Photocatalytic decomposition of ethanol on TiO₂ modified by N and promoted by metals

Gyula Halasi, Imre Ugrai, Frigyes Solymosi

Reaction Kinetics Research Group, Chemical Research Center of the Hungarian Academy of Sciences, Department of Physical Chemistry and Materials Science, University of Szeged, P.O. Box 168, H-6701 Szeged, Hungary

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Abstract
The photo-induced vapor-phase decomposition of ethanol was investigated on pure, N-doped, and metal-promoted TiO₂. The catalysts were characterized by bandgap determination and by FTIR and XPS spectroscopy. In harmony with previous findings, the bandgap of N-doped TiO₂ continuously decreased from 3.15 to 2.17 eV with elevation of the temperature of its modification. IR studies revealed that illumination of the C₂H₅OH–TiO₂ system initiated the decomposition of adsorbed ethoxy species to yield acetaldehyde. The photodecomposition of ethanol on pure TiO₂ occurs to only a very limited extent; N-doped TiO₂ displays much higher activity and gives acetaldehyde and hydrogen as the primary products. The acetaldehyde formed is photolyzed to afford methane and CO. The efficiency of the N-doped TiO₂ increased with the narrowing of the bandgap, a feature attributed to the prevention of electron–hole recombination. The deposition of Rh on pure and doped TiO₂ dramatically enhanced the extent of photodecomposition of ethanol, even in visible light.

1. Introduction

Great efforts are currently being made to produce hydrogen for fuel and for various other applications. Oxygenated hydrocarbons (methanol, ethanol, and dimethyl ether) are the most generally and conveniently used sources of hydrogen production [1–3]. A number of effective materials have been developed for the catalysis of their decomposition and reforming. Unfortunately, even on the most effective and expensive Pt metals [4–17] and on the much less expensive Mo₂C [18,19], the reactions of these oxygenated hydrocarbons occur at relatively high temperatures. Their photocatalytic decomposition may provide a solution, as in this way hydrogen might be generated even at ambient temperature. Of the semiconductors, TiO₂ is applied frequently as a photocatalyst. However, its wide bandgap (3.0–3.2 eV) requires the use of UV light during the reactions, as only 4–5% of solar energy can be utilized for photoreactions. In contrast with heterogeneous catalysis, where the catalytic efficiency of TiO₂ can be varied appreciably by altervalent cations [20,21], in photocatalysis, anionic dopants have been found to be effective due to the narrowing of the bandgap of TiO₂, leading to visible light photocatalysis [22–29]. Over the past 20 years, a tremendous amount of work has been devoted to photocatalysis, including the photolysis of ethanol (for reviews, see [30–32]). Most of the published studies have dealt with the oxidation of ethanol generated as a pollutant by industry, or automobiles fueled by ethanol, and much less with the aim of producing hydrogen [33–44]. The present paper reports on the photodecomposition of ethanol on TiO₂ modified with N and on the effects of Rh, one of the most active metals for the decomposition of ethanol [4–6,9,12–17]. Measurements were also carried out with Ag/TiO₂, which exhibited high activity in the reduction of NO with ethanol in heavily oxidizing exhaust gas [45–47]. Its catalytic efficiency was earlier found to be greatly increased by illumination with a 15 W germicide lamp [48].

2. Experimental

2.1. Materials

Two types of TiO₂ were used: Degussa, P 25 (50 m²/g) and Hombikat, UV 100 (300 m²/g). For the preparation of N-doped TiO₂, we applied several methods. Following the description of Beranek and Kisch [28], titania powder was placed into 230-ml Schlenk tube connected via an adapter with 100-ml round-bottom flask containing 1 g of urea and heated in a muffle furnace for 30 min at different temperatures [28]. Samples prepared by this general method are denoted with “SK”. In other cases, TiO₂ was treated with NH₃. Following the method of Yates et al. [27], Hombikat TiO₂ powder was heated in a flow reactor system in an argon gas atmosphere up to 870 K. The heating rates were 7 K/min. For doping, the argon flow was replaced by NH₃ for 30 min, after the target temperature had been reached. Subsequently, the
powder was kept in flowing argon for 1 h at 870 K and then cooled in flowing argon over a time period of 2–3 h to room temperature. This sample was marked “SY”. N-modified TiO2 sample (named “SX”) was also produced following the description of Xu et al. [25]. Titanium tetrachloride was used as a precursor. After several steps, the NH3-treated TiO2 slurry was vacuum dried at 353 K for 12 h, followed by calcination at 773 K in flowing air for 3 h. Ag/TiO2 and Rh/TiO2 samples were prepared by impregnation of pure and various N-doped titania in the solution of AgNO3 or RhCl3. The suspension was dried at 373 K and annealed at 573 K for 1 h. For IR studies, the dried samples were pressed in self-supporting wafers (30 × 10 mm 〜10 mg/cm²). For photocatalytic measurements, the sample (70–80 mg) was sprayed onto the outer side of the inner quartz tube of the catalytic reactor from aqueous suspension. The surface of the catalyst film was 168 cm². The catalysts were oxidized at 573 K and reduced at 573 K in the IR cell or in the catalytic reactor in O2 or H2 stream for 1 h. The dispersion of Rh was determined by H2 adsorption at 300 K. We obtained a value of 26.6%. Ethanol with purity of 99.7% was supplied by Sharlau.

