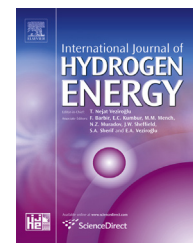


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Photocatalytic decomposition of formic acid and methyl formate on TiO₂ doped with N and promoted with Au. Production of H₂

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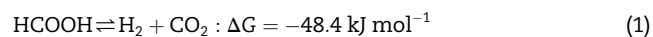
ABSTRACT

The photo-induced vapor-phase decompositions of formic acid and methyl formate were investigated on pure, N-doped and Au-promoted TiO₂. Infrared (IR) spectroscopic studies revealed that illumination initiated the decomposition of adsorbed formate formed in the dissociation of formic acid and located mainly on TiO₂. The photocatalytic decompositions of formic acid and methyl formate vapor on pure TiO₂ occurred to only a limited extent. The deposition of Au on pure or doped TiO₂ markedly enhanced the extent of photocatalytic decomposition of formic acid. The main process was dehydrogenation to give H₂ and CO₂. The formation of CO occurred to only a very small extent. Addition of O₂ or H₂O to the formic acid decreased the CO level from ~0.8% to ~0.088%. Similar features were experienced in the photocatalytic decomposition of methyl formate, which dissociated in part to give surface formate. Experiments over Au deposited on N-doped TiO₂ revealed that the photo-induced decomposition of both compounds occurs even in visible light.

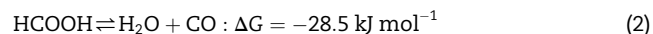
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1. Introduction

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



If the dehydration of formic acid



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

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methanol [28]. Methyl formate has been considered as a precursor in the synthesis of several compounds, such as formamide, acetic acid, cyanhydric 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 was 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 cell housed in a metal chamber was used. Infrared spectra were recorded with a Biorad (Digilab. 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. HAuCl₄SYMBOL 215 \f “Symbol” \s 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). Titanate nanotube and titanate nanowires were synthesized using a simple alkali hydrothermal method detailed elsewhere [31]. In addition, we also used a commercial 1% Au/TiO₂ (P25) sample (AUROLite, 50 m²/g). The sizes of the Au nanoparticles determined with an electron microscope: 1.5–2.0 nm for 1% Au/TiO₂ (AuroLite), 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 parawolframate (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.

Table 1 – Some characteristic data for pure and N-modified TiO₂.

Sample	Pretreatment temperature (K)	Surface area (m ² /g)	Bandgap (eV)	Notation
TiO ₂	As received	200	3.17	(Hombi)
TiO ₂	723	135	3.15	(Hombi)
TiO ₂ + N	673	96	2.30	(SK)
TiO ₂ + N	723	90	2.10	(SK)
TiO ₂	723	265	3.00	(SX)
TiO ₂ + N	723	79	1.96	(SX)
TiO ₂	873	53	3.09	(Hombi)
TiO ₂ + 2% Cr ₂ O ₃	873	51	2.87	(Hombi)
TiO ₂ + 1.5% WO ₃	873	73	3.07	(Hombi)
TiO ₂ (nanotube)	423	186	3.14	–
TiO ₂ (nanowire)	423	36	3.10	–

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 NH₃ 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)

samples. No absorption bands were seen in the IR spectra of the catalysts $\text{TiO}_2 + 1.5\% \text{Cr}_2\text{O}_3$ and $\text{TiO}_2 + 2.0\% \text{WO}_3$.

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 ~ 2953 , ~ 2870 , ~ 1561 and $\sim 1367 \text{ cm}^{-1}$, which can be attributed to the vibrations of formate species formed in the dissociative adsorption of formic acid:



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 ~ 1604 , 1376 and 1370 cm^{-1} (Fig. 1D), and also a strong band at 1737 cm^{-1} due to

Table 2 – Vibrational frequencies (in cm^{-1}) observed following the dissociative adsorption of formic acid and methyl formate.

