

Aluminium alkoxide sulphate catalyst: a computational study

R. Improta, M. Di Serio, E. Santacesaria *

Dipartimento di Chimica dell'Università di Napoli 'Federico II', via Mezzocannone 4, 80134 Napoli, Italy

Received 23 December 1997; accepted 13 March 1998

Abstract

Aluminium alkoxide sulphate catalysts have been used to promote ethoxylation of fatty alcohols with a narrow distribution of the molecular weights. Based on experimental observations, a reaction mechanism and a related kinetic model able to simulate all the performed kinetic runs have been proposed in a previous work by M. Di Serio et al. [M. Di Serio, P. Iengo, R. Gobetto, S. Bruni, E. Santacesaria, *J. Mol. Catal. A: Chem.* 112 (1996) 235]. In the present work the plausibility of the mechanism suggested and the role played by the sulphate groups in the reaction have been evaluated by a computational study. The promoting effect on the reaction rate of sulphate groups is similar to that observed in the heterogeneous catalysis for different oxides treated with sulphuric acid, so the results obtained in this work will also be applied to explain the catalytic behaviour of sulphated alumina. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aluminium alkoxide sulphate catalyst; Ethoxylation; Super acid catalysts

1. Introduction

Aluminium alkoxide sulphate catalysts have been used to promote ethoxylation of fatty alcohols with a narrow distribution of the molecular weights of the oligomers and with a very low concentration of residual unreacted alcohol [1,2]. The narrow-range ethoxylated fatty alcohols (NRE) have better properties than those obtained with the traditional alkaline catalysts KOH or NaOH and for the low ethylene oxide/substrate molar ratio they can be sulphonated without forming undesired dioxane [3].

In a previous work, this catalytic system has been studied by M. Di Serio et al. [4] with regard to the structure of the catalyst and its kinetic behaviour. Based on experimental observations, a reaction mechanism and a related kinetic model, able to simulate all the performed kinetic runs, have been proposed.

The aims of the present work are to evaluate by a computational study the plausibility of the mechanism suggested in the previous work and to investigate the role played by the sulphate groups in the reaction.

The promoting effect of the sulphate group introduced in the aluminium alkoxide molecules shown in this homogeneous reaction is due to the increased acidic properties of the catalytic complex obtained. This promoting effect is similar to that observed in the heterogeneous catal-

* Corresponding author.
E-mail: santacesaria@chemna.dichi.unina.it

ysis for different oxides treated with sulphuric acid.

Despite the importance of the sulphated oxides in many heterogeneous catalytic reactions, very few theoretical works have been addressed to the study of the effect of the sulphate group in catalytic systems of industrial interest [5], so the obtained results of this work will also be applied to explain the catalytic behaviour of sulphated alumina [6].

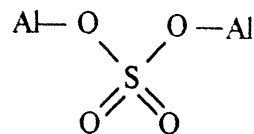
2. Main previous experimental results and suggested mechanism [4]

In the previous work [4] we prepared the catalyst by reacting aluminium isopropoxide with 1-dodecanol in stoichiometric amounts at 130°C, obtaining aluminium tridodecanoxide. After the exchange reaction, we added sulphuric acid (100%) dropwise at 50°C under vigorous stirring of the solution until the molar ratio H_2SO_4/Al between 0 and 1 was reached.

The acidity of the prepared catalysts were calculated as suggested by Benesi [7] and correspond to a weak Bronsted acidity.

The spectroscopic analysis (IR and ^{27}Al NMR) indicates that the addition of sulphuric acid strongly favours the formation of six-coordinate aluminium atoms with respect to the four-coordinate atoms of aluminium tridodecanoxide.

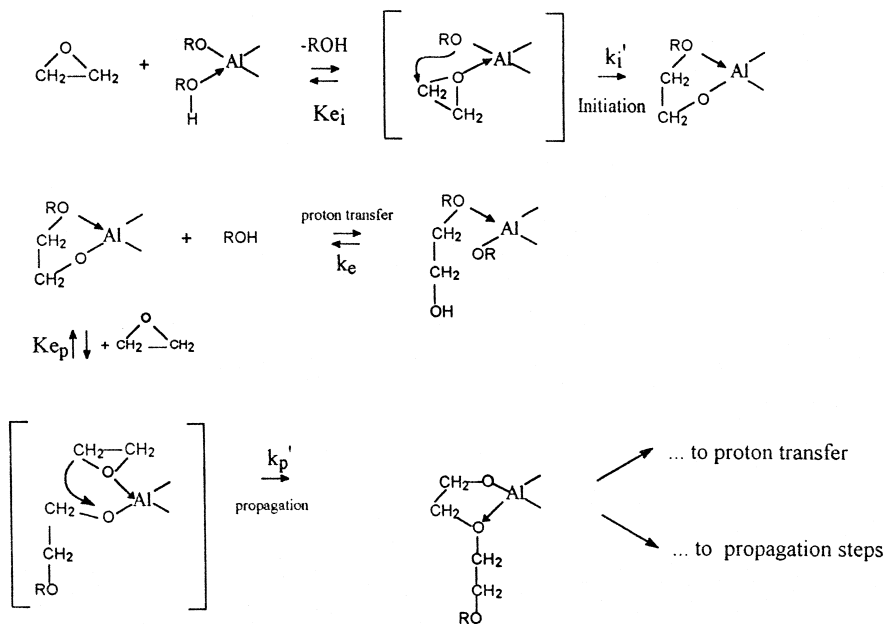
Moreover, after adding sulphuric acid, a bidentate structure of the type



seems to be dominant.

The bidentate structure should have Lewis superacidic properties in analogy with a similar structure proposed by Arata [8] for zirconium oxide treated on the surface with sulphuric acid.

From the experimental results of the kinetic runs, we have concluded that the presence of sulphuric acid strongly increases the activity of the catalyst with respect to untreated aluminium tridodecanoxide. The reaction starts at a very high rate, but after the addition of about one



Scheme 1.

