

FTIR study of adsorption and photochemistry of amide on powdered TiO₂: Comparison of benzamide with acetamide

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FTIR has been used *in situ* to investigate the adsorption, thermal transformation, and photoreactions of benzamide on TiO₂. The reaction pathways are compared to the case of acetamide. Our reaction system is focused on the vapor–solid surface reactions, which are complementary to the reactions catalyzed in the solution phase. Benzamide is adsorbed molecularly or dissociatively to generate C₆H₅CONH by losing one amino hydrogen at 35 °C. Upon raising the TiO₂ surface temperature, C₆H₅CN and C₆H₅COO are produced. Under photoirradiation in O₂, adsorbed benzamide and C₆H₅CONH are transformed into surface species of NCO, C₆H₅COO, and C₆H₅CN and gaseous CO₂, revealing versatile photoreaction pathways. These surface intermediates were not found in a previous study of benzamide photodecomposition catalyzed by TiO₂ in the solution phase. Similar reaction pathways were found for acetamide on TiO₂. It is worthy of note that –CONH₂ on TiO₂ is transformed into –CN thermally and photochemically. –CN reacts reversibly with surface OH groups to form –CONH₂.

Introduction

Semiconductor oxides are of much interest in electrochemistry, photocatalysis, energy conversion, and sensor technology. Heterogeneous photocatalysis by TiO₂ appears promising for transforming organic pollutants in aqueous solution into environmentally innocuous species and has attracted much attention recently.¹ Photoreactions of organic compounds with special functionality, such as carboxylate^{2–10} and amide groups,^{11–13} have been studied in solution in the presence of TiO₂. In a previous study of the photodegradation of benzamide to CO₂ and nitrate ions in aerated TiO₂ aqueous suspensions, trihydroxybenzamide and trace amounts of parabenzquinone and hydroxyquinone were detected, by a combination of HPLC, GC/MS, and UV spectroscopy, as reaction intermediates present in the aqueous solutions.¹¹ However in these previous studies of benzamide catalyzed by TiO₂ in suspension systems, the subjects of adsorption and surface intermediate are not described, presumably due to the limitation of surface analytical techniques. In the present research, we apply *in situ* Fourier-transform infrared spectroscopy to study the adsorption and reactions of benzamide on TiO₂ with the focus being on the surface chemistry. The results obtained are also compared with our previous study of acetamide using the same technique.¹⁴ We investigate these two compounds as a model for amide (the –CONH₂ amide group is attached to methyl for acetamide and to phenyl for benzamide) and find similar reaction pathways for the amide group on TiO₂.

Experimental

The preparation of TiO₂ powder supported on a tungsten fine mesh (~6 cm²) has been described previously.¹⁵ In brief, TiO₂ powder (Degussa P25, ~50 m² g^{–1}, anatase 70%, rutile 30%) was dispersed in water/acetone solution to form a uniform mixture which was then sprayed onto a tungsten mesh. The TiO₂ sample was then mounted inside the IR cell for

simultaneous photochemistry and FTIR spectroscopy. The IR cell with two CaF₂ windows for IR transmission down to 1000 cm^{–1} was connected to a gas manifold which was pumped by a 60 l s^{–1} turbomolecular pump with a base pressure of ~1 × 10^{–7} Torr. The TiO₂ sample in the cell was heated to 450 °C under vacuum for 24 h by resistive heating. The temperature of the TiO₂ sample was measured by a K-type thermocouple spot-welded on the tungsten mesh. Before each run of the experiment, the TiO₂ sample was heated to 500 °C in vacuum for 2 h. After the heating, 10 Torr O₂ was introduced into the cell as the sample was cooled to 70 °C. When the TiO₂ temperature reached 35 °C, the cell was evacuated for gas dosing. The TiO₂ surface after the above treatment still possessed residual hydroxy groups. O₂ (99.998%) was purchased from Matheson. Benzamide (95%, Wako) and acetamide (98%, Merck) are solid at room temperature and were well-outgassed in vacuum before introduction to the cell. Benzonitrile (>99%, Merck) and acetonitrile (99.97%, Tedia) were purified by several freeze–pump–thaw cycles. The pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the UV and IR beams were set at 45° to the normal of the TiO₂ sample. The UV light source used was a combination of a Hg arc lamp (Oriol Corp.) operated at 350 W, a water filter, and a band pass filter with a band width of ~100 nm centered at 320 nm (Oriol 51650) or 400 nm (Oriol 51670). Infrared spectra were obtained with a 4 cm^{–1} resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO₂-free dry air. The spectra presented here were ratioed against a clean TiO₂ spectrum providing the metal oxide background.

