Structure and relative Lewis acidity of the catalytic sites of an aluminium-modified silica gel
A theoretical study

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Abstract

Silica gel treated with $AlClEt_2$ is a solid with a strong Lewis acidity, which can be efficiently used to promote Diels–Alder reactions. Furthermore, this solid can be recovered and reused, as well as stored in the open air for at least one month. The possible presence of aluminium dimers grafted on the silica surface and their evolution in the presence of a carbonyl compound is studied by means of theoretical (semiempirical and ab initio) calculations.

1. Introduction

The preparation of new solid acid catalysts is an active area of research, not only for 'traditional' applications, such as cracking, isomerization, methanol to gasoline, etc. [1], but also for the preparation of fine chemicals [2].

In this context, we have described the preparation of a new family of solid acids, consisting of silica gel or alumina modified with titanium or aluminium derivatives [3,4]. These solids have been successfully tested as catalysts in Diels–Alder reactions of several dienes with non-chiral [3,5–8] and chiral [4,5,7,8] dienophiles. In particular, silica gel modified with $AlClEt_2$ is an excellent solid acid, with strong Lewis acid

sites, as shown by the large frequency shift (14.8 cm^{-1}) of the Lewis acid IR band of pyridine adsorbed onto the solid [3]. Furthermore, this catalyst can be stored in the open air and recycled, without a noticeable decrease in its overall catalytic activity. It is even possible with this solid to carry out some reactions which are very difficult in homogeneous conditions [6]. In other cases, activation by microwaves leads to better results than those previously reported using homogeneous catalysts [9].

Despite this, very little is still known about the structure of the active sites of this interesting catalyst. In this paper we will present some experimental and theoretical results dealing with the possible structure of the aluminium active centers and their relative acidity towards carbonyl compounds.

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2. Experimental

Preparation of the catalyst and reaction procedures have been described elsewhere [3,7].

Theoretical calculations were carried out at the semiempirical level using the MNDO [10] and AM1 [11] Hamiltonians, as implemented in the MOPAC 6.0 program [12]. Ab initio calculations were carried out with the Gaussian 94 program [13]. Full geometry optimization of all structures was performed at the RHF theory level using the split-valence 3-21G and 6-31G* basis sets. For the last geometries, single point energy calculations were carried out at the MP2 theory level using the 6-311G** (6-311G* for hydrogenless compounds) basis set.

3. Results and discussion

3.1. Experimental results

The silica gel, modified with $AlClEt_2$ as previously described [3], was used as a catalyst in the benchmark Diels–Alder reaction of cyclopentadiene with methyl acrylate (Scheme 1). In the first series of experiments, we used a freshly prepared solid, which was recovered and reused three more times after the first reaction. The results obtained in these experiments are gathered in Table 1.

As can be seen, the initial rate of the reaction suffer an important decay with recovering, but the conversion at longer reaction times is almost constant in all runs. In any case, most of the reaction is catalyzed by the solid, as shown by the high endo/exo selectivities observed ($\geq$ 95: $\leq$ 5), which do not change with time (the endo/exo of the non-catalyzed process is about 70:30 [3]).

Table 1
Results obtained in the Diels–Alder reaction between cyclopentadiene and methyl acrylate, catalyzed by silica gel modified by $AlClEt_2$

| Catalyst	Run	Conv. at 30 min (%) [a]	Conv. at 24 h (%) [a]	Endo/ exo [a]
Freshly prep.	1	90	99	95:5
	2	30	93	95:5
	3	15	85	96:4
	4 [b]	46	99	96:4
Aged [c]	1	35	91	95:5
	2	32	91	95:5
	3	18	92	95:5

[a] Determined by gas chromatography [3].
[b] The molar ratio diene:dienophile was increased from 1:1 to 3:1 in this run.
[c] Stored in the open air for one month.

In the second series of experiments, the catalyst was 'aged' by storing it for one month in the open air, prior to use. After the first reaction, the solid was recovered and reused two more times. The results obtained in these experiments are gathered in Table 1.

As can be seen, the conversion obtained at short reaction times is similar with the aged and with the recovered catalyst in the first series of experiments. Also, the conversion at longer reaction times is high, and does not decrease upon recovering. The endo/exo ratios are 95:5 in all cases, indicating that most of the reaction takes place through a catalytic pathway.

