Diffuse Reflectance Laser Flash Photolysis Study of Titanium-Containing Zeolites

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A series of porous titanosilicates (Ti-preferrierite, Ti-ferrierite, Ti/ITQ-6, Ti/ITQ-2, and silylated Ti/MCM-41), all of them active as alkene epoxidation catalysts, have been submitted to diffuse reflectance laser flash photolysis. The transient spectra in the microsecond time domain exhibit characteristic absorption bands at 350 nm (sharp) and 450−800 nm (featureless) attributable to triplet ligand-to-metal charge-transfer state and ejected electrons, respectively. It is proposed that the relative intensity of these two bands is a reflection of the presence of isolated, tetrahedral Ti atoms versus Ti aggregates, the former being considered the most active titanium sites in olefin epoxidation. Our study shows the applicability of laser flash photolysis to the characterization of titanium atoms in titanosilicates.

Introduction

Titanosilicates are catalysts that have found industrial application for alkene epoxidations, ammoxidation of ketones, and benzene hydroxylation.[1,2] In addition, these solids are also efficient heterogeneous catalysts for heteroatom oxygenations, degradative C═C double bond cleavage, and oxidative oxime hydrolysis at a laboratory or preindustrial scale.[3−12] Given the importance of titanosilicates as catalysts, an intense research has been developed aimed at optimizing their catalytic performance. Numerous reports have established that the chemical composition, preparation procedure, and structural modifications play a significant role in the activity and selectivity of these catalysts by varying the coordination of Ti atoms and their distribution in the solid. Thus, comparative studies have revealed that the optimum titanium catalyst must contain isolated, tetrahedral framework Ti atoms and that the intrinsic activity of the titanosilicate TS-1 is higher than Ti/Beta and mesoporous Ti/MCM-41.[13]

To improve catalyst preparation, the nature of the Ti active sites, i.e., coordination and crystallographic location of Ti atoms, has to be known and correlated with their catalytic activity. To do this, different techniques have been applied up to now. Thus, the predominant tetrahedral coordination of Ti atoms in titanosilicates has been inferred from neutron diffraction,[14,15] the narrow peak at 4967 eV in XANES spectroscopy,[16] combined with a narrow absorption band at 225 nm in the diffuse reflectance UV spectrum[17] and 960 and 1024 cm^{-1} bands appearing in IR and Raman spectroscopy.[5,18−20] The fact that Ti isotopes are silent in NMR, combined with the low Ti content of catalytically active titanosilicates, results in the inability of NMR techniques to provide any useful information on the coordination of Ti atom. In view of the above comments, it is evident that there is a need for experimental techniques that could specifically probe Ti atoms in the solid. Electrochemistry of a zeolite modified electrode has

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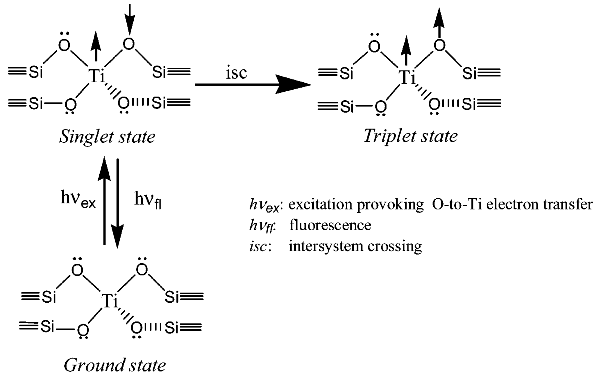
Scheme 1. Possible Excited States of Porous Titanosilicates



revealed the presence of a single Ti atom site in TS-1 and two different populations in Ti/Beta zeolites.[21−25] Unfortunately, electrochemical techniques are limited by the fact that they only report on the shallow outermost boundary of a zeolite particle and this region is most likely to contain specific Ti atoms different from the predominant Ti population present in the bulk particle.