Results and discussion

Adsorption of benzamide

Fig. 1 shows the IR spectra of benzamide after adsorption on TiO₂ at 35 °C and brief annealing at the indicated temperatures

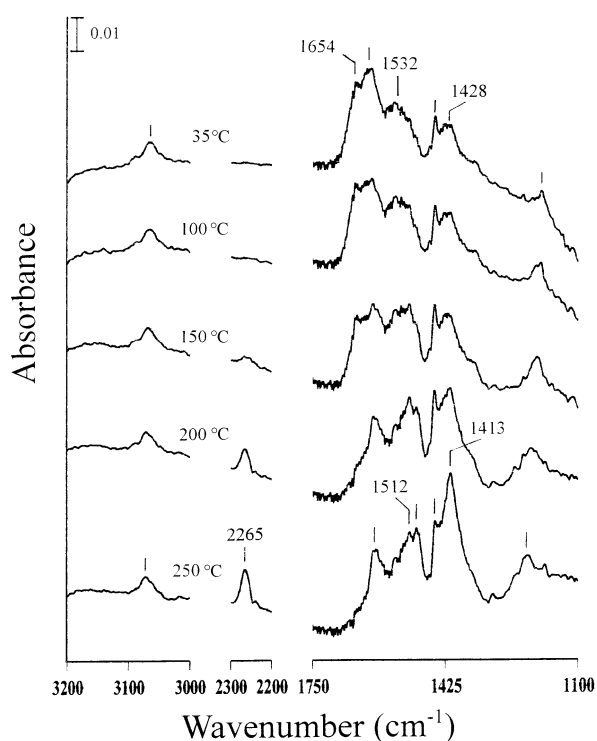


Fig. 1 IR spectra of TiO₂ surface exposed to benzamide vapor for ~42 h at 35 °C and then evacuated at the indicated temperatures for 1 min. During the benzamide dosing, the cell was evacuated from time to time to minimize possible surface contamination. All of the spectra were taken at ~35 °C with 50 scans. The frequencies at the marked positions and their vibrational assignments are listed in Table 1. The TiO₂ sample used was 76 mg.

in vacuum. In the 35 °C spectrum, absorption bands appear at 1190, 1428, 1451, 1532, 1606, 1654, and 3065 cm⁻¹. The 1654 cm⁻¹ bands, characteristic of the carbonyl stretching frequency, indicating the presence of benzamide molecules on TiO₂ at this temperature. However this frequency is lower than the carbonyl absorption frequency at 1677 cm⁻¹ for benzamide in CHCl₃ and CS₂ solutions or at 1715 cm⁻¹ from calculation,¹⁶ revealing the interaction of the carbonyl oxygen with surface Lewis acid sites.¹⁴ The adsorbed benzamide also contributes to the IR absorptions at 1190 and 1451 cm⁻¹ due to C–C stretching and C–H rocking, 1606 cm⁻¹ due to C–C and N–H stretching, and 3065 cm⁻¹ due to C–H stretching. These band assignments are given on the basis of previously measured and calculated IR absorptions of benzamide.¹⁶ However adsorbed benzamide cannot account for the two other bands at 1428 and 1532 cm⁻¹ in the 35 °C spectrum. The simultaneous appearance of two strong bands at ~1430 and ~1530 cm⁻¹ suggests the formation of the functional group of –CON–. In the adsorption of acetamide on TiO₂, CH₃CONH_(a) is generated with frequencies of 1439 and 1541 cm⁻¹ due to symmetric and antisymmetric –CON– stretching.¹⁴ In Fig. 1, the spectral feature after heating to 100 °C is about the same as that of the 35 °C spectrum. However, the carbonyl peak at 1654 cm⁻¹ is decreased upon further heating to 150 °C, indicating the desorption or decomposition of adsorbed benzamide. Meanwhile the absorptions located at 1413, 1512, and 2265 cm⁻¹ are enhanced. This trend continues to 250 °C at which the bands appear at 1225, 1413, 1450, 1494, 1512, 1598, 2265, and 3070 cm⁻¹. As to the bands at 1413, 1512, and 2265 cm⁻¹, the former two bands are likely due to the symmetric and antisymmetric –COO– group,¹⁷ the 2265 cm⁻¹ band is likely due to CN stretching based on the characteristic frequencies of specific functional groups. Fig. 2 and 3 obtained after adsorption of benzoic acid and benzonitrile

