Photocatalytic decomposition of formic acid and methyl formate on TiO₂ doped with N and promoted with Au. Production of H₂

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1. Introduction

Great efforts are currently being made to produce H₂, if possible free of CO. As a source of H₂, the most extensively studied compound is ethanol [1–10]. However, complete freedom from CO can not be achieved even in the presence of H₂O. Attention recently turned to formic acid: one pathway of its decomposition results in the formation of H₂ and CO₂

\[
\text{HCOOH} \rightarrow \text{H₂} + \text{CO₂} \quad \Delta G = -48.4 \text{ kJ mol}^{-1}
\]

If the dehydration of formic acid

\[
\text{HCOOH} \rightarrow \text{H₂O} + \text{CO} \quad \Delta G = -28.5 \text{ kJ mol}^{-1}
\]

can be avoided, this compound will be suitable for the generation of pure, CO-free H₂. Recent studies proved that, under certain conditions, the production of CO can be markedly reduced over some supported metal catalysts at elevated temperatures [11–16]. Further progress was made by the photolysis of formic acid on TiO₂-based catalysts at room temperature [17–26]. In harmony with the early findings of Haruta [27] concerning the high catalytic performance of Au nanoparticles in several reactions, Au supported on various oxides is also an effective catalyst for the thermal decomposition of formic acid at 423–573 K [11,13,16]. It is an open question whether Au deposited on TiO₂ in nanosize is also capable of accelerating the photocatalytic decomposition of formic acid at room temperature. The primary aim of the present work was to elaborate the experimental conditions for the production of H₂ with lowest CO content on Au catalysts. We additionally studied the photolysis of methyl formate, which is one of the products of the photocatalytic reaction of...
methanol [28]. Methyl formate has been considered as a precursory in the synthesis of several compounds, such as formamide, acetic acid, cyanohydrin acid [29], therefore the knowledge of its formation and decomposition represents technological importance. Attempts will be made to decrease the bandgap of TiO₂ by anionic doping, making possible the occurrence of photoreactions even in visible light. The effects of cationic doping, which considerably affects the defect and electronic structure of TiO₂, were also examined.

2. Experimental

2.1. Methods

In the determination of the bandgaps of the TiO₂ samples we applied the same procedures as described in previous papers [25,26]. The surface area of the catalysts was determined by Brunauer–Emmet–Teller (BET) method with N₂ adsorption at ~100 K. Data are listed in Table 1. The sizes of the Au nanoparticles were determined by an electron microscope (Philips CM 20).

Photocatalytic reaction was followed in the same way as described in our previous papers [29,30]. Formic acid (~5.4%, 990 μmol) and methyl formate (~3.0%, 610 μmol) were introduced in the reactor through an externally heated tube avoiding the carrier gas Ar, which was bubbled through pure formic acid or methyl formate at room temperature until their concentrations reached the above values. The gas-mixture was circulated by a pump. The reaction products were analyzed with a HP 5890 gas chromatograph. The conversion was calculated on the amount formic acid reacted. We obtained practically the same values when the calculation was based on the H or C contents of the products. For IR studies a mobile IR instrument (Biorad, Div. FTS 155) instrument.

2.2. Materials

Formic acid was the product of British Drug Houses (BDH) with purity of 99.5%. Methyl formate (purity 97%) was purchased from Alfa Aesar. Supported Au catalysts were prepared by a deposition-precipitation method. HAuCl₄·[254·5·215 ε “Symbol” vs 12-aq (p.a., 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the aqueous HAuCl₄ solution had been adjusted to 7.5 by the addition of 1 M NaOH solution, a suspension was prepared with the finely powdered oxidic support, and the system was kept at 343 K for 1 h under continuous stirring. The suspension was then aged for 24 h at room temperature, washed repeatedly with distilled water, dried at 353 K and calcined in air at 573 K for 4 h. The following oxides were used as catalysts or supports: TiO₂ (Hombikat, UV 100, 200 m²/g), TiO₂ (Degussa P25, 51 m²/g), and SiO₂ (Cabosil, 198 m²/g). Titane nanotube and titane nanowires were synthesized using a simple alkali hydrothermal method detailed elsewhere [31]. In addition, we also used a commercial 1% Au/TiO₂ (P25) sample (AUORolite, 50 m²/g). The sizes of the Au nanoparticles determined with an electron microscope: 1.5–2.0 nm for 1% Au/TiO₂ (AUORolite), 8.0–9.0 nm for Au/TiO₂ (P25), 10–15 nm for 1% Au/TiO₂ (Hombi) and 6.0–7.0 nm for 1% Au/SiO₂ (Cabosil).

