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Photoisomerization of Norbornadiene to Quadricyclane Using Ti-Containing Photocatalysts

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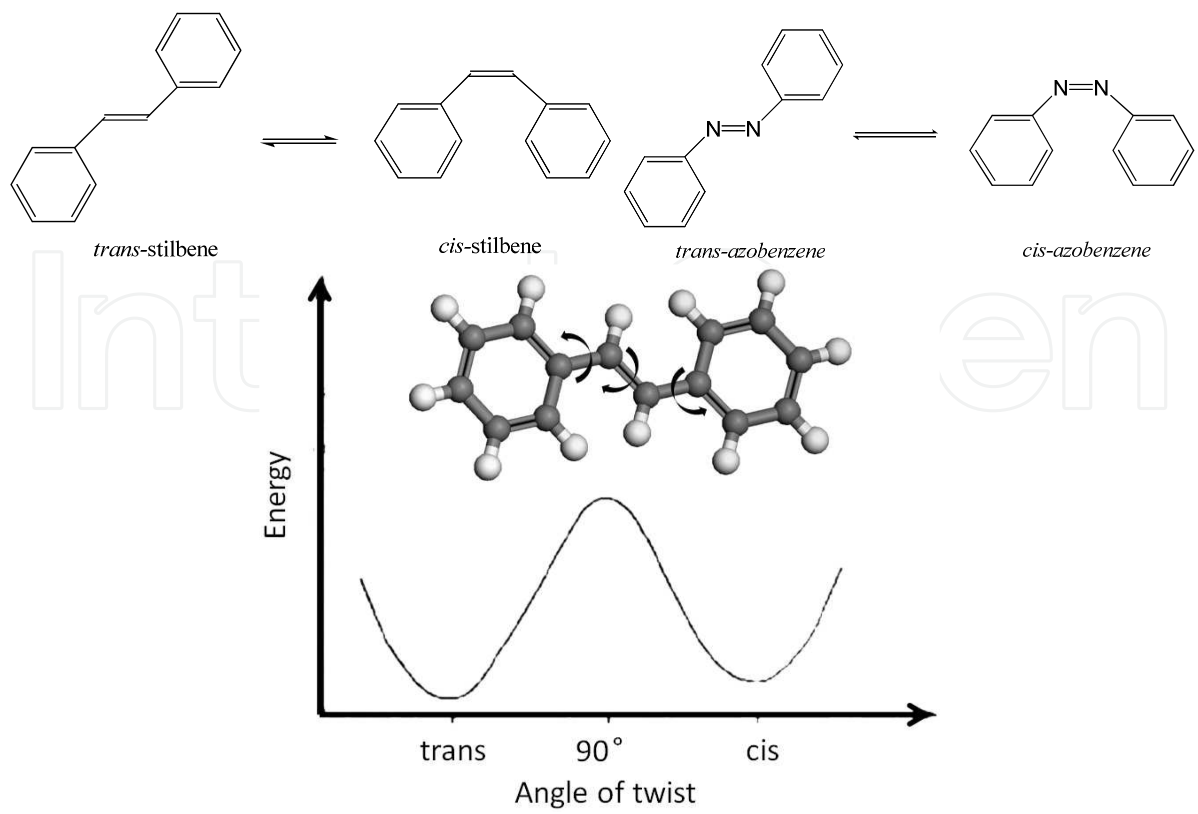
1. Introduction

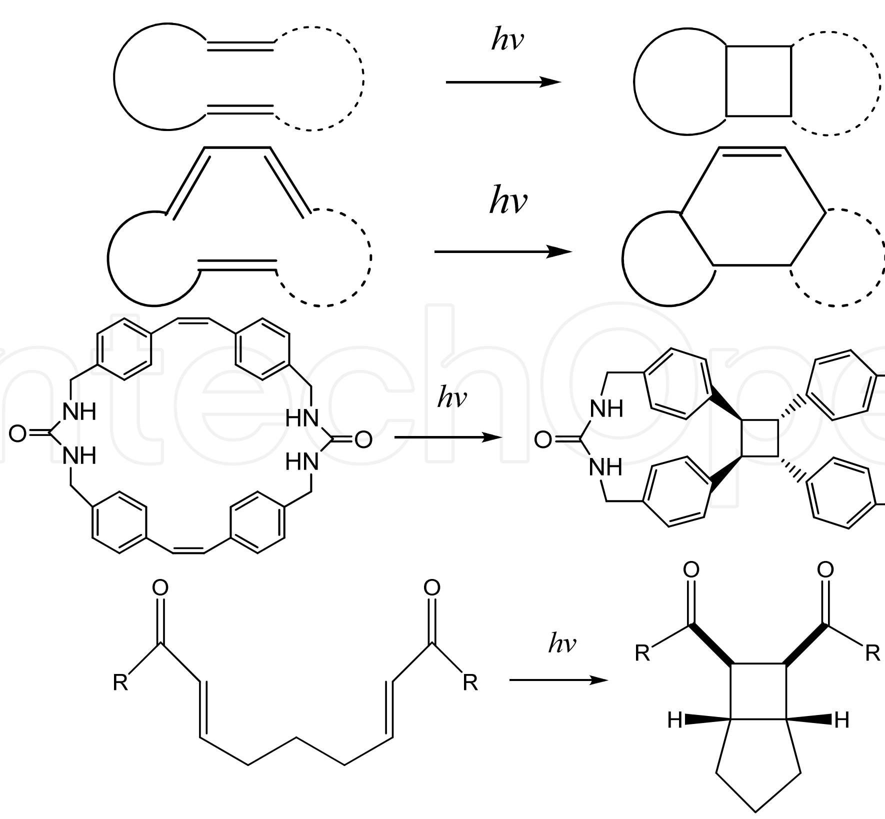
Photoisomerization, an important aspect of photochemistry, is molecular behavior in which the structural change between isomers is caused by photoexcitation. Photoisomerization is already applied or has potential in many fields, such as the synthesis of compounds that can not be obtained by other methods, pigments in digital data storage and recording, solar energy harvesting, and nanoscale devices and materials with photo-modulable properties.

Conformation transformation, especially the *trans-cis* photoisomerization of alkenes, see Scheme 1, is the most studied photoisomerization (Waldeck, 1991; Dou & Allen, 2003; Quenneville & Martínez, 2003; Minezawa & Gordon, 2011). Stilbene is a prototypical molecule that has been extensively investigated by both experimental and theoretical approaches. The primary mechanism of isomerization is through the excited singlet state starting from either the *cis* or the *trans* geometry. After photoexcitation, the molecule can overcome a small activation barrier and twist about its central C=C bond to form a twisted intermediate. This intermediate then decays with equal probability to either ground state *cis*-stilbene or ground state *trans*-stilbene. Similarly, the torsion around N=N bond also induces photoisomerization (Ciminelli et al., 2004; Mita et al., 1989), with azobenzene as the prototype. Moreover, compounds with photoisomerizable core have been designed for some special purposes. For example, highly branched dendrimers containing azobenzene core can be excited and converted to isomers by infrared irradiation, which represents a strategy for harvesting low-energy photons via chemical transformation (Jiang & Aida, 1997).

Geometric isomerization is another important type of photoisomerization that involves bond cleavage and creation in alkenes, see Scheme 2. One typical transformation is intramolecular cycloaddition such as [2+2] and [2+3] cycloadditions (Xu et al., 2009; Filley et al., 2001; Lu et al., 2011; Somekawa et al., 2009), which is very attractive in synthetic applications. In addition, the cycloaddition may produce strained and energy-rich products, which has received attention as a way to store solar energy.



Scheme 1. Examples of conformation photoisomerization of alkenes along with the prototype surface diagram of stilbene isomerization.