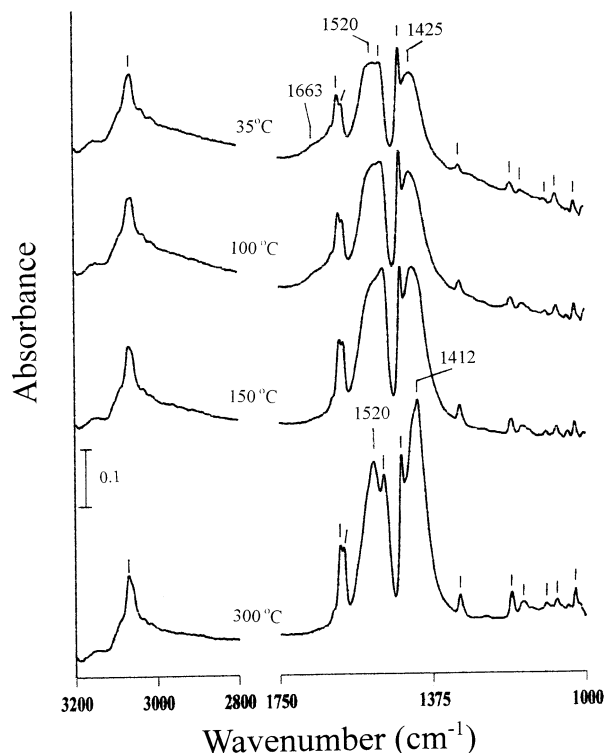


Fig. 2 IR spectra of TiO₂ surface exposed to benzoic acid vapor for 21 h at 35 °C and then evacuated at the indicated temperatures for 1 min. All of the spectra were taken at ~35 °C with 50 scans. The frequencies at the marked positions and their vibrational assignments are listed in Table 2. The TiO₂ sample used was 76 mg.

trile confirm the assignment by the appearance of similar bands. Table 1 summarizes the observed band frequencies for the 35 °C and 250 °C spectra in Fig. 1 and their approximate vibrational mode assignment.

Fig. 2 shows the IR spectra of benzoic acid after adsorption on TiO₂ at 35 °C and brief annealing at the indicated temperatures in vacuum. Absorption bands appear at 1025, 1070, 1094, 1155, 1181, 1307, 1425, 1452, 1500, 1520, 1592, 1604, 1663, and 3062 cm⁻¹ in the 35 °C spectrum. The characteristic carbonyl stretching band of 1663 cm⁻¹ indicates the presence of benzoic acid molecules on TiO₂. Similar to the case of benzamide on TiO₂, the interaction of the carbonyl group of benzoic acid with surface Lewis acid sites leads to its lower frequency compared to the pure benzoic acid at 1695 cm⁻¹.¹⁸ In this 35 °C spectrum, except for the two bands at 1425 and 1520 cm⁻¹, adsorbed benzoic acid also contributes to all the other bands attributable to its C–C bending and stretching and C–H rocking and stretching. The amount of the surface benzoic acid decreases with increasing temperature, as indicated by the loss of intensity at 1663 cm⁻¹, almost disappearing at 150 °C. In contrast, the 1425 and 1520 cm⁻¹ bands grow simultaneously with increasing temperature. In comparison to the –COO– symmetric and antisymmetric stretching frequencies for sodium benzoate (1421 and 1548 cm⁻¹)¹⁹ and for acetate on TiO₂ (1423 and 1532 cm⁻¹),¹⁷ the 1425 and 1520 cm⁻¹ bands are assigned to –COO– stretching of benzoate on TiO₂. Table 2 summarizes the observed band frequencies for the 35 °C and 300 °C spectra in Fig. 2 and their approximate vibrational mode assignment based on the IR frequencies of pure benzoic acid.¹⁸ The results of Fig. 2 show that adsorbed benzoic acid is decomposed into benzoate with increasing temperature.

