Photocatalytic Reduction of NO with Ethanol on Ag/TiO$_2$

Gy. Halasi · A. Kecskeméti · F. Solymosi

Abstract The effect of illumination on the surface interaction and the reaction between NO + C$_2$H$_5$OH was investigated on TiO$_2$ and Ag/TiO$_2$. By means of Fourier transform infrared spectroscopy the formation of an absorption band at 2,210 cm^{-1} was observed on pure TiO$_2$, which was attributed to the NCO species. Similar measurements on Ag/TiO$_2$ produced another spectral feature at 2,170 cm^{-1}, which was assigned to the vibration of NCO bonded to Ag. These absorption bands formed more easily on oxidized than on reduced surfaces. Study of the catalytic reduction of NO with ethanol showed that the illumination of the system induced the reaction even at room temperature.

Keywords Surface interaction between NO and ethanol · Photoinduced formation of isocyanate · Photocatalytic reduction of NO · Ag/TiO$_2$ photocatalyst

1 Introduction

In the last decades extensive research has been performed on photocatalytic reactions mainly using TiO$_2$ as catalyst or support [1, 2]. It appeared clearly that the semiconducting properties of TiO$_2$ play an important role in its photocatalytic activity. In our laboratory we found that changing the work function of TiO$_2$ by doping influences the rate of H$_2$O + CO$_2$ reaction to yield formic acid,

formaldehyde and methane on pure and Rh-containing TiO$_2$ [3]. This feature also appeared in the photoinduced activation of CO$_2$ on the same samples [4]. In this short paper we report the effect of illumination of the NO + C$_2$H$_5$OH reaction on pure and Ag-containing TiO$_2$ catalyst. The increasing use of oxygenated organic compounds, particularly ethanol, as fuel or additives for automotive vehicles required the study of the reaction between NO and ethanol. Ethanol was found to be extremely effective for NO$_x$ reduction over Ag/Al$_2$O$_3$, which displays high tolerances to water and SO$_2$ [5–15]. By means of FTIR spectroscopy two absorption bands were detected at 2,228–2,235 and 2,255–2,260 cm^{-1}, which were attributed to NCO species. As regards the location of NCO different views were expressed. The first band was attributed to the vibration of Ag–NCO, whereas the second one to that of Al–NCO [5, 8]. Alternatively both bands were ordered to Al–NCO [9, 10]. Based on the previous works on the chemistry of NCO species on metals and supporting oxides [16–19], it appeared more certain that both bands are due to NCO attached to alumina [20].

2 Experimental

TiO$_2$ was the product of Degussa (P 25, 50 m^2/g). Ag/TiO$_2$ samples were prepared by impregnation of titania in the solution of AgNO$_3$. The suspension was dried and pressed into self-supporting wafers (30 × 10 mm ∼ 10 mg/cm^2) for IR studies. For photocatalytic studies the sample 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 in certain cases reduced at different temperatures in the IR cell or in the catalytic reactor for 1 h. Ethanol was the product of

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Sharlau with purity of 99.7%. NO was the product of MESSER with purity of 99.8%.

For FTIR studies a mobile IR cell housed in a metal chamber was used. The sample can be heated and cooled to 150–200 K in situ. The IR cell can be evacuated to 10^{-5} Torr using a turbo molecular pumping system. The samples were illuminated by the full arc of a Hg lamp (LPS-220, PTI) outside the IR sample compartment. The IR range of the light was filtered by a quartz tube (10 cm length) filled with triply distilled water applied at the exit of the lamp. The filtered light passed through a high-purity CaF$_2$ window into the cell. The light of the lamp was focused onto the sample. The output produced by this setting was 300 mW cm^{-2} at a focus of 35 cm. The maximum photon energy at the sample is ca. 5.4 eV (the onset of UV intensity from the lamp.) 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 wavenumber accuracy of ±4 cm^{-1}. All the spectra presented in this study are difference spectra.

Photocatalytic reaction was followed in a thermostatically controllable photoreactor, equipped with a 15 W germicide lamp (type GCL307T5L/CELL, Lighttech Ltd., Hungary) as light source. This lamp emits predominantly in the wavelength range of 250–440 nm. The reactor (volume: 970 mL) consists of two concentric Pyrex glass tubes fit one into the other and a centrally positioned lamp. The reactor is connected to a gas-mixing unit serving for the adjustment of the composition of the gas or vapor mixtures to be photolized in situ. The carrier gas was Ar, which was bubbled through ethanol at room temperature. Afterwards Argon containing ~1.3% ethanol and 1.0% NO were introduced in the reactor through an externally heated tube