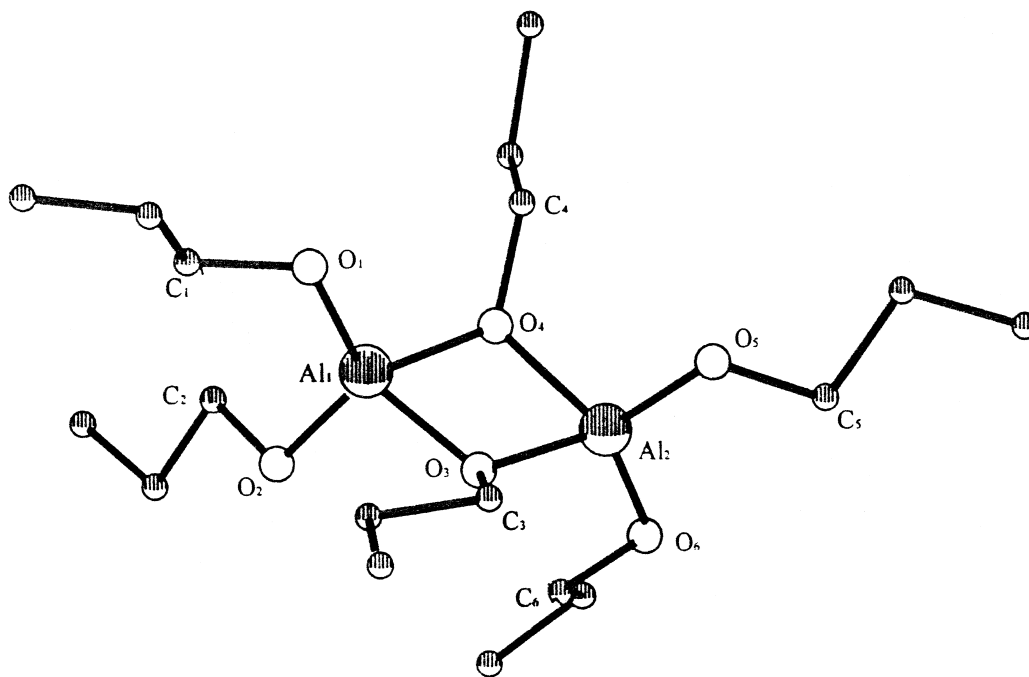
mole of ethylene oxide per mole of the substrate, the activity of the catalyst strongly decreases. As a consequence, fatty alcohol is quickly consumed and the obtained distribution is narrow. In the previous work, we have also shown that the addition of a Lewis base strongly depresses the rate of ethoxylation and that the deactivation of the catalyst is a consequence of the modification of the reaction environment.

On the basis of the experimental observations, the coordinative mechanism shown in Scheme 1 has been suggested. Ethylene oxide initially competes with dodecanol in coordinating the aluminium electron vacancy, then coordinated ethylene oxide reacts with an alkoxide bound to aluminium. The chain can grow further or exchange the proton with a free hydroxyl group. While the first equilibrium expressing the competition of ethylene oxide with alcohol is completely shifted to the right, the second one between two ethereal oxygen atoms, i.e., ethylene oxide or ethylene oxide adduct, is probably almost equivalent in the two directions.

However, as the slow steps are successive to these mentioned equilibria, the effective kinetic constants are affected by the corresponding equilibrium constants.

3. Preliminary considerations and computational details

Though if previous works provide that, under catalytic conditions, sulphuric acid favours the formation of species in which aluminium atoms are esacoordinated, the dimeric species depicted in Scheme 2 and in Figs. 1 and 2 can be considered good models for the real catalytic system, preserving the most important features suggested by the experimental results. The sulphate group of species IA and IIA (Fig. 1A and Fig. 2A) shows indeed a bridging bidentate coordination to the aluminium atoms and all the oxygen atoms coordinated to aluminium belong to OR groups, with R = alkylic group or hydrogen atom.



Scheme 2.