For the preparation of N-doped TiO₂ we applied the description of Beranek and Kisch, who treated titania powder with urea at different temperatures [32]. This sample is noted with “SK”. As regards the crystal structure of TiO₂, they found that all samples treated with different temperatures revealed only anatase peaks. In another case TiO₂ was prepared from titanium tetrachloride, and the oxide obtained was reacted with NH₃ [33]. This sample is marked with “SX”. TiO₂ was also doped with W⁶⁺ and Cr³⁺ ions following the procedure described in early papers [34]. Briefly TiO₂ was suspended in the aqueous solution of (NH₄)₂C₂O₇ or ammonium para-wolframate (NH₄)₁₀H₂(W₂O₇)₆xH₂O, dried at 373 K, and calcined at 573 K. In order to achieve a complete incorporation of the above cations, the samples have been sintered at 873 K for 5 h. As shown in Table 1, this treatment led to a significant lowering of the surface area of the catalysts.

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 cm². For IR studies the dried samples were pressed in self-supporting wafers (30 × 10 mm−10 mg/cm²). The catalysts were oxidized at 573 K and reduced at 573 K in the IR cell or in the catalytic reactor for 1 h.

3. Results

3.1. Characterization of the samples

Bandgaps of several N-doped TiO₂ samples prepared by different methods were determined and presented in our previous papers [26,30]. When the preparation was repeated, the bandgaps of the new samples were likewise determined. The largest lowering of the bandgap of TiO₂ was achieved by using NH₄ for N incorporation. Doping TiO₂ with metal cations had much less effect. Data are presented in Table 1. Whereas the IR spectra of TiO₂ + N (SK) revealed several absorption bands due to the presence of NCO, CN and NH species formed in the reaction of TiO₂ with urea [26,28], there was no sign of residual adsorbed species in the IR spectra of TiO₂ + N (SX).

<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>(Hombi)</td>
</tr>
<tr>
<td>TiO₂ + N</td>
<td>673</td>
<td>96</td>
<td>2.30</td>
<td>(SK)</td>
</tr>
<tr>
<td>TiO₂ + N</td>
<td>723</td>
<td>90</td>
<td>2.10</td>
<td>(SK)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>723</td>
<td>265</td>
<td>3.00</td>
<td>(SX)</td>
</tr>
<tr>
<td>TiO₂ + N</td>
<td>723</td>
<td>79</td>
<td>1.96</td>
<td>(SX)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>873</td>
<td>53</td>
<td>3.09</td>
<td>(Hombi)</td>
</tr>
<tr>
<td>TiO₂ + 2% Cr₂O₃</td>
<td>873</td>
<td>51</td>
<td>2.87</td>
<td>(Hombi)</td>
</tr>
<tr>
<td>TiO₂ + 1.5% WO₃</td>
<td>873</td>
<td>73</td>
<td>3.07</td>
<td>(Hombi)</td>
</tr>
<tr>
<td>TiO₂ (nanotube)</td>
<td>423</td>
<td>186</td>
<td>3.14</td>
<td>–</td>
</tr>
<tr>
<td>TiO₂ (nanowire)</td>
<td>423</td>
<td>36</td>
<td>3.10</td>
<td>–</td>
</tr>
</tbody>
</table>
samples. No absorption bands were seen in the IR spectra of the catalysts TiO$_2$ + 1.5% Cr$_2$O$_3$ and TiO$_2$ + 2.0% WO$_3$.

3.2. Adsorption and reaction of formic acid

3.2.1. IR spectroscopic measurements
The adsorption of formic acid on TiO$_2$ and Au/TiO$_2$ samples and subsequent degassing produced intense absorption bands at $\sim$2953, $\sim$2870, $\sim$1561 and $\sim$1367 cm$^{-1}$, which can be attributed to the vibrations of formate species formed in the dissociative adsorption of formic acid:

\[
\text{HCCOH}_\text{(a)} \rightarrow \text{HCOO}_\text{(a)} + \text{H}_\text{(a)} 
\]  

At the beginning of irradiation, a new weak spectral feature also developed at 1412 cm$^{-1}$, the intensity of which remained unaltered on prolonged illumination. The most important region of the spectra is shown in Fig. 1. A sudden decline in the intensity of the absorption bands occurs at the beginning of photolysis, followed by their slower attenuation. The assignments of the absorption bands are presented in Table 2.