Fig. 1 a Effects of illumination time on the FTIR spectra of TiO$_2$ (T_R = 473 K) in the presence of NO + C$_2$H$_5$OH mixture: a, 5 min; b, 15 min; c, 30 min; d, 60 min; e, 90 min; f, 120 min. b Effects of the reduction temperature of TiO$_2$ on the integrated absorbance of the 2,210 cm^{-1} band: a, 773 K; b, 673 K; c, 573 K; d, 473 K
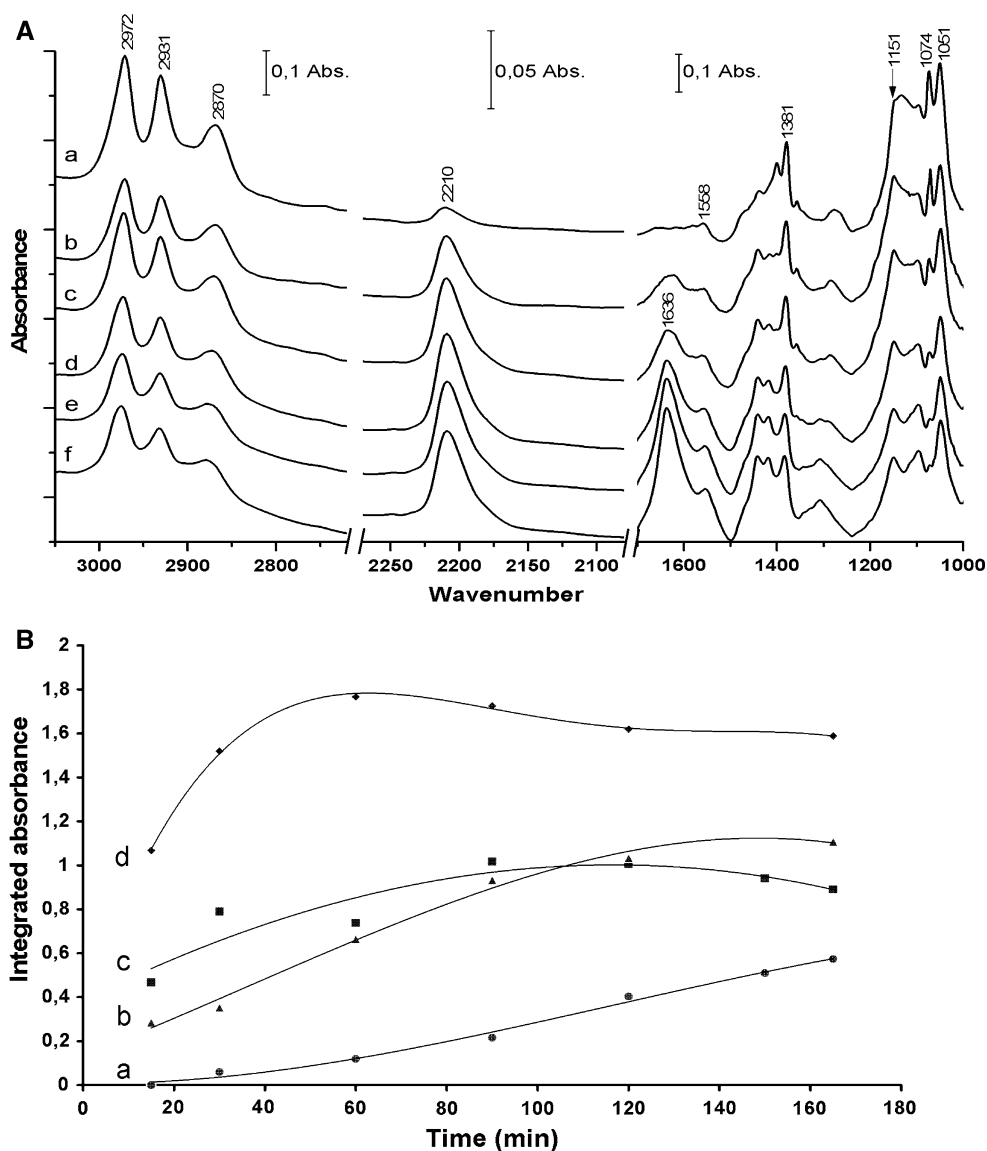
avoiding condensation. The gas-mixture was circulated by a pump. The reaction products were analyzed with a HP 5890 gas chromatograph equipped with PORAPAK Q and PORAPAK S packed columns.