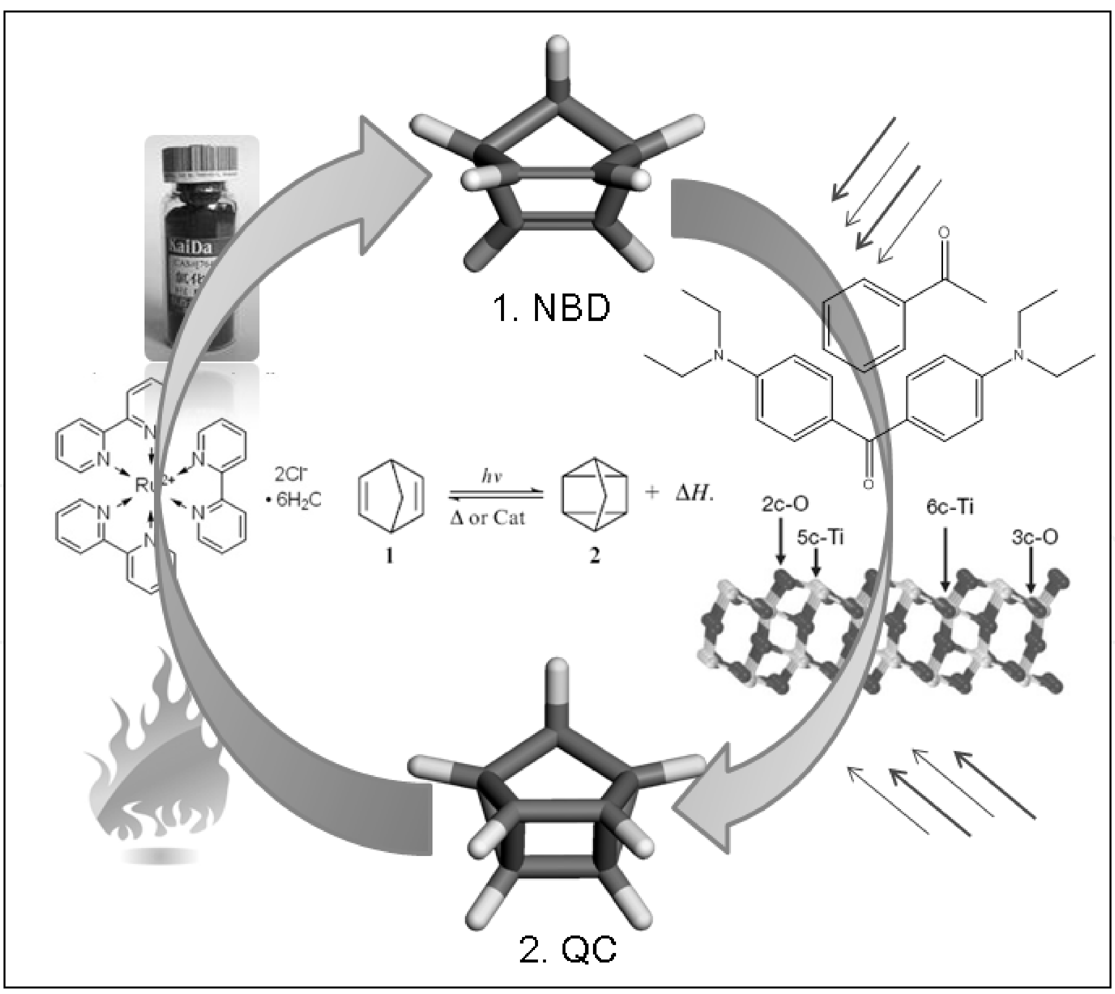


Scheme 2. Examples of geometric photoisomerization of alkenes

Generally, photoisomerization is sensitized by homogenous organics and/or metal complexes. However, solid semiconductors and even zeolites have been found to effective for these photo-induced processes. For example, CdS has been extensively studied for the *trans-cis* transformation of alkenes (Gao et al., 1998; Yanagida et al., 1986; Al-Ekabi & Mayo, 1985). Unfortunately, the instability of CdS under irradiation is a big problem for application.

2. Photosensitized isomerization of norbornadiene

Photoisomerization of norbornadiene (NBD) to quadricyclane (QC) is typical intramolecular [2+2] cycloaddition. It continues to be an interesting field as potential way for storage and conversion for solar energy (Hammond et al., 1964; Bren' et al., 1991; Dubonosov et al., 2002). The photoisomerization of NBD results in metastable structure that contains highly strained cyclobutane and two cyclopropane fragments. When one mole of NBD is transformed to QC, 89 kJ of solar energy could be stored in form of strain energy. Under some catalytic conditions, the inverse QC→NBD transformation occurs easily, accompanied with considerable thermal effect (ΔH=-89 kJ/mol). This represents an idea cycle for energy conversion and storage, see Scheme 3.



Scheme 3. Solar energy harvesting cycle based on photoisomerization of norbornadiene.

Recently, QC has been identified as a very promising high-energy compound as replacement for, or additive to, current hydrocarbon-based rocket propellants, because the extraordinary high strain energy offers a very high specific impulse (Kokan et al., 2009; Striebich & Lawrence, 2003). It is reported that QC-based fuels provide more propulsion than most of the hydrocarbon fuels like rocket propellant RP-1. QC is also designed for satellite propulsion system to replace highly toxic fuels like hydrazine and dinitrogen tetroxide. Moreover, QC is thermally and chemically stable, which means that it can be easily stored and transported like other hydrocarbon fuels.

The quantum yield of pure NBD photoisomerization is extremely low because the absorption edge of NBD is less than 300nm. Many efforts have been done to drive this photoisomerization using longer light and improve the quantum yield, which can be categorized into three directions: use of sensitizer, modification of NBD molecule and use of NBD-containing compounds. Dubonosov *et al* already presented two comprehensive reviews on the photoisomerization of NBD and its derivatives in 1991 and 2001 (Bren' et al., 1991; Dubonosov et al., 2002). This chapter focuses on the synthesis of QC from NBD, so only a brief summary is given to the direct photoisomerization of NBD, i.e. the first direction. The photosensitized isomerization of NBD occurs via triplet, so many carbonyl compounds like acetophenone, benzophenone and Michlers' ketone were used as triplet sensitizers. Actually, a recent patent claimed a solution phase photoisomerization process of NBD based on substituted Michlers' ketone (Cahill & Steppel, 2004). However, since the energy of the triplet state of NBD (^{3}NBD) is very high (~257 kJ/mol), only small amount of sensitizers are qualified. Then, metal complexes and derivatives of carbonyl compounds were studied. In this case, the isomerization proceeds through the formation of sensitizer-NBD complexes in electron-excited states, with or without the formation of ^{3}NBD.

However, the photosensitized reaction suffers from many drawbacks. First, homogenous reaction brings some difficulties in product purification and sensitizer recycling. Second, sensitizer tends to decompose under UV irradiation and induces some side-reactions like polymerization of NBD. In fact, in the past decade, work on the direct photoisomerization of NBD is very scare, and only some NBD derivatives were synthesized to prepare photo-responsive materials (Chen et al., 2007; Vlaar et al., 2001).

Heterogeneous semiconductors are extensively used in photocatalytic processes such as degradation of pollutants, hydrogen generation, and solar cell. They are also attractive for photoisomerization when considering the easy purification of product and reuse of catalyst. In fact, zeolites and semiconductors were already found to be active for the photoisomerization of NBD. In a brief communication, Lahiry and Haldar firstly reported that NBD can be isomerized over semiconductors like ZnO, ZnS and CdS (Lahiry & Haldar, 1986). Then Gandi et al. reported that Y-zeolites exchanged with K^+, Cs^+ and Tl^+ ions can sensitize the intramolecular addition of some dienes like NBD and afford the corresponding triplet products through heavy atom effect (Ghandi, 2006). In this case the reactant is pre-adsorbed in the micropores. Similarly, Gu and Liu compared La-, Cs-, Zn- and K-exchanged Y zeolites for the photoisomerization of NBD in liquid phase, and found LaY shows relatively high activity (Gu & Liu, 2008). They postulated that the heavy atom effect and Brönsted acid account for the result.

3. Photoisomerization of NBD over Ti-containing photocatalysts

Among the photocatalysts studied, TiO_2 is the most widely used material owing to its low-cost, non-toxicity, chemical and biological inertness, and photostability. Previous literatures already hint that TiO_2 can facilitate the photoisomerization of NBD. Although the activity of TiO_2 is relatively low due to the low optical absorbance and high charge–hole recombination rate, many methods such as doping with metal and nonmetal atoms and preparation of highly dispersed Ti-O species have been established to overcome this problem.

Recently, we focused on the photocatalytic isomerization of NBD using Ti-containing materials including metal-doped TiO_2 (Pan et al., 2010; Zou et al., 2008a), Ti-containing MCM-41 molecule sieves (Zou et al., 2008b) and metal-incorporated Ti-MCM-41 (Zou et al., 2010). These photocatalysts do show improved activity compared with pure TiO_2, suggesting that the photocatalysts used in environmental photocatalysis can be applied in the photoisomerization. In the following sections, a mini review of our work will be given, with the aim to show a new and promising way for photoisomerization.

3.1 Synthesis of materials and evaluation of activity

Three kinds of photocatalysts, including metal doped TiO_2 (M-TiO_2), Ti-substituted (Ti-MCM-41) and Ti-grafted MCM-41(TiO_2-MCM-41), and metal incorporated Ti-MCM-41 (M-Ti-MCM-41) were studied. M-TiO_2 materials were synthesized using sol-gel method with tetrabutyl titanate, $VO(SO_4)$, $Fe(SO_4)_3$, $Cu(NO_3)_2$, $Cr(NO_3)_3$, $Ce(NO_3)_3$ and $ZnSO_4$ as the metal resources (Pan et al., 2010; Zou et al., 2008a). Ti-MCM-41 and M-Ti-MCM-41 materials were synthesized via hydrothermal method using cetyltrimethyl ammonium bromide and tetrathyorthosilicate as the structure director and Si resource, respectively (Zou et al., 2008b, 2010), and TiO_2-MCM-41 materials were prepared through chemical grafting (Zou et al., 2008b). All the prepared materials were calcined at 500°C for 3 or 5 hours. The abbreviation of materials was suffixed with a symbol x in parentheses to describe the original molar Ti/M or Si/M ratio in starting synthetic mixtures.

The photoisomerization reaction was conducted under UV irradiation in closed quartz reactor with magnetic stirring (Pan et al., 2010; Zou et al., 2008a, 2008b, 2010). For M-TiO_2(M=V, Fe, Cu, Ce and Cr), a quartz chamber was irradiated vertically by a 300 W high-pressure xenon lamp located on the upper position. The wavelength was limited in the range of 220-420 nm by an optical filter and dimethyl sulfoxide was used as the solvent. For M-TiO_2(M=Zn) and Ti-contaning MCM-41 materials, a cylindrical quartz vessel was irradiated by a 400 W high pressure mercury lamp positioned inside the vessel. In this case the wavelength was not controlled and p-xylene was used as the solvent. The composition of the resulted mixture was determined by a gas chromatograph equipped with BP-1 capillary column and flame ionization detector. The rate constant k for each photocatalyst was calculated via kinetics fitting, assuming that the reaction obeys the first-order law. Since the reaction conditions for different type of photocatalysts are a little different, TiO_2 was used as the baseline to compare the photocatalytic activity of all materials. Therefore, the reaction constant k of one material was divided by that of TiO_2 (k_0) under identical reaction conditions, and the obtained relative reaction rate constant, i.e. k/k_0, was used in this chapter.

