Experimental and Theoretical Studies on Structure−Reactivity Relationships of Titanium-Modified Silicas in the Hydrogen Peroxide-Promoted Oxidation of Cyclohexene

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Theoretical calculations demonstrate that the presence of ligands with different basicity modifies the Lewis acidity (expressed both as the LUMO energy and the enthalpy of coordination of a NH_3 molecule) of the active centers in silica-supported titanium catalysts. Several catalysts containing different organic ligands bonded to the titanium centers have been prepared, characterized, and tested in the benchmark reaction of cyclohexene with hydrogen peroxide. Both the activity and the selectivities of the catalysts depend on the relative basicity of the ligands and their variation is proportional to the calculated Lewis acidity, expressed as the LUMO energy. With more basic ligands, hydrolysis of the epoxide to diol occurs to a lesser extent at the expense of the catalytic activity and the epoxidation/allylic oxidation selectivity, showing the coincidence of the active sites for epoxidation and hydrolysis reactions.
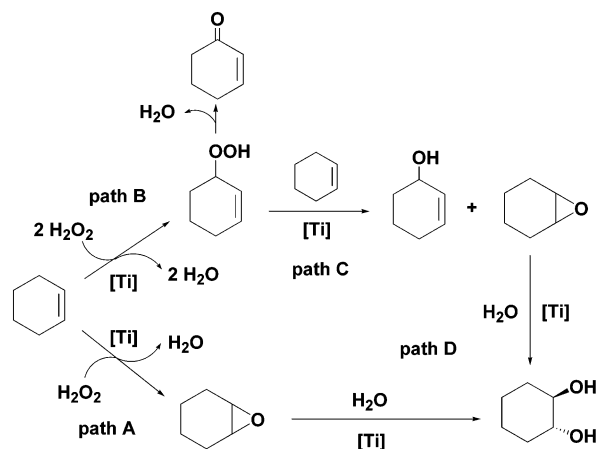
Introduction

Epoxidation is one of the most important reactions in organic synthesis, even from an industrial point of view. Among the possible oxidants, hydrogen peroxide[1] is one of the more suitable from both economic and environmental[2] considerations. Although several kinds of catalysts are able to promote epoxidation with hydrogen peroxide, titanium heterogeneous catalysts are probably the most studied, following the success of TS-1 (titanium silicalite) as catalyst for the epoxidation of small olefins.[3]

However, catalytic epoxidation with hydrogen peroxide is usually a complicated process due to the concurrence of several reactions. In addition to the direct epoxidation with hydrogen peroxide (path A in Scheme 1), at least three more reactions take place.[4] The formation of free radicals leads to allylic hydroperoxides (path B), which can be used as oxidants for other epoxidation reaction with generation of equimolecular amounts of epoxide and allylic alcohol (path C). Moreover, the epoxide suffers hydrolysis (and in some cases solvolysis) (path D) due to the presence of water. The two different epoxidations, with H_2O_2 and allylic hydroperoxide, are only catalyzed by titanium centers. Although free radicals can be thermally or photochemically generated, their formation is also accelerated by titanium. Finally, the epoxide solvolysis is acid-catalyzed, but it is not clear whether titanium centers or other sites on the solid surface are responsible for this reaction, although the role of titanium seems to be important. Thus the control of the titanium environment should be the way to optimize the results of the epoxidation reaction.

In most of the titanium catalysts the modifications have been introduced on the surface, usually a silica-like surface. One

SCHEME 1

possibility is the postsynthesis modification of the catalyst, either to change the hydrophilic−hydrophobic character of the solid[5] or to introduce polar/basic groups.[6] Another strategy is the modification during the catalyst preparation, using functionalized monomers[7] or an appropriate synthesis medium.[8] A third strategy consists of the modification of the catalytic performance by addition of different substances (molecular sieves, inorganic salts, amines, ...) to the reaction medium.[9] However, a more suitable approach would seem to be the direct modification of the near environment of titanium.

In our approach to the preparation of titanium catalysts[10] the conservation of isopropoxy groups,[11] in contrast with the Shell catalyst[12] and other related solids,[13] allows their substitution by other organic groups. This possibility has been already demonstrated with diols, such as ethylene glycol or tartaric acid derivatives. This kind of modification varied the catalytic activity of this solid in epoxidation[14] and sulfide oxidation[15] with hydrogen peroxide.

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In this contribution we present the modulation of the catalytic activity by substitution of isopropoxy groups with molecules of different basic properties. First a prediction of the properties of the new titanium centers is carried out by theoretical calculations. The catalysts were then prepared, characterized, and finally tested in the cyclohexene epoxidation with aqueous hydrogen peroxide.

Experimental Section

Theoretical Calculations. The ab initio theoretical calculations were carried out using the Gaussian 98 program.[16] Full geometric optimizations of the catalyst models and the same models with one NH_3 coordinated molecule were performed within the Hartree−Fock theory framework, using the standard split-valence double-ζ 6-31G(d) basis set.[17] Thermodynamic parameters at 25 °C were obtained through frequency calculations at the same level. NBO analyses were carried out with the NBO 3.1 program,[18] as implemented in Gaussian 98. Lowest unoccupied molecular orbital (LUMO) cube files for the catalyst models were generated at the same theory level, and plotted with the GOpenMol program.[19]

Preparation of the Catalysts. All the silica-based solids were dried at 140 °C under vacuum for 12 h prior to any treatment or use as catalysts. Si−Ti(O^{i}Pr) was prepared by treatment of silica (Merck 60) with Ti(O^{i}Pr)$_4$ in toluene under reflux, as described previously.[10] Si−Ti(**OO**) was prepared under Ar atmosphere by treatment of Si−Ti(O^{i}Pr) (1.5 g) with decane-1,2-diol (1.3 mmol) in anhydrous toluene (25 mL) under reflux for 6 h. A 15 mL aliquot of the solvent was distilled off and the reaction mixture was cooled to room temperature. The solid was separated by filtration, washed with anhydrous toluene and dichloromethane, and dried under vacuum. Si−Ti(**ON**), Si−Ti(**NN**), and Si−Ti(**ONON**) were prepared by following the same procedure with (1R,2S)-α-[1-(methylamino)ethyl]benzyl alcohol (ephedrine), N,N'-diethylethylenediamine, and 1,4-bis-(dimethylamino)butane-2,3-diol, respectively.