Fig. 3 shows the IR spectra of benzonitrile after adsorption on TiO₂ at 35 °C and brief annealing at the indicated temperatures in vacuum. In the 35 °C spectrum, absorption bands are

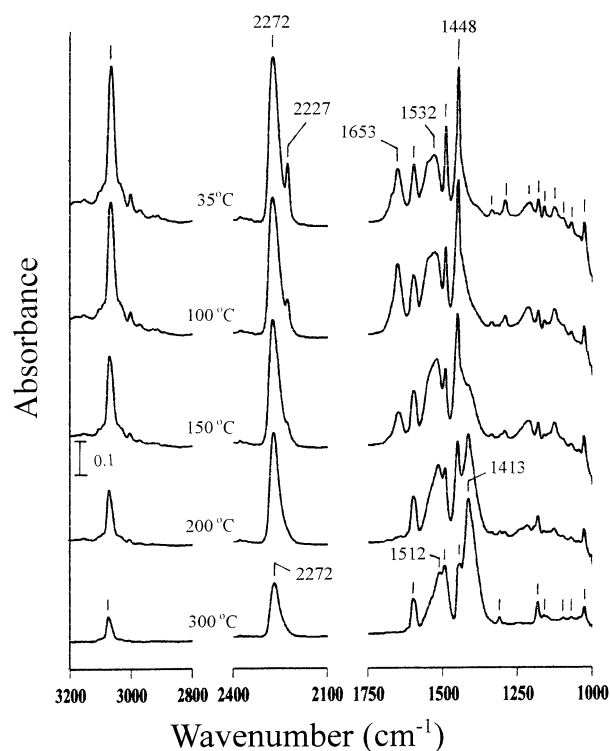


Fig. 3 IR spectra of TiO_2 surface exposed to ~ 0.7 Torr benzonitrile vapor at 35°C and then evacuated at the indicated temperatures for 1 min. All of the spectra were taken at $\sim 35^\circ\text{C}$ with 50 scans. The frequencies at the marked positions and their vibrational assignments are listed in Table 3. The TiO_2 sample used was 96 mg.

located at 1026, 1069, 1096, 1125, 1159, 1179, 1209, 1290, 1336, 1448, 1491, 1532, 1599, 1653, 2227, 2272, and 3066 cm^{-1} . The characteristic CN stretching bands of 2227 and 2272 cm^{-1} indicate the presence of benzonitrile on TiO_2 . The small CN band at 2227 cm^{-1} is close to the 2230 cm^{-1} band of pure benzonitrile in the liquid state,²⁰ therefore it is attributed to physisorbed surface benzonitrile. The other CN band at 2272 cm^{-1} is 45 cm^{-1} higher than that of the physisorbed benzonitrile and is attributed to benzonitrile bonded to surface OH or Ti ion *via* its nitrogen lone-pair. This phenomenon is also observed in the case of CH_3CN on TiO_2 .²¹ In the 35°C spectrum, except for the 1532 and 1653 cm^{-1} bands, adsorbed benzonitrile contributes to all the other bands on the basis of the IR frequencies of pure benzonitrile.²⁰ The appearance of the 1653 cm^{-1} band indicates that a compound with a carbonyl group is formed.