Assignment	HCOOH		HCOOCH ₃	
	TiO ₂ (P25)	Au/TiO ₂ (Aurolite)	TiO ₂ (P25)	Au/TiO ₂ (Aurolite)
ν_{CH} (CH ₃ O)			2957	2949
ν_{CH} (HCOO)	2958	2956		
ν_{CH} (CH ₃)			2930	2926
ν_{CH} (HCOO)	2886	2870		
ν_{CH} (CH ₃ O)			2843	~ 2880
ν_{CH} (CH ₃ O)			2831	2831
ν (O)	1676	1664	1668	1666–1649
ν_{a} (OCO)	1552	1561	1602–1546	1590–1540
ν_{s} (OCO)	1377	1367	1368	~ 1362
CO	1277	–	1279	–

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

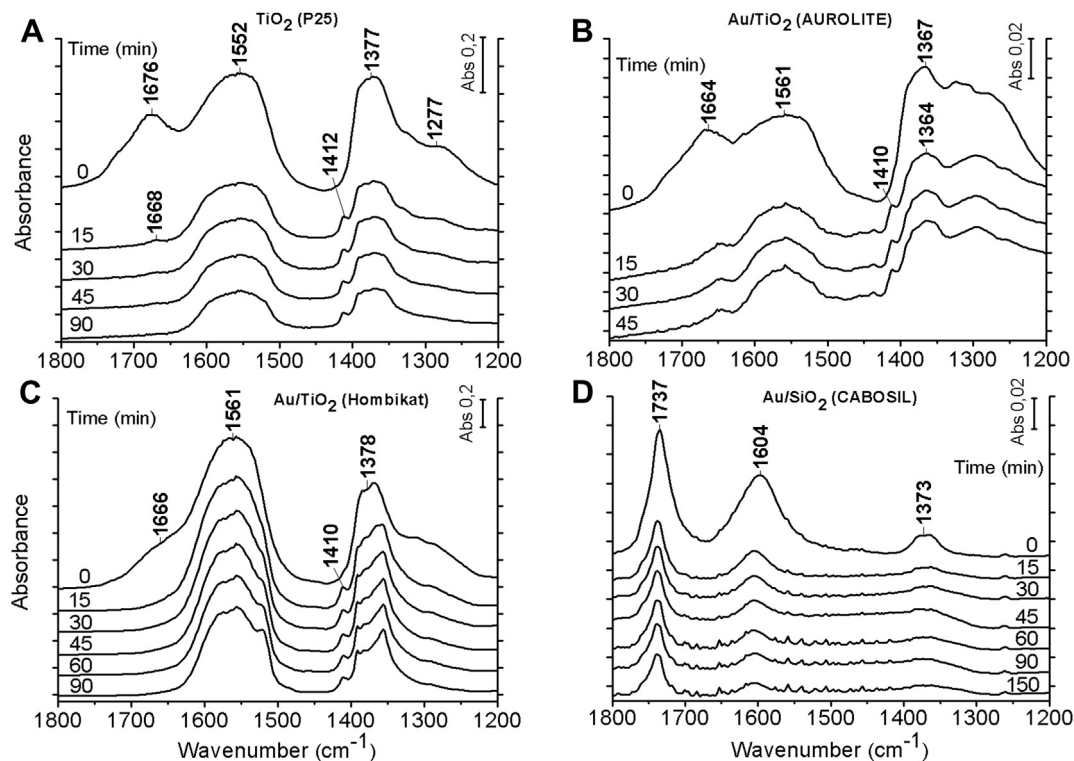


Fig. 1 – IR study of the effects of illumination time on adsorbed HCOOH TiO_2 (P25) (A), 1% Au/TiO_2 (Aurolite) (B), 1% Au/TiO_2 (Hombi) (C), and 1% Au/SiO_2 (Cabosil) (D). Illumination was performed after adsorption of HCOOH vapor for 15 min at 300 K. From time to time the irradiation was interrupted and spectral changes were registered at 300 K. All the spectra are difference spectra.

photocatalytic decomposition of formic acid on TiO₂ was enhanced by N-doping, similarly to the photolysis of ethanol [30]. The activity of N-doped TiO₂ relative to the surface area was twice that of undoped TiO₂ [26]. As the electric conductivity of n-type TiO₂ can be significantly altered by doping with higher- and lower-valence cations [34], it appeared interesting to investigate the photoactivity of cation-doped TiO₂. The results presented in Table 3 show that the doping of TiO₂ with 1% WO₃ slightly enhanced, whereas doping with 1% Cr₂O₃ lowered the photocatalytic decomposition of formic acid. We also tested the photoactivity of nanowire and nanotube TiO₂. Neither of them exhibited an extended activity (Table 3).