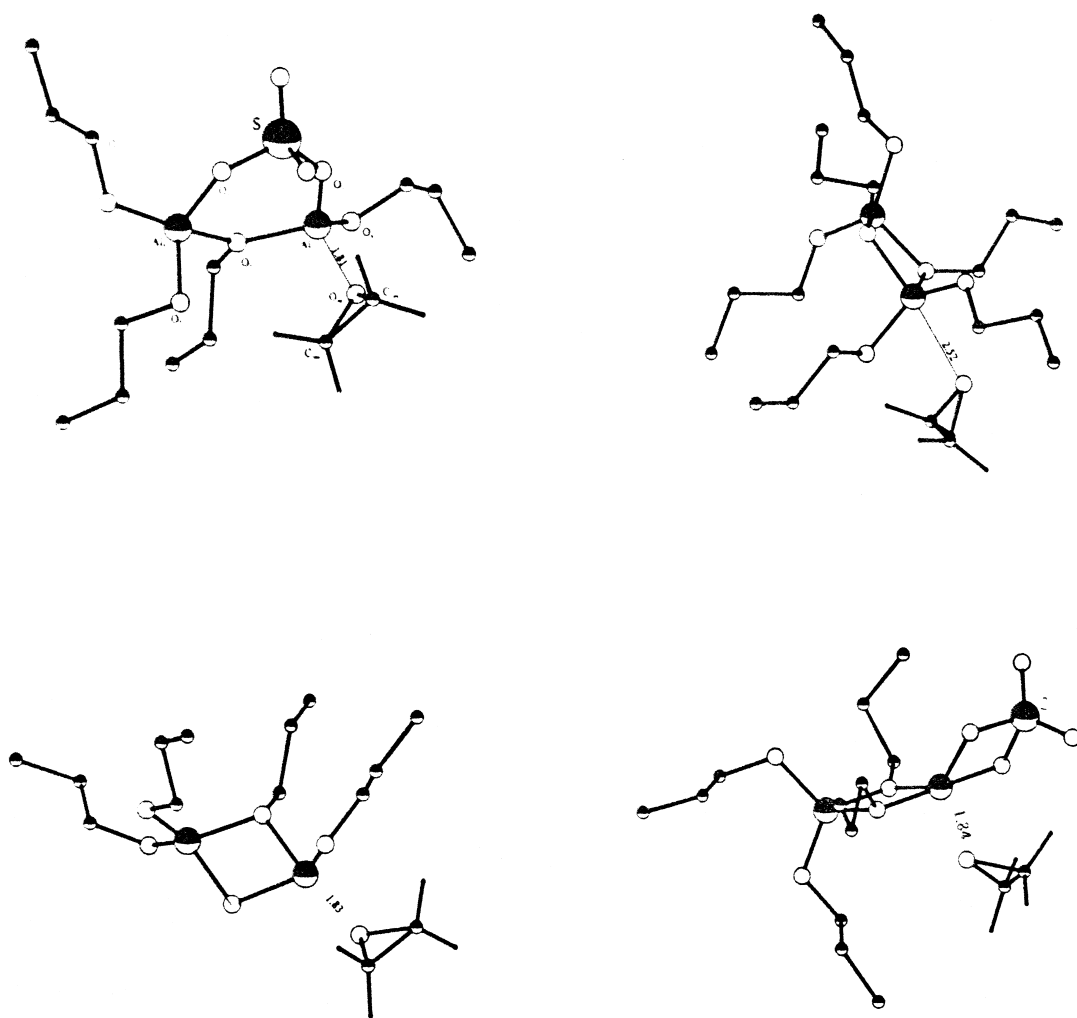


Fig. 1. (A) Coordination of the ethylene oxide adduct to the species 1A. (B) Coordination of the ethylene oxide adduct to the species 1B. (C) Coordination of the ethylene oxide adduct to the species 1C. (D) Coordination of the ethylene oxide adduct to the species 1D.

Moreover an increase in the aluminium coordination seems to be related to the catalytic activity: the results (e.g., barrier heights for the insertion reaction) of this study can thus be considered an upper limit with respect to the real values.

The system depicted in Scheme 1 and in Fig. 1B, where the sulphate group is substituted by an OR group, has been chosen instead as model for the catalytic species in the absence of sulphuric acid, in order to investigate the influence of the latter on the ethoxylation reaction.

The MNDO method in the AM1 parameterization [9,10] (MOPAC package) [11] has been applied in the study of the species IA and IB with R = propyl group, modelling the dodecanolic group of the real catalytic system.

In order to evaluate the reliability of the geometry obtained by AM1 calculations, it is useful to compare our results (see Scheme 2) with the structure obtained by X-ray diffraction [12] of $\text{Al}_2(\text{O}-t\text{-Bu})_6$, a compound very similar to those studied in the present paper (see Table 1).

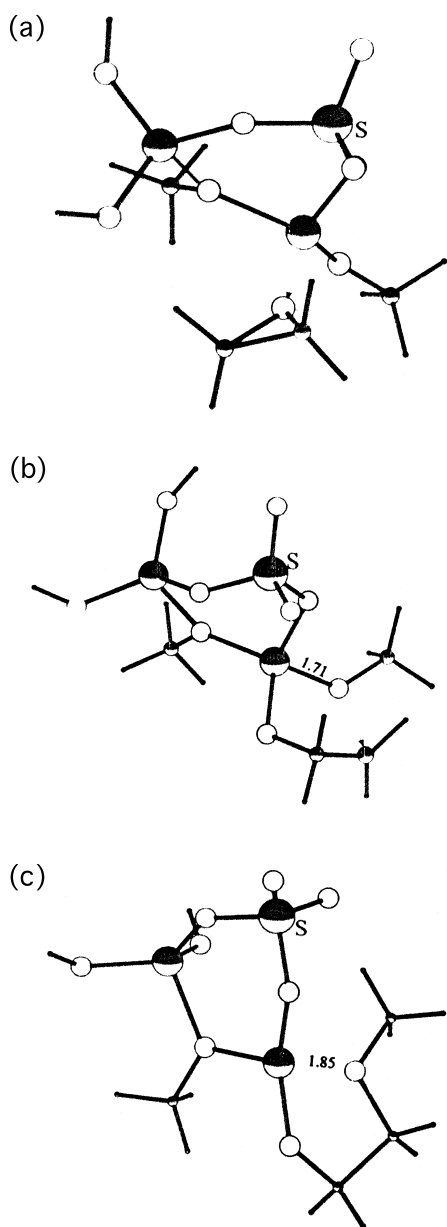


Fig. 2. (A) Minimum for the coordination of the oxirane adduct 2A. (B) Saddle point for the insertion reaction 2B. (C) Product of the ethoxylation reaction 2C.

Table 1 shows that the calculated geometrical parameters are in good agreement with the experimental ones. The differences in the bond distances are never greater than a few hundredths of an angstrom and differences in the bond angles hardly exceed 3–4°: moreover,

those little discrepancies can easily be explained on the grounds of the steric hindrance of the bulky *t*-butylic substituents in the compound of Ref. [12].

Whenever it was necessary to obtain reliable energies, we resorted to SCF-LCAO-MO Hartree–Fock ab initio calculations performed using the GAMESS package [13,14]: in this case, for computational convenience, we have substituted the propyl with methyl groups or with hydrogen atoms. The sulphated catalytic species has thus been modelled by the species IIA (see Fig. 2A), whereas the species IIB, where sulphate is substituted by an OH group, is the model of the catalyst in the absence of sulphuric acid. All the geometries have been optimized with the gradient method. In the ab initio calculations, we have used 3-21G basis sets, augmented with two d functions on sulphur and aluminium atoms [15,16], treating explicitly

Table 1
Comparison between the calculated AM1 and experimental geometrical parameters for an $\text{Al}_2(\text{O-alkyl})_6$ compound