3.2 Photoisomerization of NBD over metal-doped TiO_2: Effect of metal dopants

TiO_2 is widely used in photocatalytic reactions due to its low cost and chemical stability, but suffers from the fast recombination of photoinduced electron-hole pairs. Doping with metal ions is regarded as an effective method to improve the efficiency of TiO_2 (Yang et al., 2007; Adán et al., 2007). So metal (Cu, Cr, Ce, V, Fe, Zn)-doped TiO_2 was studied firstly for the photoisomerization of NBD.

The structural parameters of prepared materials characterized using XRD, EDX, XPS and N_2-adsorption are shown in Table 1. According to the bulk composition from EDX data and surface composition from XPS data, V, Fe and Ce are dispersed in the inner part of prepared materials whereas Cu, Cr and Zn ions are enriched on the particle surface. Specifically, only a small amount of Cu is introduced into the material. Generally, there are three possible dispersion modes for dopants, namely substitutional, interstitial and surface positions. The local structure of dopants ions can be deduced based on their ionic radii, that is, Fe and V ions with radii close to Ti ions in substitutional sites, large Ce ions in interstitial positions, whereas Cu ions with largest radii on the surface. The surface enrichment of relatively small Cr and Zn ions that have comparable radii with Ti ions is a little surprising because they could enter the lattice, but consistent with results reported by other researchers (Zhu et al., 2010; Jing et al., 2006). The reason may be that these ions are originally inside the lattice but diffuse to the surface through oxygen vacancies during the calcination process, or the hydrolysis rate of these ions is much slower than that of Ti ions.

Materials	Grain size (nm)	S_{BET} ($m^2 \cdot g^{-1}$)	Ti/M ratio	
			EDX	XPS
TiO_2	21.5	21.5	-	-
Cu-TiO_2(15)	19.9	13.1	90.4	3.8
Cr-TiO_2(15)	14.7	40.9	20.0	3.0
Ce-TiO_2(15)	11.4	64.3	16. 9	19.8
V-TiO_2(15)	9.9	102.7	19.0	15.6
Fe-TiO_2(15)	7.0	120.6	18.5	19.8
Zn-TiO_2(100)	8.1	84.9	-	7.1

Table 1. Structural characteristics of metal-doped TiO_2
(Pan et al., 2010; Zou et al., 2008a).

When metal dopants are dispersed in the substitutional site, some Ti-O-M structures are expected to form, which will cause a shift in the binding energy of Ti species because the difference in Pauling electronegativity can induce electron transfer from Ti to M ions. As shown in Fig. 1, the XPS signal (binding energy) of Ti is shifted to higher values after doping with V and Fe, while for other doping the shift is not so obvious because the metals are not located in the substitutional sites with no, or only a few, M-O-Ti structures formed.

Doping can restrain the growth of particle to some degree no mater what the doping mode is, but the mechanism may be different. Fe and Zn-doping produces considerably small particles, see Table 1 and Fig. 2. For the substitutional doping like Fe- and V-doping, dopants in the lattice can destroy the crystal structure and restrain its growth. For the surface deposition or interstitial mode, like Ce- and Zn-doping, dopants may prevent the direct contact of TiO_2 crystallites and retard them agglomerating into big particle.

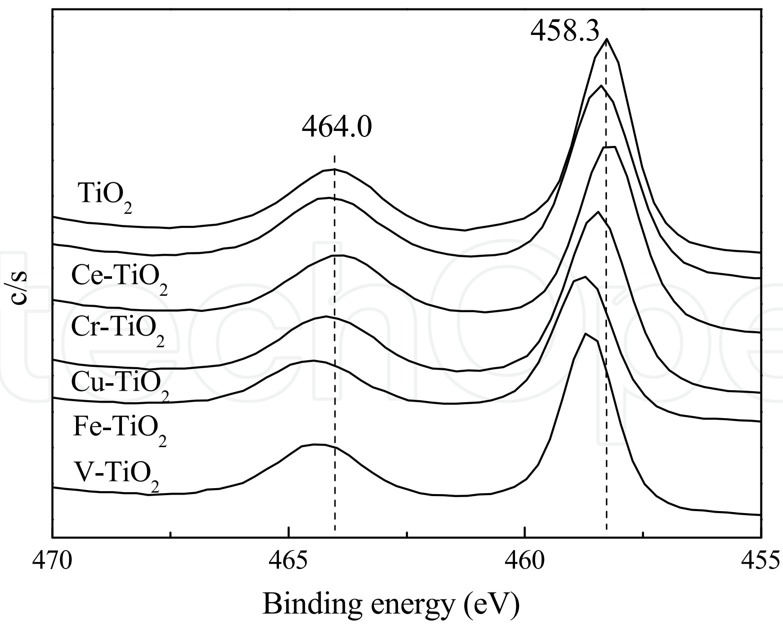


Fig. 1. Ti2p XPS spectra of metal-doped TiO_2. Reprinted with permission from Pan, L.; Zou, J.-J; Zhang, X. & Wang, L. (2010), *Industrial & Engineering Chemistry Research,* Vol.49, No.18, pp. 8526-8531. Copyright @ 2010 American Chemical Society.

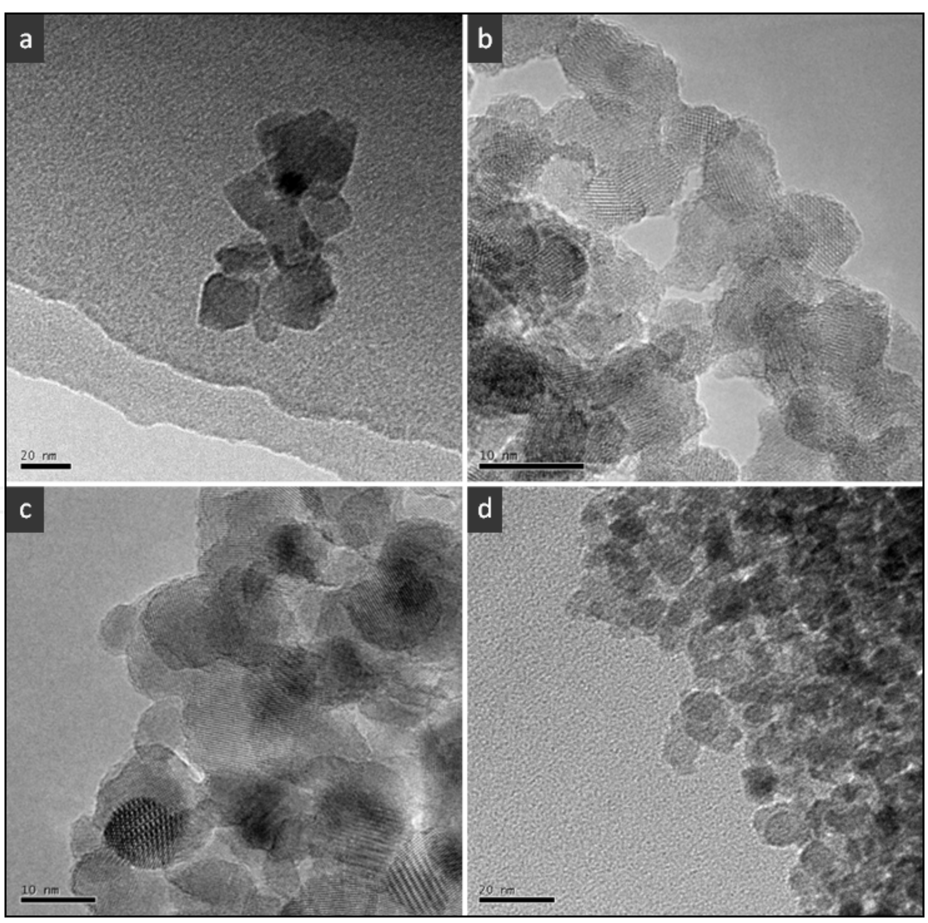


Fig. 2. TEM images of (a) pure TiO_2, (b) Fe-TiO_2(15), (c) V-TiO_2(15) and (d) Zn-TiO_2(100). (a) & (d) reprinted with permission from Zou, J.-J.; Zhu, B.; Wang, L.; Zhang, X. & Mi, Z.

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The relative photocatalytic activity of doped TiO_2 (k/k_0) is also shown in Fig. 3. Except Cu, doping metal ions show positive effect on the photoisomerization of NBD, among which Zn-TiO_2 and Fe-TiO_2 are specifically active. The photoisomerization reaction is a complex process, and the physicochemical properties of photocatalyst such as grain size, type of dopant ions as well as their local structure are very important. Small particle is of course desired because it provides large active surface. It has been reported that the surface doping of Zn ions produces many surface OH groups that greatly enhance the intensity of surface photovoltage spectrum and photoluminescence and improve the photoactivity (Jing et al., 2006). As shown in Fig. 4, the activity of NBD photoisomerization is also closely relative to the concentration of surface OH.