2.2. Methods

Diffuse reflectance spectra of TiO2 samples were obtained relative to the reflectance of a standard (BaSO4) using an UV/Vis spectrophotometer (OCEAN OPTICS, Typ.USB 2000) equipped with a diffuse reflectance accessory. The samples were pressed pellets of a mixture of 2 g of BaSO4 with 50 mg of the powder. X-ray photoelectron spectroscopy (XPS) measurements were performed with a Kratos XSAM 800 instrument, using non-monochromatic Al Kα radiation (hv = 1486.6 eV) and a 180° hemispherical analyzer at a base pressure of 1 × 10⁻⁹ mbar. Binding energies were referenced to the C1s binding energy (BE) (285.1 eV). The surface area of the catalysts was determined by application of the BET method with N2 adsorption at ~100 K. Data are listed in Table 1. 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). After illumination, the IR cell was moved to its regular position in 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). 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 GCL 307T5/L, Lighttech Ltd., Hungary) as light source. This lamp emits predominantly in the wavelength range of 250–440 nm. Its maximum intensity is at 234 nm. For the visible photocatalytic experiments, another type of lamp was used (Lighttech GCL 307T5/GOLD) with 400–640 nm wavelength range and two maximum intensities at 453 and 545 nm. We note that this lamp also emits below 400 nm. The approximate light intensity at the catalyst films is 3.9 mW/cm² for the germicide lamp and 2.1 mW/cm² for the other lamp. The reactor (volume: 970 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. The width of annulus between them was 42 mm, and that of the photocatalyst film was 89 mm. Ethanol (~1.3%) was introduced in the reactor through an externally heated tube avoiding condensation. The carrier gas was Ar, which was bubbled through ethanol at room temperature. 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.

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 presents plots of the Kubelka-Munk function F(Rn) vs. wavelength, obtained from diffuse reflectance data. Similarly, as observed by Beranek and Kisch [28], the color changed from yellowish to intense yellow and orange on increase of the pretreatment temperature. Correspondingly, the absorption edge shifted significantly to the visible range. In the determination of bandgap energies, Eg, we followed the calculation procedure of Beranek and Kisch [28], who used the equation \[ \alpha = A (hν - E_g)^n \] / C0, where \( \alpha \) is the absorption coefficient, \( A \) is a constant, \( hν \) is the energy of light, and \( n \) is a constant depending on the nature of the electron transition [49]. Assuming an indirect bandgap (\( n = 2 \)) for TiO2 [50], with \( \alpha \) proportional to \( F(R_n) \), the bandgap energy can be obtained from the plots of \( F(R_n) \) vs. \( hν \), as the intercept at \( [F(R_n)hν]^{1/2} = 0 \) of the extrapolated linear part of the plot (Fig. 1). The bandgap for pure TiO2 was 3.17 eV, while that for N-doped TiO2 sintered at 573 K was slightly less and continuously decreased to 2.17 ± 0.03 eV with increase in the temperature of its modification. We did not perform elemental analysis, but the results of Beranek and Kisch [28] revealed that beside N, its maximum amount was 11.8% in the sample modified 773 K, carbon has been also incorporated in the surface layer of TiO2. Accordingly, this C also contributes to the lowering of the bandgap of TiO2. We found smaller red shifts for N-doped TiO2 prepared by the reaction of TiO2 with NH3 (Table 1).