A much higher photoactivity was measured for Au/TiO₂ catalysts. The extent of decomposition of formic acid depended sensitively on the mode of preparation of the Au/TiO₂ samples and on the size of the Au particles. Au/TiO₂ (Auroilite) with Au nanoparticles measuring 1.5–2 nm was found to be the most active catalyst. In this case the decomposition was complete in ~100 min. Dehydrogenation was the predominant process. The amount of CO formed was about 0.8% (CO/CO₂ = ~0.02). Much lower photoactivity was measured for Au/TiO₂ (P25) and Au/TiO₂ (Hombi) containing larger Au particles. On both of these latter samples, a larger amount of CO (~6.4%) was evolved. Fig. 2 illustrates the conversion of formic acid and the formation of various products as a function of the illumination time. As the photoactivity of TiO₂ depends sensitively on its origin and preparation, it seemed necessary to examine the activity of the TiO₂ (P25) sample used for the preparation of the most active Au/TiO₂ (Auroilite) catalyst. This TiO₂ sample exhibited photoactivity, but at a much lower level than that of the Au-containing samples. The conversion of formic acid reached only ~14% in 210 min. For comparison, we examined the possible effects of illumination on the reaction of formic acid on the Au/SiO₂ sample. We observed only a slight decomposition: the conversion attained ~10% in 220 min. In this case, the relative amount of CO reached a value of 17.7% (Fig. 2).

Although the amount of CO formed on the Au/TiO₂ (Auroilite) sample was only about 0.8%, an attempt was made to reduce or eliminate it by adding H₂O and O₂ to the formic acid. Oxygen is known to be able to oxidize CO selectively in the presence of H₂ over a Au/TiO₂ catalyst, even at room temperature [27]. When H₂O/HCOOH (1:1) vapor was photolyzed, the formation of CO was reduced from 0.8% to 0.6%. With increase of the H₂O/HCOOH ratio to 5:1, the CO value

diminished to 0.25% (CO/CO₂ ratio ≈ 0.005). Addition of O₂ to formic acid also decreased the formation of CO to 0.23% at O₂/HCOOH (1:10) and to 0.088% at O₂/HCOOH (1:7). Some selected results are plotted in Fig. 3.

In the following experiments, the influence of N-doping of the TiO₂ on the photoactivity of the Au/TiO₂ catalysts was examined. The effect of N-incorporation proved to depend on the preparation method. Samples prepared by the reaction of TiO₂ with urea were less active, probably because of the presence of various N-containing surface compounds formed during the preparation [26]. The largest enhancement in the photoactivity of Au/TiO₂ 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. Whereas Au/TiO₂ (SX) exhibits little activity in visible light, the photoactivity of the Au/TiO₂ + N sample (SX) was 3–4 times higher.

It is important to mention that the illumination caused a temperature rise of only a few degrees in the catalyst. In order to access the contribution of a thermal reaction, the decomposition of formic acid on the most active Au/TiO₂ (Auroilite) catalyst was also followed without illumination. We found merely ~2% decomposition at 373 K and ~10% at 423 K in 60 min. Extensive 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 as in the case of formic acid. IR spectra of adsorbed methyl formate on pure and Au-promoted TiO₂ are presented in Fig. 5. As regards the pure TiO₂ (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/TiO₂ (Auroilite) sample, with slight alterations in the position of the bands. Absorption bands observed on pure TiO₂ and Au/TiO₂ 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 TiO₂ samples.

Catalyst	Conversion		Formation of CO ₂ (in nmol) related to the surface area of the sample	
	in 60 min	in 210 min	in 60 min	in 210 min
TiO ₂	1.8	8.1	0.42	1.70
TiO ₂ + 1.5% WO ₃	2.6	6.6	0.44	0.93
TiO ₂ + 2% Cr ₂ O ₃	1.2	3.6	0.28	0.77
TiO ₂ (nanotube)	1.3	39.2	0.14	0.47
TiO ₂ (nanowire)	3.9	31.5	0.44	1.38

Characteristic data for these samples are presented in Table 1.

