Available online at www.sciencedirect.com

ScienceDirect

Mendeleev Commun., 2017, **27**, 248–250

Mendeleev Communications

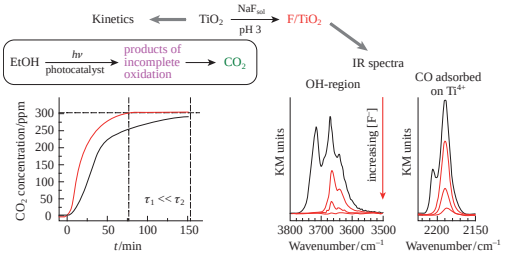
Beneficial effect of TiO_2 surface fluorination on the complete photooxidation of ethanol vapor

Denis V. Barsukov,* Aleksey V. Saprykin, Irina R. Subbotina and Nikolay Ya. Usachev

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 499 135 5328; e-mail: barsden@ioc.ac.ru

DOI: 10.1016/j.mencom.2017.05.010

The treatment of titanium dioxide with acidified NaF solution results in a more than twofold increase in photocatalytic efficiency in the complete oxidation of ethanol vapor. This treatment was accompanied by considerable changes in the surface structure of TiO_2, which were detected by diffuse scattering IR spectroscopy.



Titanium dioxide is an ideal photocatalyst for practical applications because it is stable, nontoxic, safe to handle and inexpensive.[1] However, the overall photocatalytic efficiency of TiO_2 is limited due to its relatively wide band gap and considerable recombination of photogenerated charge carriers. Various methods are used to improve the photocatalytic activity of TiO_2 and to increase its efficiency: doping with metal (Cu, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, Au, Ag and Pt) or nonmetal (N, S, C, B, I and F) ions and the preparation of composites with semiconductors or adsorbents (TiO_2–C, TiO_2–SiO_2, TiO_2–ZnO and TiO_2–CdS). As a result, the catalyst adsorption properties and the kinetics of interphase charge transfer can also change.[2–5] However, except for doping with precious metals[6] and photocatalyst–adsorbent combinations,[7] these approaches as a whole proved to have poor efficiency in complete oxidation reactions,[8] though they increase efficiency of some reactions.[8–10]

Doping with nonmetals became especially popular in recent years, in part due to economical reasons.[5] Doping with fluorine deserves special attention because it increases the activity in the UV range.[11] The effect of modification with fluorine on the photocatalytic activity of TiO_2 has been studied rather little, especially for complete oxidation reactions in a gas phase.[11,12] Here we found that a simple procedure of post-synthesis fluorine doping of a highly active commercial TiO_2 sample makes it possible not only to increase its photocatalytic activity in a model reaction of ethanol vapor oxidation but also to enhance the sample efficiency in the control of partial oxidation products and considerably change the surface structure.

The samples were obtained by a modified Kim and Choi technique.[13] A significant difference from the cited technique is that TiO_2 was not calcined at 450 °C before fluorination, thus preserving the large catalyst surface area and the number of OH groups that can serve as substitution centers.†

It is well known that the formation of hard-to-remove products of incomplete oxidation is among the main problems in the photocatalytic oxidation of volatile organic compounds (VOCs). The most undesirable and commonly occurring compounds are acetaldehyde, formaldehyde, acetic and formic acids.[14] This problem is particularly important in the oxidation of alcohols.[14] For this reason, we studied the oxidation of ethanol vapor on the photocatalysts synthesized.‡ This allowed us to estimate the activity of the photocatalysts during the oxidation of alcohols in the gas phase and predict their efficiency in the prevention of the above problem.

The photocatalytic oxidation of ethanol vapor to carbon dioxide on TiO_2 occurs *via* a series of intermediate compounds, the main of which (in terms of quantity) is acetaldehyde.[15] Therefore, this compound, along with ethanol and CO_2, was chosen to monitor the kinetics of oxidation. The time dependences of the concentrations of ethanol, acetaldehyde and carbon dioxide in the gas phase are presented in Figure 1.