Characterization of the Catalysts. Titanium analyses were carried out by plasma emission spectroscopy on a Perkin-Elmer Plasma 40 emission spectrometer. Carbon and nitrogen analyses were carried out on a Perkin-Elmer 2400 elemental analyzer. Infrared spectra were recorded on a Mattson Genesis Series FTIR spectrometer. Self-supported wafers were treated under vacuum ($<10^{-5}$ Torr) at 140 °C in a cell equipped with NaCl windows. Acidity was determined by calorimetry of NH_3 adsorption using a Setaram C80 differential microcalorimeter. Samples were evacuated at 150 °C for 2 h and ammonia was introduced in successive doses at the same temperature.

Catalytic Tests. All the catalysts were dried at 140 °C under vacuum for 12 h prior to use. The catalyst (200 mg) was added to a solution of cyclohexene (5 mL, 50 mmol), H_2O_2 (0.28 mL, 30%, 2.5 mmol), and ethylene glycol dimethyl ether (1 mL, internal standard) in *tert*-butyl alcohol (5 mL). The reaction mixture was heated at 80 °C for 24 h and monitored by GC (FID from Hewlett-Packard 5890 II; helium as a carrier gas, 20 psi; cross-linked methyl silicone column, 25 m × 0.2 mm × 0.33 μm; oven temperature program, 45 °C (4 min), 25 °C/min, 250 °C (2 min); retention times, internal standard 2.9 min, cyclohexene 3.5 min, cyclohexene oxide 6.5 min, 2-cyclohexenol 6.9 min, 2-cyclohexenone (from cyclohexenyl hydroperoxide decomposition) 7.3 min, *trans*-1,2-cyclohexanediol 8.7 min). The products were detected in the reaction mixture by ^{1}H NMR spectroscopy, identified in the chromatogram by comparison with authentic samples, and calibrated against the internal standard. After 24 h the catalyst was filtered off, washed
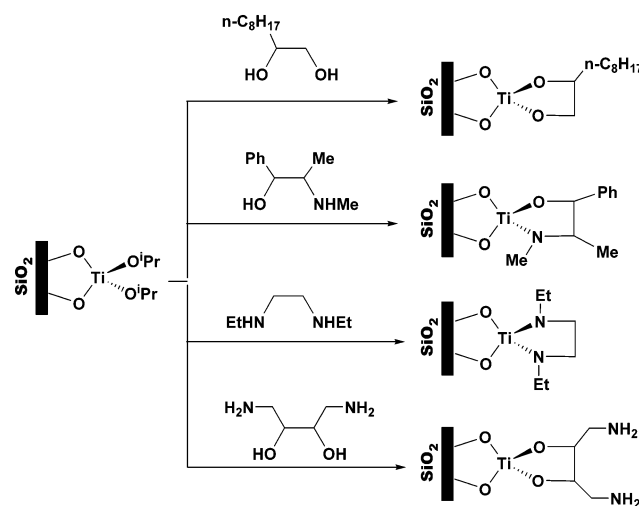
SCHEME 2

TABLE 1: Analysis of the Catalysts

| | mmol/g | | |
catalyst	Ti	C	N
Si−Ti(O^{i}Pr)	1.07	3.46	0.00
Si−Ti(**OO**)	1.10	9.46	0.00
Si−Ti(**ON**)	0.87	6.86	0.67
Si−Ti(**NN**)	0.85	4.57	0.90
Si−Ti(**ONON**)	0.89	6.23	1.42

with dichloromethane (5 × 5 mL), dried under vacuum, and reused under the same conditions. The absence of H_2O_2 in the final solution was confirmed by iodometric titration.

Results

Preparation and Characterization of the Catalysts. Initially, the chosen ligands for the preparation of the modified titanium−silica catalysts were decane-1,2-diol (**OO**), (1R,2S)-α-[1-(methylamino)ethyl]benzyl alcohol (ephedrine) (**ON**), and N,N'-diethylethylenediamine (**NN**). These ligands were made to react (Scheme 2) with the parent Si−Ti(O^{i}Pr) solid[10,11] in toluene under reflux, with distillation of the toluene/2-propanol azeotrope. A fourth ligand was further considered, by reasons explained in the discussion, namely, the N,N'-diethylethylene-diamine and 1,4-bis(dimethylamino)butane-2,3-diol (**ONON**), which was made to react with the Si−Ti(O^{i}Pr) under the same conditions.

The catalysts were first analyzed and the results are listed in Table 1. The carbon and nitrogen contents are in agreement with a partial (54−80%) complexation of titanium with the organic ligand. As we will see later, even if the complexation is not complete, the modification in catalytic activity and selectivity is so important that the nonmodified titanium centers seem to have very little participation in the activity of the solid, because of either lack of accessibility or presence in inactive form.