Recent studies have shown that photoluminescence spectroscopy can be applied to determine the distribution of Ti atom in titanosilicates.[26−28] The photoluminescence has been ascribed as arising from the emissive Ti(III) → Ti(IV) transition, Ti(III) being generated from Ti(IV) upon excitation through ligand-to-metal photoinduced electron transfer. A controversy about whether the emission of tetrapodal "closed" Ti(OSi≡)$_4$ appears at ~490 or 390 nm has recently been issued.[26,29]

Although photoluminescence is an extremely sensitive spectroscopy that can be very useful in many instances, it suffers from the general limitation that it cannot report on the fraction of excited states that decay through radiationless pathways or on the existence of any photogenerated nonemissive transient species (Scheme 1).[30,31] Thus, upon light excitation a commonly occurring process is a "spin flip" of unpaired electrons. This process termed as intersystem crossing leads to a new species in a spin manifold different from the singlet state (Scheme 1). Triplet excited states having two unpaired electrons with parallel spins, as those arising from intersystem crossing from the singlet, have considerably longer lifetimes (several orders of magnitude) than singlet transients.[30,31] Triplet species, if formed, could not be detectable by photoluminescence spectroscopy simply because they do not emit. The same lack of fluorescence detection applies to any other secondary species generated from the initial emitting singlet excited state.

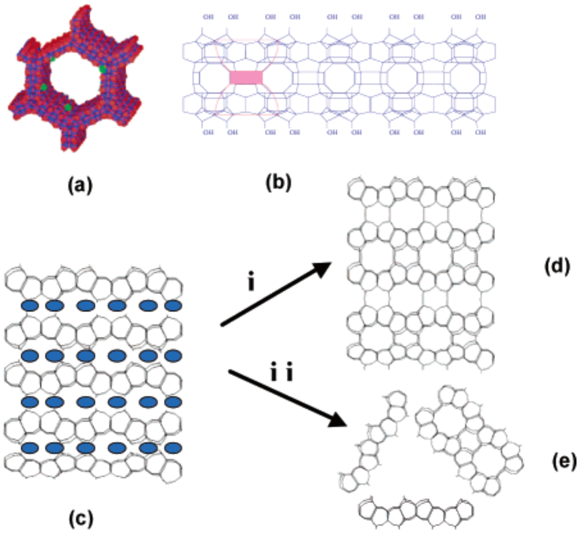


Figure 1. Crystal structure of the Ti-containing zeolites: MCM-41 (a), ITQ-2 (b), preferrierite (c), ferrierite (d), and ITQ-6 (c). (i) Calcination. (ii) Swelling and sonication.

A much more versatile photochemical technique is laser flash photolysis.[32] This technique has been adapted to the study of solid opaque samples by monitoring after a laser pulse the changes of the diffuse reflectance of the solid in the submillisecond time scale.[33] In this time-resolved, diffuse-reflectance, laser flash photolysis technique, species having a distinctive optical spectra in the available UV−vis region (250−800 nm) can be detected, even if they do not emit. In the present study, we provide the first laser flash photolysis transient spectra of porous titanosilicates having activity as oxidation catalysts. These transient spectra provide spectroscopic evidence for the presence of other photogenerated titanium species decaying in the microsecond time scale never detected previously in any fluorescence study. Our observation opens the way to kinetic measurements based on the laser flash that can eventually be of relevance in catalysis.

Results and Discussion

The samples that are the subject of the present study include Ti/preferrierite, Ti/ferrierite, Ti/ITQ-6, and Ti/ITQ-2; all four samples exhibit high catalytic activity for alkene epoxidation by organic hydroperoxides.[2] Figure 1 shows the crystal structure of the Ti-containing zeolites used in the present study. This series was rationally selected to have a consistent set of titanosilicates. Starting from the layered Ti/preferrierite and