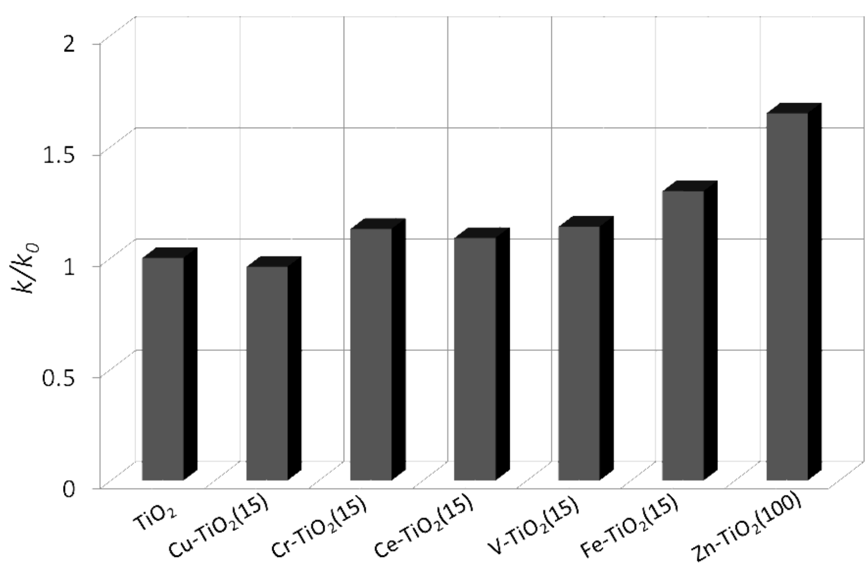


Fig. 3. Activity of metal-doped TiO_2 for the photoisomerization of norbornadiene (Pan et al., 2010; Zou et al., 2008a).

However, the role of surface OH seems invalid for the materials with substitutional doping. As shown in Fig. 5, the activity of Fe- and V-doped TiO_2 and their lattice oxygen concentration, not the surface OH, change in identical manner, strongly suggesting there is an inherent correlation between the photoisomerization and lattice oxygen. It is still not clear why two doping modes induce contrary result, probably because the reactant molecule is adsorbed on different site that will be discussed in section 4. As to the role of substitutional dopants, it has been reported that metal ions in substitutional sites can improve the photoinduced charge transfer and separation (Wang et al., 2009). It is believed that this process is very likely to occur through the M-O-Ti structure in which the metal dopants mainly serve as charge trapping and transferring center. Taking Fe-TiO_2 as example, the role of Fe is shown as follows: (1) Fe ions temporarily trap photoinduced charges in the neighboring Ti-O moiety:

$$Ti^{4+} - O^{2-} - Fe^{3+} - O^{-} - Ti^{3+} \rightarrow Ti^{4+} - O^{2-} - Fe^{2+} - O^{-} - Ti^{4+}$$

$$Ti^{4+} - O^{2-} - Fe^{3+} - O^{-} - Ti^{3+} \rightarrow Ti^{4+} - O^{2-} - Fe^{4+} - O^{2-} - Ti^{3+}$$

(2) The trapped charges are transferred to sideward Ti-O species, resulting in separated charges:

$$Ti^{4+} - O^{2-} - Fe^{2+} - O^{-} - Ti^{4+} \rightarrow Ti^{3+} - O^{2-} - Fe^{3+} - O^{-} - Ti^{4+}$$

$$Ti^{4+} - O^{2-} - Fe^{4+} - O^{2-} - Ti^{3+} \rightarrow Ti^{4+} - O^{-} - Fe^{3+} - O^{2-} - Ti^{3+}$$

In this way, the charge induced in one Ti-O moiety is quickly transferred to another Ti-O moiety through the Fe-O-Ti structure, thus effectively separating the charge and retarding the recombination.

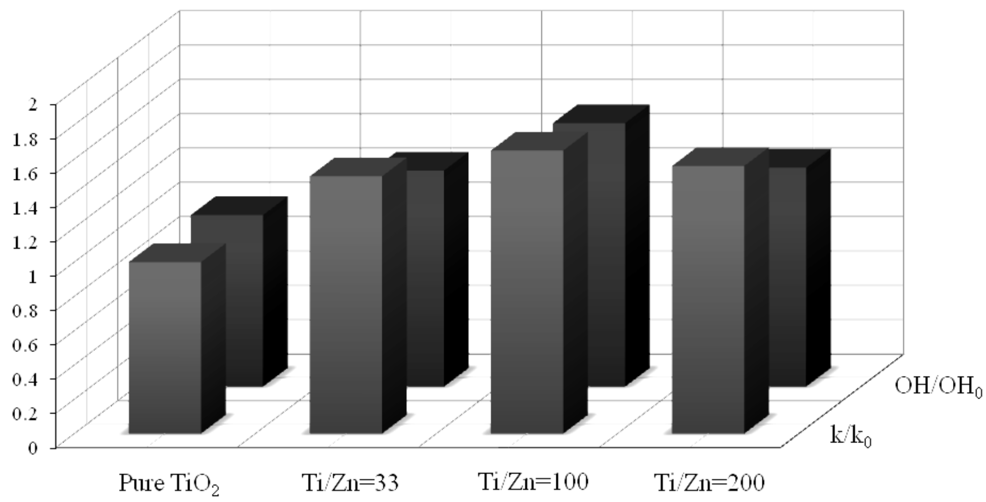
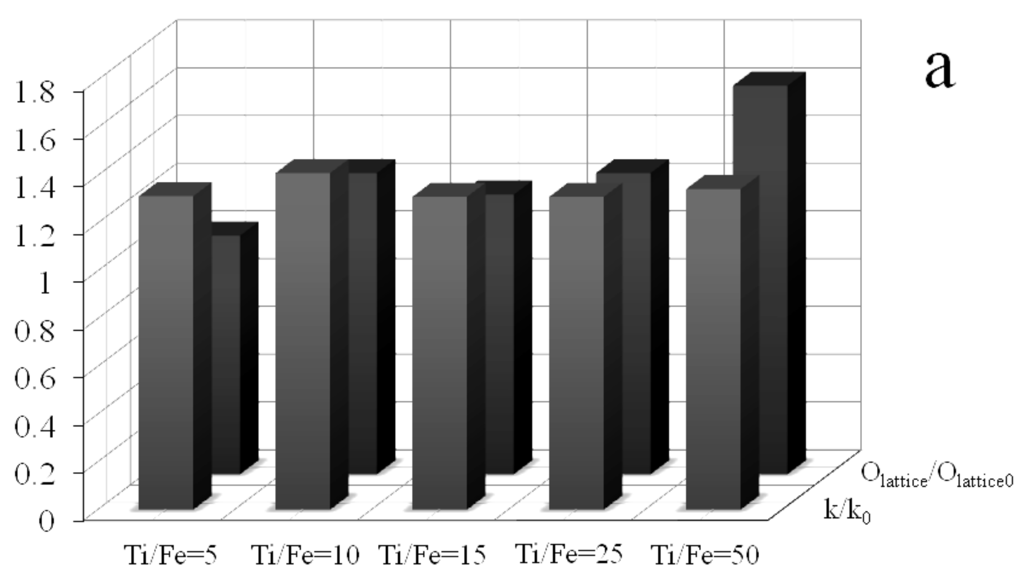


Fig. 4. Relationship of activity for the photoisomerization of norbornadiene and the relative surface OH concentration of Zn-TiO_2 (Zou et al., 2008a). OH, the content of surface OH; OH_0, the OH content of pure TiO_2.



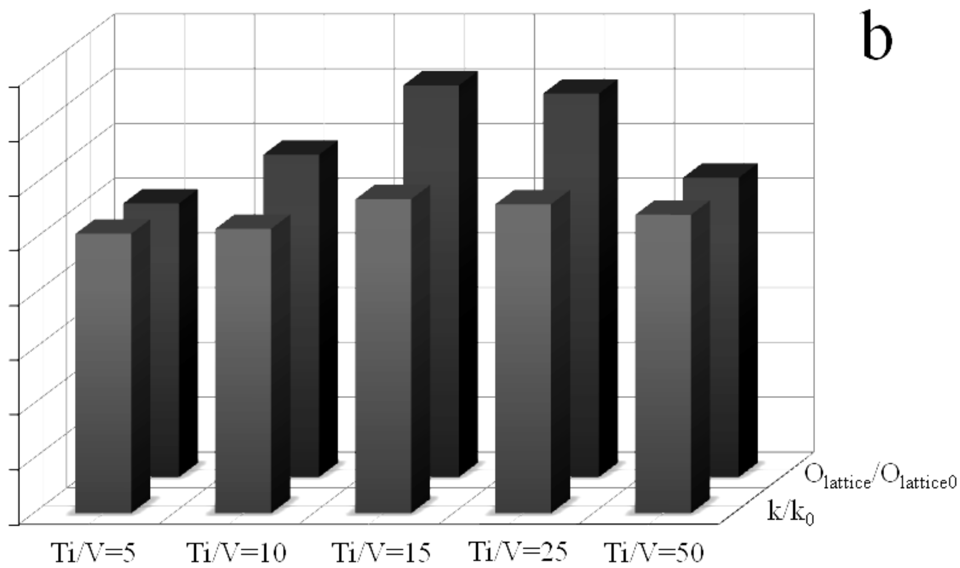


Fig. 5. Relationship of activity for the photoisomerization of norbornadiene and the relative lattice oxygen concentration of (a) Fe-TiO_2 and (b) V-TiO_2 (Pan et al., 2010).

