



# Surface organometallic chemistry of zirconium Chemical reactivity of the $\equiv\text{Si}-\text{O}-\text{ZrNp}_3$ surface complex synthesized on dehydroxylated silica and application to the modification of mordenite

Mariko Adachi<sup>a</sup>, Christophe Nédez<sup>b</sup>, Xu Xu Wang<sup>a</sup>, François Bayard<sup>a</sup>,  
Véronique Dufaud<sup>a</sup>, Frédéric Lefebvre<sup>a,\*</sup>, Jean-Marie Basset<sup>a,1</sup>

<sup>a</sup> Laboratoire de Chimie Organométallique de Surface, UMR CNRS-CPE 9986,  
43 Boulevard du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

<sup>b</sup> Procatalyse, BP 8, 30340 Salindres, France

Received 17 October 2002; received in revised form 26 February 2003; accepted 27 February 2003

Dedicated to Prof. Renato Ugo on the occasion of his 65th birthday

## Abstract

The organometallic complex  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  was synthesized on the surface of silica dehydroxylated at 500 °C and its reactivity towards oxygenated molecules was studied. The materials were characterized by IR, <sup>13</sup>C CP-MAS NMR, analysis of evolved gases and elemental analysis. Reaction with neopentyl alcohol ((CH<sub>3</sub>)<sub>3</sub>CCH<sub>2</sub>OH) leads to the quantitative formation of  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3$ . Similarly, reaction with pivalic acid ((CH<sub>3</sub>)<sub>3</sub>CCOOH) leads to the quantitative formation of  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{OCOC}(\text{CH}_3)_3)_3$ . Addition of dry oxygen at 25 °C to  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  leads to the formation of  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3$ . When heated at 200 °C under oxygen, the alkoxy ligands transform into carboxylate species ((CH<sub>3</sub>)<sub>3</sub>CCOO)<sup>-</sup> probably coordinated to zirconium. These results, together with molecular modelling studies of the adsorption of hydrocarbons on mordenite modified by such complexes, explain the different behaviours observed in presence of air or inert gases.

© 2003 Elsevier Science B.V. All rights reserved.

**Keywords:** Zirconium; Solid-state NMR; Organometallic; Mordenite; Oxidation

## 1. Introduction

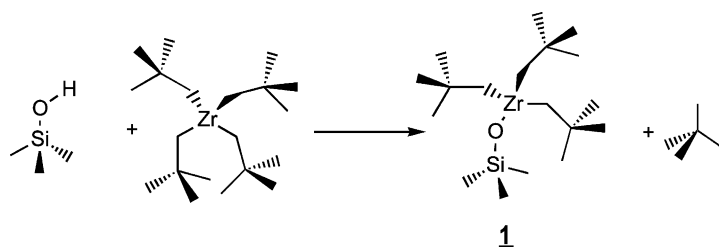
Molecular sieves, and more specifically zeolites, offer many applications including catalysis (e.g. catalytic cracking, isomerization of xylenes and alkyla-

tion of aromatics), separation processes (such as the preparation of oxygen or the removal of water from gases, solvents, ...), without excluding one of their most important applications as detergent builder in replacement of phosphate compounds. Their cage-like structure of precise geometry with pores of uniform shape throughout the entire crystal renders them very useful for all these applications. Indeed, the limited size of the channels avoids the formation of some intermediates in the catalytic reactions, allowing then

\* Corresponding author. Tel.: +33-4-72-43-18-07;  
fax: +33-4-72-43-17-95.

E-mail address: [lefebvre@cpe.fr](mailto:lefebvre@cpe.fr) (F. Lefebvre).

<sup>1</sup> Co-corresponding author.



Scheme 1.

unexpected selectivities (shape form selectivity). In addition, the constant value of the channels size leads to similar properties over the whole crystal. However, it is not possible to synthesize zeolites with given pore entrances and sorption properties, due to the limited number of structures of these compounds [1]. This resulted in numerous studies on the post-synthesis modification of these materials [2]. One can classify them into three groups: (i) modification by cation exchange; (ii) modification by adsorption of polar molecules; and (iii) modification of the zeolite itself, for example, by dealumination or reaction with silanes. We have developed a new method for the modification of zeolites by reaction of their external hydroxyl groups with organometallic complexes and formation of well-defined grafted organometallic fragments [3–7]. It is then possible, by simple molecular modelling calculations, to determine a priori the sorption characteristics of the resulting materials. Evidently, for this purpose it is necessary to suppose that the grafted organometallic fragment will retain its integrity upon the adsorption phenomena. Unfortunately, this is not always the case due to the fact that the organometallic groups are not always chemically inert or thermally stable. From this point of view, the following solutions can be proposed:

- to graft, on the external surface of the zeolite, more stable organometallic fragments;
- to transform the grafted organometallic fragment into a more stable species.

Previous studies with alkyltin compounds showed that these grafted organometallic fragments are thermally stable up to 150–200 °C [3,6]. A first improvement was achieved by reaction of organometallic complexes of germanium at the pore entrance of mordenite [5]. Indeed GeBu<sub>4</sub> gives more thermally stable

surface organometallic fragments, ≡Si–O–GeBu<sub>3</sub> being stable up to 400 °C under vacuum.

A second possibility should be the transformation of the metal–alkyl surface complex to more chemically stable species. Indeed, alkyl–transition metal complexes of elements from the left of the periodic table are generally very unstable. Typically, not only do they decompose in presence of oxygen but they can also undergo a β–H abstraction followed by reductive elimination [8]. The second type of reactions can be avoided by use of ligands such as –CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, –CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>, –CH<sub>2</sub>Ph which do not have hydrogen in β–position. This methodology was applied to mordenite which was modified by reaction of the silanol groups present on its external surface with tetra-neopentyl zirconium (ZrNp<sub>4</sub>). The grafted complex ≡Si–O–Zr(CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub> (**1**) (Scheme 1) which was fully characterized on silica dehydroxylated at 500 °C [8], is stable under vacuum up to about 80 °C, but it decomposes at higher temperatures. Above 200 °C, almost all alkyl groups are removed [9].

In addition, this complex is not air-stable and decomposes rapidly. One solution could be to replace metal–carbon bonds by metal–oxygen bonds, which are more stable for these transition metals. This strategy was then applied to mordenite modified by ≡Si–O–Zr(CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub> (**1**). Noteworthy, while 2,2,4-trimethyl-pentane and *n*-hexane diffused at different rates over mordenite modified by **1** [10], such discrimination was lost after exposure of the material to oxygen. As a consequence, we undertook the study of the reaction of **1** with oxygen and compared the data to those obtained with other well-defined grafted zirconium complexes. A molecular modelling study of the adsorption of hydrocarbons on mordenite modified by reaction with **1** was then performed on the basis of these results.