The presence of the organic ligands was confirmed by IR spectroscopy (Figure 1). The substitution of isopropoxy groups was shown by the disappearance of the typical bands at 1466−1452 and 1385−1375 cm^{-1}. Some new bands in the same zone appeared, coming from the hydrocarbon skeleton of the new ligands. A prominent band at 1670 cm^{-1} was obtained in the amine-containing ligands. In the case of Si−Ti(**ON**), the presence of the aromatic group of ephedrine is confirmed by the bands at 3068 and 3033 cm^{-1} (C$_{ar}$−H) and 1602 cm^{-1}

TABLE 2: Calculated Total Energies, Enthalpies (at 25 °C), Free Energies (at 25 °C), Coordination Energies of a NH_3 Molecule, and LUMO Energies of the Structures Described in This Work

structure	ΔE_0 (au)[a]	ΔH (au)[a]	ΔG (au)[a]	$\Delta H_{coor}(NH_3)$ (kcal mol^{-1})	E_{LUMO} (au)[a]	ΔE_{LUMO} (kcal mol^{-1})
Ti(**OO**)	−1807.44634	−1807.29848	−1807.35721		0.07529	0.0
Ti(**ON**)	−1787.59195	−1787.43145	−1787.49125		0.07658	0.8
Ti(**NN**)	−1767.73515	−1767.56215	−1767.62363		0.08024	3.1
Ti(**ONON**)$_{tet}$	−1995.56753	−1995.31572	−1995.38660		0.07970	2.8
Ti(**ONON**)$_{bip}$	−1995.56758	−1995.31546	−1995.37911		0.08725	7.5
NH_3	−56.18436	−56.14355	−56.16534			
Ti(**OO**)-NH_3	−1863.66304	−1863.47089	−1863.53415	−18.1		
Ti(**ON**)-NH_3 (N$_{ax}$)	−1843.80634	−1843.60161	−1843.66527	−16.7		
Ti(**ON**)-NH_3 (O$_{ax}$)	−1843.80563	−1843.60065	−1843.66363	−16.1		
Ti(**NN**)-NH_3	−1823.94691	−1823.74946	−1823.79284	−14.9		
Ti(**ONON**)-NH_{3-bip}	−2051.78265	−2051.48659	−2051.56213	−17.1		
Ti(**ONON**)-$NH_{3-oct-1}$	−2051.78140	−2051.48500	−2051.55459	−16.3		
Ti(**ONON**)-$NH_{3-oct-2}$	−2051.78604	−2051.48891	−2051.55607	−18.6		

[a] 1 au = 627.5 kcal mol^{-1}.
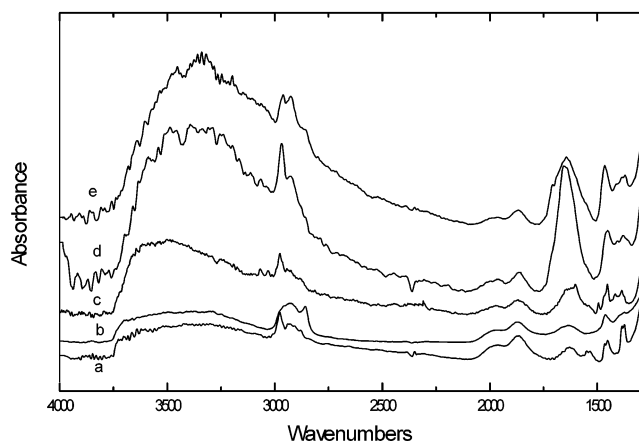
Figure 1. IR spectra of titanium catalysts: (a) Si-Ti(O^{i}Pr)$_2$; (b) Si-Ti(**OO**); (c) Si-Ti(**ON**); (d) Si-Ti(**NN**); (e) Si-Ti(**ONON**).
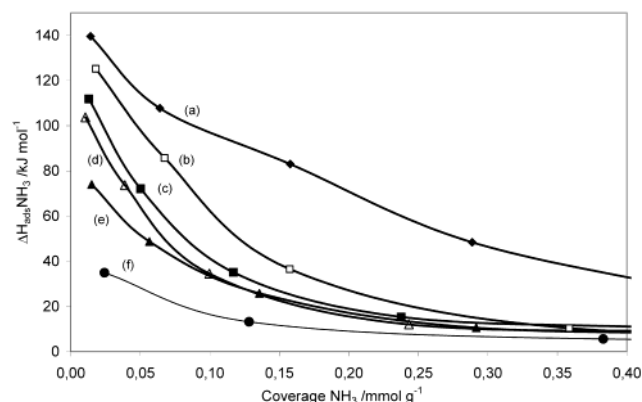
Figure 2. Differential Heat of ammonia adsorption for the different solids described: (a) Si-Ti(O^{i}Pr)$_2$; (b) Si-Ti(**OO**); (c) Si-Ti(**ON**); (d) Si-Ti(**NN**); (e) Si-Ti(**ONON**); (f) SiO$_2$.

(C$_{ar}$−C$_{ar}$). Moreover, the zone 1500−1350 cm^{-1} presents the same bands as in the spectrum of pure ephedrine.

The presence of organic ligands in the catalysts precludes the use of IR spectroscopy of adsorbed pyridine as a method for acidity determination. Calorimetric measurement of ammonia adsorption was chosen instead, and the results are plotted in Figure 2.