From these experimental results we can guess that there is at least two different kinds of catalytic sites in the solid. On the one hand, there are some catalytic sites, very active, which are formed when the solid is freshly prepared, and that are still present if the catalyst is immediately used after preparation. These sites are deactivated the first time that the catalyst is
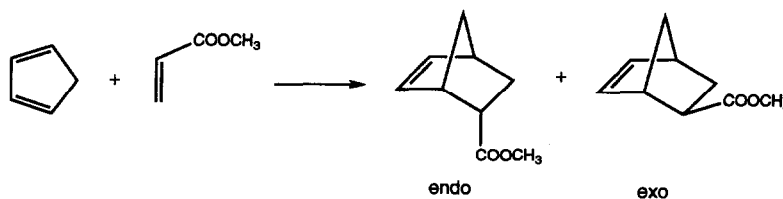
Scheme 1.

Scheme 2.
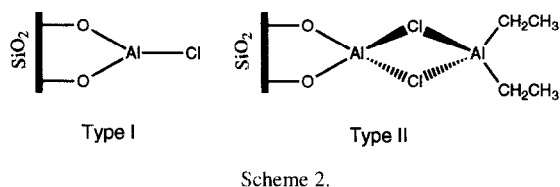
used or when it is stored in the open air. On the other hand, there are some other catalytic sites which are fully recoverable, and that lead to high conversions and endo/exo selectivities at longer reaction times.

It has recently been proposed [14], based on ^{27}Al- and ^{29}Si-NMR measurements, that in the preparation of aluminium chloride grafted on a silica surface, some of the aluminium sites correspond to dimeric Al_2Cl_5 species. Given that it is known that alkylaluminium compounds are also present as dimers in solution, a possible explanation for our results would be the simultaneous presence of dimeric and monomeric aluminium species in the freshly prepared catalyst, the first being more reactive and therefore short-lived (Scheme 2).

3.2. Theoretical results

Theoretical calculations offer a powerful tool to test the validity of the above hypothesis. However, for theoretical results to be of chemical significance, first of all it is necessary to be sure that the correct level of theory is being used. For this reason, several computational levels, ranging from semiempirical to ab initio with the inclusion of electronic correlation effects, will be considered. Given the size of the systems, we started with the most simple models of monomeric and dimeric aluminium species, i.e., $AlCl_3$, Al_2Cl_6, $AlClMe_2$, and $Al_2Cl_2Me_4$. The acidity of these species was calculated from their interaction energy with a molecule of formaldehyde. Basis set superimposition errors (BSSE) were not corrected in any case.

The system formaldehyde-$AlCl_3$ has previously been studied by other authors at ab initio Hartree–Fock [15,16], and DFT levels [17], so

that some comparisons of the structural and energetic results can be done in this case.

Some selected geometrical parameters of the four aluminium species are given in Fig. 1, and the total energies are gathered in Table 2.

As can be seen, both $AlCl_3$ and $AlClMe_2$ have trigonal planar geometry, and the calculated bond angles are similar at the MNDO, AM1, RHF/3-21G and RHF/6-31G* levels. However, the AM1 method leads to Al–Cl bonds which are too short with regard to that calculated by ab initio methods. For the $AlCl_3$, the ab initio and the MNDO results are much closer to the experimental value of 2.06 Å [18]. The DFT values recently reported by Bran-
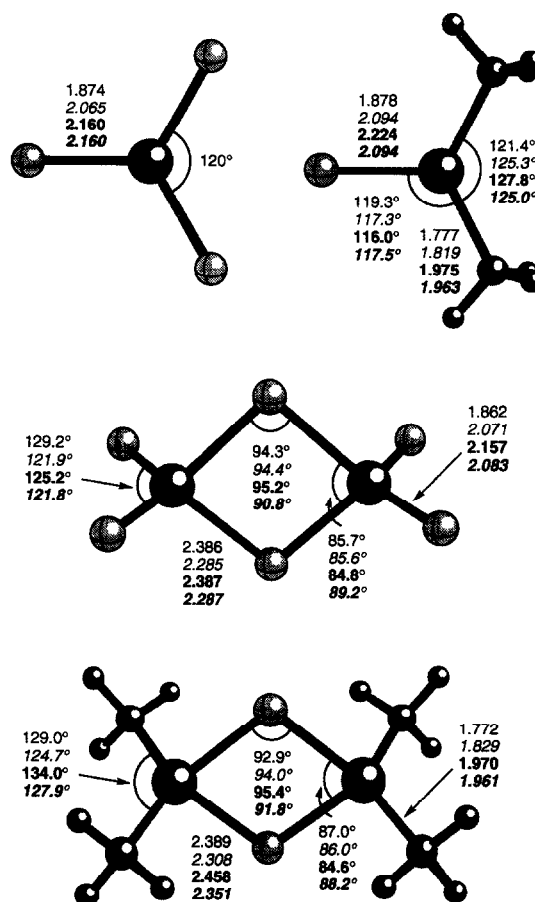