Table 1 Infrared frequencies and approximate assignments for adsorbed benzamide on TiO_2 at 35°C and 250°C

Temperature		Assignment
35°C	250°C	
3065	3070	C–H stretch
—	2265	$\text{C}\equiv\text{N}$ stretch from $\text{C}_6\text{H}_5\text{CN}_{(\text{a})}$
1654	—	C=O stretch
1606	1598	C–C, N–H stretch
1532	—	CON stretch from $\text{C}_6\text{H}_5\text{CONH}_{(\text{a})}$
—	1512	COO stretch from $\text{C}_6\text{H}_5\text{COO}_{(\text{a})}$
—	1494	C–C stretch, C–H rock
1451	1450	
1428	—	CON stretch from $\text{C}_6\text{H}_5\text{CONH}_{(\text{a})}$
—	1413	COO stretch from $\text{C}_6\text{H}_5\text{COO}_{(\text{a})}$
—	1225	C–C stretch, C–H rock, C–O, N–H bend
1190	—	C–C stretch, C–H rock

Table 2 Infrared frequencies and approximate assignments for adsorbed benzoic acid on TiO_2 at 35°C and 300°C

Temperature		Assignment
35°C	300°C	
3062	3071	C–H stretch
1663	—	C=O stretch from $\text{C}_6\text{H}_5\text{COOH}_{(\text{a})}$
1604	1602	C–C stretch
1592	1592	
1520	1520	COO stretch from $\text{C}_6\text{H}_5\text{COO}_{(\text{a})}$
1500	1495	C–C stretch, C–H rock
1452	1451	
1425	1412	COO stretch from $\text{C}_6\text{H}_5\text{COO}_{(\text{a})}$
1307	1310	C–C stretch, C–H rock
1181	1180	
1155	1152	
1094	1094	C–C stretch, C–C bend
1070	1170	
1025	1026	

The broad band at 1532 cm^{-1} is also observed in the benzanide adsorption in Fig. 1 and is assigned to the antisymmetric stretching of $-\text{CON}-$ of $\text{C}_6\text{H}_5\text{CONH}_{(\text{a})}$. The $-\text{CON}-$ symmetric stretching band (expected to be at $\sim 1428\text{ cm}^{-1}$) seems to overlap with the 1448 cm^{-1} band and appears as a shoulder on the right-hand side of this band in the 35°C spectrum in Fig. 3. After heating the surface to 100°C , the amount of benzonitrile decreases, as evidenced by the reduction of the CN integrated intensity. Furthermore the ratio of the peak areas, $2227\text{ cm}^{-1}/2272\text{ cm}^{-1}$, is less than that at 35°C , indicating that the 2227 cm^{-1} band is thermally less stable. Increasing the temperature to 100°C also enhances the bands due to C=O at 1653 cm^{-1} and CNO at 1532 cm^{-1} . After further heating the surface to 300°C , some benzonitrile molecules are still present on the surface, as shown by the residual CN band at 2272 cm^{-1} . Most importantly, the compounds with C=O or CNO groups vanish and the absorption feature of benzoate with the bands at 1413 cm^{-1} and 1512 cm^{-1} appears. Clearly, Fig. 3 shows that adsorbed benzonitrile is thermally transformed into benzoate. It is proposed that this process is through benzamide and $\text{C}_6\text{H}_5\text{CONH}_{(\text{a})}$ as suggested by the observation of the C=O (1653 cm^{-1}) and $-\text{CNO}-$ (1532 cm^{-1}) bands. Thermal transformation of acetonitrile, through acetamide and $\text{CH}_3\text{CONH}_{(\text{a})}$, to acetate has been observed on TiO_2 , ZnO , $\alpha\text{-Fe}_2\text{O}_3$, and $\delta\text{-Al}_2\text{O}_3$.^{22–24} The reaction of acetonitrile on the metal oxides to form acetamide and $\text{CH}_3\text{CONH}_{(\text{a})}$ is attributed to the involvement of surface OH groups.^{22–24} Table 3 lists the frequencies observed in Fig. 3 and their corresponding vibrational modes. In Fig. 1, as adsorbed benzamide is heated to 250°C , a CN band at 2265 cm^{-1} appears due to the formation of benzonitrile. This is a dehydration reaction of benzamide which can be viewed as the reverse route of benzonitrile attacked by surface OH to form benzamide at 35°C as shown in Fig. 3.