3.3 Photoisomerization of NBD over Ti-containing MCM-41: Effect of Ti coordination

MCM-41 has uniform hexagonal mesopores with large internal surface area, exhibiting great potential as the supporting materials of TiO_2. It has been reported that incorporating Ti ions into framework or loading them on the wall of MCM-41 gives unique photocatalytic activity (Hu et al., 2003, 2006). So both Ti-incorporated and Ti-grafted MCM-41 materials were prepared for the photoisomerization of NBD.

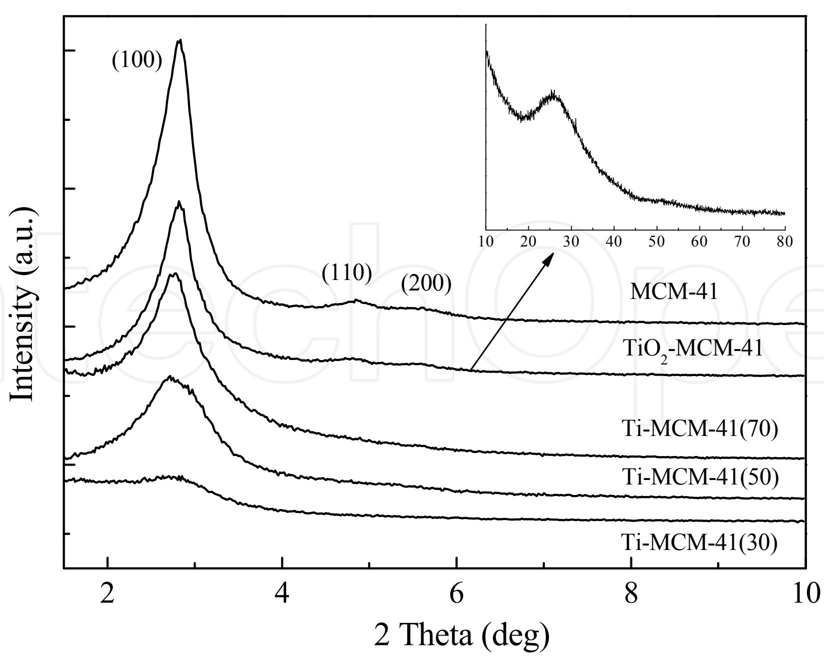


Fig. 6. XRD patterns of Ti-MCM-41 and TiO_2-MCM-41. Reprinted with permission from Zou, J.-J.; Zhang, M.-Y.; Zhu, B.; Wang, L.; Zhang, X. & Mi, Z. (2008), *Catalysis Letters*, Vol.124, No.12, pp. 139-145, Copyright @ 2008 Springer Netherlands.

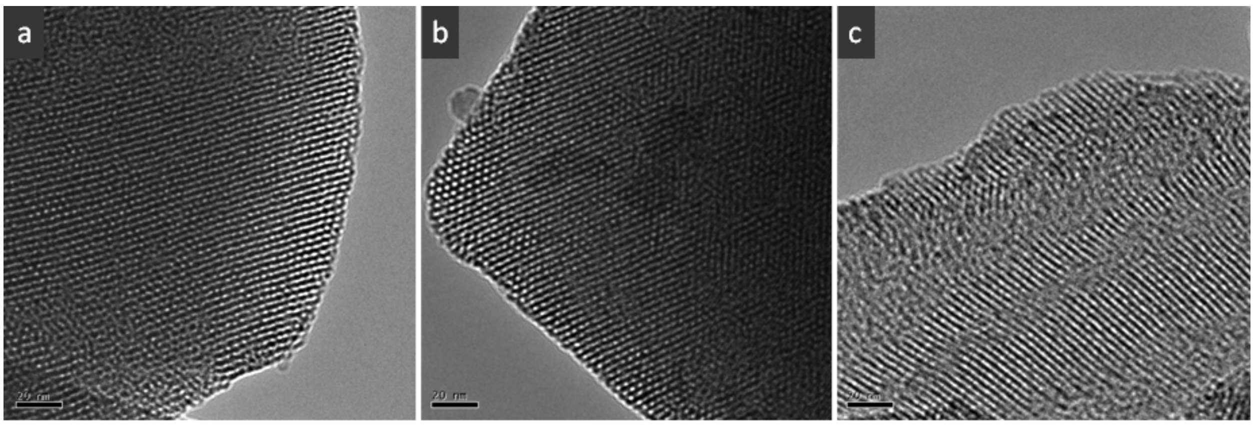


Fig. 7. TEM images of (a) MCM-41, (b) TiO_2-MCM-41 and (c) Ti-MCM-41(50). Reprinted with permission from Zou, J.-J.; Zhang, M.-Y.; Zhu, B.; Wang, L.; Zhang, X. & Mi, Z. (2008), *Catalysis Letters*, Vol.124, No.12, pp. 139-145, Copyright @ 2008 Springer Netherlands.

Grafting TiO_2 in the pore of MCM-41 does not influence the ordered hexagonal structure of support as its XRD patterns in the low-angle region are identical to MCM-41, see Fig. 6. An additional peak corresponding to the (101) reflex of anatase TiO_2 is observed at 25.5° but the intensity is extremely weak, so TiO_2 crystallites are highly dispersed in the pore of MCM-41. Incorporating Ti ions in the MCM-41 framework slightly impairs the structural integrity of MCM-41 but the ordered structure is well retained, shown by the weakened but obvious diffractive peaks. Also, the cell unit of Ti-MCM-41 is enlarged because the Ti-O bond distance is longer than the Si-O bond distance. TEM images in Fig. 7 further confirm the XRD result. No TiO_2 nanoparticles are observed for TiO_2-MCM-41 and its pore structure is identical to MCM-41, but some linear tubular pores of Ti-MCM-41 collapse into irregular pores.

The nature and coordination of Ti^{4+} ions was deduced according to the UV-vis diffuse reflectance spectra shown in Fig. 8. The absorption peak at 220 nm is ascribed to tetra-coordinated Ti whereas the peak at ~270 nm represents species in higher coordination environments (penta- or hexa-coordinated species). For Ti-MCM-41, most of the Ti species are dispersed in the framework (Ti-O-Si) when Ti content is low, but polymerized Ti species (Ti-O-Ti) present in case of higher Ti content. TiO_2-MCM-41 contains highly dispersed quantum-size TiO_2 nanodomains, see the blue-shifted absorption compared with bulk TiO_2.

The overall activity for the photoisomerization of NBD is Ti-MCM-41(30) > Ti-MCM-41(50) > TiO_2-MCM-41 > Ti-MCM-41(70) >TiO_2, see Fig. 9a. Since the amount of Ti species is different in these materials, the activity based on TiO_2 was also calculated to compare the inherent activity of different Ti species, with the order of Ti-MCM-41(50) ≈ Ti-MCM-41(70) > Ti-MCM-41(30) > TiO_2-MCM-41 > TiO_2, see Fig.9b. Considering the local structure of Ti, it can be seen that framework Ti species are most active in the photoisomerization of NBD, polymerized species follows and bulk TiO_2 has the lowest activity.

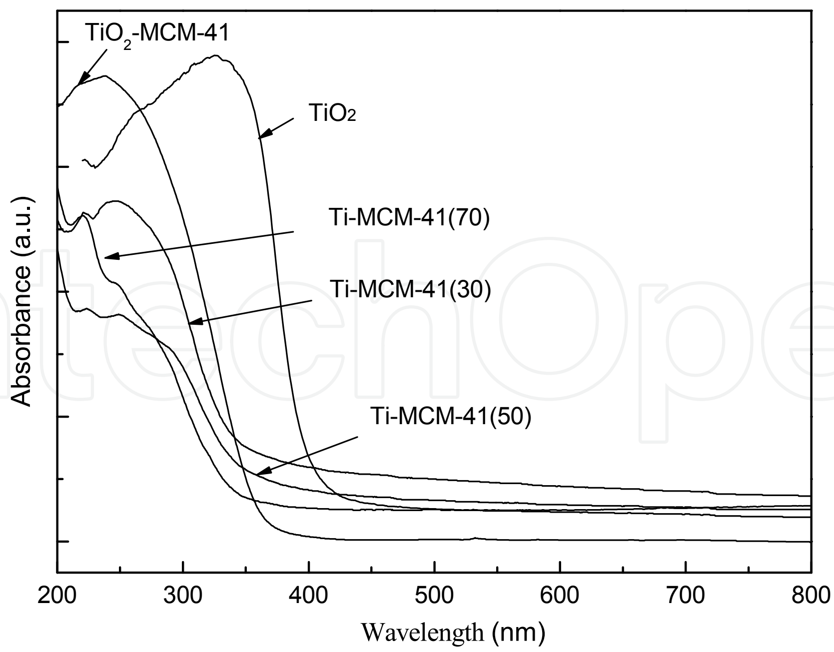


Fig. 8. UV-Vis diffuse reflectance spectra of Ti-MCM-41 and TiO_2-MCM-41. Reprinted with permission from Zou, J.-J.; Zhang, M.-Y.; Zhu, B.; Wang, L.; Zhang, X. & Mi, Z. (2008), *Catalysis Letters*, Vol.124, No.12, pp. 139-145, Copyright @ 2008 Springer Netherlands.