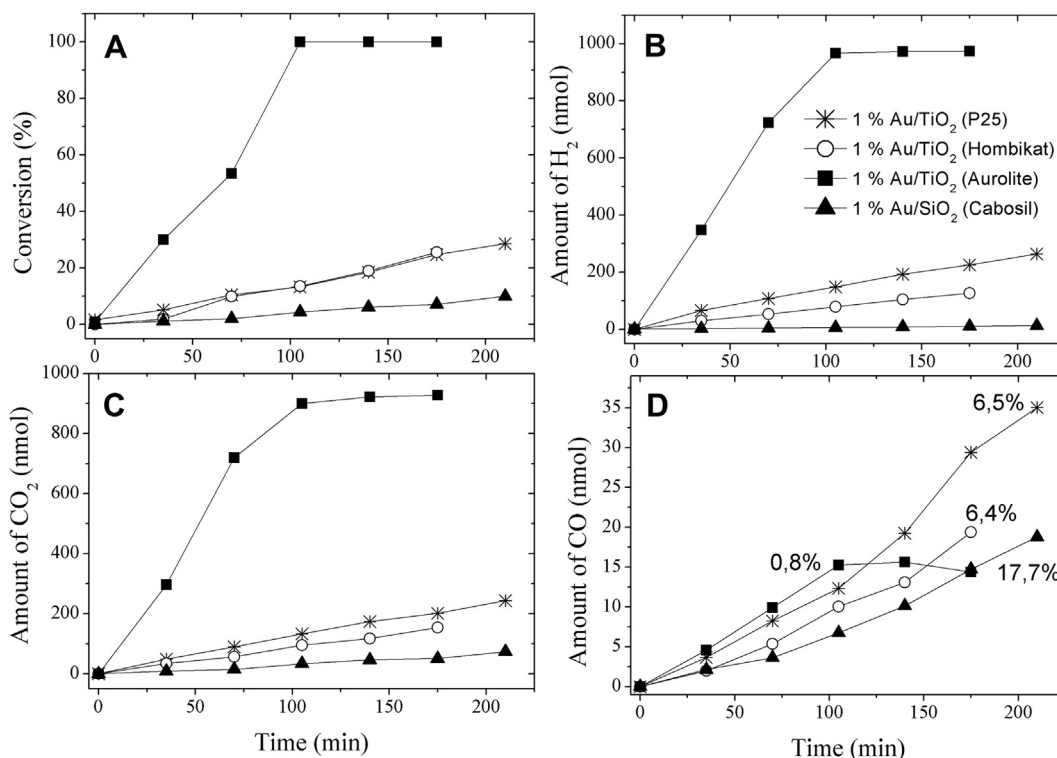


Fig. 2 – Effects of illumination time on the photocatalytic decomposition of HCOOH on various 1% Au/TiO₂ samples. Conversion of HCOOH (A), formation of H₂ (B): CO₂ (C) and CO (D).

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.