Figure 1(*a*) shows that ethanol vapor is completely removed from the gas phase in 25–30 min on all the tested TiO_2 samples modified with fluorine. Note that, at the starting concentration, a considerable fraction of ethanol is adsorbed on the catalyst

† Weighed portions of TiO_2 (2.0 g each) of Hombifine N brand (Sachtleben Chemie GmbH, 100% anatase, S_{BET} = 300 m^2 g^{-1}) were suspended in 60 ml of NaF solutions (analytical grade) with concentrations of 40, 100 and 300 mmol dm^{-3}; then, dilute nitric acid was added with stirring to pH 3. The required amounts of the dilute (0.6 wt%) acid solution were 5, 12 and 37 ml for the 40, 100 and 300 mmol dm^{-3} NaF solutions, respectively. On reaching the required pH, the suspension was stirred regularly, followed by the decantation of mother liquor and washing the precipitate with distilled water. After that, the suspension was dried at room temperature. Fluorine in modified samples was detected by energy-dispersive X-ray spectroscopy. Hereinafter, the samples obtained in this manner are designated as F/TiO_2-*x*, where *x* is the NaF concentration during sample preparation.

‡ Catalytic experiments were carried out in a sealed plastic box equipped with UV- and IR-transparent glasses for sample irradiation and the *in situ* recording of the IR spectra of a gas phase, respectively. The samples (200 mg of the catalyst applied on a Petri dish) were irradiated with a fluorescent mercury lamp (λ_{max} = 365 nm, I = 5 mW cm^{-2}). Before the photocatalytic reaction was performed, the air humidity inside the box was adjusted to a relative humidity (RH) of 37.5 ± 0.5% at 20.0 ± 0.5 °C. Ethanol (1 μl, 96%) was injected into the cabinet chamber using a microsyringe. The ethanol concentration was 150 ppm. The concentrations of ethanol and reaction products were monitored using the IR spectra of the gas phase.

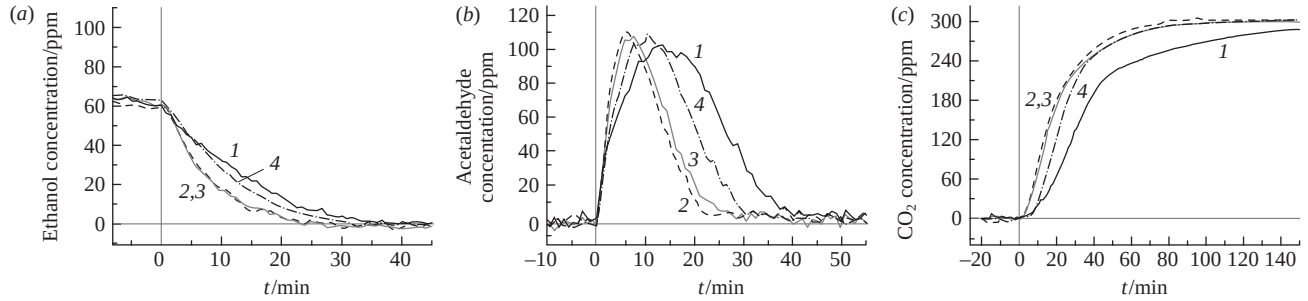


Figure 1 Concentrations of (*a*) ethanol, (*b*) acetaldehyde and (*c*) CO_2 during the photocatalytic oxidation of ethanol vapor (150 ppm) on (*1*) pure TiO_2, (*2*) F/TiO_2-40, (*3*) F/TiO_2-100 and (*4*) F/TiO_2-300.

surfaces even before irradiation is started. Ethanol remaining in the gas phase is removed more quickly on F/TiO_2 than on pure TiO_2, where complete oxidation occurs in ~40 min.

Figure 1(*b*) demonstrates a plot of acetaldehyde concentration during the reaction. Acetaldehyde was completely removed from the gas phase almost twice faster on F/TiO_2 than on pure TiO_2. F/TiO_2-40 was the best in the photocatalytic oxidation of acetaldehyde among the doped samples, while the activity of F/TiO_2-100 was slightly lower. F/TiO_2-300 showed the lowest activity.

A similar picture is observed in terms of the formation of CO_2. However, in this case the differences between the samples are observed at the initial stage only [Figure 1(*c*)]. For all the modified samples, complete conversion of ethanol vapor into CO_2 occurs more than twice faster as compared to the pure TiO_2. This indicates that the concentration of NaF in the treating solution, and hence the concentration of F^- surface ions on TiO_2, affects the conversion rate of acetaldehyde without a considerable effect on the oxidation rates of other intermediate products (acetic and formic acids).

