Probing the Titanium Sites in Ti−MCM41 by Diffuse Reflectance and Photoluminescence UV−Vis Spectroscopies

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Ti−MCM41 catalysts prepared by anchoring titanocene onto the inner walls of MCM-41 exhibit high catalytic performance in the epoxidation of cyclohexene and in oxidation of bulky cyclic and aromatic compounds because of the presence, as revealed by means of XANES and EXAFS spectroscopy, of a high concentration of accessible, well-spaced, and structurally well-defined Ti tetrahedral active sites (see Maschmeyer et al. *Nature,* **1995,** *378,* 159). These results have prompted us to study the nature and the coordinative environment of Ti active sites in MCM-41 also by means of diffuse reflectance UV−visible and luminescence spectroscopy. We revealed, particularly by means of photoluminescence spectroscopy, the presence of more than one kind of tetrahedral titanium site.

Introduction

There is a growing interest in titanium-containing zeolitic catalysts for a wide range of selective oxidations of alkenes (to epoxides) and of alkanes (to hydroxylated products).[1−7] Thus, in addition to surface immobilization of titanium oxide on amorphous silica (as utilized in some industrial processes), titanium ions have been incorporated also in the microporous framework of, e.g., ZSM-12,[8] ZSM48, [9,10] zeolite β,[11] and silicalite I and II (i.e., TS-1 and TS-2, respectively, introduced by Enichem Company)[1] and into the framework of mesoporous silicas such as MCM-41[4,5,12] and MCM-48.[13] Additionally, a recent report by Maschmeyer et al.[14] introduced a novel surface grafting methodology that allows placement of atomically dispersed, tetrahedral titanium sites onto the inner walls of mesoporous MCM-41.

It is by now widely accepted that the active site for epoxidations in all of the above materials is of tetrahedral nature. Catalytic and spectroscopic studies have revealed that the surface sites need to be isolated and tetrahedral to give the best activity/selectivity performance as the presence of titanium dimers or oligomers is thought to accelerate decomposition of the peroxide and octahedrally coordinated titanium is inactive for the epoxidation of alkenes since it lacks free coordination sites.[2,14−16]

For surface-grafted Ti−MCM41, it was possible to establish unequivocally by in situ XAS (X-ray absorption spectroscopy) that the *averaged* structure of the catalytic site is tetrahedral, containing around three Ti−O−Si bonds.[14,16] However, the fundamental question (which might also have some bearings on catalytic performance) of whether all of the grafted tetrahedral titanium centers are of the same nature, or whether they might be composed of a mixture of different tetrahedral species, still needs to be addressed.

We have endeavored to clarify this question using UV−vis reflectance and photoluminescence spectroscopies to study the titanium environment in surface-grafted Ti−MCM41 catalysts. These techniques have been applied previously in a related field (i.e., the study of anchored titanium oxide catalysts[17−19] and TS-2[20]) notably by Anpo and co-workers. Photoemission spec-

tra containing features in the range of 400−600 nm were reported and interpreted as arising from isolated tetrahedral titanium centers. However, only one corresponding UV−vis reflectance spectrum was published, containing a broad band centered around 300 nm, which indicated at least some disturbance to the tetrahedral environment.[15,21−24] This is most likely due to the presence of Ti−O−Ti connectivities and/or five or six-coordinated titanium species. Materials of a more well-defined nature might result in more detailed spectral information.

Thus, we report investigations of two differently prepared Ti−MCM41 catalysts, which have both been characterized extensively by in situ X-ray absorption and UV−vis spectroscopies as well as by catalytic evaluations.[14,16]

Experimental Section

Ti−MCM41 catalysts containing close to 2 wt % Ti have been prepared by following two different preparation routes. The one, labeled Ti−MCM41[Ar], was obtained with the strict exclusion of water under an argon atmosphere using conventional Schlenk line techniques, dehydrating the MCM41catalyst precursor at 250 °C under a dynamic vacuum prior to titanium loading.[14] The other, labeled Ti−MCM41[air], was prepared under atmospheric conditions without MCM41 pretreatment.