Fig. 1. Selected geometrical parameters for $AlCl_3$, $AlClMe_2$, Al_2Cl_6, and $Al_2Cl_2Me_4$, calculated at the AM1 (normal), MNDO (italic), RHF/3-21G (boldface), and RHF/6-31G* (boldface italic) theoretical levels.

Table 2
Total energies (in atomic units) of $AlCl_3$, $AlClMe_2$, Al_2Cl_6, $Al_2Cl_2Me_4$, formaldehyde, and of the complexes of $AlCl_3$, $AlClMe_2$, and $Al_2Cl_2Me_2$ with formaldehyde, calculated at several theoretical levels

Compound	AM1	MNDO	RHF/3-21G// 3-21G	RHF/6-31G */ / 6-31G *	MP2/6-311G **// 6-31G * [a]
$AlCl_3$	−43.228532	−41.053829	−1612.696088	−1620.576087	−1621.123026
$AlClMe_2$	−28.098353	−27.431105	−776.787040	−780.703379	−781.279001
Al_2Cl_6	−86.518132	−82.130900	−3225.435664	−3241.181217	−3242.292100
$Al_2Cl_2Me_4$	−56.265725	−54.888235	−1553.622861	−1561.437800	−1562.606170
HHCO	−17.477287	−17.570404	−113.221810	−113.866331	−114.233748
HHCO–$AlCl_3$	−60.716856	−58.658327	−1725.998033	−1734.487740	−1735.399508
HHCO–$AlClMe_2$	−45.584625	−45.023875	−890.066644	−894.701204	−895.546511
HHCO–$Al_2Cl_2Me_4$	−72.458941	−73.743911	−1666.897229	−1675.326073	−1676.853963

[a] 6-311G * for $AlCl_3$ and Al_2Cl_6.

chadell et al. [17] are also very close to this experimental value, both at the local density approximation (LDA) level (2.039 Å) and with non-local corrections (NL-SCF) (2.049 Å). With regard to the Al–C bond in $AlClMe_2$, the AM1 value is again shorter than the corresponding MNDO and ab initio values. There is no experimental information for this compound, but the Al–C distance in the related compound $AlMe_3$ is 1.88 Å [18], a value closer to that found using the MNDO and ab initio methods.

Concerning the dimeric species, the situation is similar to that observed for the monomers. The Al–Cl bond distance calculated by the AM1 method is shorter than the rest, which are in turn closer to the experimental value of 2.06 Å [18]. The calculated Al–Cl bridge distance, however, is similar for all the methods. In this case, the MNDO result is the closest to the experimental value of 2.25 Å [18]. There are

also no remarkable differences in the bond angles of these structures.

The AM1 calculations lead to a dimerization energy for $AlCl_3$ to Al_2Cl_6 of −38.3 kcal mol^{-1} (Table 3), which overestimates the experimental value of −30.8 kcal mol^{-1} [18]. On the other hand, the MNDO calculations lead to an underestimated value of −14.6 kcal mol^{-1}. With regard to ab initio calculations (Table 3), the change from a small to an extended basis set leads to an important decrease in the dimerization energy of $AlCl_3$, but the inclusion of electronic correlation has the contrary effect, so that the RHF/3-21G and the MP2/6-311G*//6-31G* values are indeed close to each to other, which confirms the 'semiempirical flavour' of the former [19]. In any case, the MP2 value is in good agreement with the experimental one.