An analysis of the literature shows that the origins of the increase in the photocatalytic activity of titanium dioxide upon doping with fluorine remain little studied so far. Various factors were considered, such as a change in the catalyst acidity, crystallinity, adsorption properties, and an increase in the lifetime of photogenerated charge carriers.[11,13,16,17] Lately, researchers tend to believe that doping with fluorine changes the kinetics of generation of reactive oxygen-containing radicals and molecules ($O_2^{\bullet-}$, $HO_2^{\bullet}$, H_2O_2 or $OH^{\bullet}$).[17–19] However, the particular role of these species in photocatalytic processes is not always clear, especially in the oxidation of molecules in a gas phase.[5,20]

Adsorbed water can considerably affect the oxidation kinetics of organic vapors. Dual effect of water on photocatalytic oxidation was reported previously:[21–23] the competitive adsorption of water and VOC molecules and prevention of catalysts deactivation. Based on CO as an example, we found that other contributions of a water effect could take place.[20] In the case of ethanol vapor oxidation on pure TiO_2, an increase in the water vapor pressure (above 20% RH) and, hence, the amount of adsorbed water on the catalyst enlarges both the amount of acetaldehyde as the intermediate product and the time required for complete conversion of ethanol to CO_2.[24] The amount of surface water was measured by IR spectroscopy. The area of the absorption band from combination vibrations of adsorbed water at 5000 cm^{-1} was considered.[20] It has been found that fluoride treatment of TiO_2 samples raises the amount of adsorbed water (Figure 2), which agrees with previous results.[25] An increase in NaF concentration under our modification conditions results in a symbatic growth in the amount of adsorbed water. Thus, an increase in the amount of adsorbed water enhances the ethanol oxidation rate. The presence of a large amount of adsorbed water still affects the F/TiO_2-300 sample, where the starting oxidation stage occurs somewhat more slowly than on the two other doped samples.

The IR spectra of F/TiO_2 samples after thermal vacuum treatment demonstrate the changes in the range of OH groups, as

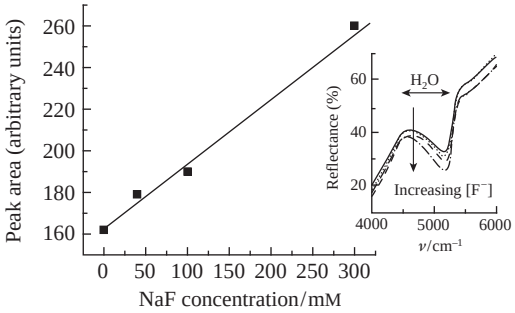


Figure 2 Plot of the combination vibration peak of water adsorbed on TiO_2 in a range of 4500–5400 cm^{-1} *vs.* the concentration of the NaF solution used in the treatment. Zero concentration of NaF corresponds to the original TiO_2. The inset shows the raw IR spectra of diffuse scattering in the range of water combination vibrations.

well as Lewis acid sites on the basis of CO probe molecule. Such IR spectroscopic data on the surfaces of doped TiO_2 are scarce in the literature.[25–27] The results of our studies are presented in Figures 3 and 4. After vacuum treatment of samples at 150 °C (the spectra are not shown) and 250 °C, the IR spectra revealed the disappearance of a high-frequency bands in the range of OH (~3716 cm^{-1})[25–27] and adsorbed CO (~2206 cm^{-1})[25] vibrations (Figure 3).

According to literature,[25–27] disappearance of the band at 3716 cm^{-1} is attributed to the replacement of terminal OH groups by F^- ions during TiO_2 treatment with NaF solution. We failed to find reported direct confirmations that the replacement occurs at room temperature. However, a number of indirect indications, such as the change in the fluoride concentration in the solution during TiO_2 treatment[26,27] and the large equilibrium constants of this reaction[28] allow us to accept this statement. The high-frequency band of adsorbed CO at 2206 cm^{-1} is attributed to the Ti^{4+} tetracoordinated center.[29] Such a Ti atom can be located on the crystal edges and vertices.[30] The band at 2188 cm^{-1} in the spectrum of adsorbed CO corresponds to the pentacoordinated Ti^{4+} ion. The disappearance of the high-frequency band of adsorbed CO was explained[25] by blocking the strong Lewis acid centers in

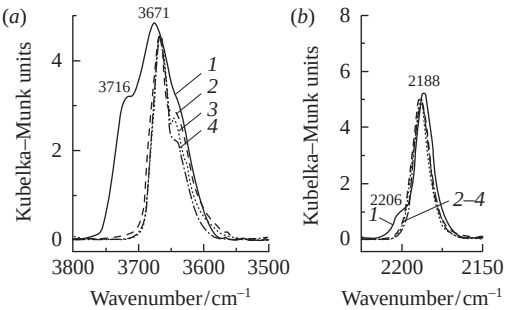


Figure 3 IR diffuse reflectance spectra of (*1*) pure TiO_2, (*2*) F/TiO_2-40, (*3*) F/TiO_2-100, and (*4*) F/TiO_2-300 in the range of (*a*) OH groups after thermal vacuum treatment at 250 °C for 30 min, and (*b*) CO (10 Torr) adsorbed at room temperature.