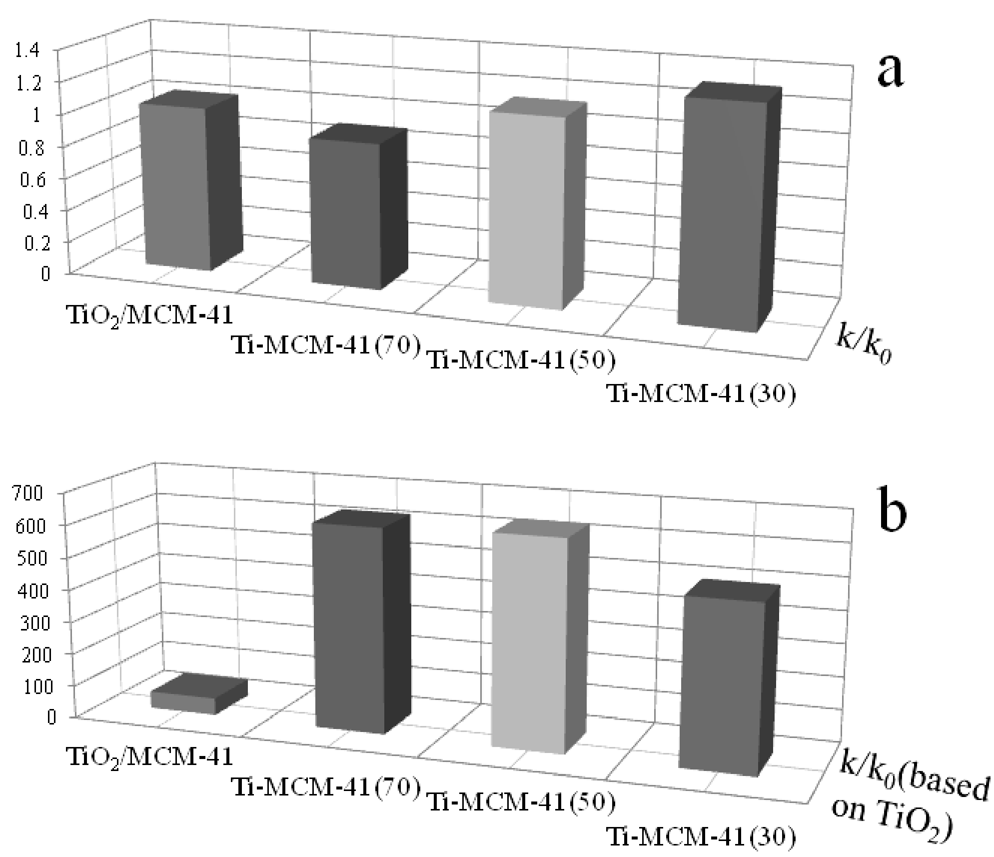


Fig. 9. Activity of Ti-MCM-41 and TiO_2-MCM-41 for the photoisomerization of norbornadiene (Zou et al., 2008b).

3.4 Photoisomerization of NBD over M-Ti-MCM-41: Combination of metal doping and framework Ti species

Transition-metal-incorporated MCM-41 generally shows high photocatalytic activity due to the high dispersion of photoactive sites and effective separation of electrons and holes (Hu et al., 2007; Yamashita et al., 2001; Matsuoka & Ampo, 2003; Davydov et al., 2001). Since Ti-MCM-41 produces highly active photocatalysts for the photoisomerization of NBD, it is expected that introducing second transition metal ion into Ti-MCM-41 may further enhance the activity. So series of transition-metal-incorporated (V, Fe and Cr) Ti-MCM-41 were synthesized for the photoisomerization of NBD, with Si/Ti ratio of 30.

According to the UV-vis spectra in Fig. 10, V and Fe ions are well dispersed in the materials whereas the dispersion of Cr ions is very poor. For V-Ti-MCM-41(150), V ions are highly dispersed in MCM-41 framework at atomic level with tetrahedral coordination, with some species in 6-fold (absorption around 370 nm) and higher coordination or even polymerized environments (absorption in >400 nm region) formed with the increase of V content. This tendency is also observed for Fe-Ti-MCM-41. However, for Cr-Ti-MCM-41, the absorption at

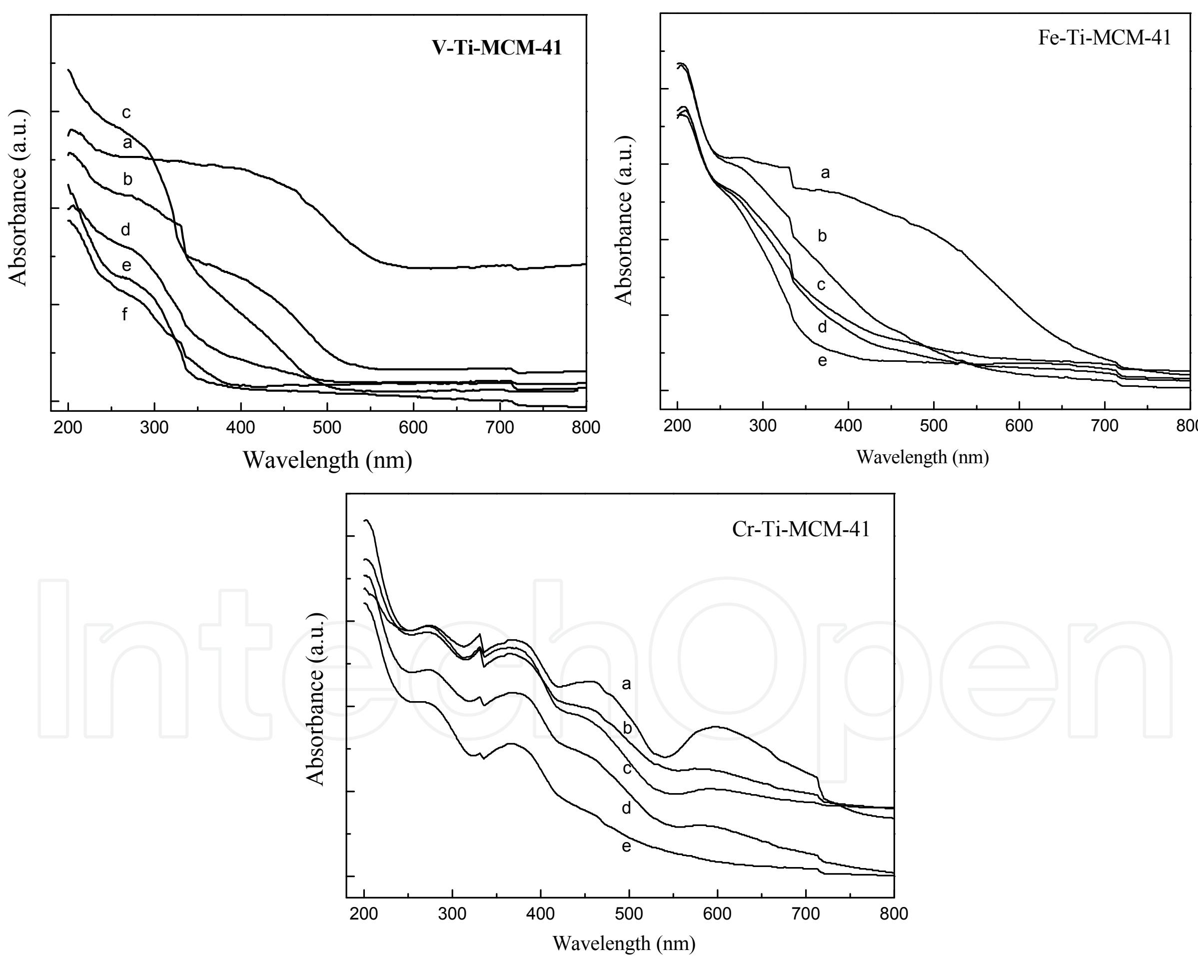


Fig. 10. UV-Vis diffuse reflectance spectra of M(V, Fe and Cr)-Ti-MCM-41 (a: Si/M=10, b: Si/M=33, c: Si/M=75, d: Si/M=100, e: Si/M=150, f: Ti-MCM-41). Reprinted with permission from Zou, J.-J.; Liu, Y.; Pan, L.; Wang, L. & Zhang, X. (2010), *Applied Catalysis B: Environmental*, Vol.95, No.3-4, pp. 439-445. Copyright @ 2010 Elsevier.

470 nm and 610 nm ascribed to poly- and bulk Cr_2O_3 is very intensive. The local structure of Cr ions are also testified by the IR spectra in Fig. 11. All Cr-Ti-MCM-41 samples show a shoulder band at 880-900 cm^{-1} assigned to Cr^{6+} species, according to the literature (Awate et al., 2005; Zhu et al., 1999). Specifically, Cr-Ti-MCM-41(10) has two bands at 630 and 570 cm^{-1} belonging to extra-framework Cr_2O_3 oxides.