N-doped TiO2 (sample SK) was also examined by FTIR measurements. The spectrum revealed that several adsorbed species remained on the solid surface after preparation, yielding intense absorption bands in the ranges 1900–2300 and 1300–1700 cm⁻¹ (Fig. 2A). The positions of the bands and their intensities were very sensitive to the preparation of the samples. As shown in Fig. 2B, they could not be eliminated by treating the sample with oxygen at different temperatures; moreover, the band at 2186–2199 cm⁻¹ intensified somewhat on treatment up to 573 K and decayed considerably only at 673 K. At the same time, the color of the sample

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pretreatment temperature (K)</th>
<th>Surface area (m²/g)</th>
<th>Bandgap (eV)</th>
<th>Notation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>As received</td>
<td>200</td>
<td>3.17</td>
<td>Hombikat</td>
</tr>
<tr>
<td>TiO2</td>
<td>723</td>
<td>135</td>
<td>3.15</td>
<td>Prepared by Kisch et al. (SK) [28]</td>
</tr>
<tr>
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<td>115</td>
<td>3.15</td>
<td>Prepared by Kisch et al. (SK) [28]</td>
</tr>
<tr>
<td>TiO2 + N</td>
<td>673</td>
<td>96</td>
<td>2.35</td>
<td>Prepared by Yates et al. (SY) [27]</td>
</tr>
<tr>
<td>TiO2</td>
<td>673</td>
<td>90</td>
<td>2.15</td>
<td>Prepared by Yates et al. (SY) [27]</td>
</tr>
<tr>
<td>TiO2</td>
<td>870</td>
<td>81</td>
<td>2.17</td>
<td>Prepared by Yates et al. (SY) [27]</td>
</tr>
<tr>
<td>TiO2 + N</td>
<td>870</td>
<td>53</td>
<td>3.12</td>
<td>Prepared by Yates et al. (SY) [27]</td>
</tr>
<tr>
<td>TiO2 + N</td>
<td>723</td>
<td>265</td>
<td>3.00</td>
<td>Prepared by Xu et al. (SX) [25]</td>
</tr>
<tr>
<td>TiO2 + N</td>
<td>723</td>
<td>79</td>
<td>1.96</td>
<td>Prepared by Xu et al. (SX) [25]</td>
</tr>
</tbody>
</table>
progressively changed from yellow to orange and brown. The intense absorption bands are very probably due to isocyanate, cyanide, and other products of the pyrolysis of urea. Their formation and presence were also considered in the original paper describing the preparation [28]. The characteristic absorption band of NCO bound to TiO$_2$ is situated at 2205–2210 cm$^{-1}$, and that of CN is at

Fig. 1. Plots of Kubelka–Munk function vs. wavelength of powders modified at different temperatures (A) and bandgap determination using $(\frac{k(hv)}{R_1})^{1/2}$ vs. $hv$ plots (assuming indirect optical transition) for unmodified TiO$_2$ and TiO$_2$–N modified at different temperatures.
3.2. FTIR study of photolysis of ethanol

The interaction of ethanol with TiO$_2$ has been extensively studied by IR spectroscopy, and the effect of illumination of the system of C$_2$H$_5$OH + O$_2$ over TiO$_2$ has likewise been thoroughly examined [39]. The adsorption of ethanol on pure TiO$_2$ produced intense absorption bands in the IR spectrum (Fig. 4A), which can be attributed to the vibrations of adsorbed ethoxy species (Table 2). As a result of irradiation, a broad weak band developed between 1500 and 1600 cm$^{-1}$, which can be separated into two peaks at 1549 and 1579 cm$^{-1}$. The first is ascribed to \(\nu_{as}(\text{CO})\) vibration of adsorbed acetate and the second one to \(\nu_{as}(\text{CO})\) vibration of formate (Table 2). Note that there was no peak at 1718–1723 cm$^{-1}$ due to acetaldehyde.

Similar measurements were carried out with N-doped TiO$_2$ (sample SK, 673 K). The positions of the bands in the C–H stretching vibration region remained the same. In the interval 1500–1600 cm$^{-1}$ vibration bands appeared at 1551 and 1584 cm$^{-1}$ (Fig. 4B).

