-doping. This made possible the reaction to occur in visible light. Note that the effect of electron transfer from TiO_2 to metal was demonstrated first in the decomposition of HCOOH on Ni/TiO_2 catalysts [45,46].

5. Conclusions

(i) Deposition of Au on TiO_2 greatly enhances its effect in the photocatalytic reduction of NO with C_2H_5OH at room temperature.

(ii) At the same time, NO slows down the occurrence of the photo-induced decomposition of C_2H_5OH.

(iii) The photocatalytic reduction of NO was also promoted by the products of the photocatalytic decomposition of C_2H_5OH, namely CH_3CHO, H_2, CO, and CH_4 in decreasing efficiency.

(iv) Lowering the band gap of TiO_2 by incorporation of N enhanced the photoactivity of Au/TiO_2 and made possible the occurrence of the reaction in visible light.

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