Si−Ti(O^{i}Pr), shows a higher molar heat of ammonia adsorption at low coverage (around 33.5 kcal mol^{-1}) than the catalysts modified with more basic ligands. Values of molar heat of ammonia adsorption decrease to 30.0, 27.5, and 18 kcal mol^{-1} for Si−Ti(**OO**), Si−Ti(**ON**), and Si−Ti(**NN**), respectively. The

corresponding value for Si−Ti(**ONON**) is 24.8 kcal mol^{-1}, i.e., an intermediate value between Si−Ti(**ON**) and Si−Ti(**NN**).

In all cases, the titanium based catalysts are more acidic than silica, demonstrating the important role of titanium for the final acidity of the catalysts.

Theoretical Calculations. Model compounds were selected, forming chelate complexes, which have shown higher stability than the open chain complexes.[14] Simple molecules were chosen as models for the ligands: ethylene glycol Ti(**OO**), 2-aminoethanol Ti(**ON**), and 1,2-ethylenediamine Ti(**NN**). The remaining free valences of the titanium atom were filled with silyloxy groups, to mimic the grafting onto the silica surface. This strategy has been largely used in previous modeling studies of titanium heterogeneous catalysts.[20] Ab initio calculations were performed on these model compounds, and their structures were optimized at the HF/6-31G(d) theory level. Frequency calculations at the same level were also carried out on the stationary points found. Calculated total energies, enthalpies, and free energies are given in Table 2. Some structural features of these compounds are shown in Figure 3.

Concerning Ti(**ONON**), this ligand is a diol-type ligand, and thus, it is linked to the titanium by two covalent bonds, analogously to Ti(**OO**). However, the presence of two amino groups allows the possibility of an additional coordination of one or two nitrogen atoms to the titanium atom.

Theoretical calculations were carried out at the HF/6-31G-(d) level to investigate the possible structures for the catalytic centers. Two minimum energy structures were located at this level, namely a bipyramidal one with an amino group coordinated to titanium atom (Ti(**ONON**)$_{bip}$), and a tetrahedral one, in which none of the amino groups are coordinated to the titanium atom (Ti(**ONON**)$_{tet}$). These structures are shown in Figure 4, and the corresponding energies are given in Table 2. As can be seen, somewhat unexpectedly, both structures have practically the same internal energy (E_0) and enthalpy at 25 °C, but the tetrahedral structure is entropically favored, so that it is 4.7 kcal mol^{-1} more stable in terms of Gibbs free energy at 25 °C.

The adequacy of these models for describing the acidity of the titanium centers was also tested by considering the enthalpy of coordination of a NH_3 molecule. To this end, the corresponding structures of the ammonia-model complexes were optimized at the HF/6-31G(d) level, and frequency calculations were carried out at the same level, to get the thermodynamic parameters at 25 °C. In the case of **ON**, an unsymmetrical ligand, two possibilities for the coordination of the NH_3 molecule, namely, in an axial position with regard to a nitrogen atom or in an axial position with regard to an oxygen atom
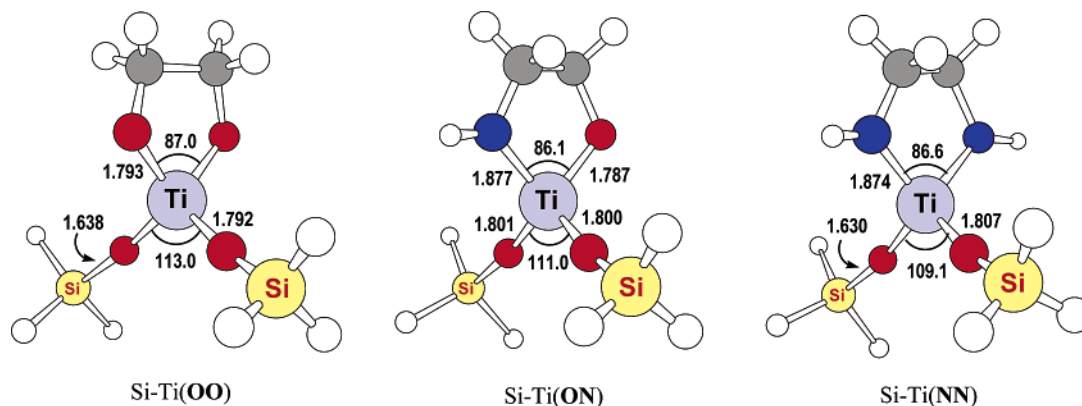
Figure 3. Some structural features of the model catalytic centers, calculated at the HF/6-31G(d) theoretical level.
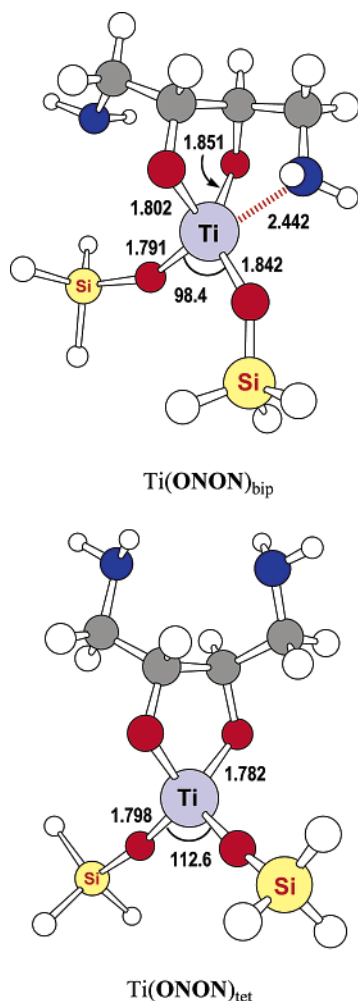

Figure 4. Some structural features of the model catalytic centers of Ti(**ONON**), calculated at the HF/6-31G(d) theoretical level.

were considered. In this case, the average coordination enthalpy was estimated by considering the population of each possible complex, on the basis of a Boltzmann distribution. In the case of **ONON**, three different structures were located and characterized. One of them corresponds to a bipyramidal structure, Ti-(**ONON**)-NH$_{3-bip}$, and two to octahedral structures, Ti(**ONON**)-NH$_{3-oct-1}$ and Ti(**ONON**)-NH$_{3-oct-2}$, in which one of the amino groups of the diamine is also coordinated to the titanium atom. These structures are shown in Figure 5, and the corresponding energies are given in Table 2.