The situation for the dimerization of $AlClMe_2$ to $Al_2Cl_2Me_4$ exactly parallels that of

Table 3
Dimerization energies (in kcal mol^{-1}) of Al_2Cl_6 and $Al_2Cl_2Me_4$, and interaction energies (in kcal mol^{-1}), of the complexes of $AlCl_3$, $AlClMe_2$, and $Al_2Cl_2Me_4$ with formaldehyde, calculated at several theoretical levels

Compound	AM1	MNDO	RHF/3-21G//3-21G	RHF/6-31G *//6-31G *	MP2/6-311G **//6-31G * [a]
Al_2Cl_6	−38.3	−14.6	−27.3	−18.2	−28.9
$Al_2Cl_2Me_4$	−43.3	−16.3	−30.6	−19.5	−26.0
HHCO–$AlCl_3$	−6.9	−21.4	−50.3	−28.4	−26.8
HHCO–$AlClMe_2$	−5.6	−14.0	−36.3	−20.1	−21.2
HHCO–$Al_2Cl_2Me_4$	−0.7	−1.5	−33.0	−13.8	−8.8

[a] 6-311G * for Al_2Cl_6.

$AlCl_3$ (Table 3), so that we can consider the $MP2/6\text{-}311G^{**}//6\text{-}31G^*$ value as the closest to the 'true' dimerization energy value. If we assume this, it can be concluded that the dimer of $AlCl_3$ is more strongly bonded than that of $AlClMe_2$.

Let us now consider the interaction of these aluminium compounds with formaldehyde. The corresponding calculated structures are shown in Fig. 2. In the case of the monomers, the most striking feature is the long Al–O distance (2.447 Å for $AlCl_3$ and 2.450 Å for $AlClMe_2$) calculated by the AM1 method with regard to the rest. This suggest a weak interaction between the formaldehyde and the aluminium compound, which is confirmed by the almost planar structure (Al pyramidal angle ca. 165° in both cases) of the latter, and the small interaction energy calculated (Table 3).

On the other hand, MNDO results are again in much better agreement with ab initio ones, not only for the geometrical features, but also for the interaction energies. In this respect, the highest level ab initio results indicate that $AlCl_3$ is a stronger acid than $AlClMe_2$ (Table 3). It is interesting to compare the results of the formaldehyde-$AlCl_3$ complex with those obtained in DFT calculations [17]. Whereas bond lengths are similar in all cases, the DFT bond C=O–Al angle is somewhat smaller (ca. 125°) and closer to that obtained in the AM1 calculation (122.2°).

On the other hand, the pyramidalization angle is almost the same than that obtained at the HF/6-31G* level. However, the most striking difference lies in the interaction energy. At the LDA level, the calculated interaction energy $(-28.4$ kcal $mol^{-1})$ is very similar to that obtained at the HF/6-31G* level, but at the NL-SCF level, this energy decreases to a value of -17.7 kcal $mol^{-1})$, far from that we find at the $MP2/6\text{-}311G^{**}//6\text{-}31G^*$ level, and also from the value obtained at the $MP4/CEP\text{-}31G^*//CEP\text{-}31G^*$ level $(-26.1$ kcal $mol^{-1})$ [16].