## 2. Experimental

- (i) Reagents: Silica (Aerosil from Degussa,  $200 \text{ m}^2 \text{ g}^{-1}$ ) was compacted to a disk (7.0 mg) for IR studies, or was hydrated, dried and crushed to prepare large quantities (1–1.5 g) for NMR studies and elemental analysis. Tetra-n-propyl zirconium was synthesized by reaction of  $\text{NpMgCl}$  with  $\text{ZrCl}_4$  [11]. It was sublimed in vacuo (10–4 mbar) before use. Its purity was checked by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Trimethylacetic acid (pivalic acid,  $\text{Me}_3\text{CCOOH}$ ) (99%, Aldrich) and 2,2-dimethyl-1-propanol (neopentyl alcohol,  $\text{NpOH}$ ) (99%, Fluka) were used after purification by fractional distillation in vacuum at room temperature and at  $0^\circ\text{C}$ , respectively.
- (ii) Synthesis of  $\equiv\text{Si-O-ZrNp}_3$  (**1**): The surface complex  $\equiv\text{Si-O-ZrNp}_3$  was synthesized by reaction of  $\text{ZrNp}_4$  with the hydroxyl groups of silica dehydroxylated at  $500^\circ\text{C}$ , as described previously [8,12]. Unreacted  $\text{ZrNp}_4$  was removed by heating at  $70^\circ\text{C}$  in vacuum during 3 h, in presence of a liquid nitrogen trap.  $\equiv\text{Si-O-ZrNp}_3$  was characterized by analysis of evolved gases, IR and  $^{13}\text{C}$  CP-MAS NMR spectroscopies and elemental analysis (see Section 3).
- (iii) Oxidation of  $\equiv\text{Si-O-ZrNp}_3$ : The oxidation of the  $\equiv\text{Si-O-ZrNp}_3$  complex was performed under strict exclusion of air, using standard break-seal glass apparatus. Oxygen (500 mbar) was dried over molecular sieves prior to use. The reaction was monitored by IR,  $^{13}\text{C}$  CP-MAS NMR spectroscopies and chromatographic analysis of the gas phase.
- (iv) Synthesis of  $\equiv\text{Si-O-Zr(ONp)}_3$  (**2**) and  $\equiv\text{Si-O-Zr(OCOCMe}_3)_3$  (**3**): These two compounds were prepared by sublimation of neopentyl alcohol and pivalic acid, respectively, at  $70^\circ\text{C}$  onto **1**. The unreacted compounds were removed by heating under dynamic vacuum at  $70^\circ\text{C}$ . **2** and **3** were characterized by IR,  $^{13}\text{C}$  CP-MAS NMR spectroscopies, GC analysis of evolved gases and elemental analysis.
- (v) Physico-chemical methods: Infrared spectra were recorded on a Nicolet 550-FT spectrometer equipped with a custom infrared cell allowing in situ studies. The  $^{13}\text{C}$  CP-MAS NMR spectra were recorded on a Bruker DSX-300 spectrom-

eter equipped with a standard double-bearing probehead. The spinning rate was typically 6000 Hz, the  $90^\circ$  value for proton  $3.8 \mu\text{s}$ , the contact time 10 ms (in order to detect the quaternary carbon atoms) and the recycle delay 2 s. Typically 20 000–50 000 scans were accumulated. All chemical shifts are given relative to external TMS. Analysis of gas phases was made with a gas chromatograph equipped with a  $\text{KCl/Al}_2\text{O}_3$  capillary column (for hydrocarbons) and with a catharometer (for  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ).

- (vi) Molecular modelling studies: Molecular modelling studies were performed on a Silicon Graphics Indy workstation with the Sybyl<sup>®</sup> software package. The Sybyl force field parameters for the O–Zr–O and O–Zr–C angles were modified to  $\theta_0 = 109.48^\circ$  and  $K = 0.024$  in order to obtain a tetrahedral geometry around zirconium. In a first series of calculations the two fragments  $\text{ZrNp}_3$  and  $\text{Zr(ONp)}_3$  were bonded to mordenite via the four possible positions at the surface. In each case, a systematic optimization of the structure was made by rotating the grafted complex around the Si–O bond linking it to the surface. The best conformation was then kept and compared to those obtained with the other grafting positions. In a second series of experiments the organometallic fragment ( $\text{ZrNp}_3$  or  $\text{Zr(ONp)}_3$ ) was placed on the most stable position and a dynamic study of the diffusion of *n*-hexane or methyl-pentane through the pore was undertaken. For this purpose, a force constant was created between the organic molecule and a virtual atom inside the pore structure. After several tests, a force constant equal to  $0.5 \text{ kcal mol}^{-1} \text{ \AA}^2$  was chosen and a 10 ps dynamics were made, allowing the determination of the energy barrier at the pore entrance.

## 3. Results and discussion

- (a) Synthesis and characterization of  $\equiv\text{Si-O-Zr(ONp)}_3$  (**2**). When  $\equiv\text{Si-O-ZrNp}_3$  (**1**) is exposed to neopentyl alcohol vapor at room temperature, its IR spectrum is immediately modified in the 1600–1300  $\text{cm}^{-1}$  region (Fig. 1). The bands at 1466, 1392 and 1363  $\text{cm}^{-1}$  which are characteristic

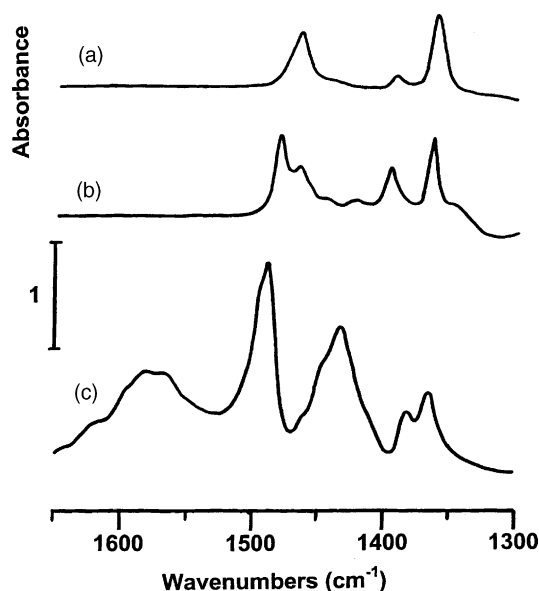


Fig. 1. Infrared spectra, in the 1600–1300  $\text{cm}^{-1}$  region of:  $\equiv\text{Si-O-Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  (**1**);  $\equiv\text{Si-O-Zr}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3$  (**2**);  $\equiv\text{Si-O-Zr}(\text{OCOC}(\text{CH}_3)_3)_3$  (**3**).