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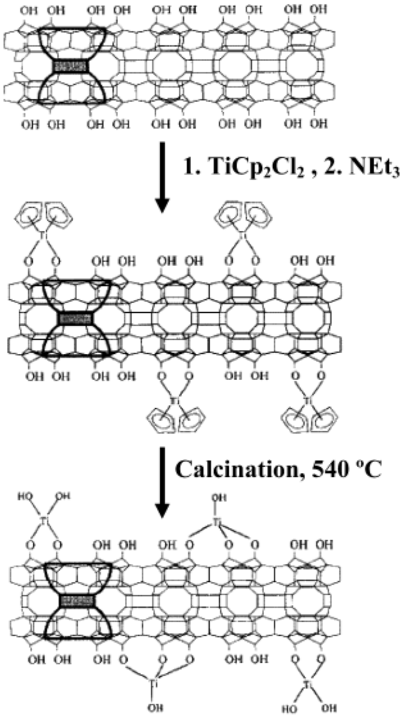
Scheme 2. Illustration of the Grafting of Titanium Atoms on the ITQ-2 Surface[a]



[a] $TiCp_2Cl_2$ corresponds to titanocene dichloride.

depending on the treatment, two samples are derived. The relationship between these crystalline titanosilicates is depicted in Figure 1. Microporous Ti/ferrierite is obtained by calcination of Ti/preferrierite (i in Figure 1), and the resulting solid has a crystal structure isomorphic with ferrierite, characterized by an array of parallel 10-membered ring channels. Novel Ti/ITQ-6 is a delaminated zeolite obtained by sonication of Ti/preferrierite after it is swollen through ion exchange with cetyltrimethylammonium, and its structure is formed by disordered layers of preferrierite (ii in Figure 1). The Ti/ITQ-6 was also calcined in the presence of air to decompose completely the organic quaternary ammonium ions. Thus, the three samples are synthetically closely related either as precursor (Ti/preferrierite) or derived after alternative treatments (Ti/ferrierite and Ti/ITQ-6). It is therefore of interest to correlate the Ti atom distribution of these samples to determine possible variations or similarities. Ti/ITQ-2 is a delaminated zeolitic material analogous to Ti/ITQ-6, but with a different layer crystal structure (Figure 1). Ti/ITQ-2 is obtained by delamination of the layered precursor of MCM-22, but in this case Ti atoms in Ti/ITQ-2 have been introduced on the silicate layer by grafting dichloro titanocene on the silanol groups[34] and subsequent calcination (Scheme 2).

For the sake of comparison, a sample of mesoporous titanosilicate MCM-41 that has been submitted to exhaustive silylation of the silanol groups (Ti/MCM-41-(sil))[29] has also been included in the study. The reason Ti/MCM-41(sil) was also considered here is because it has been shown that Ti/MCM-41(sil) exhibits the most intense titanium fluorescence among a series of related Ti/MCM-41, and that the intensity of the emission correlates well with the catalytic activity for alkene epoxidation.[29] Table 1 lists the main analytical and physicochemical parameters of the titanosilicates studied. The low Ti content of the samples subject to study is noteworthy, as that is characteristic of the solids employed as oxidation catalysts.[2]

Table 1. Analytical and Textural Properties of the Titanosilicates Studied in the Present Work

sample	Ti (%)[a]	particle size (μm)	S_{BET} ($m^2\ g^{-1}$)	V_{micro} ($cm^3\ g^{-1}$)
Ti/ferrierite	1.37	flat 0.5 × 0.5	278	0.12
Ti/ITQ-6	0.65	0.2	591	0.025
Ti/ITQ-2	0.7	flat 0.5	806	0.009
Ti/preferrierite	1.37	flat 2 × 5	*b*	*b*
Ti/MCM-41	2.0	> 0.1 spherical	805	0.44

[a] In weight percent as TiO_2. [b] Not measurable.