	AM1	Experimental
$\text{Al}_1\text{--Al}_2$	2.81	2.78
$\text{O}_1\text{--Al}_1$	1.73	1.70
$\text{O}_2\text{--Al}_1$	1.73	1.68
$\text{O}_3\text{--Al}_1$	1.80	1.82
$\text{O}_4\text{--Al}_1$	1.80	1.83
$\text{O}_3\text{--Al}_2$	1.80	1.83
$\text{O}_4\text{--Al}_2$	1.79	1.83
$\text{O}_5\text{--Al}_2$	1.74	1.69
$\text{O}_6\text{--Al}_2$	1.74	1.68
$\text{O}_1\text{--C}_1$	1.40	1.42
$\text{O}_2\text{--C}_2$	1.40	1.42
$\text{O}_3\text{--C}_3$	1.42	1.47
$\text{O}_4\text{--C}_4$	1.42	1.47
$\text{O}_5\text{--C}_5$	1.40	1.42
$\text{O}_6\text{--C}_6$	1.40	1.42
$\text{O}_1\text{--Al}_1\text{--O}_3$	111.8	111.7
$\text{O}_1\text{--Al}_1\text{--O}_4$	113.9	109.8
$\text{O}_3\text{--Al}_1\text{--O}_4$	76.9	81.1
$\text{O}_3\text{--Al}_2\text{--O}_4$	72.2	81.1
$\text{O}_3\text{--Al}_2\text{--O}_5$	107.3	98.9
$\text{O}_3\text{--Al}_2\text{--O}_6$	116.5	117.8
$\text{Al}_1\text{--O}_3\text{--Al}_2$	102.8	98.9
$\text{Al}_1\text{--O}_4\text{--Al}_2$	102.8	98.9

Bond distances are in Ångstrom, angles in degrees; for atom numbering, see Scheme 2.

all the core electrons. No constraint has been imposed in the optimization and saddle point search runs.

To our knowledge, there are no theoretical studies in literature of systems in which a sulphate group is bound to aluminium alkoxides: however, the geometries we obtained at the 3-21G level very well agree with those predicted for the sulphate group [6] and the $\text{Al}_2(\text{OH})_6$ dimer [12] using more extended basis sets.

4. AM1 results

4.1. Coordination step

First, we have compared the coordination to the species IA of ethylene oxide and of the octanol molecule (modelling a dodecanol molecule). AM1 results predict that the coordination of the latter is slightly more exothermic than that of the former. The difference is, however, very small (less than 1 kcal/mol) and it is very likely that the situation will completely be reversed if all the steric effects are considered. We have indeed surely underestimated the repulsion between the catalytic species and dodecanol using propoxide groups and octanol molecules, far less sterically hindered than real dodecanoxide and dodecanol; moreover, the average coordination of sulphur in the catalytic system is 5–6, thus reducing still more the conformational space available to the coordination of the bulky dodecanol. All these approximations are likely far less important for the compact ethylene oxide than for the dodecanol molecule, the coordination of which, owing to its long hydrocarbon tail, is very disfavoured from a steric and an entropic point of view.

On balance, the small value of the difference predicted by AM1 calculations supports thus the experimental findings which show that an ethylene oxide adduct can quite easily replace a dodecanol molecule from the coordination to an aluminium atom.

The results of the AM1 (Tables 2 and 3) computations predict that the coordination of an ethylene oxide adduct to the species IA is exothermic for 14.0 kcal/mol. The binding to the aluminium atom produces a nonnegligible variation in the geometry of the ethylene oxide molecule: AM1 calculations predict that OC bond distances increase by 5 pm with respect to the value they assumed in the free molecule, favouring its opening and the ethoxylation reaction. The Mulliken population analysis performed on this system shows that the ethylene oxide moiety appears to be positively charged for 0.235 a.u.: this result can be related with an electronic depletion of the OC bonds and, thus, with a decrease in strength of these bonds. The distance $\text{Al}-\text{O}^{\text{ox}}$ is predicted to be rather low (ca 1.81 Å), close to the distances between the aluminium and the alkoxydic oxygens, confirming the strength of the coordination of ethylene oxide to aluminium in the presence of sulphuric acid. This picture drastically changes when examining the coordination of ethylene oxide to the species IIA (Tables 4 and 5): in the absence

Table 2

Computed ab initio AM1 geometrical parameters of minimum energy configurations for the coordination of ethylene oxide to the specie IA and for the product of the insertion reaction

	Coordination	Product
O_1-Al_1	1.74	1.74
O_2-Al_1	1.74	1.74
O_3-Al_1	1.80	1.80
O_4-Al_1	1.74	1.73
O_3-Al_2	1.77	1.76
O_5-Al_2	1.71	1.69
O_6-Al_2	1.73	2.40
$\text{O}^{\text{ox}}-\text{Al}_2$	1.82	1.73
O_4-S	1.52	1.52
O_5-S	1.59	1.61
O_7-S	1.37	1.36
O_8-S	1.36	1.36
$\text{O}_4-\text{S}-\text{O}_5$	95.2	94.3
$\text{O}^{\text{ox}}-\text{C}_1^{\text{ox}}$	1.47	1.40
$\text{O}^{\text{ox}}-\text{C}_2^{\text{ox}}$	1.47	2.43
$\text{C}_1^{\text{ox}}-\text{C}_2^{\text{ox}}$	1.48	1.53
$\text{O}_6-\text{C}_2^{\text{ox}}$	4.08	1.43
E(SCF)	199.1380	199.1902

Bond distances are in Ångstrom, angles in degrees, energies in atomic units; for atom numbering see Scheme 2.

Table 3

Computed ab initio 3-21G geometrical parameters of minimum energy configurations for the coordination of ethylene oxide to the specie IIA, of transition states for the insertion reactions, of the product of the insertion reaction, of the minimum for the coordination of a second ethylene oxide adduct and of the saddle point for the second insertion reaction