Photooxidation of adsorbed benzamide

Fig. 4 shows the IR spectra before and after the indicated light exposure times for adsorbed benzamide initially in 10 Torr of O_2 . In the region of $2100\text{--}2450\text{ cm}^{-1}$, it is found that two absorption bands at 2202 and 2265 cm^{-1} quickly appear and continue to be present on the surface during the 180 min light irradiation. A few tens of minutes after the UV lamp is turned on, a band at 2349 cm^{-1} is generated and assigned to gaseous CO_2 . The bands at 2202 and 2265 cm^{-1} belong to CN stretching. The 2202 cm^{-1} is attributed to $\text{NCO}_{(\text{a})}$ which is also observed in the photodissociation of CH_3CN on TiO_2 ²¹ due

Table 3 Infrared frequencies and approximate assignments for adsorbed benzonitrile on TiO₂ at 35 °C and 300 °C

Temperature		Assignment
35 °C	300 °C	
3066	3074	C–H stretch
2272	2272	C≡N stretch from C ₆ H ₅ CN _(a)
2227	—	
1653	—	C=O stretch
1599	1600	C–C stretch
1532	—	CON stretch from C ₆ H ₅ CONH _(a)
—	1512	COO stretch from C ₆ H ₅ COO _(a)
1491	1494	C–C stretch, C–H rock
1448	1441	
—	1413	COO stretch from C ₆ H ₅ COO _(a)
1336	—	C–C stretch, C–H rock, C–N stretch from C ₆ H ₅ CONH _{2(a)}
1290	1309	C–C stretch, C–H rock
1209	—	
1179	1181	
1159	1161	
1125	—	C–C stretch, C–C bend
1096	1094	
1069	1071	
1026	1025	

to the C–C bond scission and is identified on various surfaces.²¹ The other band at 2265 cm^{−1} is also observed in the surface heating of adsorbed benzamide in Fig. 1 and assigned to the CN stretching frequency of benzonitrile. In the region of 1250–1800 cm^{−1}, the spectrum features also change with light irradiation. After 180 min, absorption IR bands appear

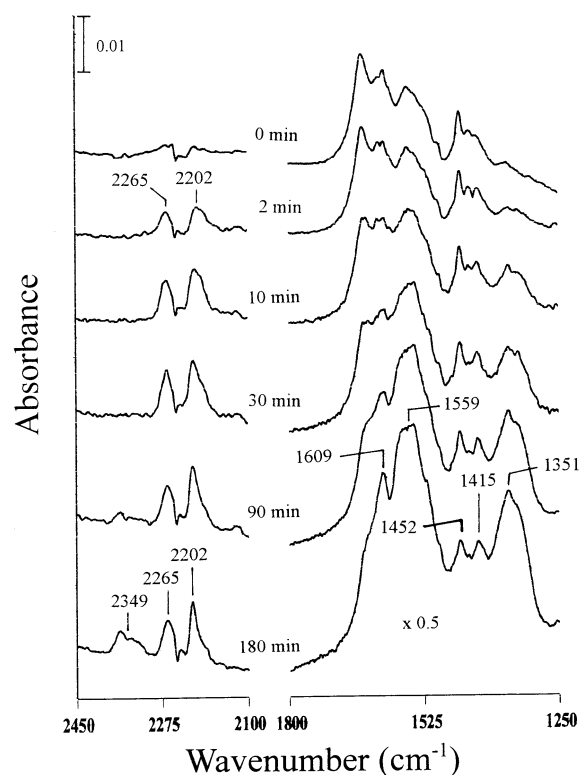
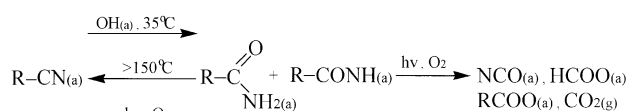


Fig. 4 IR spectra taken before and after the indicated times during photoirradiation of adsorbed benzamide in 10 Torr of O₂. The benzamide-adsorbed TiO₂ surface was prepared by exposing a clean TiO₂ surface to benzamide vapor for ~42 h followed by evacuation at 35 °C. All of the spectra were taken with 5 scans. The wavelength used was centered at 320 nm. The TiO₂ sample used was 90 mg.