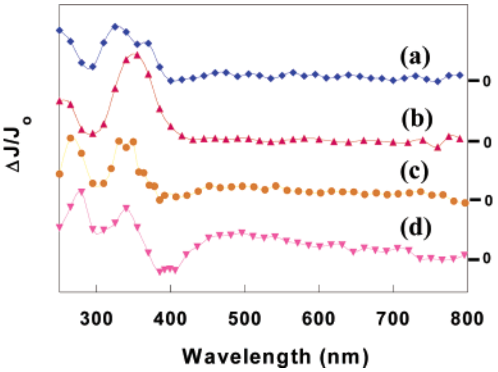


Figure 2. Transient diffuse reflectance UV−vis absorption spectra of Ti/preferrierite (a), Ti/ferrierite (b), Ti/ITQ-6 (c), and Ti/MCM-41(sil) (d) recorded 10 μs after 266 nm laser excitation. The spectra have been shifted in the vertical axis for clarity.

All the titanosilicates exhibit a transient signal decaying in the submillisecond time scale upon excitation with a laser operating at 266 nm. The transient spectra plotted as the relative variation of the detector intensity ($\Delta J/J_0$) versus time recorded a few microseconds after laser excitation of nitrogen-purged samples are shown in Figure 2. Relevant to the following discussion is that the range of wavelengths available to our laser flash photolysis setup covers the UV region where the ground-state absorption of isolated Ti atoms occurs (~220 nm). The emissive ligand-to-metal charge-transfer state of Ti/MCM-41 (sil) has been shown to live about 10 ns.[29] Therefore, the transient spectrum shown in Figure 2 for Ti/MCM-41 (sil) cannot correspond to the emissive primary singlet charge transfer state, but to other Ti species that are much longer lived. Similarly, the emission lifetime of other titanosilicates has been measured also in the nanosecond time scale.[27,28] Hence the time-resolved spectra shown in Figure 2 must correspond in all cases to other Ti transient species that have never been previously reported for titanosilicates. Blank controls using all silica ITQ-2 and MCM-41 do not give any transient signal upon 266 nm excitation. Given that different sources of Ti atoms give identical transient spectra, it is unlikely also to attribute the origin of these transients to impurities from the Ti source.

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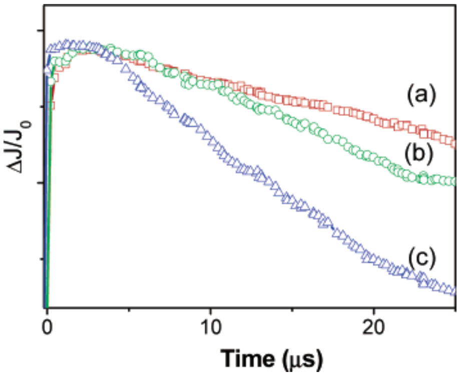
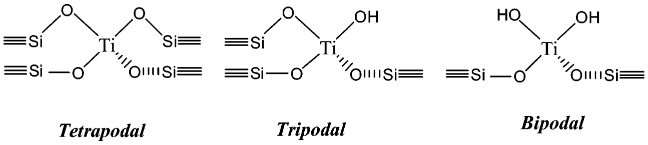


Figure 3. Decays monitored at 260 (a), 340 (b), and 500 (c) nm for Ti/preferrierite after a 266 nm laser pulse.

Scheme 3. Different Types of Ti Atoms Depending on Its Bonding to the Silicate Framework



Inspection of the transient diffuse reflectance spectra shown in Figure 2 reveals common spectroscopic features present in all the titanosilicates. There are two intense, sharp absorption bands at about 220−260 and 330−360 nm accompanied by a structureless, broad absorption from 400 to 800 nm with smaller intensity. Comparison of the normalized decays monitored at the corresponding λ_{max} indicates that for each sample they correspond to at least three different transient species. Obviously, none of these three species has ever been anticipated on the basis of photoluminescence studies (Figure 3). Kinetic analysis of the temporal profiles is complex, and the decays cannot be fitted to a monoexponential equation. Better fits result when the temporal profiles are adjusted to two consecutive exponential terms. This fact is common for photochemical studies in heterogeneous media and is attributed to the existence of a distribution of sites in the solid.