	Coordination	Saddle point	Product	2 Coordination	2 Saddle point
O ₁ -Al ₁	1.67	1.68	1.69	1.68	1.68
O ₂ -Al ₁	1.71	1.68	1.69	1.71	1.68
O ₃ -Al ₁	1.83	1.85	1.84	1.83	1.85
O ₄ -Al ₁	1.75	1.79	1.77	1.75	1.79
O ₃ -Al ₂	1.78	1.75	1.76	1.78	1.75
O ₅ -Al ₂	1.74	1.75	1.71	1.74	1.75
O ₆ -Al ₂	1.64	1.71	1.85	1.65	1.72
O ^{ox} -Al ₂	1.81	1.75	1.70	1.81	1.75
O ₄ -S	1.53	1.54	1.53	1.53	1.54
O ₅ -S	1.55	1.56	1.57	1.55	1.56
O ₇ -S	1.42	1.43	1.42	1.42	1.43
O ₈ -S	1.44	1.43	1.42	1.44	1.43
O ^{ox} -C ₁ ^{ox}	1.51	1.45	1.43	1.51	1.45
O ^{ox} -C ₂ ^{ox}	1.51	2.07	2.40	1.51	2.08
C ₁ ^{ox} -C ₂ ^{ox}	1.47	1.48	1.54	1.47	1.48
O ₆ -C ₂ ^{ox}	4.23	2.35	1.48	4.21	2.37
O ₁ -Al ₁ -O ₂	116.9	119.6	119.2	116.2	120.4
Al ₁ -O ₃ -Al ₂	119.6	115.2	123.7	120.0	115.2
O ₆ -C ₁ ^{ox} -C ₂ ^{ox}	60.9	90.0	107.9	60.8	90.6
E(SCF)	1705.1427	1705.0746	1705.1796	1857.2090	1857.1426

Bond distances are in Ångstrom, angles in degrees, energies in atomic units; for atom numbering see Scheme 2.

of sulphuric acid, AM1 calculations do not predict any energy stabilization coming from the coordination of ethylene oxide.

The distance Al-O^{ox} increases up to 252 pm, 70 pm more than in the preceding case, and the

Table 4

Computed ab initio geometrical parameters of minimum energy configurations for the coordination of ethylene oxide to the species IIB (3-21G) and IB, IC (AM1)

	3.21G	AM1 (IB)	AM1 (IC)
O ₁ -Al ₁	1.68	1.74	1.74
O ₂ -Al ₁	1.68	1.73	1.74
O ₃ -Al ₁	1.81	1.80	1.82
O ₄ -Al ₁	1.80	1.80	1.74
O ₃ -Al ₂	1.89	1.81	1.78
O ₄ -Al ₂	1.83	1.80	1.71
O ₅ -Al ₂	1.72	1.75	
O ₆ -Al ₂	1.70	1.74	1.73
O ^{ox} -Al ₂	2.00	2.52	1.83
O ^{ox} -C ₁ ^{ox}	1.49	1.44	1.47
O ^{ox} -C ₂ ^{ox}	1.50	1.44	1.47
C ₁ ^{ox} -C ₂ ^{ox}	1.47	1.48	1.48
O ₆ -C ₂ ^{ox}	4.06	4.13	4.06

Bond distances are in Ångstrom, angles in degrees; for atom numbering see Scheme 2.

O-C bond distances in the ethylene oxide moiety are much more similar to those typical of the insulated molecule.

Besides, the charge donation from ethylene oxide to aluminium decreases by 0.25 a.u.

These results are in a good agreement with the experimental finding that the ethoxylation reaction is much faster in the presence of sulphuric acid. The influence of the sulphur atom is twofold.

(1) The electronegativity of the sulphate group makes the Al₂ atom much more electrophilic: in IA its Mulliken charge is 1.25 a.u., compared with 1.05 a.u. in IB. The coordination of the nucleophilic oxygen of ethylene oxide is thus much more favoured in the former case.

(2) The presence of the sulphate group increases the space locally available for the coordination of ethylene oxide to aluminium. Indeed, though the presence of the sulphuric acid increases the average coordination number of aluminium, it is likely that the substitution of the bulky propoxide substituents (and, even

Table 5

Computed ab initio geometrical parameters of minimum energy configurations for species ID in the absence (a) and in the presence (b) of an ethylene oxide adduct

	(a)	(b)
O ₁ –Al ₁	1.73	1.74
O ₂ –Al ₁	1.73	1.74
O ₃ –Al ₁	1.80	1.80
O ₄ –Al ₁	1.80	1.79
O ₃ –Al ₂	1.77	1.79
O ₄ –Al ₂	1.78	1.80
O ₅ –Al ₂	1.76	1.79
O ₆ –Al ₂	1.76	1.78
O ₅ –S	1.64	1.62
O ₆ –S	1.64	1.62
O ₅ –S–O ₆	82.5	83.5
O ^{ox} –Al ₂		1.84
O ^{ox} –C ₁ ^{ox}		1.47
O ^{ox} –C ₂ ^{ox}		1.47
C ₁ ^{ox} –C ₂ ^{ox}		1.48

Bond distances are in Ångstrom, angles in degrees; for atom numbering, see Scheme 2.

more, of the dodecanoxide group of the catalytic system) with the compact sulphate group makes the coordination of an ethylene oxide molecule to aluminium easier. This hypothesis is supported by the experimental finding that introducing sulphuric acid restores local symmetry around the aluminium atom whereas the dodecanoxide group produces local disorder, due to its long hydrocarbon tail [4].

In order to evaluate the relative contribution of electronic vs. geometrical effect of the sulphate group, the coordination of ethylene oxide to the species IC (Fig. 1C) has been studied: in this system, Al₂ is tricoordinated as in the system IA, but sulphate is substituted by an ethereal bridge. AM1 calculations (Table 4, third column) predict a geometry of coordination of ethylene oxide very similar to that observed in the system IA. However, the energy stabilization coming from the coordination of ethylene oxide to aluminium, though substantially higher than IB, is less exothermic (more than 5 kcal/mol) than case IA. The partial charge on Al₂ atom has indeed a value of 1.05 a.u. and this atom is less electrophilic than in the presence of the sulphate group. On balance ca. 40%

of the difference between case IA and IB comes from the electron-withdrawing effect of the sulphate group. Our results thus provide that, in the presence of sulphuric acid, aluminium is very electron deficient and, so has rather strong Lewis acidic properties, essential for a good outcome of the ethoxylation reaction. To our knowledge, these are the first computational results available in literature on sulphated aluminium.

AM1 calculations support the hypothesis that this catalyst sulphate group can have a bridging bidentate coordination to aluminium atoms similar to that proposed by Arata [8] for zirconium oxide treated on the surface with sulphuric acid. That structure is indeed predicted to be a stable minimum: the results of geometry optimization have been checked by the vibrational analysis performed on the minimum energy geometry of the species IA, which showed that all the eigenvalues are positive, confirming that the structure IA is a real minimum in the potential energy surface.