More dramatic spectral changes occurred when Rh was deposited on TiO$_2$. In order to avoid the disturbance caused by the absorption bands in the region 2000–2300 cm$^{-1}$ for the N-doped TiO$_2$ prepared by the decomposition of urea, experiments were performed with the sample SY. Spectra are presented in Fig. 4C. In the high-frequency region, almost the same absorption bands were observed as for pure TiO$_2$. Additionally, however, relatively strong CO bands due to linearly bonded CO (Rh$_2$–CO) and bridging CO (Rh$_2$–CO) appeared at 2008 and 1837 cm$^{-1}$ even without illumination; their intensities increased appreciably as a consequence of irradiation. There was no sign of the absorption bands at 2030 and 2100 cm$^{-1}$, indicative of the formation of Rh$(\text{CO})_2$ as a result of the oxidative disruption of Rh nanoparticles [52]. A possible reason is that the H$_2$ formed prevented this process [52]. Similar spectral features were experienced for Rh deposited on sample SY (Fig. 4D). In the low-frequency range, the picture was the same as for TiO$_2$. In order to eliminate the thermal effect, measurements were repeated at \(\sim 200\) K. Without irradiation, no absorption features were registered between 1800 and 2150 cm$^{-1}$. Even at the beginning of the photolysis, however, a well-detectable peak due to adsorbed CO appeared at 2045 cm$^{-1}$. Its absorbance slightly increased with elevation of the duration of irradiation.

3.3. Photocatalytic decomposition on pure and N-doped TiO$_2$

The results obtained following the photolysis of ethanol on pure TiO$_2$ are displayed in Fig. 5A. Even at room temperature, illumination initiated the decomposition of ethanol, to give acetaldehyde, hydrogen, methane, and CO as the major products. The predominant reaction pathway was clearly dehydrogenation. The conversion of ethanol was very low: \(\sim 4\%\) in 240 min. The results were well reproducible in the repeated measurements. Previous [39] and the present IR studies have clearly revealed that ethanol readily dissociates on TiO$_2$ to give adsorbed ethoxy species even at room temperature:

\[
2090–2150 \text{ cm}^{-1} [51]. \text{Both surface species, and particularly the CN group, are very stable on TiO}_2. \text{The absorption feature at } \sim 1618 \text{ cm}^{-1} \text{ is very likely due to } \delta_{\text{as}} \text{ vibration of NH groups.}
\]

Since the first preparation of N-doped TiO$_2$, it has been subjected to extensive XPD and XPS studies [22–29]. The nature of the incorporated N and its place in the TiO$_2$ lattice are still debated. It is not a purpose of the present paper to contribute to this debate. Nevertheless, for the characterization of our samples, we also performed informative XPS measurements. We found only slight shifts in the binding energies (BE) of Ti2p and N1s on the XPS spectra of N-doped TiO$_2$ (sample SK) prepared at different temperatures. These results are in good agreement with those obtained previously [28]. Treatment of the N-doped TiO$_2$ in vacuum at various temperatures resulted in very minor changes in the XPS spectrum. As the IR studies revealed a considerable amount of carbon-containing compounds on the surface, we also examined the influence of oxygen treatment on the XPS spectrum of TiO$_2 + N$ (SK) modified at 573 K (a), 673 K (b), and 773 K (c). (B) Effects of oxidation of TiO$_2 + N$ modified at 673 K. Unoxidized (a); 300 K (b); 373 K (c); 473 K (d); 573 K (e); 673 K (f).
C₂H₅OH(g) = C₂H₅OH(a) (1)

C₂H₅OH(a) = C₂H₅O(a) + H₂ (2)

This process does not need illumination. As only traces of acetaldehyde were detected on pure TiO₂ without irradiation, it may be assumed that the slow step in the dehydrogenation of ethanol to acetaldehyde and hydrogen is the decomposition of ethoxy species or more precisely the cleavage of one of the C–H bonds. Photolysis of the C₂H₅OH–TiO₂ system, however, initiated the decomposition of ethoxy on TiO₂, very probably involving the donation of a photo-electron formed in the photo-excitation process:

TiO₂ + hv = h⁺ + e⁻ (3)

to the ethoxy species:

C₂H₅O(a) + e⁻ = C₂H₅O⁻ (a) (4)

This step is followed by the photo-induced decomposition of ethoxy to acetaldehyde and hydrogen:

C₂H₅O⁻ (a) = CH₃CHO⁻ (a) + H₂ (5)