of **1** are replaced by four bands at 1481, 1466, 1398 and 1366  $\text{cm}^{-1}$ . Simultaneously, neopentane is evolved (3 mol  $\text{mol}^{-1}$  of grafted zirconium as determined by gas chromatography, elemental analysis and IR). Chemical analysis, after removal of unreacted neopentyl alcohol, gives a ratio  $\text{C}/\text{Zr} = 13 \pm 2$  ( $2.3 \pm 0.2$  wt.% Zr,  $3.9 \pm 0.2$  wt.% C; expected  $\text{C}/\text{Zr}$  ratio for  $\equiv\text{Si-O-Zr}(\text{ONp})_3 = 15$ ) for the solid. The  $^{13}\text{C}$  CP-MAS NMR spectrum of the resulting material is quite different from that of  $\equiv\text{Si-O-ZrNp}_3$  (Fig. 2a and b and Table 1). The  $-\text{CH}_3$  peak has shifted from 33.9 to 24.7 ppm and the  $-\text{CH}_2-$  peak from 95.5 to 81.7 ppm. In addition, the quaternary carbon atom in **2** is observed at 32.2 ppm. Although the  $^{13}\text{C}$  chemical shifts of the methyl and quaternary carbon atoms are very close to those of neopentyl alcohol, that of the methylene group is shifted by ca. 10 ppm with respect to the starting material, confirming the occurrence of the reaction. These peaks are attributed to neopentoxo ligands of a surface zirconium complex. The above results allow to propose that  $\equiv\text{Si-O-ZrNp}_3$  **1** reacts with neopentyl alcohol to form a tris-neopentoxo surface complex according to Scheme 2.

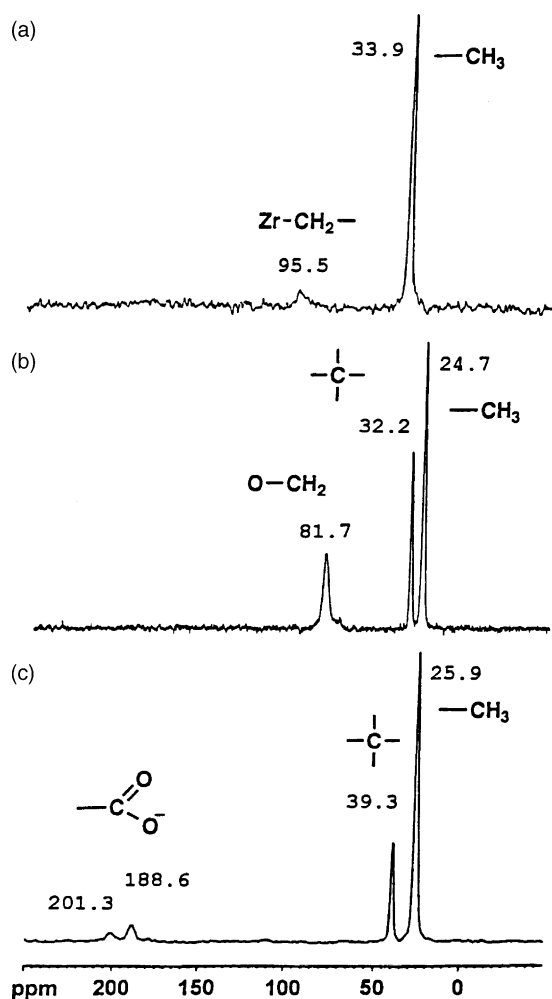
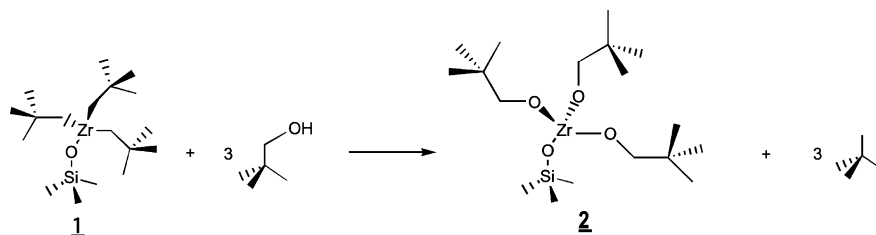


Fig. 2.  $^{13}\text{C}$  CP-MAS NMR spectra of:  $\equiv\text{Si-O-Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  (**1**);  $\equiv\text{Si-O-Zr}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3$  (**2**);  $\equiv\text{Si-O-Zr}(\text{OCOC}(\text{CH}_3)_3)_3$  (**3**).

(b) Synthesis and characterization of  $\equiv\text{Si-O-Zr}(\text{OCOCMe}_3)_3$  (**3**). When  $\equiv\text{Si-O-ZrNp}_3$  is reacted with pivalic acid, neopentane is evolved (3 mol  $\text{mol}^{-1}$  of grafted zirconium) and the IR spectrum is drastically modified in the 1600–1300  $\text{cm}^{-1}$  region (Fig. 1c). The sharp bands at 1466, 1392 and 1363  $\text{cm}^{-1}$  are replaced by bands at 1489, 1434, 1383 and 1367  $\text{cm}^{-1}$ . Simultaneously, a sharp  $\nu(\text{C}=\text{O})$  band appears at 1715  $\text{cm}^{-1}$ , due to the physisorbed acid, and two bands, characteristic of carboxylate ions are observed at 1583 and 1570  $\text{cm}^{-1}$ . The  $^{13}\text{C}$  CP-MAS



Scheme 2.

Table 1

$^{13}\text{C}$  chemical shifts of supported zirconium complexes and of some organic molecular compounds

Compound	$^{13}\text{C}$ chemical shift (ppm)		
	$-\text{CH}_3$	$-\text{C}(\text{CH}_3)_3$	$-\text{C}-\text{C}(\text{CH}_3)_3$
Neopentane <sup>a</sup>	31.7	28.1	
Neopentyl alcohol <sup>a</sup>	26.3	32.6	72.6
Pivalic acid <sup>b</sup>	26.9	38.6	186.2
<b>1</b> $\equiv \text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$	33.9	n.d. <sup>c</sup>	95.5
<b>2</b> $\equiv \text{Si}-\text{O}-\text{Zr}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3$	24.7	32.2	81.7
<b>3</b> $\equiv \text{Si}-\text{O}-\text{Zr}(\text{OC}(=\text{O})\text{C}(\text{CH}_3)_3)_3$	25.9	39.3	188.6
<b>1</b> + $\text{O}_2$ at 25 °C	25.0	33.0	82.5
<b>1</b> + $\text{O}_2$ at 200 °C	25.4	39.3	189

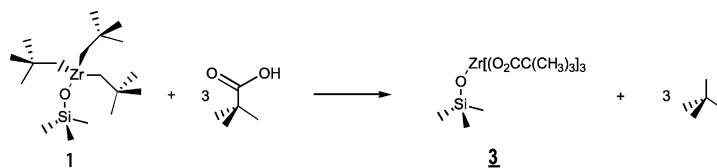
<sup>a</sup> [8].

<sup>b</sup> In  $\text{C}_6\text{D}_6$ .

<sup>c</sup> Not detected.