Diffuse reflectance UV−vis spectra were recorded by means of a Perkin-Elmer (Lambda 19) spectrometer equipped with an integrating sphere attachment and photoluminescence spectra by using a SPEX FLUOROLOG-2 1680 spectrometer. The powdered samples were placed in quartz cells that were permanently connected to a vacuum line (ultimate pressure $\leq$ 10^{-5} Torr) for in situ experiments.

All the samples were calcined in 100 Torr of O_2 at 550 °C for 5−10 h in order to eliminate the organic fraction of the Ti−cyclopentadienyl complexes anchored onto the surface of MCM41; successively, the samples were also evacuated at 550 °C.
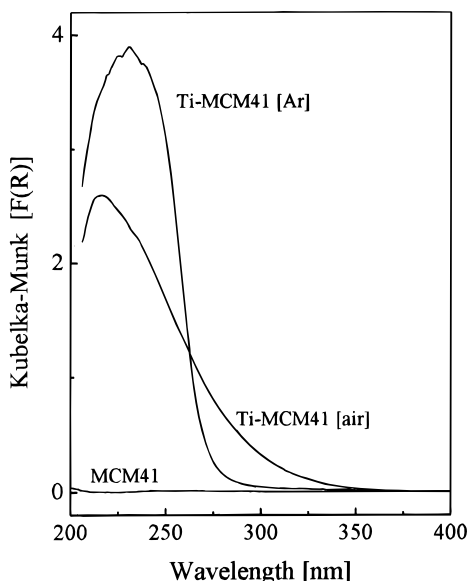
Results and Discussion

Diffuse Reflectance Spectra. In Figure 1 we show the diffuse reflectance UV spectra (collected in situ after calcination at 550 °C) of the two Ti−MCM41 catalysts and, for comparison, of the purely siliceous MCM-41. Ti−MCM41[Ar] has a very intense and narrow UV absorption centered at around 230 nm,

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Figure 1. Diffuse reflectance spectra of the different Ti−MCM41 catalysts and of pure MCM41.

Figure 2. Photoemission spectra of Ti−MCM41[Ar] obtained by exciting the sample at 298 K with different wavelengths. The spectrum of pure MCM41 is also reported for comparison.

which indicates that the titanium exists mainly in tetrahedral coordination.[23−25] It is well-known, in fact, that bands in the 210−240 nm region arise from oxygen to tetrahedral titanium-(IV) ligand to metal charge transfer[21−27] (LMCT) as represented in the eq 1 (from left to right).

$$Ti^{4+}/O^{2-} \underset{- h\nu_{emission}}{\overset{+ h\nu_{excitation}}{\rightleftharpoons}} Ti^{3+}/O^{-} \qquad (1)$$
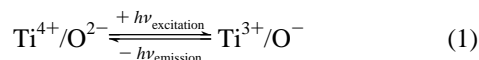
[The first Laporte-allowed CT for TiX$_4$ complexes is related to $\pi t_1 \rightarrow$ de or $(\pi+\sigma)t_2 \rightarrow$ de electron transfer.[28]]

Even though the position of the maximum of the band cannot be detected precisely for Ti−MCM41[Ar] because of the very high $F(R)$ values that are close to the limit of applicability of the Kubelka−Munk function,[29] we demonstrated unambiguously that this band is affected by the presence of adsorbates. It is, in fact, gradually replaced, upon water and/or ammonia adsorption, by new broader bands at $\lambda \geq 240$ nm, and this was explained as due to *tetrahedral Ti(IV) sites that undergo a coordination change to octahedra* by insertion of water (or ammonia) molecules as extraligands.[25−27] These results are consistent with reported X-ray absorption data (XANES and EXAFS).[14]

For the Ti−MCM41[air] sample the absorption is not only of lower intensity, with the peak centered around 217 nm, it also exhibits a shoulder at ca. 230 nm and an additional broad shoulder in the range of 250−320 nm; this latter feature would be consistent with a decrease in the tetrahedral character of the titanium environment[21−23] monitoring an incipient oligomerization of Ti^{4+} species (also observed in the XANES[30]). One might reasonably advance, when comparing the shapes of the two spectra, that they are of composite nature, i.e., in addition to the Ti−MCM41[air] broad shoulder in the range of 250−320 nm, both consist of at least two different contributions (at 217 and 230 nm) giving rise to the different overall band profiles.