The geometry of the dimeric aluminium alkoxide species is indeed not much perturbed from the bridged coordination of the sulphate group. The main difference is obviously found in the Al–O₃–Al angle which has to open (from 100° to 120°) in order to permit the coordination of the sulphate group to aluminium atoms: however, the latter results should not have dramatic effects on the stability of the bridging bidentate species, since the values of the bond angles substantially greater than 100° are rather common for bonds of the metal–oxygen–metal (Ref. [17] and references therein) or Al–O–Al [18,19] type. For example, in γ -alumina the bond angle corresponding to an oxygen atom bridging one aluminium atom in a tetrahedral cavity and another one in an octahedral cavity has the value of about 125° [18,19]. The sulphate group has a geometry which is rather similar to that experimentally determined for sulphuric acid [20]: the differences in the SO bond distances are never greater than 5 pm and the comparison of the computed and experimental bond angles confirms either the reliability of the AM1 re-

sults or the stability of the bridging coordination (see below).

In order to reach a deeper comprehension on the relationship between the geometry of coordination of the sulphate group to the aluminium and the superacidic properties of the catalyst, we have studied the coordination of ethylene oxide to the species ID, in which the sulphate group exhibits a bidentate coordination to a single atom of aluminium (bidentate chelate coordination). The results of the geometry optimizations in the presence and in the absence of the ethylene oxide adduct are summarized in Table 5. Computational results predict that the chelate coordination of the sulphate group is less stable than the bridging one: in the former, the OSO bond angle is constrained up to 82.5° , 19° smaller than that of the experimental value for the free sulphuric acid [20], whereas in the bridging bidentate coordination, it assumes a value of 95.2° . Following semiempirical calculations, the coordination of sulphate in the species ID is thus disfavoured both from an electronic and steric point of view, explaining the experimental finding that most of the sulphate groups have a bridging bidentate coordination to two aluminium atoms [4].

Moreover, the ΔE of the coordination of the oxirane molecule to the species ID is just of 1.5 kcal/mol, i.e., 12 kcal/mol less than the coordination to IA; besides, the Al_2 atom bear a Mulliken positive charge of 1.19 a.u., being 0.06 a.u. less positively charged than in the presence of a bridging coordination. The superacidic properties of the species ID seem thus to be far less pronounced than those of the species IA. Computational results strongly suggest that the superacidic behaviour of a sulphate catalyst critically depends on the geometry of coordination of the sulphate group to the catalytic species.

4.2. Insertion step

At semiempirical level, the ethoxylation reaction is predicted to be very exothermic. AM1

calculations predict indeed that the opening of the ethylene oxide cycle and the insertion of a carbon atom in the Al–OR ($Al-O_6$ in Fig. 1A) bond produces an energy stabilization of about 37 kcal/mol.

As previously suggested, after the insertion reaction has occurred, the ethoxylated chain folds on itself in order to permit the coordination of the ethereal oxygen to the aluminium atom (Table 2 and Fig. 3). Following AM1 calculations, the $Al-O_6$ bond distance is 240 pm, allowing a strong coordination interaction between those atoms.

Indeed, AM1 calculations provide an energy stabilization of 14 kcal coming from the coordination of the ethereal oxygen to aluminium.

Another hint on the strength of the latter interaction comes from the distances between O_6-C in the ethoxylated chain: they are predicted to be slightly longer than standard ethereal O–C bonds. All the other geometrical parameters are instead very similar to those typical of the coordination step.

4.3. Coordination of another ethylene oxide molecule

The last step in our analysis of the ethoxylation mechanism was to study the coordination of another ethylene oxide molecule to the system IA, after the insertion reaction has occurred. Indeed, we remind that the narrow range of distribution of the oligomers has been explained on the ground of the difficulty for other ethylene oxide adducts to shift the ethereal oxygen of the ethoxylated chain from the coordination with aluminium electronic vacancy.

In this case, a simple energetical analysis is not enough, because the transition from the chelate bicoordination of the ethoxylated chain towards a coordination of two different units (growing chain plus ethylene oxide adduct) is disfavoured from an entropic point of view. As matter of fact, AM1 calculations predict that the reaction,



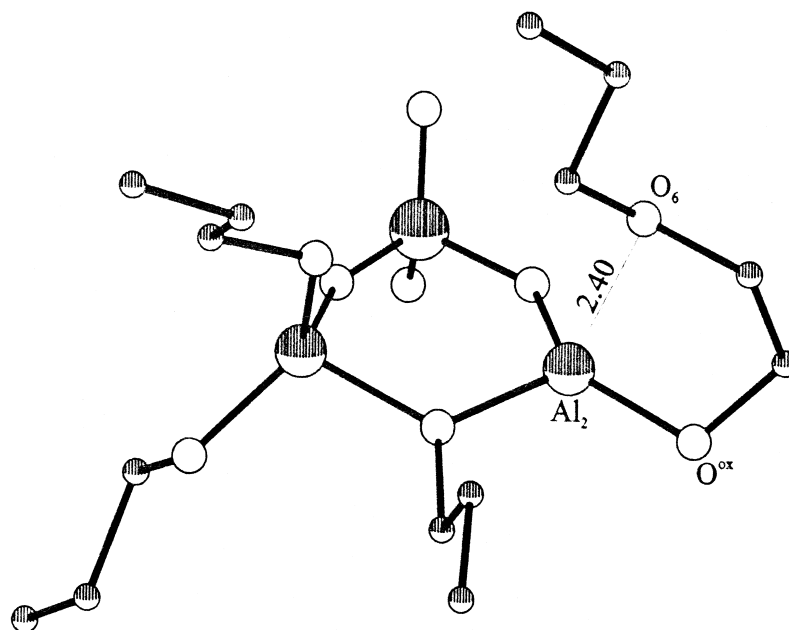


Fig. 3. Product of the ethoxylation reaction in the presence of species IA.

where C = catalytic species with an ethoxylated chain, Ox = ethylene oxide adduct, COx = catalytic species with coordinated ethylene oxide, is exothermic for 3.2 kcal/mol.