NMR spectrum (after elimination of pivalic acid in excess) is very different from that of **1** (Fig. 2, Table 1). The  $-\text{CH}_3$  peak has shifted from 33.9 to 25.9 ppm while the  $-\text{CH}_2-$  resonance has disappeared and has been replaced by two peaks at 201.3 and 188.6 ppm attributed to a carboxylate carbon atom. In addition, the peak of the quaternary carbon is observed at 39.3 ppm.

All these results combined with elemental analysis ( $\text{C} = 4.2 \pm 0.2$  wt.%,  $\text{Zr} = 2.3 \pm 0.2$  wt.%,  $\text{C}/\text{Zr} = 14 \pm 2$ ) allow us to conclude that **1** reacted with pivalic acid according to Scheme 3.



Scheme 3.

The presence of two  $^{13}\text{C}$  NMR peaks for the carboxylate carbon atom indicates that the three  $(\text{CH}_3)_3\text{CCOO}^-$  ligands are not equivalent. As the ratio of the two peaks is ca. 2:1, we can reasonably suppose that one of the three  $(\text{CH}_3)_3\text{CCOO}^-$  ligands is different from the two others. This may be related various reasons such as a terminal versus bidentate form of the ligands or, for the same coordination of the ligands, to different surroundings. For example, it had been shown by EXAFS that in  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{acac})_3$  zirconium is heptacoordinated [13]. If we assume that we have also a heptacoordination in the case of **3**, then all carboxylates cannot be equivalent. Solution data could help to elucidate this point.

(c) Oxidation of  $\equiv\text{Si}-\text{O}-\text{ZrNp}_3$  (**1**) by dry oxygen at room temperature. When dry oxygen (500 mbar) is added at room temperature to  $\equiv\text{Si}-\text{O}-\text{ZrNp}_3$ , great variations of the infrared spectrum are observed in the  $1600\text{--}1300\text{ cm}^{-1}$  region without any gas evolution. The IR bands at 1466, 1392 and  $1363\text{ cm}^{-1}$  are replaced by peaks at 1480, 1467, 1398 and  $1366\text{ cm}^{-1}$  (Fig. 3b), very close to those reported for  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{ONp})_3$  (**2**). Volumetric determination at equilibrium (after 24 h reaction) gives a consumption of 1.5 mol of oxygen per mole of grafted zirconium, in agreement with the formation of  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{ONp})_3$  while the  $^{13}\text{C}$  CP-MAS NMR spectrum is quite comparable to

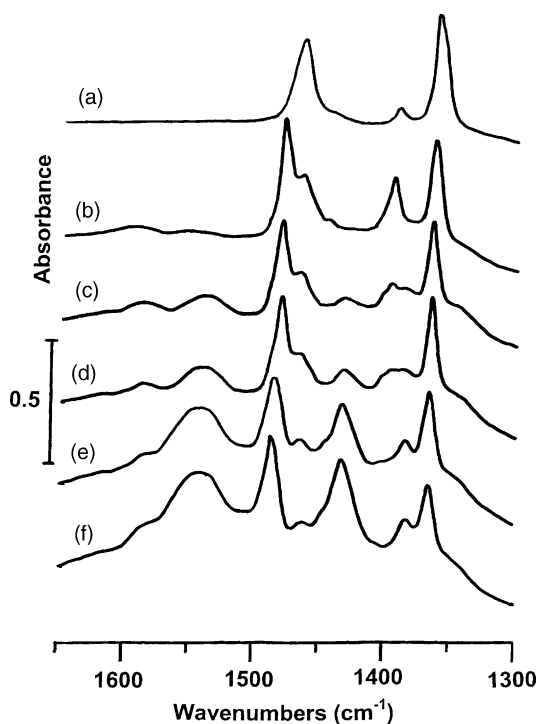
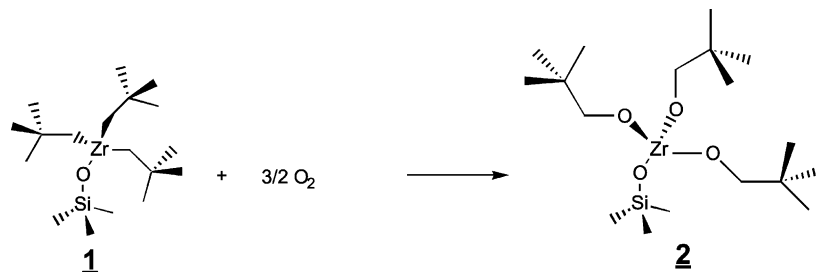


Fig. 3. IR spectra (after subtraction of silica) in the 1600–1300  $\text{cm}^{-1}$  region of  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  (**1**) contacted with dry oxygen: (a)  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$ ; (b) just after introduction of oxygen (500 mbar) at 25 °C; (c) after heating at 200 °C during 3 h; (d) after heating at 200 °C during 8 h; (e) after heating at 200 °C during 23 h; (f) after heating at 200 °C during 30 h.

that of **2** (Fig. 4a). Extraction by HCl in ether is in agreement with this conclusion, only neopentyl alcohol being detected ( $2.5 \text{ mol mol}^{-1}$  of grafted zirconium). Reaction of **1** with dry oxygen at room temperature can then be represented by



Scheme 4.

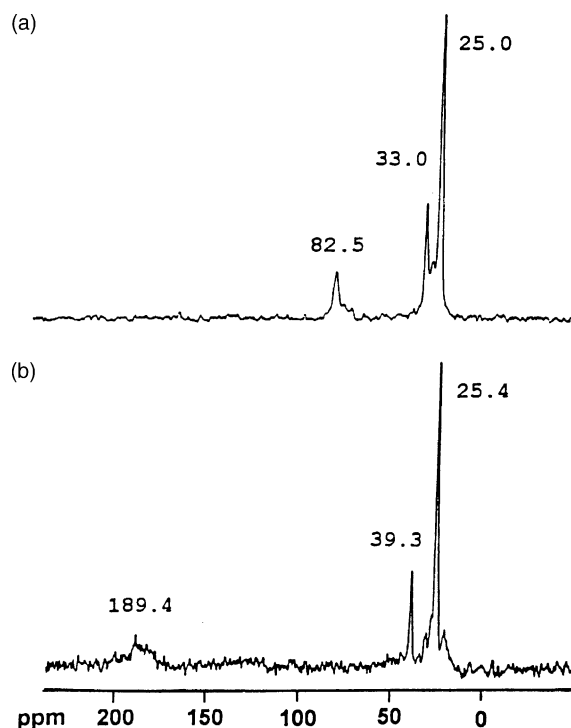
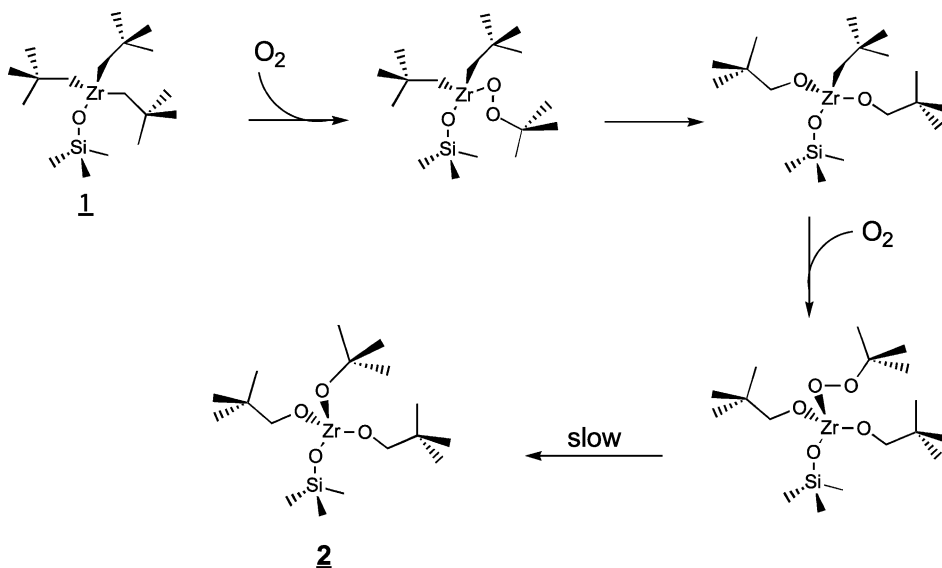