We have also considered the behaviour of the formaldehyde with regard to the $Al_2Cl_2Me_4$ compound. If we consider the dimerization and the interaction energies given in Table 3, it can be concluded that the equilibrium $Al_2Cl_2Me_4 + 2HHCO \rightleftarrows 2HHCO\text{-}AlClMe_2$ is completely shifted to the right. However, the possible structures of a molecule of formaldehyde interacting with Al have also been calculated (Fig. 3a). In the case of AM1, the Al–O distance is even longer than that calculated for the monomer complex, and this leads to a very small interaction energy (less than 1 kcal mol^{-1}) between both molecules (Table 3). The behaviour is completely different in the case of MNDO (Fig. 3b), for which a partial dissociation of the $Al_2Cl_2Me_4$ molecule is observed, in agreement with the behaviour expected from the dimerization and interaction energies. In fact, if a second
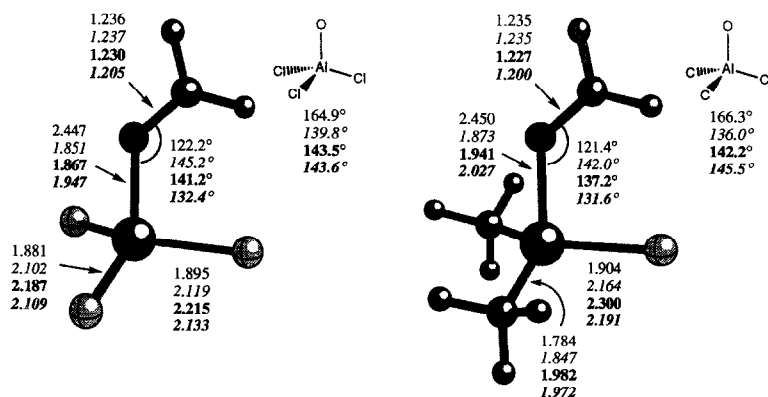

Fig. 2. Selected geometrical parameters for the complexes of formaldehyde with $AlCl_3$ and $AlClMe_2$, calculated at the AM1 (normal), MNDO (italic), RHF/3-21G (boldface), and RHF/6-31G * (boldface italic) theoretical levels.
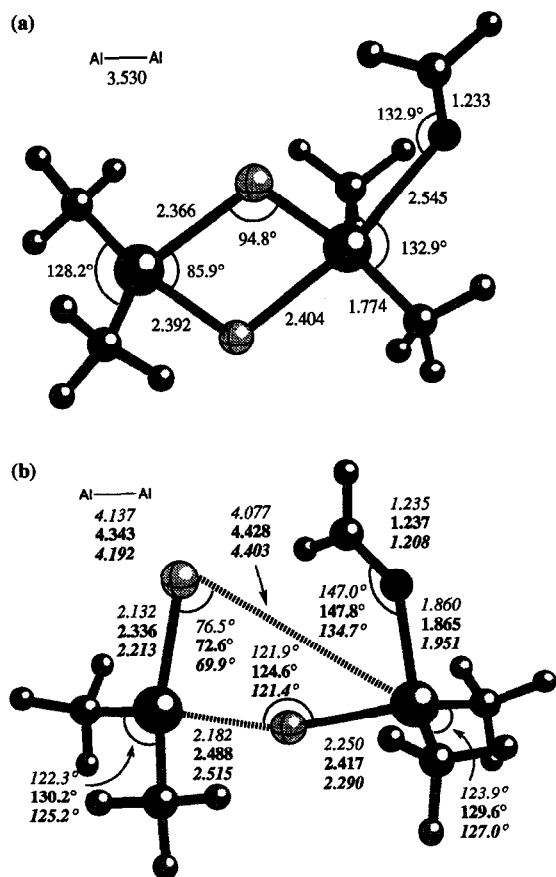
(a)

(b)

Fig. 3. Selected geometrical parameters for the complex of formaldehyde and $Al_2Cl_2Me_4$, calculated at the AM1 (normal) (a), and the MNDO (italic), RHF/3-21G (boldface), and RHF/6-31G * (boldface italic) (b) theoretical levels.

molecule of formaldehyde is coordinated to the free aluminium, the dimer fully dissociates into two HHCO–AlClMe$_2$ complexes. The interaction energy between one molecule of formaldehyde and the $Al_2Cl_2Me_4$ is as low as -1.5 kcal mol^{-1}, which agrees with the highly improbable existence of this species in solution.

The ab initio calculations confirm the precedent analysis, and also show the importance of the theoretical level used to study these kind of complexes. In all cases the complex is partially dissociated (Fig. 3b), and the coordination of a second molecule of formaldehyde gives rise to a total dissociation, but the interaction energy changes dramatically with the theoretical level used (Table 3). Thus, at the RHF/3-21G level,

the interaction energy between formaldehyde and $Al_2Cl_2Me_4$ is as high as -33.0 kcal mol^{-1}, but when both the more extended basis sets and electronic correlation are considered, the interaction energy strongly decreases until reaching a value of -8.8 kcal mol^{-1} at the MP2/6-311G**//6-31G* level. This strong variation suggests that geometry optimization with inclusion of correlation corrections would further change the geometry towards a dissociated complex. The size of the system, however, at the moment prevents this calculation from being carried out.