However, it has been revealed that in addition to a band at 200−210 nm, a strong shoulder at 230 nm is always present also in dehydrated Ti−silicalites even in the case of samples in which, as suggested by accurate EXAFS, XANES,[24,27] XPS, and ^{1}H and ^{29}Si NMR[24] investigations, virtually all the titanium exists in tetrahedral coordination. Le Noc et al. suggested that the two bands at 200−210 and 230 nm are due to two different framework sites [Ti(OH)(OSi)$_3$ and Ti(OSi)$_4$, see structures **A** and **C** in Scheme 1], which have different TiOSi angles, the
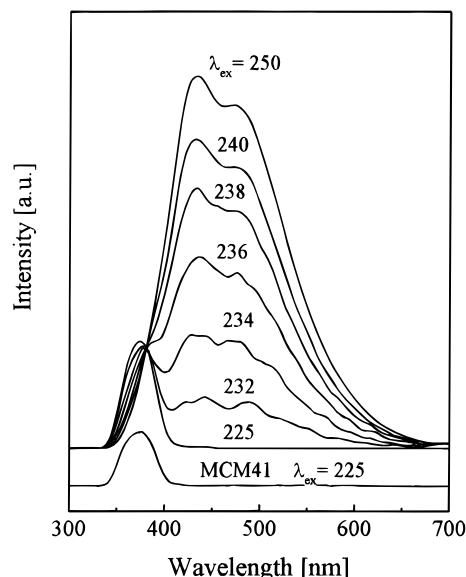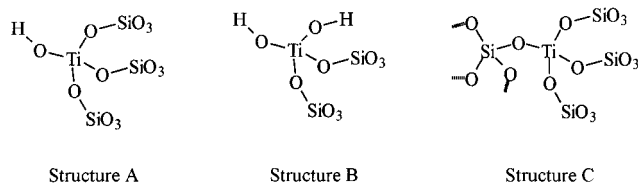
sites with the larger angles being responsible for the band at lower wavelengths.[24]

To probe these different contributions more deeply, we examined the Ti−MCM41 materials with photoluminescence spectroscopy, which allows monitoring of the relaxation of excited states by collecting the emitted radiation (eq 1, from right to left).

Photoluminescence Spectra. A series of emission spectra at 298 K of Ti−MCM41[Ar] by exciting with different wavelengths are shown in Figure 2. With an excitation of 225 nm only one band at 372 nm is observed in the emission spectrum. However, since this feature is also found in the emission spectrum of purely siliceous MCM41, we conclude that it is not directly related to the presence of titanium, and so it is not discussed further. With an excitation of 232 nm we observe only a weak, broad, and composite absorption in the range 400−600 nm, but by exciting between 234 and 250 nm distinct features emerge. As the emission intensities are greatest with excitation at 250 nm for both the Ti−MCM41[air] and the Ti−MCM41[Ar] samples, the emission spectra of the two compounds are compared using this excitation, cf. Figure 3.

In the emission spectrum of Ti−MCM41[Ar], two overlapped bands at 430 and 480 nm are clearly distiguishable (curve a). These bands have shoulders at ca. 400 and 550−600 nm. For Ti−MCM41[air] two main overlapped bands at 430 and 490 nm are observed, the latter of which is asymmetric in the high-wavelength region (550−600 nm), indicating the presence of a third component. However, the high-wavelength component at 550−600 nm is more intense in the case of Ti−MCM41-[air], and this suggests, according also to the reflectance spectra of Figure 1, that this small contribution to the overall photoluminescence might be due to oligomerized Ti^{4+} sites.