Fig. 4.  $^{13}\text{C}$  CP-MAS NMR spectra of the oxidation products of  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  (**1**). (a) After 120 h under oxygen at 25 °C; (b) After 168 h under oxygen at 200 °C.

**Scheme 4**, the three neopentyl ligands being transformed into neopentyl oxygens.

Insertion of oxygen into a metal–carbon bond, leading finally to alkoxy ligands, has been observed for molecular compounds displaying similar structures, such as  $(\text{tritox})_n\text{MNp}_{4-n}$  with  $n = 0-2$  and  $\text{M} = \text{Ti}, \text{Zr}$  and  $\text{Hf}$  [14–16]. The generally accepted mechanism involves a radical



Scheme 5.

pathway with a cleavage of the O–O bond of oxygen [16–19]. However this mechanism necessitates a bimolecular step between two complexes, a reaction which is quite improbable when the complexes are grafted on a support. More probably, in this particular case, the first step is the insertion of one oxygen molecule in a Zr–C bond, leading to a monoperoxo complex which, after reorganization gives a mononeopentyl bis-neopentoxo complex. The insertion of the second oxygen molecule and the transformation into the tris-neopentoxo complex is more difficult to explain, and up to now we have no simple mechanism to propose explaining it (Scheme 5).

All attempts to isolate and/or characterize the intermediate peroxy species (for example, by the observation of a M–O–O bond by Raman spectroscopy or by reaction with olefins, phosphines, ...) failed, in contrast to what was observed with titanium where the titration of  $\equiv\text{Si}-\text{O}-\text{TiNp}_3$  by molecular oxygen gave a consumption of four oxygen atoms [20].

- (d) Oxidation of  $\equiv\text{Si}-\text{O}-\text{ZrNp}_3$  (**1**) by dry oxygen at 200 °C. Heating at 200 °C under oxygen results in a new modification of the IR spectrum (Figs. 3 and 5). The  $\nu(\text{CH}_3)$  bands at ca.  $3000\text{ cm}^{-1}$  decrease in intensity (Fig. 5) while the IR spec-

trum is modified in the  $1600\text{--}1300\text{ cm}^{-1}$  domain (Fig. 3). Simultaneously,  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  are evolved in the gaseous phase. This reaction occurs relatively slowly at 200 °C and can be interpreted as the combustion of the surface complex, the organic groups transforming into water and carbon oxides. However, interesting information can be obtained on the decomposition mechanism of this surface complex under oxygen. First, the infrared spectrum after heating during 30 h is very

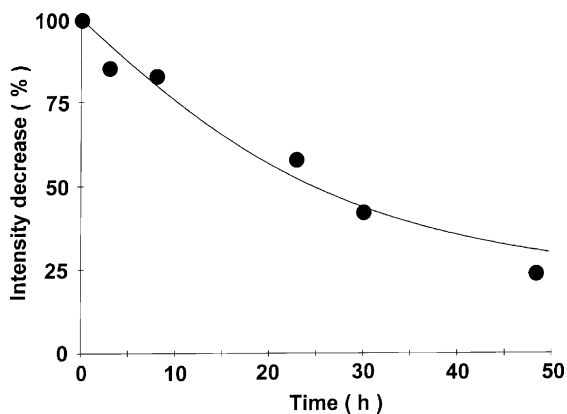


Fig. 5. Decrease of the intensity of the  $\nu_{\text{as}}(\text{CH}_3)$  band at  $2954\text{ cm}^{-1}$  as a function of time under oxygen at 200 °C.



similar to that of complex **3**, showing that, on the surface, the organic groups remain as carboxylate species. The  $^{13}\text{C}$  CP-MAS NMR spectrum is also in agreement with that conclusion. Indeed the  $^{13}\text{C}$  CP-MAS NMR spectrum of a sample of **1** (or **2**) heated at  $200^\circ\text{C}$  under dry oxygen is shown in Fig. 4b. One peak is clearly present around 190 ppm, indicating the possibility of the formation of a carboxylate species. The other peaks are also very similar to those of **3** (see Fig. 2c and Table 1), allowing us to propose that this carboxylate is coordinated to zirconium; the other possible grafting, on silicon, can be excluded given that carboxylate species are not stable on silica alone and, in presence of water, product the carboxylic acid and a silanol group. The presence of carbon oxides (arising from the decomposition of the organic ligands), the decrease of the  $\nu_{\text{as}}(\text{CH}_3)$  band down to zero (Fig. 5) and the presence of only one

NMR peak for the carboxylate carbon show that there is not a clean formation of a tris-carboxylate complex on the surface. More probably, this carboxylate species corresponds to the first step of the decomposition of the neopentoxy ligands and should be considered as an intermediate species stabilized on zirconium.

The observation of carboxylate species on a metal by heating under oxygen is not surprising and had been observed previously for tin complexes but in that case the reaction led also to other products as shown by solid-state NMR and infrared spectroscopy [10,21]. Up to now the mechanism of formation of such species is not known. Various possibilities can be proposed such as a radical reaction or reaction through a surface oxygen atom [21].