Importantly, remarkable differences are observed in the intensity of these three transients from one sample to other. On the basis of the previous knowledge on the distribution of tetrahedral Ti atoms in various populations depending on the number of covalent bonds connecting it to the framework (Scheme 3)[2] and their different photoluminescence spectra, we propose that differences in the transient spectra recorded for each sample reflect differences in the distribution for each sample of framework Ti atoms among different coordination spheres.

For some samples in which transient absorption bands do not obscure the measurement, two other features, namely, a growth of the UV absorption band at 230 nm and fluorescence recovery at 390 nm, were observed. Particularly clear was the case of Ti/preferrierite. For this sample the decay rate of the 365 nm band coincides with the growth rate in the deep UV as measured at 250 nm (Figure 4).

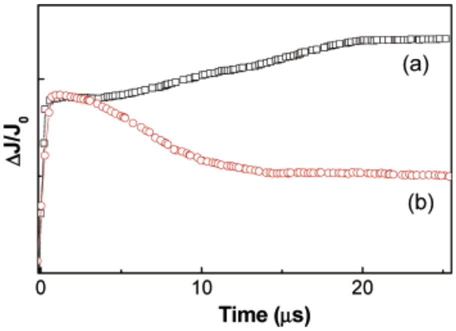


Figure 4. Growth and decay monitored at 250 (a) and 365 (b) nm, respectively, for the Ti/preferrierite sample after a 266 nm laser pulse.

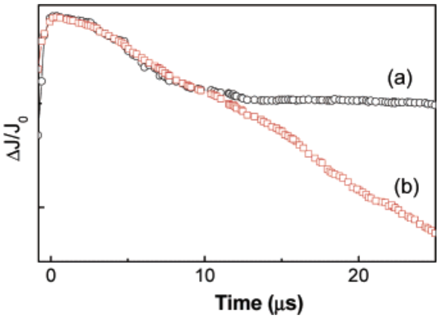


Figure 5. Oxygen quenching of the 365 nm band for Ti/preferrierite upon 266 nm excitation: N_2 (a) and O_2 (b).

On the basis of the ground state diffuse reflectance of titanosilicates which show a simple band at 230 nm, we attribute the growth of the absorption below 250 nm to the recovery of the ground state of the Ti atoms and the 365 nm band to the nonemissive triplet excited state of the ligand-to-metal charge-transfer Ti(III)(↑)−O(•)(↑)− species. This triplet state would be generated from the emissive singlet LMCT state through intersystem crossing as depicted in Scheme 1 and would be much longer lived than the singlet. A decay on the microsecond time scale is not unreasonable for this type of transient. In support of our interpretation is the oxygen's influence on the decay of this band (Figure 5). This triplet state of the charge-transfer species should decay to the initial ground state without any “net” photochemical change.

For the other samples, the kinetic analyses showing the recovery of the initial Ti ground state absorption were not so evident. We suggest that this is due to the presence of transient absorption bands in the 220−250 nm region superimposed over that corresponding to the ground state of Ti atoms (see Figure 2). These transient absorption bands would overlap and obscure the observation of ground state recovery that is occurring in the limit of the photomultiplier response. However, it has to be noted that steady-state diffuse reflectance UV spectra of the samples after laser flash photolysis do not show significant differences with respect to the initial spectra indicating that no permanent products are formed in the photochemical study.