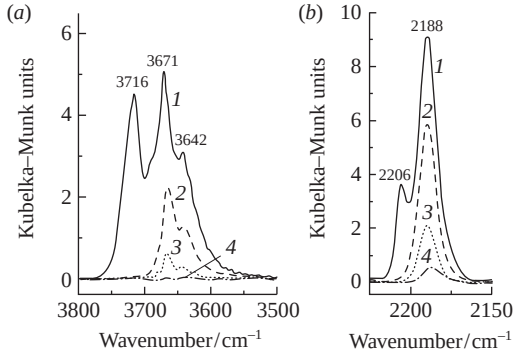


Figure 4 IR diffuse reflectance spectra of (*1*) pure TiO_2, (*2*) F/TiO_2-40, (*3*) F/TiO_2-100, and (*4*) F/TiO_2-300 in the range of (*a*) OH groups after thermal vacuum treatment at 350 °C for 30 min, (*b*) CO (10 Torr) adsorbed at room temperature.

doped TiO_2 samples due to higher water adsorption. However, we found that this explanation is insufficient. The temperature of vacuum treatment of the samples was limited to 150 °C,[25] which does not allow adsorbed water to be totally removed from the catalyst surface. Since adsorbed water is more strongly retained on fluorinated samples, one may conclude that Ti centers are blocked with water. We used a higher vacuum treatment temperature (350 °C) and fully removed adsorbed water from the F/TiO_2 surface. This was confirmed by disappearance of bands around 5000 cm^{-1} (the spectra are not shown). No vibration bands of adsorbed CO were observed at high treatment temperatures for any of the fluorinated samples [Figure 4(*b*)]. This is evidently due to significant changes of TiO_2 surface during modification and grafting of fluorine to the surface.

We also observed a decrease in the intensity of a low-frequency absorption band of CO vibrations at 2190 cm^{-1} [see Figure 4(*b*)] on F/TiO_2 after thermal vacuum treatment at 350 °C, which occurs with raising the fluoride concentration used in the modification process. The intensity of the bands of adsorbed CO for pure TiO_2 depends on CO pressure. The band at 2188 cm^{-1} represents relatively weak adsorption centers, whereas the band at 2206 cm^{-1} corresponds to strong centers but a smaller concentration. This result agrees with published data,[29,30] indicating that these bands correspond to Ti^{4+} ions located on crystal planes (2188 cm^{-1}) and crystal edges, vertices or other defects (2206 cm^{-1}). Thus, an increase in the treatment temperature of doped TiO_2 results in deeper changes in the surface structure involving defective and regular surface centers.

Considerable changes after vacuum treatment of F/TiO_2 at 350 °C also occurred in the range of OH vibrations, namely, a decrease in the intensity of the band of bridging OH groups (3666 cm^{-1}) and their complete disappearance in the case of F/TiO_2-300 sample [Figure 4(*a*)]. This is related to the presence of fluorine ions on the surface since the bands of OH groups in IR spectra of non-doped TiO_2 were observed even after vacuum treatment at 600 °C.

It is very important that the changes observed at 350 °C are reversible. When the samples vacuum-treated at 350 °C are kept at room temperature in air or in the presence of a small amount of water vapor and then evacuated at 150–250 °C, the band of bridging OH groups and the low-frequency CO band reappear in the IR spectrum. Reversibility of this kind indicates that adsorbed water strongly affects the modified surface of fluorinated samples. This effect is very likely related to surface restructuring to the original state.

In conclusion, the doping of TiO_2 by its treatment with an acidified NaF solution results in considerable changes in the physicochemical properties of the catalyst. These changes can manifest themselves either at room temperature (a higher amount of adsorbed water and an increase in photocatalytic efficiency) or at elevated temperatures (changes in the bands of OH groups and adsorbed CO). Moreover, they can be either reversible (the removal of bridging OH groups and blocking of pentacoordinated Ti^{4+} ions) or irreversible (removal of terminal OH groups, blocking of tetracoordinated Ti^{4+} ions). These changes are rather deep and they considerably increase the photocatalytic efficiency in gas-phase reactions, which makes this direction quite promising for further studies.

This study was supported by the Russian Foundation for Basic Research (project no. 16-03-00956_a). Energy-dispersive X-ray characterization was performed at the Department of Structural Studies of N. D. Zelinsky Institute of Organic Chemistry, Moscow.