Catalytic Tests. As a benchmark reaction we chose the epoxidation of cyclohexene with 30% hydrogen peroxide

(Scheme 1), due to the concurrence of all the side reactions, as explained in the Introduction. The results obtained are listed in Table 3. For the sake of comparison, Table 3 also contains the results of the reactions in the absence of catalyst, catalyzed by silica, and catalyzed by Si−Ti(O^{i}Pr).

Discussion

Concerning the theoretical results, some systematic trends can be remarked in the structures shown in Figure 3. Thus, the SiO−Ti distance increases in the same sense as does the basicity of the ligand, i.e., Ti(**OO**) < Ti(**ON**) < Ti(**NN**). Similarly, the SiO−Ti−OSi bond angle decreases in the same sense.

For epoxidation with hydrogen peroxide, titanium centers must possess Lewis acidity given that the first step is the coordination of the oxidant acting as a Lewis base. Thus, LUMO energy should give an indication of the catalytic activity. Graphic representations of the corresponding LUMO, calculated at the HF/6-31G(d) theoretical level, are shown in Figure 6, and their corresponding energies are listed in Table 2.

As can be seen, all LUMO mainly correspond to an empty d orbital centered on the titanium atom, so they can be considered as good representatives of the Lewis acidity of the titanium center. The calculated LUMO energies agree with the expected acidity of the different species. The coordination of a more basic ligand, as in Ti(**NN**), produces a less acidic species, as shown by the higher LUMO energy, and its smaller size. Thus, the Ti acidity decreases in the order Ti(**OO**) > Ti(**NO**) > Ti(**NN**).

A complementary description of the acidity of these centers can be drawn from the calculation of the coordination of a NH$_3$ molecule (Figure 5). Thus, the H$_3$N−Ti distance is shorter for Ti(**OO**) and Ti(**ON**)-O$_{ax}$ than for Ti(**ON**)-N$_{ax}$ and Ti(**NN**), which indicates a strong interaction for the former. The natural bond orbital analyses confirm this observation. Thus, the estimate of the $n_N \rightarrow n_{Ti}^*$ interaction energy between the lone pair of the ammonia nitrogen atom and the empty d orbital of the titanium atom, obtained by second-order perturbation theory analysis, is 25.8 and 26.05 kcal mol^{-1}, respectively, for Ti(**OO**) and Ti-(**ON**)-O$_{ax}$, and decreases to 12.0 and 11.2 kcal mol^{-1}, respectively, for Ti(**ON**)-N$_{ax}$ and Ti(**NN**). The calculated occupancy of the empty d orbital of the titanium is 0.1320, 0.1178, 0.0901, and 0.0652 electron, respectively, for Ti(**OO**) and Ti(**ON**)-O$_{ax}$, Ti-(**ON**)-N$_{ax}$, and Ti(**NN**), which is in line with the above results. Therefore, the presence of a nitrogen atom in the trans position to the NH$_3$ molecule results in a decrease of the titanium acidity, and hence in a lesser charge transfer from the ammonia molecule. These results roughly correlate with the calculated coordination enthalpy of a NH$_3$ molecule (Table 2), which follows the decreasing order Ti(**OO**) > Ti-(**ON**)-N$_{ax}$ ≈ Ti(**ON**)-
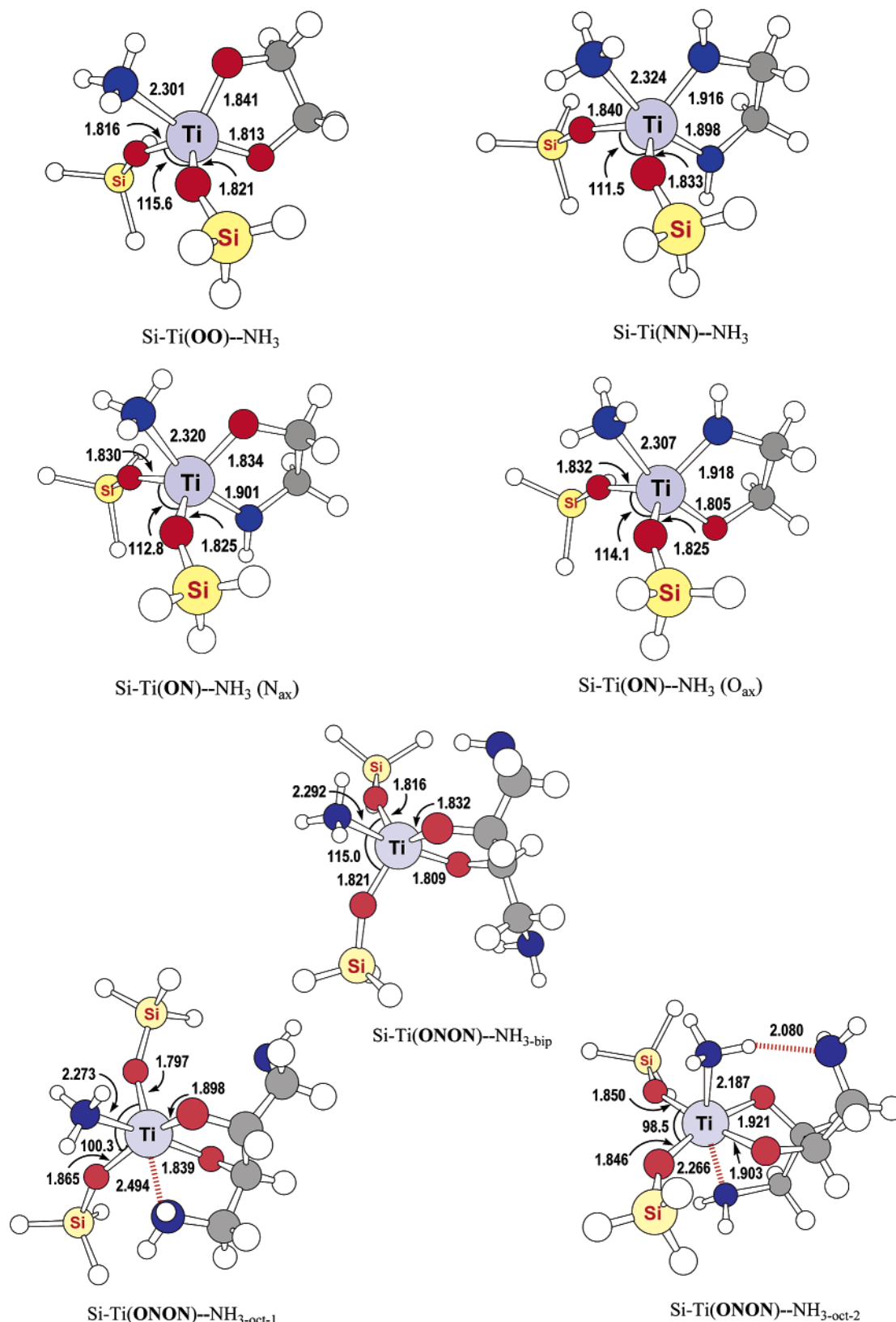
Figure 5. Some structural features of the coordination of a NH₃ molecule to the model catalytic centers, calculated at the HF/6-31G(d) theoretical level.