To probe whether the bands at 480 nm (Ti−MCM41[Ar]) and 490 nm (Ti−MCM41[air]) are of the same nature, we collected excitation spectra (Figure 3) with $\lambda_{em} = 480$ and 490

SCHEME 1

Structure A   Structure B   Structure C
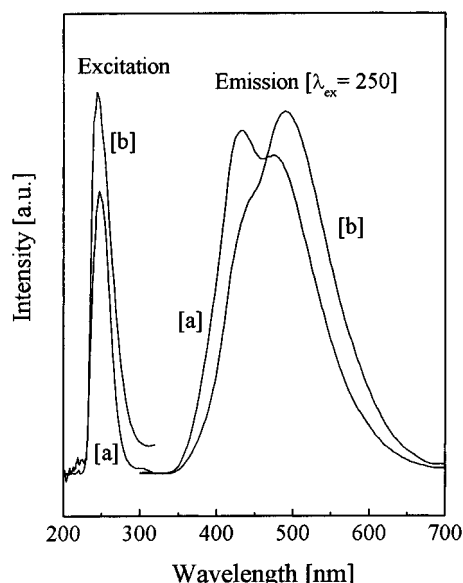
Figure 3. Photoluminescence spectra of (a) Ti−MCM41[Ar] and (b) Ti-MCM[air]. The emission spectra were obtained by exciting the samples with $\lambda_{ex} = 250$ nm; the excitation spectra at $\lambda_{em} = 480$ for Ti−MCM41[Ar] and at $\lambda_{em} = 490$ nm for Ti−MCM41[air] were obtained by varying λ_{ex} from 200 to 350 nm.

nm. Both excitation spectra contained one band centered at 245 nm for the two materials, strongly indicating that they stem from similar environments, the shift of 10 nm being caused by the overlap of peaks of different relative intensity.

Hence, for a material that contains almost exclusively tetrahedral titanium sites, as is the case in Ti−MCM41[Ar], we observe that these sites emit different signals in the range of 400−600 nm when excited at $\lambda_{ex} = 250$ nm. This can be attributed to oxygens in different environments, i.e., the identification of several components in the photoemission spectrum might be due to the presence of different oxygen sites (cf. eq 1). Since with different methods of preparation the relative intensities of these components vary, we suggest that they *mainly* stem from titanium in different tetrahedral environments and propose that a mixture of titanium siloxy−hydroxy species is present (cf. Scheme 1). Recent quantum-mechanical (DFT) cluster calculations[31] indicate that there is very little difference in energy (ca. 20 kJ/mol) between the structures in Scheme 1, underlining the potentiality of their coexistence.

Although the X-ray absorption spectra of the grafted Ti−MCM41 catalysts suggest (on the basis of second-shell analysis) that on average three silicon atoms per titanium are present throughout the grafting, thus establishing structure A of Scheme 1 as the most plausible of the averaged structures, the technique is not sensitive enough to discriminate between mixtures of this dominant species with other oxidic tetrahedral species.

It is unlikely that there are significant amounts of sites with structure **C** given that the titanium centers are grafted onto the surface, necessitating a major surface rearrangement to accommodate the fourth Ti−O−Si linkage.

However, structure **B** is an attractive suggestion in accordance with reports of limited initial leaching of titanium/silica catalysts. Recently, Abbenhuis et al.[32] have shown that homogeneous silsesquioxane-based model compounds in which titanium coordinated to only two siloxy groups are likely to hydrolyze (i.e., leach) under reaction conditions, whereas titanium centers coordinated to three siloxy groups are much more stable. The variations in the photoemission between Ti−MCM41[air] and Ti−MCM41[Ar] probably occur due to changes of the relative populations of various species (with a limited contribution, in the latter case, of oligomers). Hence, the additional sensitivity

of photoluminescence spectroscopy when compared to other techniques might serve eventually to evidence the heterogeneity in catalytic sites.

Further studies to elucidate the precise nature of the different Ti sites, using probe molecules, model compounds, and calculational methods, are currently underway to assess the correlation between **A** and **B** structures and the two main photoluminescence peaks.

In addition, the photocatalytic activity of such materials is being examined.

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