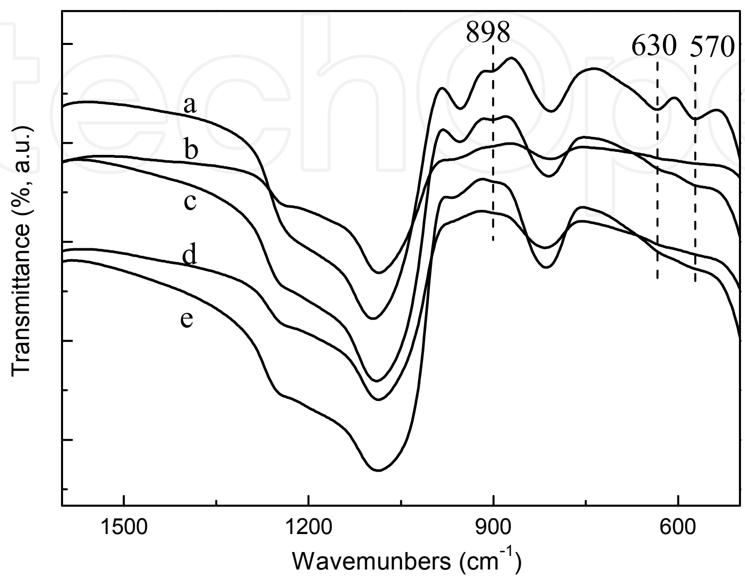
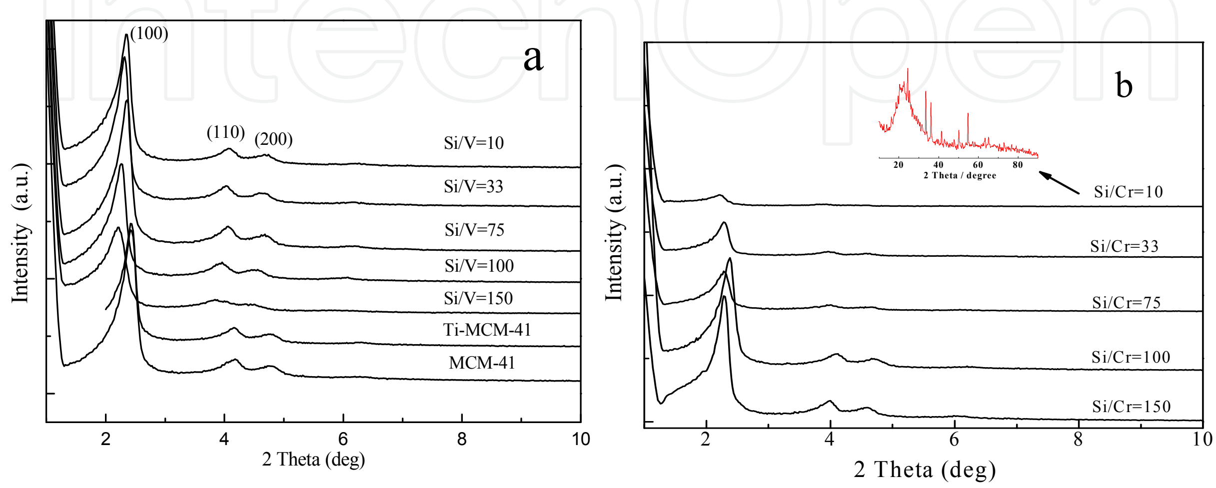


Fig. 11. IR spectra of Cr-Ti-MCM-41 (a: Si/M=10, b: Si/M=33, c: Si/M=75, d: Si/M=100, e: Si/M=150, f: Ti-MCM-41). Reprinted with permission from Zou, J.-J.; Liu, Y.; Pan, L.; Wang, L. & Zhang, X. (2010), *Applied Catalysis B: Environmental*, Vol.95, No.3-4, pp. 439-445. Copyright @ 2010 Elsevier.

The well dispersed V and Fe species show no obvious influence on the ordered structure of prepared materials, but the polymerized Cr species obviously impose negative effect on the structure, see Fig. 12. An extreme is observed for Cr-Ti-MCM-41(10), in which the characteristic diffractive peaks of ordered structure completely disappear, and a peak of bulk Cr_2O_3 appears. In TEM image, this material no longer possess hexagonal mesoporous structure, but agglomerate of many crystallites.



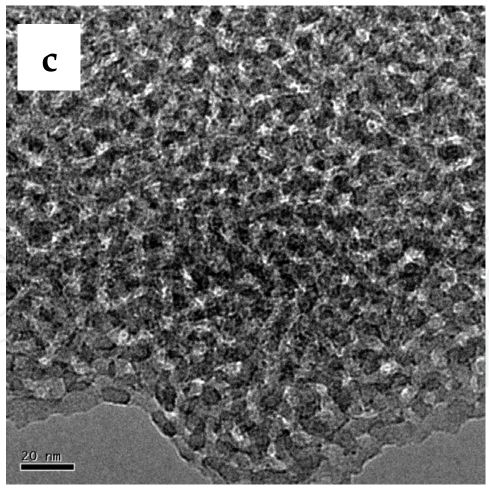


Fig. 12. XRD patterns of (a) V-Ti-MCM-41 and (b) Cr-Ti-MCM-41, and (c) TEM image of Cr-Ti-MCM-41(10). Reprinted with permission from Zou, J.-J.; Liu, Y.; Pan, L.; Wang, L. & Zhang, X. (2010), *Applied Catalysis B: Environmental*, Vol.95, No.3-4, pp. 439-445. Copyright @ 2010 Elsevier.

All the materials exhibit higher activity than Ti-MCM-41, see Fig. 13, indicating that introducing second metal is beneficial to the photoisomerization. Among the three metals, V-incorporation is most effective, Fe-incorporation follows, and Cr- incorporation is the least. The photocatalytic activity has nothing to do with the concentration of second transition metal ions, and the improvement in activity should be related to their state of dispersion and local structure. It has been reported that tetrahedrally coordinated M-oxide moieties dispersed in mesoporous materials can be easily excited under UV and/or visible-light irradiation to form corresponding charge-transfer excited states (Yamashita et al., 2001; Matsuoka & Anpo, 2003):

$$[M^{n+} - O^{2-}] \xrightarrow{hv} [M^{(n-1)+} - O^{-}]^{*} \text{ (M=V, Cr, Fe)}$$

Then M species can donate an electron to surrounding Ti-O moieties and O^- can scavenge an electron from surrounding Ti-O moieties, inducing charge separation in Ti-O species (Davydov et al., 2001). Therefore, two different excitation mechanisms exist in M-Ti-MCM-41. One is direct excitation of Ti-O moieties by UV irradiation, and the other is indirect excitation via charge transition from $[M^{(n-1)+} - O^{-}]^{*}$ species. The second process should be responsible for the high photocatalytic activity of M-Ti-MCM-41 because of its high efficiency in charge formation and separation.

V-Ti-MCM-41(150) shows specifically high activity because majority of V ions are highly dispersed in 4-fold coordination, which brings up highly efficient excitation of Ti-O species. In addition, the well retained ordered structure and high surface area can enhance the adsorption of NBD molecules and provide more active sites. With the increase of V content, the activity is decreased because some 4-fold ions are transformed into undesirable highly-coordinated species and the damaged structure and small surface area may suppress the adsorption of reactants. The low activity of Cr-Ti-MCM-41 is due to poorly dispersed chromium ions and dramatically destroyed textural structure.