The adsorbed hydrogen may reduce the TiO₂ surface or react with surface oxygen to yield OH. In the case of TiO₂ samples, it was a general observation that the amount of H₂ was much less than that of acetaldehyde. We assume that beside the reduction process, a fraction of H₂ reacts with the surface species produced by the preparation of TiO₂ + N samples. The formation of CH₄ and CO suggests the further decomposition of acetaldehyde:

CH₃CHO⁻(a) = CH₄ + CO⁻(a) (6)

CO⁻(a) + h⁺ = CO(g) (7)

This is a photo-catalyzed process as acetaldehyde does not decompose on TiO₂ at this temperature. The tiny amounts of ethylene and ethane in the products suggest that the dehydration of ethanol and the resulting hydrogenation of ethylene to ethane

C₂H₂OH = C₂H₄ + H₂O (8)

C₂H₄ + H₂ = C₂H₆ (9)

occur to only negligible extents. The level of photolysis on pure TiO₂ is very low, most likely because of the ready recombination between electrons and holes generated by light.

The incorporation of N into TiO₂ (sample SK), however, appreciably increased the extent of photodecomposition, as indicated by the higher conversion and rates of product formation (Fig. 5B,C). With the consumption of ethanol, formation of acetaldehyde apparently slowed down or even ceased. At the same time, more CH₄ and CO were produced on longer illumination, indicating the occurrence of the photodecomposition of acetaldehyde (Eq. (5)). The effect of doping TiO₂ with N depended on the pretreatment. Both the conversion and the product distribution increased with increase in the temperature of modification of N-doped TiO₂. The highest photocatalytic activity was exhibited by the sample annealed at 773 K. When the surface area of the sample was taken into account, this effect was more pronounced (Fig. 5D). In view of the change in the bandgap of N-doped TiO₂ with the modification temperature (Fig. 1), it may be concluded that the extent of photolysis of ethanol on TiO₂ is markedly enhanced by the narrowing of the bandgap of TiO₂. This can be explained by the prevention of electron–hole recombination.

As the narrowed bandgap allows TiO₂ to absorb light at lower wavelengths, measurements were performed with the use of a lamp emitting in the visible range. These experiments were carried out with TiO₂ (SX), which possesses better performance. The results presented in Fig. 6A and B show that, whereas pure TiO₂ exhibits moderate activity in the visible light, the photocatalytic activity of N-doped sample (SX) is significantly higher.
3.4. Effects of Rh and Ag

In further experiments, we examined the effects of the deposition of Rh on TiO$_2$ on the photodecomposition of ethanol. Results are shown in Fig. 7. Whereas the conversion of ethanol in 200 min on pure TiO$_2$ was less than 4.0%, in the presence of 2% Rh, it attained 90%. The dehydrogenation of ethanol remained the main reaction pathway. In this case, the amount of hydrogen greatly exceeded that of acetaldehyde, which reached a constant level at around $\sim$140 min, when its photodegradation to methane and CO became more pronounced. The amounts of these two compounds increased as the duration of illumination was lengthened. Very small amounts of ethane and CO$_2$ were also detected. The deposition of Ag on TiO$_2$ similarly significantly promoted the photoreaction, but its effect was less than that of Rh.

As concerns the explanation of the effect of Rh, it should be borne in mind that Rh is a very active catalyst for the thermal decomposition of ethanol at higher temperature [4–6,9,12–17]. This is attributed to promotion of the rupture of a C–H bond in the ethoxy species adsorbed on Rh. Although the catalyst sample was cooled during the photolysis, the possibility cannot be excluded that the illumination caused a temperature rise of the catalyst. In order to check this possibility, a thin thermocouple was attached to the catalyst layer. The temperature rose by only a
few degrees during illumination. We also examined the thermal reaction on the Rh-promoted TiO$_2$ layer used for photolysis without illumination and detected merely very slight decomposition (~1–2%) at 300 K. A measurable decomposition of ethanol (~3% in 60 min) was observed only at 423 K. The results of these control experiments lead us to exclude the contribution of thermal effects to the decomposition of ethanol induced by photolysis.