Similar spectroscopic measurements were carried out with Au/SiO$_2$ samples. Our previous IR study had revealed that, in contrast with Pt metals [25,26], a formate species exists on Au particles even at 573 K [16]. This was established by using a SiO$_2$ support, on which formic acid does not dissociate to give adsorbed formate. The adsorption of formic acid on a Au/SiO$_2$ catalyst gave intense formate bands at $\sim$1604, 1376 and 1370 cm$^{-1}$ (Fig. 1D), and also a strong band at 1737 cm$^{-1}$ due to molecularly bonded formic acid. In response to illumination, all the bands underwent significant attenuation, very likely due to the photo-induced desorption of weakly adsorbed formic acid and to the photocatalytic decomposition of formate on Au particles.

3.2.2. Photocatalytic studies
Our previous study showed that formic acid does not decompose on pure TiO$_2$ (Hombi) at 300 K, but illumination induced a slow reaction at this temperature [25,26]. The

![Fig. 1 – IR study of the effects of illumination time on adsorbed HCOOH TiO$_2$ (P25) (A), 1% Au/TiO$_2$ (Aurolite) (B), 1% Au/TiO$_2$ (Hombi) (C), and 1% Au/SiO$_2$ (Cabosil) (D). Illumination was performed after adsorption of HCOOH vapor for 15 min at 300 K. From time to time the irradiation was interrupted and spectral changes were registered at 300 K. All the spectra are difference spectra.](image-url)
The photocatalytic decomposition of formic acid on TiO$_2$ was enhanced by N-doping, similarly to the photolysis of ethanol [30]. The activity of N-doped TiO$_2$ relative to the photocatalytic activity of some TiO$_2$ was examined and the presence of H$_2$ over a Au/TiO$_2$ catalyst, even at room temperature [22]. Oxygen is known to be able to oxidize CO selectively in the presence of various N-containing surface compounds formed during the preparation [26]. The largest enhancement in the photocatalytic activities of Au/TiO$_2$ due to N-doping was observed for the samples denoted “SX”. The results are shown in Fig. 4. The photolysis of formic acid was also examined on the previous catalysts, using a lamp emitting in the visible range. Where Au/TiO$_2$ (SX) exhibits little activity in visible light, the photocatalytic decomposition of formic acid occurred at 473 K.

### 3.3. Adsorption and reaction of methyl formate

#### 3.3.1. IR spectroscopic measurements

We performed similar IR studies with methyl formate in the case of formic acid. IR spectra of adsorbed methyl formate on pure and Au-promoted TiO$_2$ are presented in Fig. 5. As regards the pure TiO$_2$ (P25), vibrations were registered at 2997, 2930, 2843, and 2831 cm$^{-1}$ in the CH frequency region. A very intense broad absorption band appeared in the interval 1500–1600 cm$^{-1}$, which can be separated into two spectral features at 1598 and 1540 cm$^{-1}$. In addition, strong peaks developed at 1367 cm$^{-1}$ and weaker ones at 1279, 1150 and 1043 cm$^{-1}$. Illumination of the adsorbed layer caused very little, if any attenuation of the above bands. We obtained similar IR spectra following the adsorption of methyl formate on the Au/TiO$_2$ (Aurolite) sample, with slight alterations in the position of the bands. Absorption bands observed on pure TiO$_2$ and Au/TiO$_2$ are listed in Table 2. Their positions agreed well with those reported by Lukaski and Muggli [20].