3 Results and Discussion

3.1 FTIR Studies

Adsorption of NO + ethanol gas mixture on TiO_2 ($T_R = 473$ K) at 300 K produced intense absorption bands at 2,972, 2,931 and 2,870 cm^{-1} in the C–H stretching region, and 1,381, 1,271, 1,151, 1,074 and 1,051 cm^{-1} in the low frequency range. Taking into account the previous

IR results for adsorbed ethanol the major bands at 2,972 and 2,870 cm^{-1} can be attributed to the vibrations of $v_a(CH_3)$, $v_s(CH_3)$ and to $v_s(CH_2)$, whereas the peaks at 1,074 and 1,051 cm^{-1} to the vibration of $v(OC)$ of ethoxy group [21, 22]. As a result of illumination the characteristic absorption bands of ethoxy gradually attenuated and new bands developed at 2,210 and 1,636 cm^{-1}; their intensities grew with the illumination time. Spectra registered on titania reduced at 473 K are presented in Fig. 1a. All the new bands remained unaltered after degassing the sample at 300 K for 15 min. The intensity of the 2,210 cm^{-1} band gradually decreased with the reduction temperature of TiO_2. In harmony with this, stronger band at 2,210 cm^{-1} was registered on oxidized sample. Control measurements showed that only a very weak band appeared at 2,210 cm^{-1}

Fig. 2 **a** Effects of illumination time on the FTIR spectra of Ag/TiO$_2$ ($T_R = 473$ K) in the presence of NO + C$_2$H$_5$OH mixture. **b** The integrated absorbance of the bands at 2,210 cm^{-1} (*white circle*) and 2,170 cm^{-1} (*filled circle*) formed in the NO + C$_2$H$_5$OH reaction on Ag/TiO$_2$ ($T_{OX} = 573$ K)
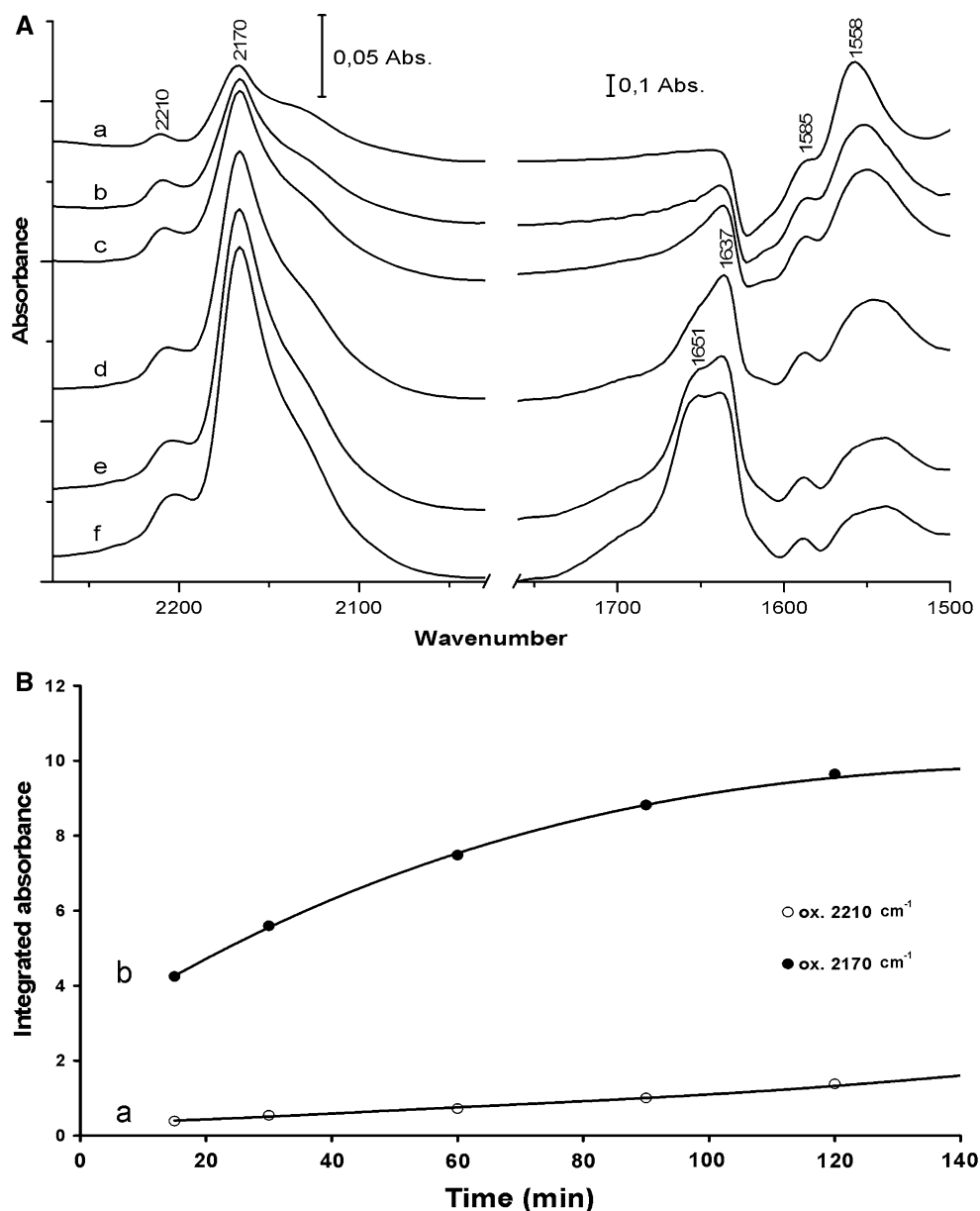
at 300 K in the IR spectrum of pure titania without illumination. The intensities of the 2,210 cm^{-1} band measured on oxidized and reduced TiO$_2$ are plotted in Fig. 1b. Based on the previous results [16–19] there is no doubt the 2,210 cm^{-1} band is due NCO species formed on TiO$_2$. Same absorption band was identified following the dissociative adsorption of HNCO on TiO$_2$ [19]. The finding that its generation is favored on oxidized surface may be connected with the enhanced dissociation of ethanol and ethoxy on the oxidized TiO$_2$ to produce reactive species for the reduction of NO. The absorption band at 1,636 cm^{-1} is assigned to the ν(C=O) vibration of the acetaldehyde.