After this preliminary study, we tackled the modelling of the catalytic centers in our modified silica gel. The two possible structures considered were a single aluminium atom bonded to two vicinal oxygen atoms of the silica surface (type I catalytic sites), as proposed in references [3] and [4], and a dimeric aluminium compound, also bonded to two vicinal oxygen atoms (type II catalytic sites). These structures were modelled as depicted in Scheme 3, at the same computational levels used in the preceding calculations. Some selected geometrical parameters are shown in Fig. 4, and the total, and the dimerization and interaction energies are given in Table 4.

With regard to the type I catalytic sites, the situation is similar to that found in the precedent cases, i.e., the MNDO results are much closer to the ab initio ones than those obtained with the AM1 Hamiltonian. In all cases, the aluminium atom is in a trigonal planar disposition, as in $AlCl_3$ and $AlClMe_2$. The acidity calculated for

Model of
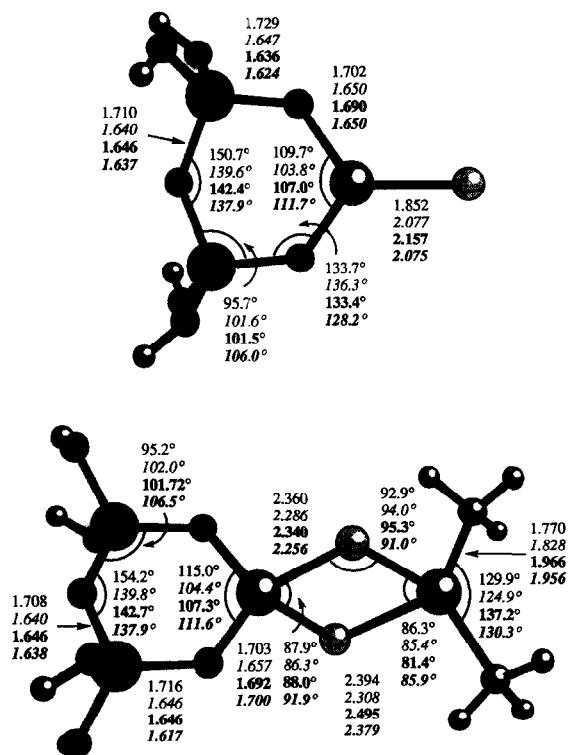type I sites

Model of
type II sites
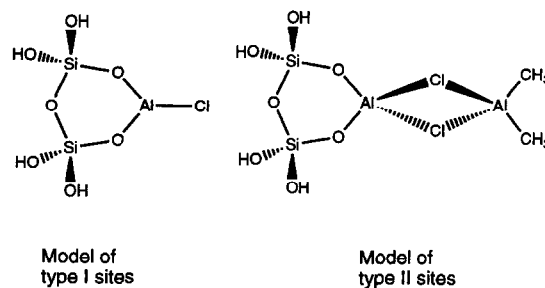
Scheme 3.

Fig. 4. Selected geometrical parameters for the type I and type II models of the modified silica catalytic sites, calculated at the AM1 (normal), MNDO (italic), RHF/3-21G (boldface), and RHF/6-31G * (boldface italic) theoretical levels.
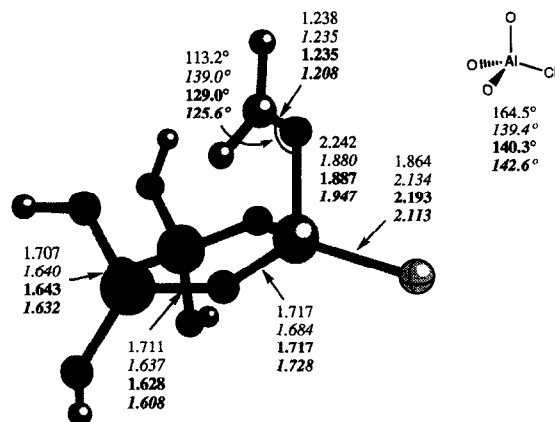

Fig. 5. Selected geometrical parameters for the complex of formaldehyde and the type I catalytic site, calculated at the AM1 (normal), MNDO (italic), RHF/3-21G (boldface), and RHF/6-31G * (boldface italic) theoretical levels.

type I sites, expressed as their interaction energy with formaldehyde, is even greater than that calculated for these two aluminium compounds at the highest theory level considered (Table 4). The long Al–O distance (2.424 Å) calculated by the AM1 method (Fig. 5), which is associated to an almost planar aluminium arrangement (Fig. 4), and to a weak interaction between the catalytic center and the formal-

dehyde (Table 4), is consistent with the previous comments on this calculation method.