### Table 3 – Data for the photocatalytic activity of some TiO$_2$ samples.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion in 60 min</th>
<th>Conversion in 210 min</th>
<th>CO$_2$ Formation (in nmol) related to the surface area of the sample in 60 min</th>
<th>CO$_2$ Formation (in nmol) related to the surface area of the sample in 210 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>1.8</td>
<td>8.1</td>
<td>0.42</td>
<td>1.70</td>
</tr>
<tr>
<td>TiO$_2$ + 1.5% WO$_3$</td>
<td>2.6</td>
<td>6.6</td>
<td>0.44</td>
<td>0.93</td>
</tr>
<tr>
<td>TiO$_2$ + 2% Cr$_2$O$_3$</td>
<td>1.2</td>
<td>3.6</td>
<td>0.28</td>
<td>0.77</td>
</tr>
<tr>
<td>TiO$_2$ (nanotube)</td>
<td>1.3</td>
<td>39.2</td>
<td>0.14</td>
<td>0.47</td>
</tr>
<tr>
<td>TiO$_2$ (nanowire)</td>
<td>3.9</td>
<td>31.5</td>
<td>0.44</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Characteristic data for these samples are presented in Table 1.
The adsorption of methyl formate on Au/SiO₂ gave only weak absorption bands at 2964, 2951, 2900, and 2851 cm⁻¹ in the CH frequency range, and at 1716, 1456, 1438 and 1383 cm⁻¹ in the low-frequency region. Illumination of the catalyst only in methyl formate vapor lead to the appearance of extremely weak formate bands at 1540–1590 cm⁻¹ and ~1370 cm⁻¹. These absorption features were seen only when the Au/SiO₂ was treated with methyl formate at 523–573 K.

Fig. 2 – Effects of illumination time on the photocatalytic decomposition of HCOOH on various 1% Au/TiO₂ samples. Conversion of HCOOH (A), formation of H₂ (B); CO₂ (C) and CO (D).

Fig. 3 – Effect of H₂O (A and B) and O₂ (C and D) addition on photocatalytic decomposition of HCOOH over 1% Au/TiO₂ (Aurolite) catalyst. Formation of H₂ (A, C) and CO/CO₂ ratio (B, D).
3.3.2. Photocatalytic studies
The main products of the photolysis of methyl formate on Au/TiO₂ (Aurolite) are H₂ and CO₂, with small amounts of CO, CH₃OH and CH₄. The extent of the decomposition was about ~85% in 240 min (Fig. 6). As in the case of formic acid, the photoactivity of Au/TiO₂ (Hombi) was less extensive. Pure TiO₂ (P25) also catalyzed the photodecomposition of methyl formate, the conversion reaching 20% in 240 min. As observed in the photocatalytic reactions of ethanol[26] and formic acid[26], the amount of H₂ was much less than that of CO₂. We assume that hydrogen may reduce the TiO₂ surface or react with surface oxygen to yield OH groups.

Following N incorporation, the photoactivity of both TiO₂ (SX) and 1% Au/TiO₂ (SX) was increased appreciably. More importantly, these catalysts exhibited photoactivity even in visible light. The interesting feature of this TiO₂-based catalyst is that the amount of CH₃OH is commensurable with that of H₂ and CO₂. We assume that hydrogen may reduce the TiO₂ surface or react with surface oxygen to yield OH groups.

In order to determine the catalytic effects of TiO₂ and Au/TiO₂ on the thermal decomposition of methyl formate, measurements were performed under exactly the same experimental conditions. Samples were kept at different temperatures for 30 min. Over pure TiO₂, reaction was first observable at 473 K. In 30 min, the extent of decomposition was ~3.0%. It increased to ~8.5% at 573 K. The main products were H₂, CH₃OH, CO₂ and CO. Note that formation of CH₂O was not detected. A much greater catalytic effect was exhibited by Au/TiO₂ (Aurolite), when the reaction occurred even at 373 K. The conversion was 15% at 373 K and 50% at 573 K.

4. Discussion

4.1. Formic acid

Infrared spectroscopic measurements clearly showed that formic acid undergoes dissociation readily on both pure and Au-promoted TiO₂, yielding the characteristic spectral features of formate species: $v_{as}$ at 1561–1562 cm⁻¹ and $v_{s}$ at 1367–1377 cm⁻¹ [16,35–38]. Illumination caused a slow decline in the intensities of both broad bands, suggesting that the slow step in the photoreaction is the decomposition of this surface intermediate, e.g. cleavage of one of the C–O bonds in the formate. As this surface compound is readily formed on TiO₂, it is an open question whether it also exists on the Au surface. The fact that we identified the 1604 and ~1370 cm⁻¹ bands in the IR spectra of Au/SiO₂ (Fig. 1) suggests that formate does exist on Au particles, too, as no dissociation of formic acid to yield formate occurs on pure SiO₂ [16,36]. It is very likely that the broad nature of the formate band at 1561 cm⁻¹ for Au/TiO₂ catalysts is a consequence that it is composed of two slightly different asymmetric stretches of formate located on the TiO₂ and Au particles. This is in contrast with SiO₂-supported Pt metals, on which formate exhibits low stability and decomposes below 300 K [16,36]. Besides formate bands, a weak feature also developed at
Fig. 5 – IR study of the effects of illumination time on adsorbed methyl formate on TiO₂ (P25) (A), 1% Au/TiO₂ (Aurolite) (B), 1% Au/TiO₂ (Homb) (C), 5% Au/TiO₂ (Homb) (D). Illumination was performed after adsorption of methyl formate vapor at 300 K. From time to time the irradiation was interrupted and spectral changes were registered at 300 K. All the spectra are difference spectra.