Same experiments were performed over 2% Ag/TiO$_2$ catalyst. Introduction of NO + C$_2$H$_5$OH mixture in the cell in dark gave identical IR spectrum as in the case of pure titania. Following the illumination, however, a new strong feature appeared at 2,170 cm^{-1}, in addition to the band at 2,210 cm^{-1}, which was somewhat less intense than measured for pure TiO$_2$. The new band was significantly larger than that of at 2,210 cm^{-1}, and it further grew with the illumination time (Fig. 2a). As in the case of pure TiO$_2$ the oxidation of the sample favored and the reduction at high temperature hindered its development. This spectral feature is ordered to surface NCO attached to Ag particles. The absorption band of isocyanate species bonded to Ag was determined by the dissociative adsorption of HNCO on Ag/SiO$_2$ in similar way as the vibration of NCO bonded to Pt

metals was established [16–19]. Dissociation of molecularly adsorbed HNCO on metal single crystal surfaces also gave a vibration loss at 2,160–2,190 cm^{-1} [23, 24]. It is important to note that the 2,170 cm^{-1} band was not detected in the high temperature reaction of NO + C$_2$H$_5$OH supported Ag catalyst [5–15]. The possible reason is that NCO formed on Ag spilt over the oxidic supports after its production, where it was stabilized [20].

As regards the formation of NCO we can exclude the step assumed in the case of supported Pt metals [16–18], when adsorbed N formed in the dissociation of NO is combined with CO

$$N_{(a)} + CO_{(a)} = NCO_{(a)} \tag{1}$$

This is particularly true for pure TiO$_2$. It is more likely that the reactive enolic species produced in the photodissociation of ethoxy

$$C_2H_5O_{(a)} = CH_2 = CH - O_{(a)} + H_{2(g)} \tag{2}$$
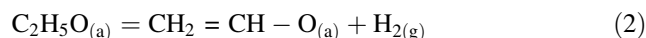
reacts with NO to give NCO, as was assumed for the thermal reaction [12, 13].