at 1351, 1415, 1452, 1559, and 1609 cm^{−1}. The two strong, broad bands at 1351 and 1559 cm^{−1} are assigned to –COO– stretching of HCOO_(a) which has been thoroughly studied on TiO₂.²⁵ The 1415 cm^{−1} may be due to the symmetric stretching of benzoate molecules. The other two bands at 1452 and 1609 cm^{−1} are likely due to C–C stretching of the benzene ring of unreacted benzamide, benzoate, or benzonitrile. Since the surface temperature is increased to ~70 °C during the light exposure, a separate experiment was carried out using the same experimental conditions as that of Fig. 4 and holding the surface temperature at 70 °C for 180 min without light exposure. The bands observed after the UV illumination in Fig. 4 are not found in this thermal control experiment, indicating that the reaction products observed in Fig. 4 are due to a photoeffect. In the present photoreaction study of adsorbed benzamide, it is possible to identify surface intermediates *in situ* during the photoirradiation. This investigation of the vapor–solid reaction is complementary to those performed in the liquid phase in which surface processes are difficult to explore and the complexity due to the presence of solvent has also to be taken into account. The reaction products of CO₂, NCO, C₆H₅COO, and C₆H₅CN observed in Fig. 4 in the photoirradiation of adsorbed benzamide show that versatile reaction pathways exist. The last three products involve chemical changes of the amide group of benzamide. NCO is formed by dehydrogenation of the –CONH₂ group and scission of the C–C bond between the benzene ring and the amide group. C₆H₅CN is formed by the loss of one oxygen and two hydrogen atoms of benzamide. C₆H₅COO results from the replacement of the NH₂ group. Although multiple reaction routes are identified, they do not necessarily account for all the reactions occurring. In our previous study of the photooxidation of benzene on TiO₂ using the same technique, phenoxy groups were identified as a reaction product.²⁶ It would not be surprising if a similar type of oxygen addition to the benzene ring might occur in the benzamide case. However due to the presence of a strong, broad absorption feature in the region of 1250–1800 cm^{−1} in Fig. 4, products other than CO₂, HCOO, NCO, C₆H₅COO, and C₆H₅CN are not detected. Scheme 1 summarizes our findings in this study for benzamide. It is found that acetamide on TiO₂ also shows similar reaction pathways.

Adsorption and photooxidation of acetamide

Fig. 5 shows the comparison of the spectral features of adsorbed acetonitrile and acetamide subjected to surface heating or photoillumination. Fig. 5(a) shows the spectra obtained after exposure of a clean TiO₂ surface to 2 Torr of acetonitrile followed by evacuation at 35 °C and 200 °C. Adsorption of acetonitrile at 35 °C produces IR bands located at 1367, 1415, 1433, 1469, 1537, 1578, 1650, 2279, and 2306 cm^{−1}. Adsorbed acetonitrile is responsible for the characteristic, strong bands of 1367, 2279, and 2306 cm^{−1} which are assigned to symmetric bending of CH₃ and stretching of CN. Adsorption of acetonitrile on TiO₂ at 35 °C, generates not only molecularly adsorbed acetonitrile but also acetamide and CH₃CONH_(a) whose formation is verified by the similar frequencies from acetamide adsorption shown in the 35 °C spectrum of Fig. 5(b) obtained by exposing a clean TiO₂ surface



Scheme 1



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Acetamide and benzamide have similar thermal and photochemical reactions for the amide group. Many organic molecules can be effectively photooxidized on TiO_2 with UV illumination. As TiO_2 accepts photons with energy higher than its bandgap (3.2 eV), electron-hole pairs can be produced and these migrate to the surface where they initiate redox reactions of adsorbates.²⁸ OH^\bullet radicals, possibly from the reaction of surface hydroxy groups or water with holes, have been proposed to be the oxidizing agent.^{29–32} In previous studies of the interaction of O_2 with the TiO_2 surface upon UV irradiation, EPR spectroscopy has shown the existence of O_2^- , O_3^- , and O_2^{3-} ,³³ which can behave as oxidants. The initiating mechanism of photooxidation for amides on TiO_2 is still under discussion.

Conclusion

Conclusion

Acknowledgements

Acknowledgements

References

- ## References

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