O_{ax} > Ti(**NN**). However, there is a slight inversion in the case of Ti(**ON**), because the Ti-(**ON**)-N_{ax} structure is somewhat more acidic than Ti-(**ON**)-O_{ax}.

By plotting the experimental enthalpies of absorption of NH₃ in front of the calculated enthalpies of coordination of a NH₃ molecule (Figure 7), one can see that there is a good correlation between both magnitudes ($r = 0.973$), indicating that the model systems chosen can be adequate to describe the acidic behavior of the catalytic centers.

Similarly with that found with the LUMO energies and the NBO analyses, the same acidity order, namely Ti(**OO**) > Ti-(**ON**) > Ti(**NN**), is found in this case. In fact, a plot of the

**TABLE 3: Results of the Epoxidation of Cyclohexene with 30% H$_2$O$_2$ Using Si−Ti(L) as Catalysts**

		% yield[a]				% select	% contr	epoxide	epox + diol
catalyst	t (h)	epoxide	diol	enol	chhp[b]	overall	H$_2$O$_2$[c]	path A[d]	diol	enol
None	24	4	2	3	8	17	25	12	67/33	67/33
SiO$_2$	24	4	2	4	34	44	78	3	67/33	60/40
Si−Ti(O^{i}Pr)	1	23	12	9	8	52	−	−	63/37	80/20
	24	2	49	19	3	73	76	42	5/95	73/27
Si−Ti(**OO**)	1	18	7	7	8	40	−	−	72/28	78/22
	24	1	39	21	3	64	67	28	3/97	66/34
Si−Ti(**ON**)	1	13	0	5	0	18	−	−	100/0	72/28
	24	11	13	23	5	52	57	2	46/54	51/49
Si−Ti(**NN**)	1	12	0	6	0	18	−	−	100/0	66/34
	24	8	7	17	4	36	40	0	53/47	47/53
Si−Ti(**ONON**)	1	3	2	6	9	20	−	−	60/40	45/55
	24	13	3	20	5	41	46	0	81/19	44/56

[a] Referred to the maximum. [b] Cyclohexenyl hydroperoxide. [c] Selectivity to oxidation products. [d] Contribution of direct epoxidation with hydrogen peroxide (path A) to hydrogen peroxide conversion. Calculated as (epox + diol − enol)/(select H$_2$O$_2$).