3.2 Photocatalytic Studies

The decomposition of ethanol on oxidized and reduced TiO$_2$ in dark was hardly observable at 300 K. Same feature was experienced for NO. Illumination of oxidized TiO$_2$
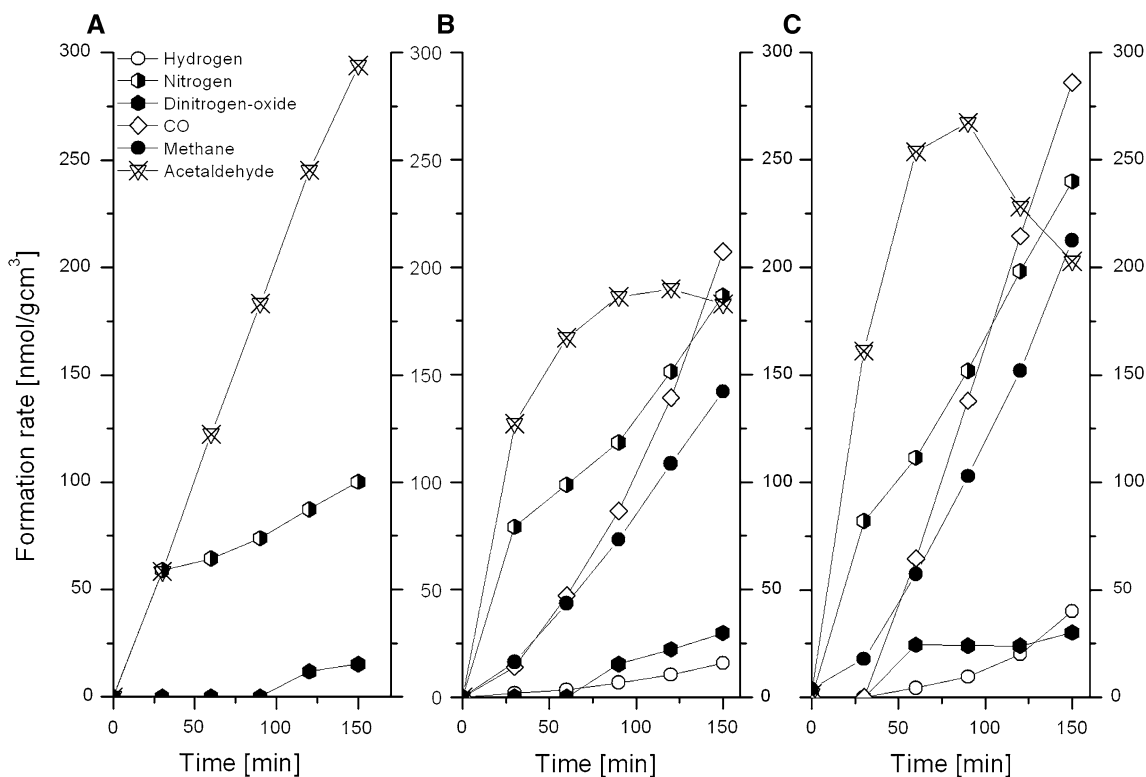
Fig. 3 Photo catalysis of NO + C$_2$H$_5$OH reaction on TiO$_2$ (T_R = 473 K) (**a**), 2% Ag/TiO$_2$ (T_R = 473 K) (**b**) and (T_{OX} = 573 K) (**c**)

(T_{OX} = 523 K), however, induced a slow consumption of ethanol to yield acetaldehyde, H_2 and smaller amount of CH_4, CO_2 and CO. A slight photo-decomposition of NO was also experienced over TiO_2. When NO + ethanol gas mixture was photolyzed on TiO_2 (T_R = 473 K) we experienced a reaction between the two compounds as indicated by the consumption of both reactants and the formation of N_2, N_2O, acetaldehyde and—in trace quantity—H_2, CO and CH_4. These compounds were produced at higher rates on oxidized TiO_2 (T_{OX} = 573 K). Results are plotted in Fig. 3a. Note that without illumination no reaction was observed between the reactants. The photo-reduction of NO with ethanol was markedly enhanced on Ag/TiO_2 catalyst: the reaction occurred at somewhat faster rate on oxidized than reduced Ag/TiO_2 surfaces (Fig. 3b, c). The main products were acetaldehyde, N_2, CO, CH_4 and H_2O (not determined), and the minor ones N_2O and H_2 indicating the occurrence of the oxidative dehydrogenation of ethanol

$$C_2H_5OH + 2NO = CH_3CHO + N_2O + H_2O \tag{3}$$
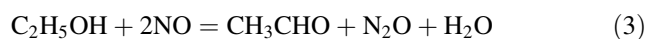
This step may be followed by the photo-decomposition of acetaldehyde and N_2O

$$CH_3CHO = CH_4 + CO \tag{4}$$

$$N_2O = N_2 + \frac{1}{2}O_2 \tag{5}$$

Further experiments are needed to establish the role of NCO and the finer mechanism of the NO + C_2H_5OH photoreaction.

4 Conclusions

(i)   Photolysis of NO + C_2H_5OH gas mixture on pure TiO_2 led to the formation of an IR band of isocyanate at 2,210 cm^{-1}, and a more intense one at 2,170 cm^{-1} on Ag/TiO_2. The latter is attributed to the vibration of Ag–NCO species.

(ii) Irradiation of the NO + C_2H_5OH on pure and Ag-containing TiO_2 induced the reduction of NO at 300 K. The rate of reaction was markedly enhanced by deposition of Ag onto TiO_2.

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