Journal of Catalysis 325 (2015) 60–67

Contents lists available at ScienceDirect

Journal of Catalysis

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

Photocatalytic reduction of NO with ethanol on Au/TiO_2

Gyula Halasi, Tamás Bánsági, Frigyes Solymosi *

MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1, H-6720 Szeged, Hungary

ARTICLE INFO

Article history:
Received 3 December 2014
Revised 25 February 2015
Accepted 26 February 2015
Available online 18 March 2015

Keywords:
Au/TiO_2 photocatalyst
Surface interaction between NO and C_2H_5OH
Photo-induced formation of NCO species
Photocatalytic reduction of NO with C_2H_5OH and CH_3CHO
Effect of N-doping of TiO_2

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.

© 2015 Elsevier Inc. All rights reserved.

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

---

* Corresponding author. Fax: +36 62 544 106.
E-mail address: fsolym@chem.u-szeged.hu (F. Solymosi).

http://dx.doi.org/10.1016/j.jcat.2015.02.019
0021-9517/© 2015 Elsevier Inc. All rights reserved.

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-

Download English Version:

https://daneshyari.com/en/article/60889

Download Persian Version:

https://daneshyari.com/article/60889

Daneshyari.com