Concerning the nature of the species responsible for the broad 450−800 nm absorption band, we notice the similarly of this featureless band with that recorded previously for photochemically generated “trapped” electrons in zeolite framework devoid of Na^+ atoms as well as others in amorphous TiO_2 samples.[35−37] The photogeneration of electrons and holes upon UV irradia-

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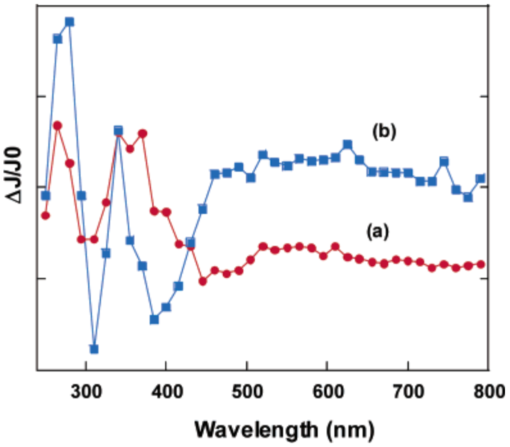

Figure 6. Transient diffuse reflectance UV−vis spectra of Ti/ITQ-2 recorded 10 μs after 266 nm laser excitation before (a) and after (b) calcination. Note the increase in the 400−800 broad band upon calcination.

tion is a general phenomenon in semiconductors, and the UV−vis spectra of these electrons are generally very broad bands in the 450−800 nm region of the spectrum. In agreement with this assignment, exposure of the titanosilicates to dichloromethane vapors causes a remarkable diminution of the intensity of this band. CH_2Cl_2 is known to be a good trap for electrons in zeolites. One possibility is that instead of a ligand-to-metal electron transfer the electron ejected from oxygen atoms is delocalized on the zeolite or on metal oxide conduction band. Delocalized electrons could indicate the presence of a nonframework Ti_xO_y cluster in the solid. In this regard it is known that TiO_2 aggregates are nonemissive or extremely weak lumophores and would be hardly detectable by emission spectroscopy.[38] Not surprisingly, TiO_2 aggregates, if present, would not be observed by photoluminescence.

In support of this correlation between the 450−800 nm band attributable to electrons and the presence of nonframework Ti species is the fact the initial Ti/preferrierite and highly crystalline Ti/ferrierite do not present this band. These two solids should only contain isolated Ti atoms lacking amorphous TiO_2. In contrast, the 450−800 nm band is already observed for delaminated Ti/ITQ-6, and its relative intensity increases significantly upon calcination over extended periods (Figure 6). This indicates that, starting from Ti/preferrierite, migration of a Ti atom from framework to out-of-framework positions and aggregation occur to a certain extent during the process of delamination, especially upon calcination. Ti/MCM-41 also exhibits a significant intensity for this band (see Figure 2). Importantly, since the catalytic activity of titanosilicates has been related to isolated tetrahedral Ti atoms[2], we propose that the absence of this 450−800 nm band can be taken as a simple spectroscopic feature to assess the absence of Ti aggregates. The absence of these TiO_2 aggregates would be related to high catalytic activity of Ti atoms of the solid. Interestingly for Ti/ITQ-2 prepared by grafting Ti atoms onto all-silica ITQ-2 layers, a very weak transient absorption spectrum exhibiting a broad 450−800 nm band was recorded. This indicates that Ti/ITQ-2 contains predominantly nonframework Ti aggregates versus isolated ≡Ti−O−.

Conclusions

We have shown that laser flash photolysis can be a valuable technique applicable to the characterization of Ti atoms in titanosilicates giving new spectroscopic information not previously provided by any other technique. Thus, upon light absorption and generation of an emissive singlet LMCT state, other secondary species decaying in the microsecond time scale have been clearly observed for the first time. We attribute them to a triplet LMCT state and to ejected electrons. The proportion of these two transients clearly varies depending on the nature of the titanosilicate. The relative intensity of the triplet LMCT versus ejected electrons is proposed to be a valid criterion of the presence of isolated, tetrahedral Ti atoms. Given the difficulty of determining Ti atoms in titanosilicates, our report can open a new methodology for characterization of these Lewis acid catalysts.