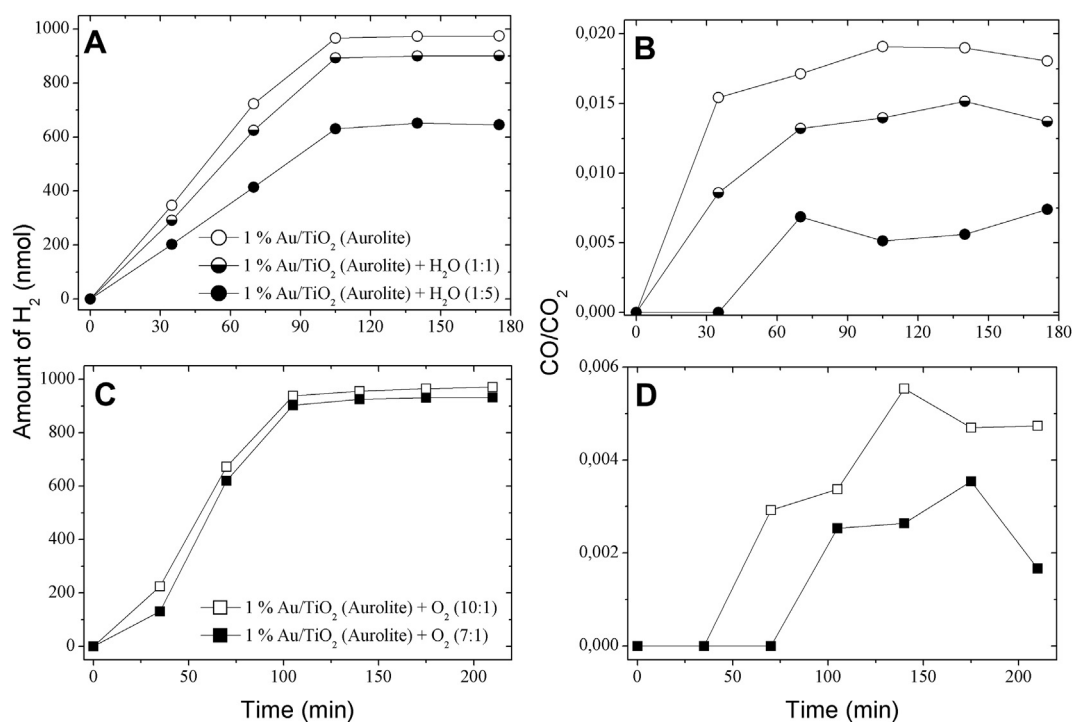


Fig. 3 – Effect of H₂O (A and B) and O₂ (C and D) addition on photocatalytic decomposition of HCOOH over 1% Au/TiO₂ (Auroilite) catalyst. Formation of H₂ (A, C) and CO/CO₂ ratio (B, D).

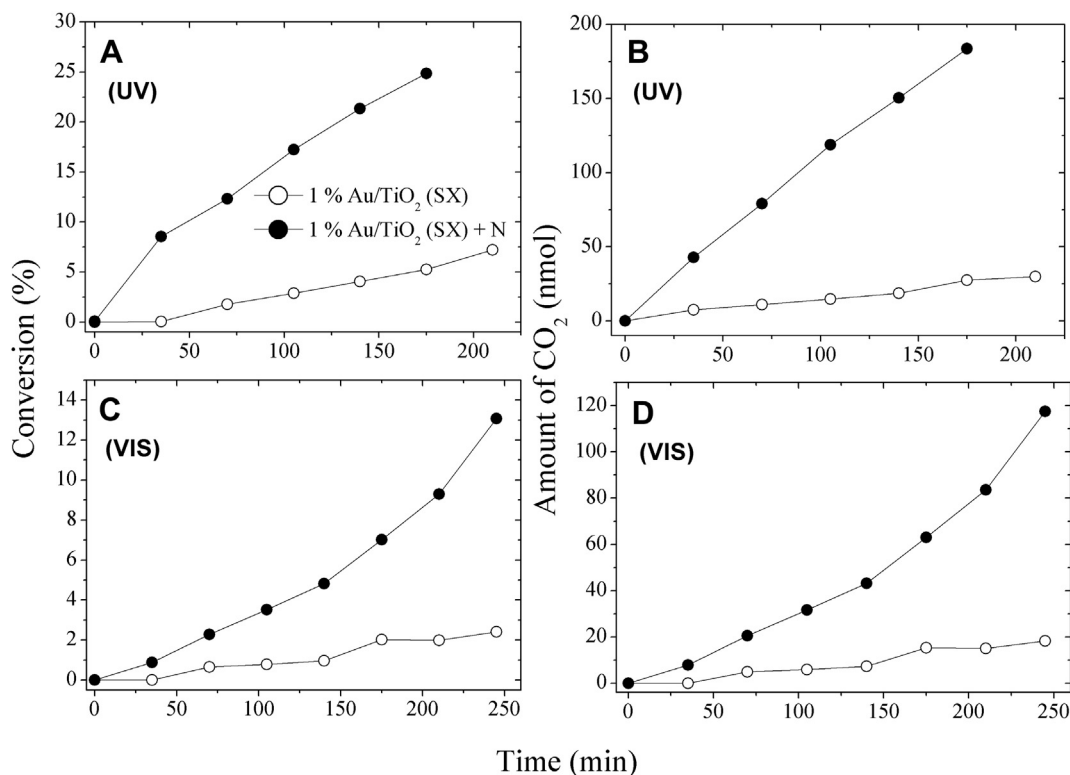


Fig. 4 – Effects of N doping of TiO₂ (SX) on the photocatalytic decomposition of HCOOH in the UV and visible light on 1% Au/TiO₂ (SX) and 1% Au/TiO₂ + N (SX). Conversion of HCOOH (A, C) and formation of CO₂ (B, D).