Ti(**OO**)

Ti(**ON**)

Ti(**NN**)
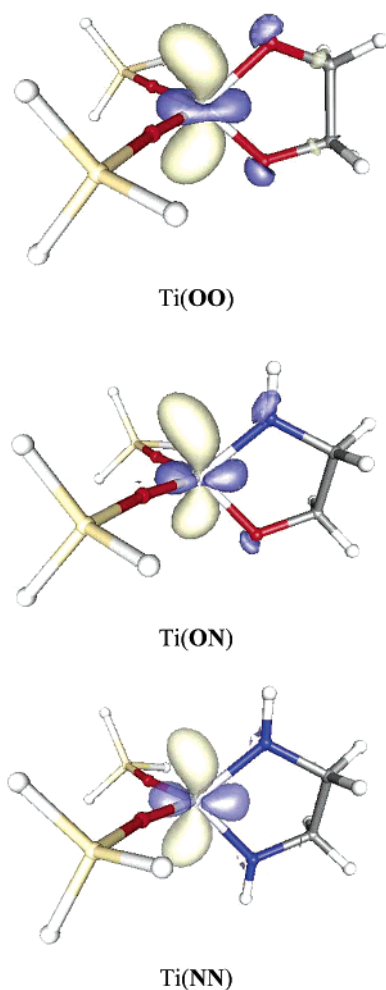
Figure 6. 0.05 au level plots of the lowest unoccupied molecular orbitals (LUMO) of the model catalytic centers, calculated at the HF/6-31G(d) theoretical level.

experimental enthalpies of absorption of NH$_3$ in front of the relative LUMO energies also shows an excellent correlation (r = 0.999, Figure 7).

As far as the catalytic tests are concerned, whose results are shown in Table 3, in the absence of catalyst the reaction is very slow and leads mainly to allylic oxidation products. The presence of silica accelerates the allylic oxidation, which must be detrimental to the reaction with Si−Ti. Despite this problem, the use of Si−Ti(O^{i}Pr) noticeably increases the consumption of H$_2$O$_2$ in direct epoxidation (path A in Scheme 1), up to 42%. When only epoxidation is taken into account, the direct
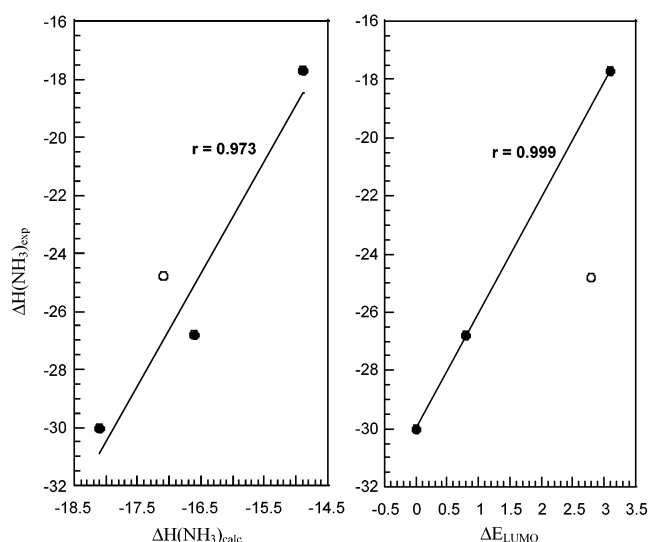
Figure 7. Linear regression plots of the experimental heat of ammonia adsorption against the calculated coordination enthalpy of an ammonia molecule and the relative LUMO energy, calculated at the HF theoretical level, for the model catalytic centers Ti(**OO**), Ti(**ON**), and Ti(**NN**) (filled circles). The relative position of Ti(**ONON**), not included in the regression analysis, is marked with an open circle. All units in kcal mol^{-1}.

mechanism is almost as efficient as the chhp-mediated epoxidation (path C), leading to a quite high epoxidation products/enol ratio. However, at long reaction times almost all the epoxide is hydrolyzed to diol, as indicated by the low epoxide/diol ratio.

Modification of the titanium centers by exchange of the isopropoxy groups has little influence in the case of decane-1,2-diol (**OO**). The overall activity and the different selectivities are similar to those observed for the original Si−Ti catalyst, although some decrease in the contribution of path A is observed. The more hydrophobic character of the diol, with the consequent difficulty in H$_2$O$_2$ coordination, may account for this decrease. However, when the exchanged ligand contains one or more amine groups, more dramatic changes in activity and selectivities are observed. In general, on passing from **OO** to **ON** and to **NN**, the overall activity of the catalysts decreases along with the selectivity in hydrogen peroxide and the contribution of path A, which practically disappears. However, hydrolysis of the epoxide to diol also decreases.

All these results point to an effective influence of the Lewis acidity of the titanium centers on the reaction results. Thus, more basic ligands lead to higher epoxide/diol ratios, given that the epoxide hydrolysis is catalyzed by Lewis acid centers. These
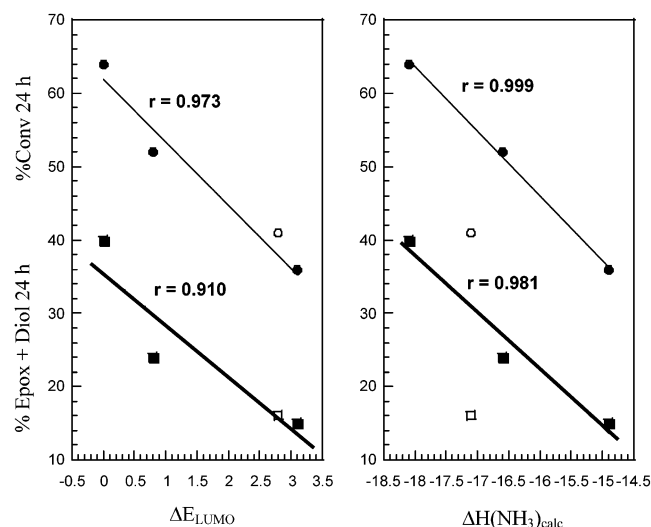
Figure 8. Linear regression plots of the overall cyclohexene conversion and total epoxidation products against the relative LUMO energy, and the coordination enthalpy of an ammonia molecule, calculated at the HF/6-31G(d) theoretical level, for the model catalytic centers Ti(**OO**), Ti(**ON**), and Ti(**NN**) (filled symbols). The relative position of Ti-(**ONON**), not included in the regression analyses, is marked with open symbols. All units in kcal mol^{-1}.

centers can be either the titanium centers themselves or some silanol groups, polarized by the presence of a near titanium atom. On the other hand, the overall activity and direct epoxidation seem to be favored by more acidic centers, and thus both decrease when the basicity of the ligands increases.