Fig. 6 – Effects of illumination time on the photocatalytic decomposition of methyl formate on TiO₂ and 1% Au/TiO₂ (Aurolite) samples. Conversion (A), formation of H₂ (B): CO₂ (C) and CO (D).
1410 cm$^{-1}$ during irradiation in the IR spectra of the TiO$_2$-based catalysts (Fig. 1). This vibration can be attributed to dioxymethylene formed in the photo-induced decomposition of adsorbed formate [39].

In the explanation of the photocatalytic decomposition of formic acid on TiO$_2$ we assumed the donation of a photo-electron formed in the photo-excitation process to the formate species [25,26]:

Fig. 7 – Effects of N doping of TiO$_2$ (SX) on the photocatalytic decomposition of methyl formate in the UV and visible light on TiO$_2$ (SX) and TiO$_2$ + N (SX) samples. Conversion (A and C), formation of CH$_3$OH (B and D).

Fig. 8 – Effects of N doping of TiO$_2$ (SX) on the photocatalytic decomposition of methyl formate in the UV and visible light on 1% Au/TiO$_2$ (SX) and 1% Au/TiO$_2$ + N (SX). Conversion (A and C), formation of CH$_3$OH (B and D).
HCOO\(_{(a)}\) + e\(^{-}\) → HCOO\(_{(a)}^\cdot\)  \(4\)

This step is followed by the photo-induced decomposition of formate to CO\(_2\) and hydrogen. As the N-modified TiO\(_2\) samples exhibited higher photoactivity compared to that of unmodified catalysts, we concluded that the extent of photolysis of formic acid on TiO\(_2\) is markedly enhanced by the narrowing of the bandgap of TiO\(_2\) [26]. This was attributed to the prevention of electron–hole recombination.

The effects of cationic doping of TiO\(_2\) requires special discussion. The incorporation of W\(^{6+}\) into TiO\(_2\) is known to increase the electric conductivity of TiO\(_2\) by two orders of magnitude [34]. TiO\(_2\) doped with Cr\(^{3+}\) exhibited special behavior. During heat treatment of TiO\(_2\) + 1% CrO\(_3\) in air, Cr\(^{3+}\) is oxidized to Cr\(^{6+}\) and Cr\(^{5+}\) [34]. As a result, the surface layer of Cr ion-doped TiO\(_2\) exhibited a p-type character. This catalyst exhibited high activity in the thermal decomposition of formic acid [34]. In the present case, however, cationic doping affected the activity of TiO\(_2\) in the photolysis of formic acid to only a slight extent. The similar negative results found in the studies of several other metal/TiO\(_2\) systems [45].

Considerably higher photoactivity was measured on Au/TiO\(_2\) catalysts (Fig. 2). The efficiency of Au/TiO\(_2\) (Aurolite) slightly exceeds that of Pt metals with the exception of Pd/ TiO\(_2\) [26]. As concerns the explanation of the effect of Au, it should be borne in mind that Au nanoparticles are very active catalysts of the decomposition of formic acid at elevated temperature [11,13,16]. This is attributed to the facilitation of the rupture of a C–H bond in the formate species adsorbed on the Au or at the Au/oxide interface. It should be also pointed out that CO formed in the photocatalytic decomposition of formic acid at room temperature does not adsorb on Au particles, whereas it forms a strong bond with Pt metals leading to the lowering of the number of active metal sites. This feature may also contribute to the comparable activity of Au nanoparticles with that of Pt metals. The promoting effect of Au in the photocatalytic decomposition of formic acid can be attributed to the better charge carrier separation induced by illumination and by improved electronic communication between Au particles and TiO\(_2\), can be explained in the same way as proposed in our previous works [26]. We believe that the electronic interaction between Au metal and n-type TiO\(_2\) also plays an important role in the enhanced photoactivity of Au/ TiO\(_2\), as demonstrated in the oxidation of CO [27,42–44] and in several other metal/TiO\(_2\) system [45]. As the work function of TiO\(_2\) (∼4.6 eV) is less than that of Au (5.31 eV), electron transfer may occur from TiO\(_2\) to Au, which increases the activation of adsorbed molecules on the Au particles [45]. We assume that illumination enhances the extent of electron transfer from TiO\(_2\) to Au at the interface of the two solids, leading to a greater degree of decomposition.