3.3.2. Photocatalytic studies

The main products of the photolysis of methyl formate on Au/TiO₂ (Auro-lite) 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 [30] 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. Note that this TiO₂ (SX) used for the incorporation of N is less active than the other TiO₂ samples. Selected results are presented in Figs. 7 and 8.

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 (Auro-lite), 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: ν_{as} at 1561–1562 cm⁻¹ and ν_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

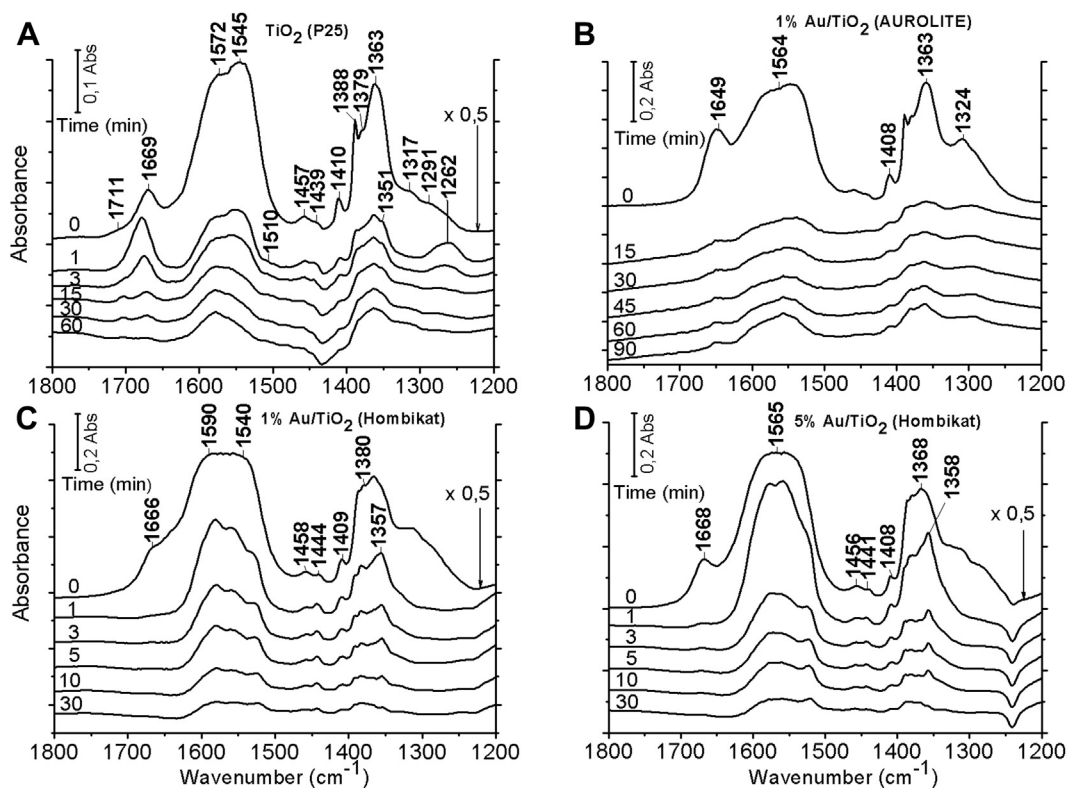


Fig. 5 – IR study of the effects of illumination time on adsorbed methyl formate on TiO₂ (P25) (A), 1% Au/TiO₂ (Aurolite) (B), 1% Au/TiO₂ (Hombi) (C), 5% Au/TiO₂ (Hombi) (D). Illumination was performed after adsorption of methyl formate vapor at 300 K. From time to time the irradiation was interrupted and spectral changes were registered at 300 K. All the spectra are difference spectra.