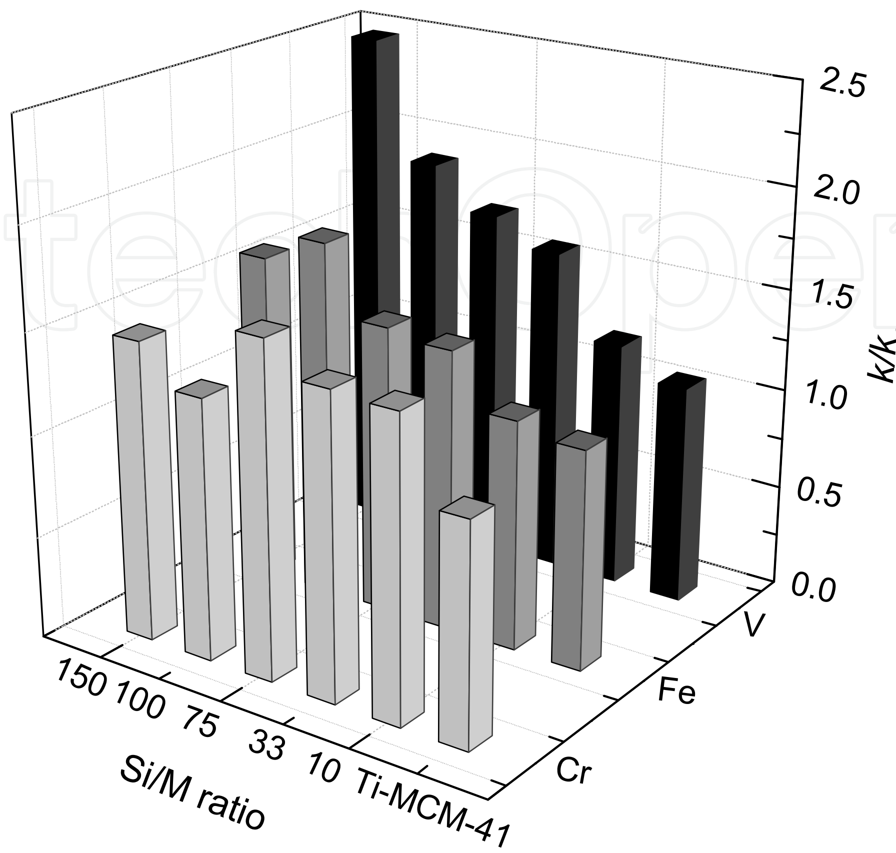
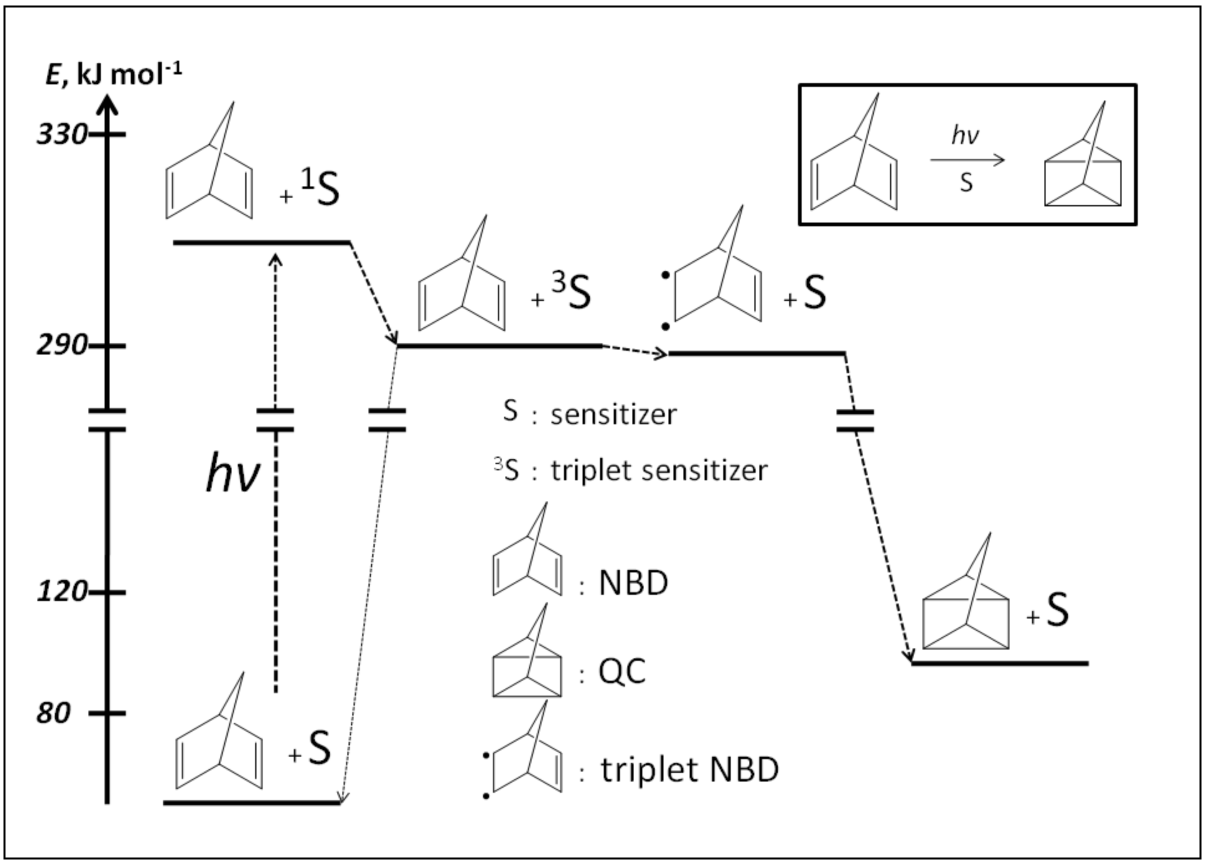


Fig. 13. Activity of M(V, Fe and Cr)-Ti-MCM-41 for the photoisomerization of norbornadiene (Zou et al., 2010).

Since some photocatalysts show absorption in visible-light region, one may wonder whether they can catalyze the isomerization under visible-light irradiation. However, there is no any observable conversion when the experiment was conducted using visible irradiation (>420 nm). This is different from the case of H_2 generation and organic degradation, where Cr-Ti-MCM-41 is reported to exhibit visible-light activity (Yamashita et al., 2001; Davydov et al., 2001; Chen & Mao, 2007). These results suggest that the reaction mechanism between the photoisomerization and other photocatalytic reactions may be very different.

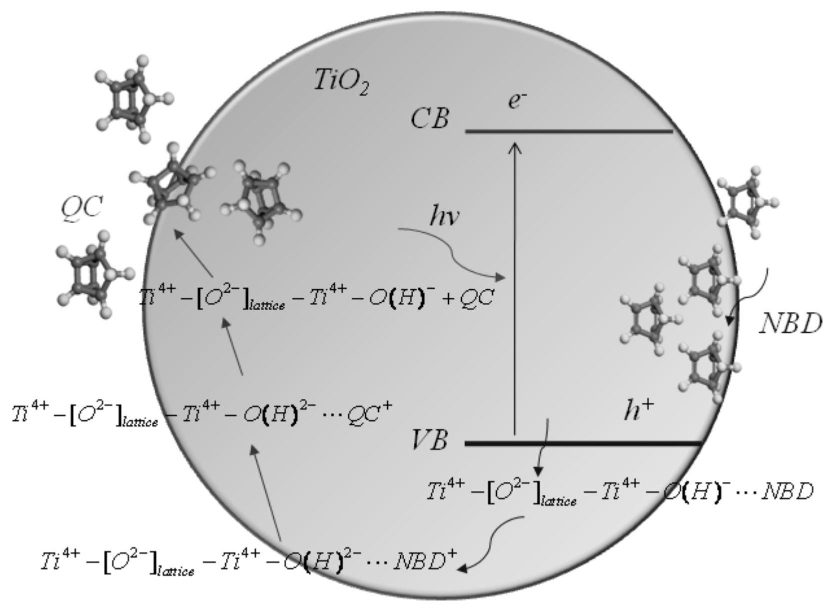
4. Mechanism for NBD photoisomerization

Photoisomerization of NBD in the presence of sensitizers generally proceeds via triplet state mechanism (Bren' et al., 1991; Dubonosov et al., 2002), see Scheme 4. Under irradiation, the sensitizer is excited to triplet state (^{3}S) via single state (^{1}S), that subsequently transfers energy to NBD molecules and excites it to triplet state (^{3}NBD). Then ^{3}NBD undergoes adiabatic isomerization and forms triplet state of QC (^{3}QC) that rapidly decays to its ground state and produces QC.



Scheme 4. Triplet sensitized photoisomerization of norbornadiene.

However, with the presence of Ti-containing photocatalyst, this mechanism is not suitable because the vertical triplet energy transfer from Ti-oxide species to NBD is very difficult. NBD molecules have to be firstly positively charged by photoinduced holes, but the free radical ion isomerization mechanism is ruled out because the energy of free $NBD^{\cdot+}$ is significantly lower than free $QC^{\cdot+}$. In fact, the transformation of QC to NBD is through the $QC^{\cdot+} \rightarrow NBD^{\cdot+}$ free radical route (Ikezawa & Kutal, 1987). So the photoisomerization of NBD over semiconductors should be an adsorption-photoexcited process, which is very likely through the exciplex (charge-transfer intermediate), see Scheme 5. First, NBD molecule is adsorbed on the photoexcited Ti-oxides. Then surface-trapped hole is transferred to adsorbed molecule and a complex with NBD positively charged is formed. Subsequently the complex is transformed to structure with QC skeleton. Finally, QC is released into the liquid phase and the charge is recombined through reverse electron transfer. In this case the adsorption and charge transfer are two critical steps. The adsorptive site on different Ti-containing materials may be different. For Zn-TiO_2, surface OH very likely serves as the site because it plays an important role in the reaction, and the excited complex may be $TiO_2^- - OH \cdots NBD^+$. For Fe-TiO_2 and V-TiO_2, however, the lattice oxygen may work as the adsorbing site with the complex of $Ti^{4+} - [O^{2-}] - Ti^{4+} - O^{2-} \cdots NBD^+$. Any charge recombination process can deactivate the complex, so the function of dopants and framework Ti species is to retard the undesired recombination.



Scheme 5. Photoisomerization of norbornadiene via adsorption-photoexcitation over semiconductor.

5. Summary

The transform of norbornadiene is typical photoisomerization and of great importance for both solar energy harvesting and aerospace fuel synthesis. Our recent work shows that the heterogeneous Ti-containing materials show activity comparable to homogeneous sensitizers, along with many additional advantages in manipulation and scale-up. Ti-containing photocatalysts are extensively used in environmental and energy science and show many exciting and rapid progress, which will undoubtedly benefit the photoisomerization of alkenes like NBD. Specially, surface modulation may be very helpful because it can tune the adsorption and even charge transfer between reactant and catalyst. Even though, the photoisomerization shows some unique characteristics and further work is necessary to understand the mechanism and substantively improve the efficiency. It is expected that the heterogeneous photocatalysis may provide a new and promising pathway for photoisomerization of alkenes.

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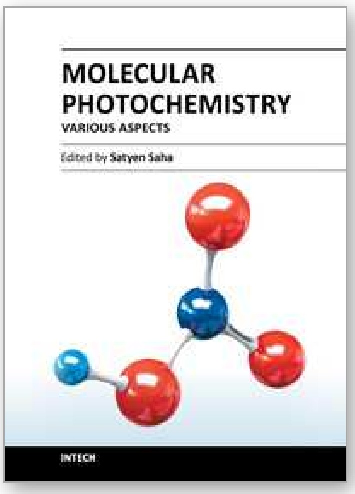

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