4.2. Methyl formate

As mentioned in the Introduction, the dissociation of methyl formate vapor was not achieved on Au/SiO\(_2\) even heating the sample to 373–623 K. Methyl formate was the main product in the photocatalytic decomposition of methanol over Pt metals/ TiO\(_2\) catalysts [28]. Its formation was also observed in the photocatalytic oxidation of methanol over TiO\(_2\) [46–50]. In an extensive IR spectroscopic study Lukaski and Muggli [20] found that methyl formate adsorbs both molecularly and dissociatively as methoxy and formate on TiO\(_2\). In the photocatalytic oxidation formate oxidizes to CO\(_2\), whereas methoxy forms CO\(_2\) through formaldehyde and formate.

The IR spectra of methyl formate adsorbed on TiO\(_2\) samples at 300 K contained the same spectral features in the low-frequency range as in the case of formic acid: intense absorption features at between 1600–1500 cm\(^{-1}\) and 1368 cm\(^{-1}\). This suggests that methyl formate underwent dissociation to result in the formation of formate species. Illumination of the adsorbed layer on TiO\(_2\) caused only a slow attenuation of these absorption bands. The effects of photolysis on Au/TiO\(_2\) samples were more pronounced. Adsorption of methyl formate on Au/SiO\(_2\) sample produced only absorption bands due to molecularly bonded methyl formate. On the effect of illumination caused only the desorption of this weakly attached molecule. A very weak signal of formate bands was attained by prolonged illumination of Au/SiO\(_2\) in methyl formate vapor.

A more complex picture emerged in the photocatalysis of methyl formate, as indicated by the product distribution. The formation of products shown in Fig. 6 suggests that we can count with the occurrence of following reactions:

\[\text{HCOOH}_\text{g} + \text{OH}_\text{a} \rightleftharpoons \text{CH}_3\text{O}_\text{a} + \text{HCOO}_\text{a} + 1/2\text{H}_2\text{O}_\text{g}\]  \(5\)

\[\text{HCOO}_\text{a} \rightleftharpoons \text{CO}_\text{a} + 1/2\text{H}_2\text{O}_\text{g}\]  \(6\)

\[\text{CH}_3\text{O}_\text{a} + \text{H}_\text{a} \rightleftharpoons \text{CH}_3\text{OH}_\text{g}\]  \(7\)

\[\text{CH}_3\text{O}_\text{a} \rightleftharpoons \text{CH}_2\text{O}_\text{a} + 1/2\text{H}_2\text{O}_\text{g}\]  \(8\)

\[\text{CH}_2\text{O}_\text{a} \rightleftharpoons \text{CO}_\text{g} + \text{H}_2\text{O}_\text{g}\]  \(9\)

Without illumination, the decomposition of methyl formate started only ∼473 K on pure TiO\(_2\) (P25) and above 373 K on Au/ TiO\(_2\) (Aurolite) catalysts.

It is important to mention that the narrowing the bandgap of TiO\(_2\) by N incorporation enhanced the activity of both TiO\(_2\) and Au/TiO\(_2\) in the photocatalytic decomposition of methyl formate, too. This can be also attributed to the prevention of electron–hole recombination. The positive influence of the narrowing the bandgap of TiO\(_2\) also appeared in the results obtained in visible light (Figs. 7 and 8).

5. Conclusions

1. IR study revealed that formate formed in the dissociation of formic acid exists on both the Au particles and the TiO\(_2\) support.
2. Au deposited on TiO\(_2\) effectively catalyzed the photodecomposition of both formic acid and methyl formate. The highest photoactivity was obtained for Au particles measuring 1.5–2.0 nm.
3. The main process in the photoreaction of formic acid is dehydrogenation to yield H\(_2\) and CO\(_2\). The small amount of CO formed can be reduced to a very low level by the addition of O\(_2\) or H\(_2\)O to the formic acid. The photocatalytic decomposition of methyl formate gave rise to different products.
4. Lowering the bandgap of TiO$_2$ by N incorporation enhanced the photoactivity of Au/TiO$_2$ catalysts and led to the decomposition of both compounds in visible light.

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References