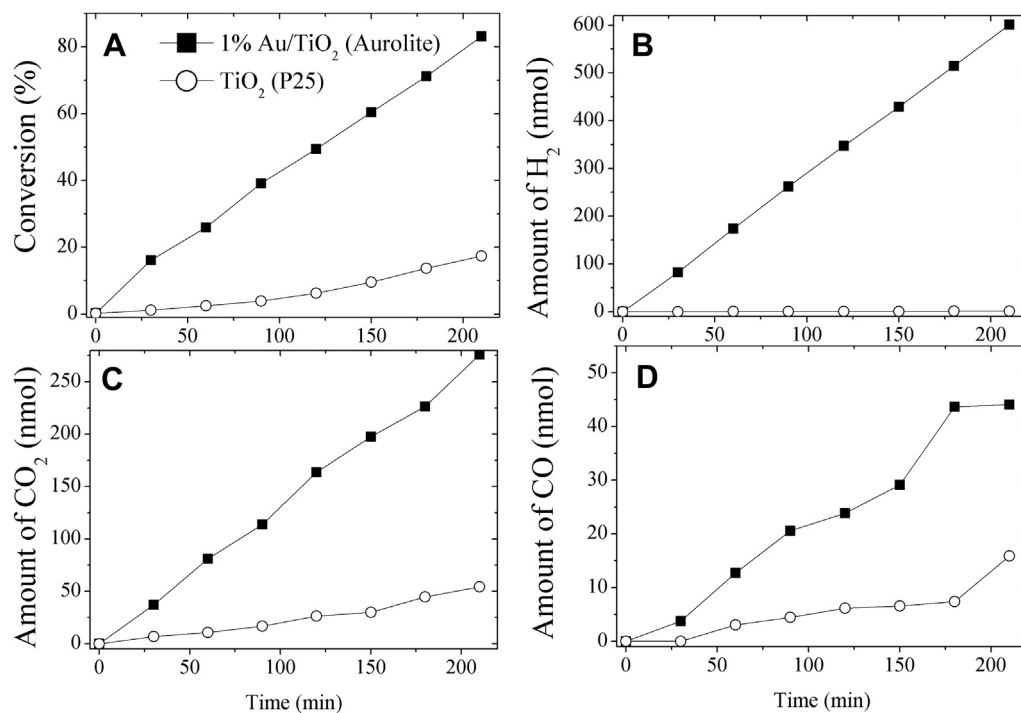


Fig. 6 – Effects of illumination time on the photocatalytic decomposition of methyl formate on TiO₂ and 1% Au/TiO₂ (Aurolite) samples. Conversion (A), formation of H₂ (B): CO₂ (C) and CO (D).

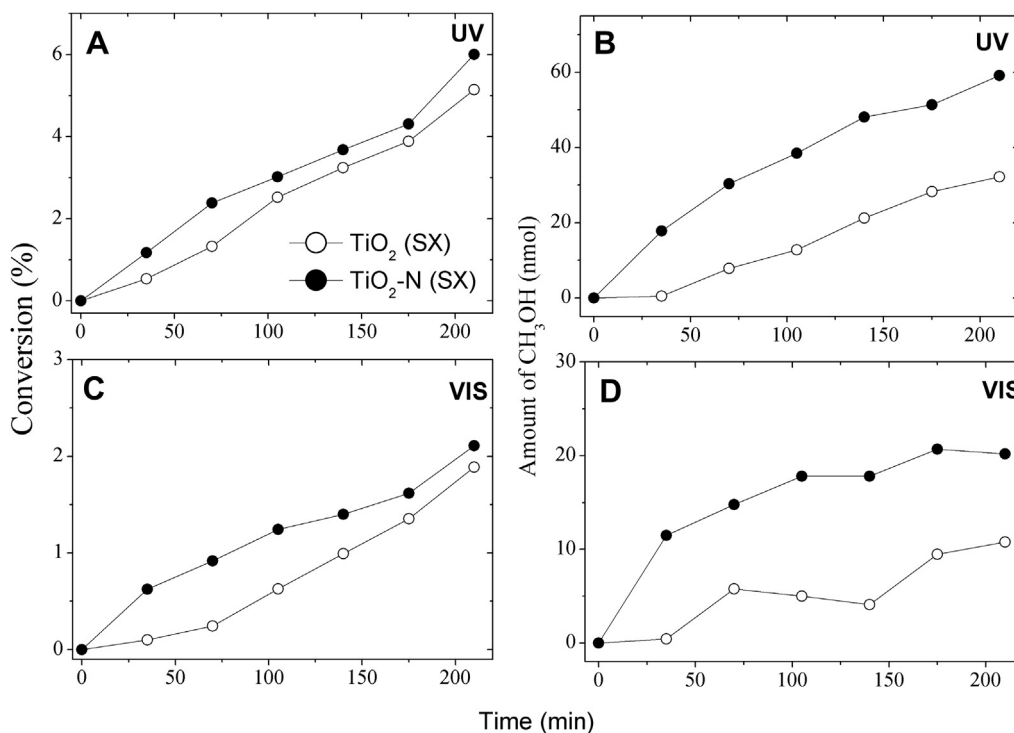


Fig. 7 – Effects of N doping of TiO₂ (SX) on the photocatalytic decomposition of methyl formate in the UV and visible light on TiO₂ (SX) and TiO₂ + N (SX) samples. Conversion (A and C), formation of CH₃OH (B and D).