(e) Application to molecular separation by mordenite modified by zirconium complexes. As described

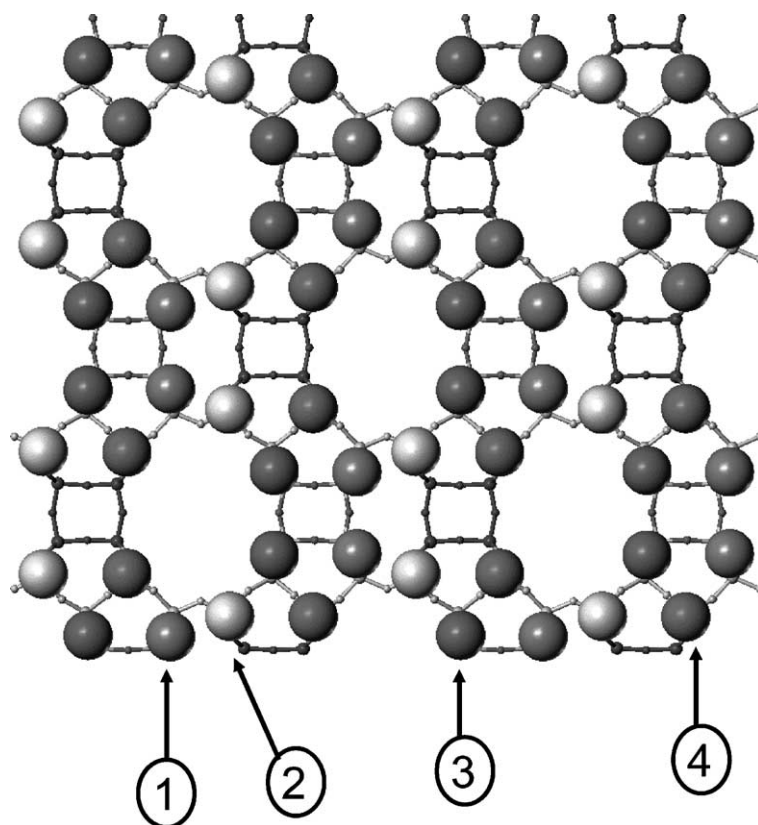


Fig. 6. Anchoring sites on mordenite near the pore entrance.



in the introduction, mordenite can be modified by the grafting reaction of tris-neopentyl zirconium groups at its pore entrances. Due to the great difficulty to characterize the resulting solids (the zirconium loading is too low), the reaction was also modelled on silica, the reactive groups at

the external surface of mordenite being silanols. The resulting modified zeolite is able to discriminate alkanes such as *n*-hexane, 2-methyl-pentane, 2,3-dimethyl-butane and *iso*-octane, in contrast to the unmodified one. However, these properties are lost when the solid is contacted with oxygen

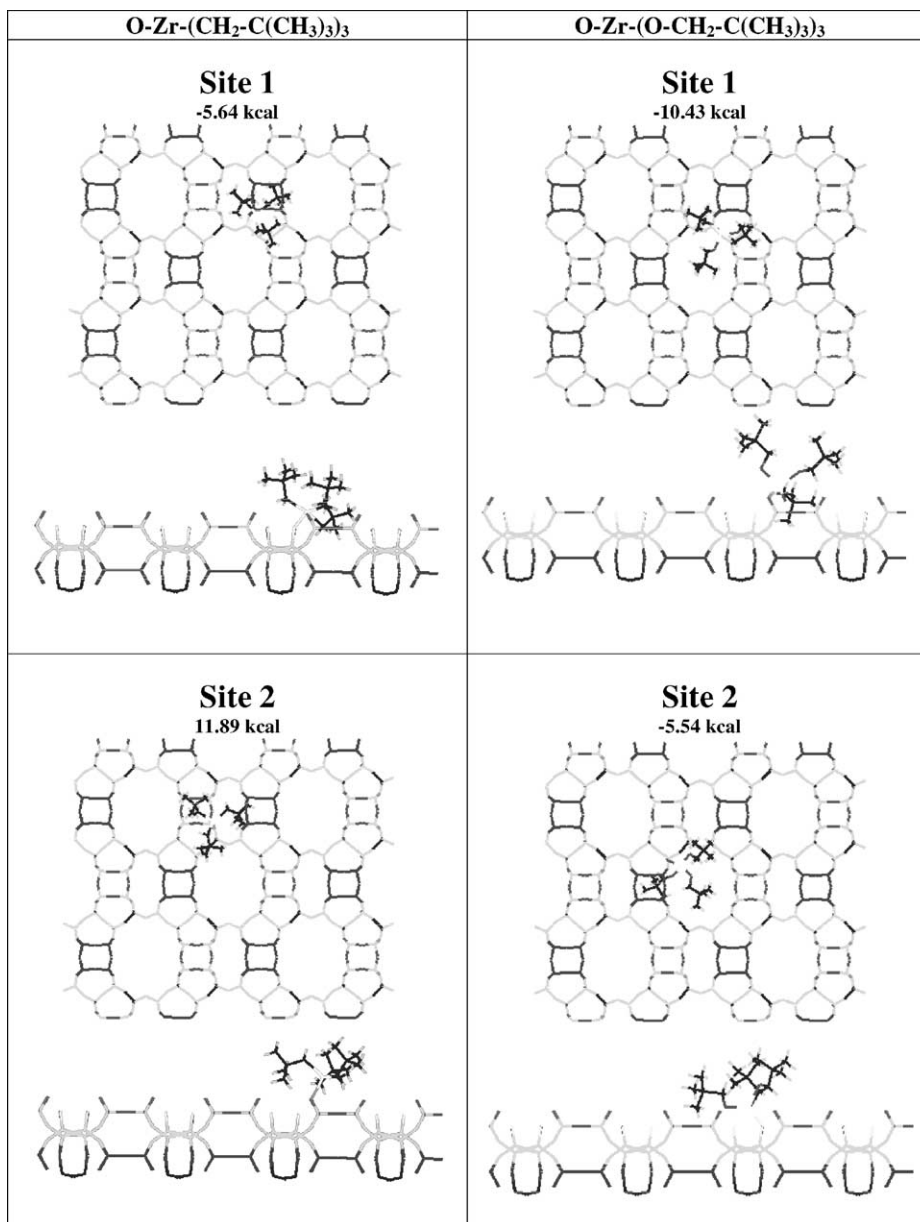


Fig. 7. Best conformations of the ZrNp<sub>3</sub> and Zr(ONp)<sub>3</sub> organometallic fragments as a function of the grafting site.