These results are in complete agreement with the acidity changes predicted by the theoretical calculations. Thus, the HF/6-31G(d) LUMO energies follow the same trend as the overall cyclohexene conversion ($r = 0.982$) or the yield of epoxidation products (epoxide + diol), taken as a measure of the catalytic activity ($r = 0.910$). Even better results are obtained when the calculated enthalpies of coordination of a NH$_3$ molecule are used as a measure of the acidity of the titanium centers ($r = 0.999$ and 0.981, respectively) (Figure 8). Therefore, both the total catalytic activity for hydrogen peroxide conversion and the activity for epoxidation, either direct (path A) or chhp-mediated (path C) correlate with the Lewis acidity of the titanium centers, showing the identity of the sites for all the reactions involved in the process of cyclohexene oxidation.

The results described hitherto clearly show that the acidity of the titanium center can be effectively modulated by the ligand covalently linked to it. A finer tuning of this acidity can be envisaged by means of more complex ligands, which allow not only covalent but also coordinative bonding to the titanium atom.

With the aim of testing this hypothesis, a new ligand, namely the 1,4-bis(dimethylamino)butane-2,3-diol (**ONON**) was used to prepare a new silica-supported titanium catalyst, Ti(**ONON**), following the same procedure used for the other ligands.

This ligand is a diol-type ligand, and thus, it is linked to the titanium by two covalent bonds, analogously to Ti(**OO**). The elemental nitrogen analyses show that the solid prepared has ca. 80% functionalization with this ligand (Table 1). The theoretical calculations have demonstrated that two types of titanium centers, with and without coordination of one of the ligand amino groups, are possible for this catalyst.

The acidity of both types of titanium centers can be theoretically estimated either by their corresponding LUMO energy, or by the enthalpy of coordination of a NH$_3$ molecule. From the LUMO energy viewpoint, Ti(**ONON**)$_{tet}$ is more acidic

than Ti(**ONON**)$_{bip}$ by 4.7 kcal mol^{-1}, as expected. More interestingly, the relative LUMO energy of Ti(**ONON**)$_{tet}$ with regard to Ti(**OO**) is 2.8 kcal mol^{-1}. This means that the catalytic activity of this center should be intermediate with regard to those observed for Ti(**ON**) and Ti(**NN**).

Similarly to what happened with Ti(**ONON**), although Ti-(**ONON**)-NH$_{3-oct-2}$ is lower in internal energy—probably due to the hydrogen bond between the NH$_3$ molecule and one of the amino groups—both octahedral structures are entropically disfavored, Ti(**ONON**)-NH$_{3-bip}$ thus being the most stable structure, in terms of Gibbs free energy at 25 °C. The calculated enthalpy of coordination of a NH$_3$ molecule for this structure is −17.1 kcal mol^{-1}, i.e., somewhat higher than that of Ti(**ON**).

Concerning the calculated acidity for this structure, Figure 7 shows as open circles the relative position of Ti(**ONON**)-NH$_{3-bip}$ with regard to the rest of structures. As can be seen, the agreement is fairly good for the calculated coordination enthalpy of a NH$_3$ molecule. On the other hand, this point is a clear outlier in the case of the calculated LUMO energy.

Concerning the acidity−catalytic activity relationships, Figure 8 analogously shows the position of Ti(**ONON**)-NH$_{3-bip}$ as open circles and squares. When the acidity is expressed as a relative LUMO energy, the agreement is good with the rest of the structures. However, when the calculated coordination enthalpy of a NH$_3$ molecule is used as the measure of acidity, the position of Ti(**ONON**)-NH$_{3-bip}$ is clearly far apart from the rest, both for the total cyclohexene conversion and for the final yield of epoxidation products.

Therefore, it can be concluded that the changes introduced in the ligand lead to a more complex description of the system. In these conditions, the thermodynamic acidity (as measured by the coordination enthalpy of a NH$_3$ molecule) is no longer valid as a reactivity index, and only the relative LUMO energy seems to keep its validity for describing the catalytic behavior of the titanium centers.

Conclusions

The Si−Ti solid can be easily modified by exchanging the isopropoxy groups with other organic functionalities. The combination of experimental and theoretical results allows the conclusion to be drawn that this modification leads to solids with different Lewis acidities, and thus with different behavior when used as catalysts in the benchmark reaction of cyclohexene with hydrogen peroxide. This behavior shows that the Lewis acidity of the titanium centers is of great importance in determining the catalytic activity in several steps of the reaction mechanism. These results also demonstrate that it is possible to achieve a "fine-tuning" of the catalytic features of the titanium-modified silicas at the molecular level, simply by choosing a suitable exchange ligand. Theoretical calculations of relatively simple catalytic center models have proven their usefulness to explain the catalysis results, with the energy of the LUMO being a good measure of the Lewis acidity of the titanium centers, and a good global reactivity index. As a consequence, the activity and selectivity of new catalyst candidates may be predicted by means of this methodology, provided they are structurally close enough to those described here.

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Supporting Information Available: Cartesian coordinates for the different structures described in this work. This material is available free via the Internet at http://pubs.acs.org.

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