Concerning type II catalytic sites, the dimerization energy is higher (more negative) than that observed for $Al_2Cl_2Me_4$ at all the ab initio levels considered. However, given the high interaction energies of formaldehyde with type I catalytic sites and with $AlClMe_2$, the complete dissociation of these aluminium species in the presence of formaldehyde can be reasonably expected.

From these results the following scenario can be depicted for the aluminium-modified silica catalysts. The freshly prepared solid has both type I and type II catalytic centers. If this solid is used immediately after its preparation, the type II sites will react with the dienophile, and

Table 4
Total energies (in atomic units) of the type I and type II aluminium sites, and the complex of the former with formaldehyde. Dimerization energy (in kcal mol^{-1}) of the type II aluminium site, and interaction energy (in kcal mol^{-1}), of the complexes of type I aluminium site with formaldehyde

Compound	AM1	MNDO	RHF/3-21G// 3-21G	RHF/6-31G *// 6-31G *	MP2/6-311G * *// 6-31G *
Type I SiO$_2$–Al	– 106.667570	– 106.777573	– 1796.848727	– 1806.213596	– 1808.197345
Type II SiO$_2$–Al	– 134.823340	– 134.229958	– 2573.686973	– 2586.950635	– 2589.526992
HHCO-type I SiO$_2$ Al	– 124.157175	– 124.368037	– 1910.150959	– 1920.128877	– 1922.479199
Type II SiO$_2$–Al	– 36.0	– 13.4	– 32.1	– 20.9	– 31.8
HHCO-type I SiO$_2$ Al	– 7.7	– 12.6	– 50.5	– 30.7	– 30.2

two kinds of aluminium–dienophile complexes will be present in the reaction. It is important to note that, unlike the behaviour described for $AlCl_3$-modified silica [14], *there is no leaching of aluminium after the reactions*, as demonstrated by the plasma emission spectra, so that the existence of pure homogeneous catalysis contributing to the reaction results can be ruled out. Probably, the $AlClEt_2$–dienophile complexes do not leave the surface of the solid, and the $AlClEt_2$ becomes available to react with a free OH of the silica surface, so that the recovery of the catalyst gives rise to a solid with a different distribution and nature of catalytic sites, and hence different activity.

On the other hand, when the catalyst is aged, the reversibility of the dimer–monomer equilibrium allows the molecules of $AlClEt_2$ to react with a free OH of the silica surface, giving rise to a catalyst more similar to that obtained after the first recovering.

Of course, in all cases, the reaction of the aluminium atoms with the ambient humidity during the storing or recovering of the catalyst, will further contribute to decrease the activity of the catalyst by the creation of octahedral aluminium sites, and the loss of the chlorine atom.

To summarize, the complementary use of experimental results and theoretical calculations has proven to be a powerful tool to study the nature of the catalytic centers of aluminium-modified silica gel, and their possible evolution by aging or recovering. The semiempirical AM1 Hamiltonian is unable to give a correct picture of the behaviour of these systems, but, somewhat surprisingly, the MNDO Hamiltonian gives results which are in qualitative agreement with those obtained at ab initio level. The results obtained with ab initio methods are, in turn, dependent on the theory level used. Both extended basis sets and the inclusion of electronic correlation energy corrections seem to be important in correctly describing these systems.

The experimental and the theoretical results suggest that at least two types of catalytic sites are present in the freshly prepared solids, con-

sisting of both monomeric and dimeric species of aluminium bonded to vicinal OH groups of the silica surface. The dimeric species evolve to monomeric ones by aging, or react with the dienophile, by dissociating a molecule of $AlClEt_2$, which further reacts with the silica surface.

Acknowledgements

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