Experimental Section

Laser flash photolysis experiments were carried out using the fourth (266 nm, 20 mJ pulse^{-1}) harmonic of a Surelite Nd:YAG laser for excitation (pulse $\leq$ 10 ns). The signal from the monochromator/photomultiplier detection system was captured by a Tektronix TDS640A digitizer and transferred to a PC computer that controlled the experiment and provided suitable processing and data storage capabilities. Fundamentals[33] and details[39] of a similar time-resolved laser setup have been published elsewhere.

Preferrierite was prepared by hydrothermal crystallization from a solution of 2.3 g of Al_2O_3 and 16.16 g of water, to which 9.24 g of NH_4F, 11.56 g of water, 3.33 g of HF (50% weight), and 26.00 g of 4-amino-2,2,6,6-tetramethylpiperidine were slowly added. The resulting liquor was stirred strongly during 1 h, and then 10.00 g of SiO_2 and 0.5 g of $Ti(OiPr)_4$ were added, the stirring was continued during 2 h, and the resulting sol−gel was autoclaved at 135 °C and 1 atm of pressure for 10 days. The preferrierite formed was filtered and washed with deionized water and dried at 60 °C for 12 h.

Ferrierite was obtained from a preferrierite sample by calcining at increasing temperatures (ramp 5 °C/min) up to 650 °C. Initially the sample was flushed with a nitrogen flow that was progressively changed to oxygen. The finally temperature was maintained for 12 h to complete the template degradation.

ITQ-6 was prepared from a preferrierite sample (2 g) that was submitted to ion exchange using 8 g of MilliQ water, 40 g of a solution of CTMA (25% weight), and 40 g of a solution of TPA (40% weight). The suspension is refluxed for 16 h at 95 °C. After this time, the solid is recovered by centrifugation and dried at 60 °C for 12 h. The swollen preferrierite was dispersed and treated with ultrasound for 12 h. Then the suspension was acidified up to a pH $\leq$ 2, and centrifuged. Finally the ITQ-6 was washed, dried at 60 °C for 12 h, and calcined at 580 °C in air flow.

ITQ-2 was prepared from the lamellar precursor MWW, that was treated with $CTMA^+Br^-$ to swell the solid before submitting it to sonication for prolonged periods as described for ITQ-6. Then, the product was recovered by centrifugation and washed. The zeolite ITQ-2 was obtained by calcination at 540

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°C. Ti was grafted on the surface of ITQ-2 by the procedure illustrated in Scheme 2. This procedure consists of dehydrating 10 g of zeolite at 300 °C under 1023 Torr over 2 h and adding a solution containing an appropriate amount of titanocene dichloride in 90.0 g of CH_2Cl_2. The suspension was stirred for 1 h at room temperature under inert atmosphere. Subsequently, triethylamine dissolved in 10 g of $CHCl_3$ giving a ratio $NEt_3/TiCp_2Cl_2 = 1$ was added. The suspension changed from orange-red to yellow-orange indicating a variation on the coordination around the Ti atoms. The solids were recovered by filtration washed with CH_2Cl_2 and calcined at 540 °C for 1 h in N_2 and then 6 h in air. The resultant Ti/ITQ-2 has the same textural and structural characteristics that the initial ITQ-2 zeolite has.

MCM-41 was prepared by stirring magnetically an aqueous ammonia solution of $CTMA^+Br^-$ to which tetraethoxyorthosilicate (TEOS) and $Ti(OiPr)_4$ were added dropwise. The resulting liquor was heated at 80 °C for 4 days in a sealed polypropylene flask. The molar composition of the precursor gels was: 1.00 TEOS/0.05 $Ti(OiPr)_4$/114 H_2O/8.0 NH_3(20 wt %)/0.12 CTABr. The resulting as-synthesized Ti/MCM-41 was collected by filtration and the template decomposed by heating the solid gradually up to 450 °C under air. Exhaustive silylation of the silanol groups of Ti/MCM-41 was accomplished after removing the template by refluxing at 110 °C a suspension of the solid (1 g) in toluene (20 mL) containing hexamethyldisilazane (2 g) under Ar atmosphere for 24 h.

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