In order to calculate the overall equilibrium constant for reaction (1), it is, however, necessary to resort to the ripartition function of the reactant and the product

$$K = \left(Q_r^{\text{COx}} Q_v^{\text{COx}} Q_t^{\text{COx}} / Q_r^{\text{C}} Q_v^{\text{C}} Q_t^{\text{C}} Q_r^{\text{Ox}} Q_v^{\text{Ox}} Q_t^{\text{Ox}} \right) \times \exp(\Delta E_0 / RT) \quad (2)$$

An exact evaluation of Eq. (2) is not an easy task, requiring the calculation of the vibrational and rotational energetic contribution: a rough estimate is, however, possible, neglecting in first approximation the contribution of the rotational and vibrational degrees of freedom and considering equal the translational contribution of C and COx which have almost the same mass. Within those approximations, at a temperature of 400 K, the equilibrium constant of Eq. (1) is 1.7. Considering that the neglected contributions favour the reactant on the product because the rotational degrees of the coordinated

ethylene oxide are lost, the theoretical results are in very good agreement with the experimental ones suggesting that the equilibrium (1) is almost equivalent in the two directions.

5. Ab initio results

The most important features of the reaction outlined at semiempirical level are validated from the results of ab initio calculations. The main geometrical parameters of the minimum energy geometry of the species IIA and IIB are indeed very similar to those predicted by AM1 calculations for the corresponding species IA and IB (see Tables 2 and 6). Moreover, the bridged bidentate structure for the sulphate group is predicted to be a minimum also at ab initio level, the difference between the geometry of the coordinated sulphate group and the experimental geometry of sulphuric acid [20] being smaller than those predicted from semiempirical results.

Ab initio results confirm the superacidic properties of the sulphated species: the coordi-

Table 6
Energetics of the main steps of the ethoxylation reaction

		ΔE for the coordination of the ethylene oxide adduct			
		IA	IB	IC	ID
AM1		-13.97	-0.0097	-9.63	-1.80
Ab initio					
		IIA	IIB		
		-45.6	-25.5		
		Energy barrier for the insertion in the Al-alkoxide bond			
		First insertion	Second insertion		
Ab initio		42.6	42.6		

Energy in kilocalories per mole.

nation of an ethylene oxide molecule to the species IIA is found to be exothermic for 45 kcal/mol, the bond distance $\text{Al}_2\text{-O}^{\text{ox}}$ has a value of 1.81 Å and, in the oxirane molecule, OC bond distances increase from 146 to 151 pm, confirming the decrease in the strength of those bonds.

On the other hand, if the sulphate group is absent, the coordination step is less exothermic for more than 20 kcal/mol and the $\text{Al}_2\text{-O}^{\text{ox}}$ bond distance increases up to 2.00 Å.

In the presence of the species IIA, the insertion reaction is exothermic for about 23 kcal/mol and the ethoxylated chain is confirmed to fold around the aluminium atom: the Al-O_6 bond distance is 185 pm, just 20 pm longer than that at the coordination step, when O_6 is directly bound to aluminium. As a consequence, the bond between O_6 and the carbon atoms in the ethoxylated chain is weakened, their bond distances increasing up to 148 pm. Ab initio calculation provide an energetical stabilization of about 25 kcal/mol coming from the coordination to the aluminium atom by the ethereal oxygen of the ethoxylated chain.

We finally resorted to ab initio calculations to locate the saddle point for the insertion reaction of one and two ethylene oxide adducts in the Al-O_6 bond. The inspection of Table 6

shows that there is no relevant difference in the geometry of the saddle point for the first (initiation) and the second (propagation) insertion step. Moreover, the activation energy for the two insertion steps has practically the same value. These results are in a good agreement with the experimentally obtained apparent kinetic parameters which show that the initiation step is faster than the propagation one mainly for the preexponential factors, whereas the activation energies are quite similar.

In the saddle point, O_6 is very close to the aluminium atom (bond distance 175 pm). Since after the ethylene oxide insertion has occurred, the O_6 atom is just 184 pm away from the Al_2 atom, ab initio calculations show that during and after the initiation step, the O_6 atom always remains bound to the aluminium atom.

It should be noted that during the first insertion step, the aluminium atom is always shielded by the starting ethoxylated chain, and, consequently, the coordination of another ethylene oxide adduct is very difficult.

Once insertion has occurred, the long and flexible hydrocarbon chain (12 carbon atoms) prevents another oxirane molecule from approaching the catalytic system at distances short enough to assist the breaking of the bond between O_6 and the aluminium atom. A second coordination step would thus let the system lose all the energy stabilization (at least about 15 kcal/mol) coming from the coordination of the ethereal oxygen of the growing chain without having any contribution from the coordination of another oxirane adduct.

The latter step thus seems to be very disfavoured from a kinetic point of view, in good agreement with experimental results.

6. Discussion and conclusion

Validating our previous suggestion [4], semiempirical and ab initio computations pre-

dict that the ethoxylation reaction proceeds through the coordinative mechanism depicted in Scheme 1.

The first step consists in the coordination of the ethylene oxide adduct to an aluminium atom, displacing a dodecanol molecule, whose coordination is more disfavoured from a steric point of view. In agreement with experimental results, our computations assign a fundamental role in the ethoxylation reaction to the presence of the sulphate group. In a bridging bidentate coordination (see below) the latter species makes the coordination step much more exothermic (from -14.00 to -0.01 kcal/mol) and increases the charge donation from the oxirane moiety to the aluminium atom of 0.25 a.u. Indeed, the electron-withdrawing effect of the sulphate group makes aluminium atoms more positively charged (0.19 a.u.) and, consequently, more electrophilic. The OC bonds in the oxirane moiety are thus remarkably weakened (cf. their bond distances) and the opening of the oxirane ring is much easier. Besides, according to AM1 results, the sulphate group favours the ethoxylation reaction also increasing the space locally available for the coordination of the oxirane adduct.