1410 cm⁻¹ during irradiation in the IR spectra of the TiO₂-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 TiO₂ we assumed the donation of a photoelectron formed in the photo-excitation process to the formate species [25,26]:

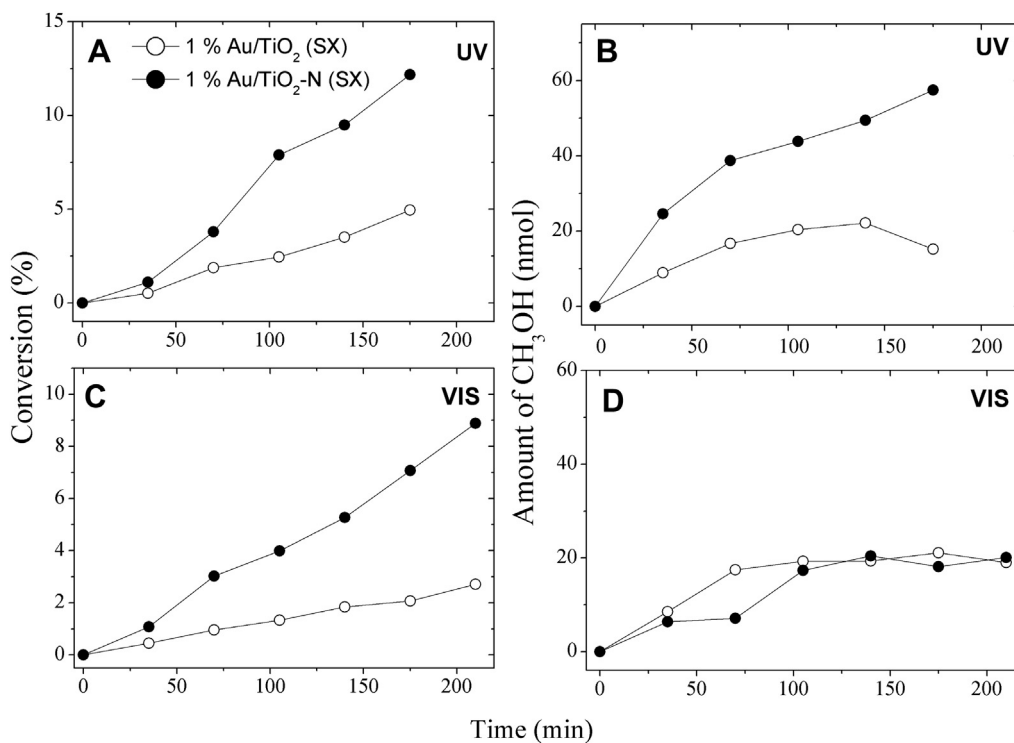


Fig. 8 – Effects of N doping of TiO₂ (SX) on the photocatalytic decomposition of methyl formate in the UV and visible light on 1% Au/TiO₂ (SX) and 1% Au/TiO₂ + N (SX). Conversion (A and C), formation of CH₃OH (B and D).



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_2O_3 exhibited special behavior. During heat treatment of $\text{TiO}_2 + 1\% \text{Cr}_2\text{O}_3$ in air, Cr^{3+} is oxidized to Cr^{4+} and Cr^{6+} [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 similarly negative results found in the studies of several photoreactions were explained by the promotion of the recombination of the charge carrier by dopant cations [40,41].

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 $1600\text{--}1500 \text{ cm}^{-1}$ 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:



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_2O to the formic acid. The photocatalytic decomposition of methyl formate gave rise to different products.

4. Lowering the bandgap of TiO₂ by N incorporation enhanced the photoactivity of Au/TiO₂ catalysts and led to the decomposition of both compounds in visible light.

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