References

1 A. Fujishima, X. Zhang and D. A. Tryk, *Surf. Sci. Rep.*, 2008, **63**, 515.
2 W. Choi, *Catal. Surv. Asia*, 2006, **10**, 16.
3 A. Zaleska, *Recent Pat. Eng.*, 2008, **2**, 157.
4 S. G. Kumar and L. G. Devi, *J. Phys. Chem. A*, 2011, **115**, 13211.
5 J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo and D. W. Bahnemann, *Chem. Rev.*, 2014, **114**, 9919.
6 D. V. Kozlov and A. V. Vorontsov, *J. Catal.*, 2008, **258**, 87.
7 D. S. Selishchev, P. A. Kolinko and D. V. Kozlov, *J. Photochem. Photobiol., A*, 2012, **229**, 11.
8 H. Park, Y. Park, W. Kim and W. Choi, *J. Photochem. Photobiol., C*, 2013, **15**, 1.
9 *Photocatalysis and Water Purification. From Fundamentals to Recent Applications*, ed. P. Pichat, Wiley-VCH, Weinheim, 2013.
10 I. V. Baklanova, V. N. Krasil'nikov, O. I. Gyrdasova and L. Yu. Buldakova, *Mendeleev Commun.*, 2016, **26**, 335.
11 M. V. Dozzi and E. Selli, *J. Photochem. Photobiol., C*, 2013, **14**, 13.
12 S. G. Kumar and L. G. Devi, *J. Phys. Chem. A*, 2011, **115**, 13211.
13 H. Kim and W. Choi, *Appl. Catal., B*, 2007, **69**, 127.
14 A. T. Hodgson, D. P. Sullivan and W. J. Fisk, *Evaluation of Ultra-Violet Photocatalytic Oxidation (UVPCO) for Indoor Air Applications: Conversion of Volatile Organic Compounds at Low Part-per-Billion Concentrations*, Lawrence Berkeley National Laboratory, LBNL-58936, Berkeley, CA, 2005.
15 M. R. Nimlos, E. J. Wolfrum, M. L. Brewer, J. A. Fennell and G. Bintner, *Environ. Sci. Technol.*, 1996, **30**, 3102.
16 J. Yu and J. Zhang, *Dalton Trans.*, 2010, **39**, 5860.
17 M. V. Dozzi, C. D. Andrea, B. Ohtani, G. Valentini and E. Selli, *J. Phys. Chem. C*, 2013, **117**, 25586.
18 M. Mrowetz and E. Selli, *New J. Chem.*, 2006, **30**, 108.
19 S. Yang, H. Hu, Y. Chen, J. Zheng and Y. Cui, *J. Environ. Sci.*, 2007, **19**, 1239.
20 D. V. Barsukov, A. N. Pershin and I. R. Subbotina, *J. Photochem. Photobiol., A*, 2016, **324**, 175.
21 T. N. Obee and R. T. Brown, *Environ. Sci. Technol.*, 1995, **29**, 1223.
22 D. V. Kozlov, A. A. Panchenko, D. V. Bavykin, E. N. Savinov and P. G. Smirniotis, *Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 1100 (*Izv. Akad. Nauk, Ser. Khim.*, 2003, 1041).
23 M. Krichevskaya, S. Jõks, A. Kachina and S. Preis, *Photochem. Photobiol. Sci.*, 2009, **8**, 600.
24 M. Takeuchi, J. Deguchi, S. Sakai and M. Anpo, *Appl. Catal., B*, 2010, **96**, 218.
25 M. Minella, M. G. Faga, V. Maurino, C. Minero, E. Pelizzetti, S. Coluccia and G. Martra, *Langmuir*, 2010, **26**, 2521.
26 J. A. R. van Veen, F. T. G. Veltmaat and G. Jonkers, *J. Chem. Soc., Chem. Commun.*, 1985, 1656.
27 J. A. R. van Veen, *Z. Phys. Chem.*, 1989, **162**, 215.
28 M. S. Vohra, S. Kim and W. Choi, *J. Photochem. Photobiol., A*, 2003, **160**, 55.
29 K. Hadjiivanov, J. Lamotte and J.-C. Lavalley, *Langmuir*, 1997, **13**, 3374.
30 C. Deiana, G. Tabacchi, V. Maurino, S. Coluccia, G. Martra and E. Fois, *Phys. Chem. Chem. Phys.*, 2013, **15**, 13391.

Received: 15th September 2016; Com. 16/5047