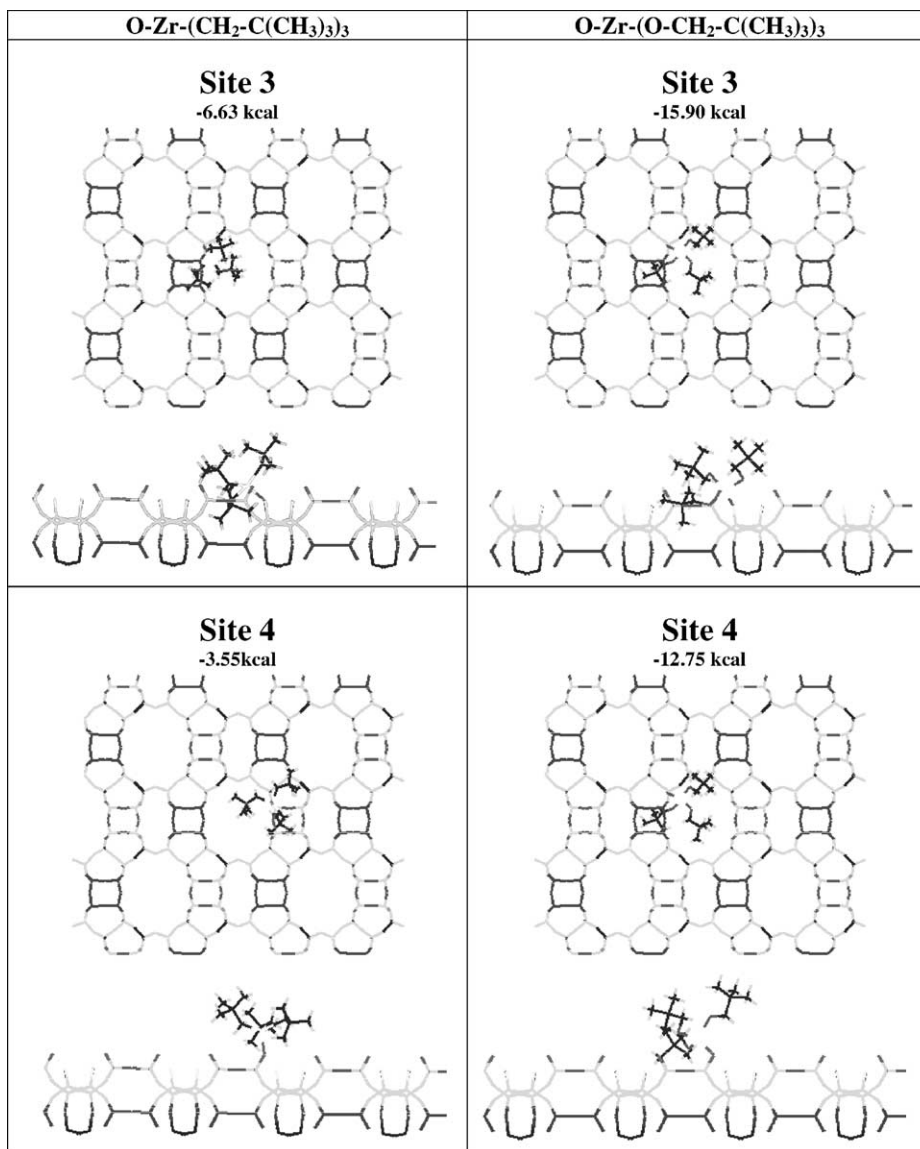


Fig. 7. (Continued).

(or air) at room temperature. In other words, the solid is not stable under air. The above data on silica allow to understand, from a chemical point of view, what happens when the modified mordenite is kept in air: the tris-neopentyl zirconium groups are transformed into tris-neopentoxy species. However, it seems difficult to understand how the insertion of one oxygen atom in the Zr–C bond can lead to such a great differ-

ence in the adsorption properties. We have then performed a molecular modelling study of the adsorption of *n*-hexane and 2-methyl-pentane on unmodified mordenite and mordenite modified by tris-neopentyl zirconium and tris-neopentoxy zirconium fragments. The main problem of such studies is that there are four possible anchoring sites on mordenite near the pore entrances. These four sites are depicted in Fig. 6. It can be seen

easily that the steric hindrance at the pore entrance will be highly dependent on the grafting position of the organometallic fragment. So, in a first series of experiments, we determined, for each complex and for each grafting position, the most stable conformation (corresponding to the larger van der Waals interaction). The results are given in Table 2 while Fig. 7 shows the most stable conformations for each grafting position.

First of all, it can be seen that whatever the organometallic complex, quite the same stability order is obtained: grafting on site 3 leads to the most stable species (note that one chain of the complex is going inside the pore channel) while grafting on site 2 leads to the less stable species. Grafting on sites 1 and 4 gives an intermediate situation but in each case the complex has no chain in the channel. These results led us to retain only

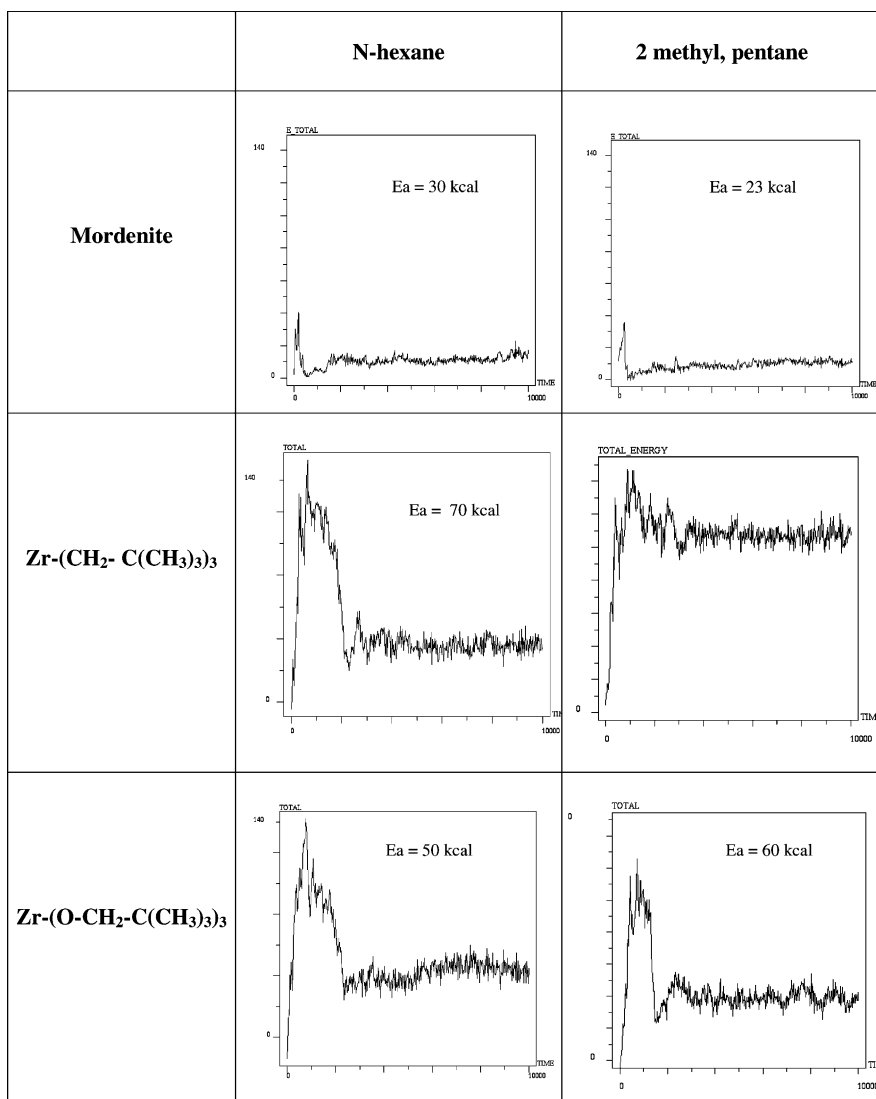


Fig. 8. van der Waals energy variation during the various dynamics of *n*-hexane (left) and 2-methyl-pentane diffusion through the pore entrance of mordenite: (a) unmodified pore entrance; (b) pore entrance modified by the  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{CH}_2\text{C}(\text{CH}_3)_3)_3$  fragment; (c) pore entrance modified by the  $\equiv\text{Si}-\text{O}-\text{Zr}(\text{OCH}_2\text{C}(\text{CH}_3)_3)_3$  fragment.