The dramatic influence of Rh was also investigated on N-doped TiO$_2$ in visible light. It was accepted that the incorporation of N into TiO$_2$ enhances its absorbance from solar light, and measurements were performed with a lamp emitting at 400–640 nm. Fig. 6C and D depict the photocatalytic effects of Rh deposited on pure TiO$_2$ and on N-doped TiO$_2$ (sample SY). A comparison immediately reveals that the photoactivity of the N-doped sample is clearly higher than that of Rh/TiO$_2$ free of nitrogen. This is reflected in the conversion of ethanol, in the amounts of the products of dehydrogenation, and in the photo-induced decomposition of acetaldehyde into CH$_4$ and CO.

The promoting effect of metal deposition on TiO$_2$ has been observed in a number of photoreactions, including the photo-oxidation of ethanol [53–55]. This effect was explained by a better separation of charge carriers induced by illumination and by improved electronic communication between metal particles and TiO$_2$ [53–55]. We believe that the electronic interaction between the metal and n-type TiO$_2$ plays an important role in the enhanced photoactivity of Rh/TiO$_2$, as demonstrated in the hydrogenation of CO and CO$_2$ [56] and in the photocatalytic reaction between H$_2$O and CO$_2$ [57]. As the work function of TiO$_2$ (~4.6 eV) is less than that of Rh (4.98 eV), electron transfer occurs from TiO$_2$ to Rh, which increases the activation of CO$_2$ in the form of CO$_2$. The role of such electronic interaction in the activity of a supported metal catalyst was first established in the case of the decomposition of formic acid.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>TiO$_2$ [39]</th>
<th>TiO$_2$ (SK) [present work]</th>
<th>TiO$_2$ + N (SK, 773 K) [present work]</th>
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<tr>
<td>Ethoxy</td>
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<td>$v_{as}$(CH$_3$)</td>
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<td>2975</td>
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<tr>
<td>$v_{as}$(CH$_2$)</td>
<td>2931</td>
<td>2929</td>
<td>2929</td>
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<tr>
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<tr>
<td>$v_{s}$(CH$_3$)</td>
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<td>1147, 1113</td>
<td>1148</td>
<td>1144</td>
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<td>1052</td>
<td>1076</td>
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<th>Vibrational mode</th>
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<th>TiO$_2$ (SK) [present work]</th>
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<td>1549</td>
<td>1551</td>
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<tr>
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Table 2

IR vibrational frequencies and their assignments for ethoxy, acetate, and formate species produced following the illumination of ethanol on TiO$_2$ catalysts at 300 K.

Fig. 5. Effects of pretreatment temperature of N-doped TiO$_2$ (SK) on the conversion of ethanol (A) and on the formation of acetaldehyde (B) and CH$_4$ (C). Rate of formation of acetaldehyde related to the surface area of the samples (D). Undoped TiO$_2$ (a); N-modified TiO$_2$ at 573 K (b); 673 K (c); 723 K (d); 773 K (e).

[Image of figures and tables]
acid on Ni/TiO$_2$. When (as far as we are aware) TiO$_2$ was first used as a support [58,59]. Variation of the electron density or the work function of TiO$_2$ doping with altervalent cations influenced the activation energy of the decomposition of formic acid. We assume that the illumination enhances the extent of electron transfer from TiO$_2$ to Rh at the interface of the two solids, leading to increased decomposition. We believe that a similar phenomenon occurs in the case of Ag/TiO$_2$.

Fig. 6. Effects of N doping of TiO$_2$ (3X) on the photocatalytic decomposition of ethanol in the visible light on TiO$_2$ (A and B) and 2% Rh/TiO$_2$ (SY) (C and D) (•, • H$_2$; ○ acetaldehyde).

Fig. 7. Conversion and product distribution of the photodecomposition of ethanol on 2% Rh/TiO$_2$ (A) and 2% Ag/TiO$_2$ (B).
4. Conclusions

(i) On the modification of TiO$_2$ through incorporation of N species containing carbon, its bandgap is markedly narrowed on elevation of the annealing temperature.

(ii) Doping TiO$_2$ with N greatly increased its photocactivity in its reaction with ethanol to give acetaldehyde and hydrogen as primary products. The acetaldehyde formed subsequently underwent photolysis to methanal and CO.

(iii) The deposition of Rh or Ag on pure or N-doped TiO$_2$ dramatically enhanced the photodecomposition of ethanol.

(iv) Lowering the bandgap of TiO$_2$ through N incorporation facilitated the photolysis of ethanol on TiO$_2$ and Rh/TiO$_2$ in visible light.

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References