Table 2

Energies of the ZrNp<sub>3</sub> and Zr(ONp)<sub>3</sub> fragments on mordenite as a function of the grafting position

Site	Energy of the grafted complex (kcal mol <sup>-1</sup> )	
	ZrNp <sub>3</sub>	Zr(ONp) <sub>3</sub>
1	-5.64	-10.43
2	11.89	-5.54
3	-6.63	-15.90
4	-3.55	-12.75

grafting on site 3 as the most probable position as: (i) it corresponds to the most stable species; and (ii) it leads to the most sterically hindered pore entrance. Naturally this choice is explained in Figs. 6 and 7, and Table 2.

Assuming the grafting position of the organometallic fragment at the surface of mordenite, it was then possible to study the diffusion of hydrocarbons (we choose *n*-hexane and 2-methyl-pentane) through the modified pore entrances. For comparison, a study was also made with unmodified pore entrances. For this purpose a molecular dynamics study was undertaken in each case (see Section 2 for details). The van der Waals energy variation for these six situations are depicted in Fig. 8.

For unmodified mordenite, there is no steric hindrance at the pore entrance and the two molecules can go in the channels. In presence of a tris-neopentyl zirconium fragment, *n*-hexane can go in the channels but the activation energy (corresponding to the interaction with the grafted organometallic complex) is ca. 70 kcal mol<sup>-1</sup>. With the same complex, 2-methyl-pentane cannot pass through the pore entrance. In presence of the tris-neopentoxy zirconium complex, there is a decrease of the activation energy for *n*-hexane to 50 kcal mol<sup>-1</sup> and 2-methyl-pentane can now go in the channels, the activation energy being 60 kcal mol<sup>-1</sup>. Qualitatively, these results are in good agreement with the experimental data. From a quantitative point of view the activation energies are probably not true, simply due to the fact that they depend on the force field used for the calculations, but relative comparisons can be made, allowing the determination of the retention order if the system was used for separation of gas mixtures.

## 4. Conclusion

The oxidation reaction of the well-defined surface species ≡Si–O–ZrNp<sub>3</sub> was studied by comparison with model species prepared selectively by reaction of neopentyl alcohol and pivalic acid with ≡Si–O–ZrNp<sub>3</sub>. These surface species were characterized by infrared spectroscopy, <sup>13</sup>C CP-MAS NMR, gas evolution and elementary analysis. The results show that at 25 °C the ≡Si–O–ZrNp<sub>3</sub> fragment is oxidized by molecular oxygen to a tris-neopentoxy species ≡Si–O–Zr(ONp)<sub>3</sub>. After heating at 200 °C the tris-neopentoxy ligands transform to *t*-butylcarboxylates (Me<sub>3</sub>CCOO)<sup>-</sup> bound to zirconium.

From the point of view of zeolites, the loss of the selectivity of branched alkanes adsorption after introduction of oxygen on a mordenite modified by grafting ≡Si–O–ZrNp<sub>3</sub> fragments on its external surface can be related to the moving of the neopentyl groups away from the surface by insertion of one oxygen atom. Molecular modelling studies are in agreement with this hypothesis.

## References

- [1] W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, Butterworths, London, 1992.
- [2] E.F. Vansant, Pore Size Engineering in Zeolites, Wiley, New York, 1990.
- [3] A. Théolier, E. Custodero, A. Choplin, J.M. Basset, F. Raatz, Angew. Chem., Int. Ed. Engl. 29 (1990) 805.
- [4] C. Nédez, A. Choplin, J. Corker, J.M. Basset, J.F. Joly, E. Benazzi, J. Mol. Catal. 92 (1994) L239.
- [5] E. Benazzi, S. de Tavernier, P. Beccat, J.F. Joly, C. Nédez, A. Choplin, J.M. Basset, ChemTech (1994) 13.
- [6] C. Nédez, A. Théolier, F. Lefebvre, A. Choplin, J.M. Basset, J.F. Joly, E. Benazzi, Microporous Mater. 2 (1994) 51.
- [7] A. Théolier, A. Choplin, J.M. Basset, E. Benazzi, Stud. Surf. Sci. Catal. 84 (1994) 1293.
- [8] F. Quignard, C. Lecuyer, C. Bougault, F. Lefebvre, A. Choplin, D. Olivier, J.M. Basset, Inorg. Chem. 31 (1992) 928.
- [9] F. Quignard, A. Choplin, J.M. Basset, J. Chem. Soc., Chem. Commun. (1991) 589.
- [10] C. Nédez, Doctoral Thesis, University Claude Bernard Lyon I, Lyon, 1992.
- [11] S.A. King, J. Schwartz, Inorg. Chem. 30 (1991) 3771.
- [12] J. Corker, F. Lefebvre, C. Lecuyer, V. Dufaud, F. Quignard, A. Choplin, J. Evans, J.M. Basset, Science 271 (1996) 966.
- [13] V. Capdevielle, Ph.D. Thesis, Lyon, 1996.
- [14] P.J. Davidson, M.F. Lappert, R. Pearce, J. Organomet. Chem. 57 (1973) 269.

- [15] T.V. Lubben, P.T. Wolczanski, *J. Am. Chem. Soc.* 109 (1987) 424.
- [16] A. van Asselt, B.D. Santarsiero, J.E. Bercaw, *J. Am. Chem. Soc.* 108 (1986) 8291.
- [17] J.A. Lanbinger, D.W. Hart, W.E. Seibert III, J. Schwartz, *J. Am. Chem. Soc.* 97 (1975) 3851.
- [18] T.F. Blackburn, J.A. Labinger, J. Schwartz, *Tetrahedron Lett.* 35 (1975) 3041.
- [19] D.J. Cardin, M.F. Lappert, C.L. Raston, P.I. Riley, in: G. Wilkinson (Ed.), *Comprehensive Organometallic Chemistry*, vol. 3, Pergamon Press, London, 1982, p. 638.
- [20] C. Vallantin-Rosier, G.P. Niccolai, R. Petroff Saint Arroman, J.M. Basset, F. Lefebvre, submitted for publication.
- [21] E.N. Clark, P.G. Harrison, *J. Organomet. Chem.* 463 (1993) 85.