As a matter of fact, in the second reaction step oxirane ring opens and enters the bond between aluminium and an alkoxydic oxygen. Both semiempirical and *ab initio* computations predict that, after the insertion reaction has occurred, the ethoxylated chain folds on itself in order to coordinate the ethereal oxygen atom to aluminium. This bonding interaction provides an energy stabilization of at least 15 kcal and decreases the probability of a successive ethylene oxide coordination. Entropic effects make indeed the transition from a bidentate to two monodentate ligands disfavoured; moreover, from a kinetic point of view, the second coordination step should have a remarkable activation energy (see Section 5). *Ab initio* computations show that, instead, the first and the second insertion steps have the same activation energy.

On the ground of the difficulty in the second coordination step, it is therefore possible to give

a convincing explanation to the narrow range distributions of oligomers obtained.

Computational results strongly suggest that the superacidic behaviour of a sulphate catalyst critically depends on the geometry of coordination of the sulphate group to the catalytic species.

The most acid sites, indeed, are those in which the sulphate group shows a bridging bidentate coordination to two aluminium atoms, forming structures similar to those ones suggested for heterogeneous sulphated catalysts by Arata [8].

Structures in which the sulphate group has a bidentate chelate coordination to a single aluminium atom are instead far less stable and show less pronounced acidic properties.

The finding that there is such a close relationship between the structure of a sulphated site and its acidity, though surely not new (see, for instance, Ref. [5]), could also be a promising key towards a deeper comprehension of the behaviour of the heterogeneous sulphated catalyst. As a matter of fact, despite the great number of papers devoted to the study of the sulphated metal oxide (Ref. [8] and references therein; Ref. [21]) due to the industrial interest for their high acidity [22], there are many unsettled questions. For example, what are the reasons for the influence of the procedure of preparation of a heterogeneous catalyst on its acidic properties? Why does the sulphated aluminium alkoxide catalyst have, in the homogeneous phase, a behaviour similar to that of sulphated zirconium alkoxide whereas sulphated alumina shows features very different from sulphated zirconium oxide? The enhancement in acidity, up to superacidity by sulphated addition on the amorphous forms, followed by calcination to the crystallization was indeed observed [8] on ZrO_2 and on the oxides of elements of the same group (Ti and Hf) [8]. On the other hand, the crystalline forms of these oxides treated by sulphate ion do not show any remarkable superacidic properties [8]. Alumina has instead an opposite behaviour: it was found that the superacid Al_2O_3 was prepared from the crystal-

lized oxide, by exposing $\gamma\text{-Al}_2\text{O}_3$ to H_2SO_4 and calcinating in air [5] whereas the activity enhancement of Al_2O_3 by sulphate addition on the amorphous forms followed by calcination was not observed [23].

In the homogenous phase, it has been instead observed that the zirconium alkoxide sulphate catalyst can be used in the narrow range ethoxylation, and its behaviour is very similar to that of the sulphate aluminium alkoxide catalyst [24]. Besides, heterogeneous catalysts obtained by grafting zirconium and aluminium alkoxide sulphate on silica and subsequent calcination show a very strong acidity because they are able to promote hydrocarbon isomerization and cracking at relatively low temperatures [25].

On the basis of our computational results, we suggest that these peculiar features can be explained admitting that in ZrO_2 and Al_2O_3 the active acid sites have structures which have a different coordination geometry of the sulphate group.

Indeed, regarding this aspect, Saur et al. [26] have shown that the bidentate chelate species were not present on sulphated δ -alumina, in agreement with the findings of IR spectra of aluminium alkoxide sulphate [4] and with the calculation reported above in this paper. On sulphated zirconium alkoxide, Di Serio et al. [24] have instead shown by I.R. spectroscopy that besides bidentate bridged complexes bidentate chelate complexes were also present in the homogeneous phase.

The latter kind of structure is probably present also on amorphous zirconia treated with H_2SO_4 [27,28] which shows IR spectra very similar to that of homogeneous catalysts; moreover, the possible existence of this structure on sulphated zirconia is confirmed by theoretical calculations [6]. According to Saur et al., bidentate chelate species are instead absent on sulphated TiO_2 obtained by sulphatation of crystalline TiO_2 [26]; besides, a closer inspection of the data by Morterra et al. [27] shows that the intensity of the signal at 1200 cm^{-1} , which is present also in the IR spectra of zirconium

alkoxide sulphate and has been attributed to chelate bidentate sulphate [24], decreases in intensity by increasing the crystallinity of the ZrO_2 precursor.

Since the catalysts obtained by sulphatation of the group IV crystalline metal oxide do not exhibit any remarkable superacidic behaviour [8], we suggest that, on sulphated zirconia, the superacidic sites are those in which the sulphate group has a bidentate chelate coordination.

As we have seen on aluminium alkoxides the most acid species show a bidentate bridging coordination of the sulphate group.

Our computations provide that the creation of superacidic sites by sulphatation of aluminium thus requires the presence of pairs of aluminium atoms with a bond distance of about 3.1 \AA in order to allow the formation of a stable bridging bidentate species. This is indeed the case of $\gamma\text{-Al}_2\text{O}_3$ where the distance between two neighbour aluminium atoms ranges between 2.7 and 3.2 \AA [18,19], whereas starting from amorphous aluminium hydroxide, the probability of Al–Al pairs with that favourable distance should decrease. Bridging bidentate structures can be formed upon sulphatation also on crystalline ZrO_2 , HfO_2 , and TiO_2 , but, for these compounds, they compete with the more acid chelated species, and, thus decrease the superacidic properties of the catalyst. On the catalyst obtained by sulphatation and calcination of amorphous oxide, the presence of bidentate chelate species seems more probable, for the latter involve just a single metal atom and are compatible with more disordered structures, too.

The lower acidity of the bidentate structures likely depends on the fact that the simultaneous interactions of sulphate groups with more than one atom of metal make the sites less electrophilic than in the bidentate chelate structure.

By now, these are almost qualitative conclusions; moreover, the problem of the transferability of considerations and concepts from the homogeneous to the heterogeneous catalysis is surely a delicate and still open question.

However, we think that the attempt of bridg-

ing these two worlds has been and will be of fundamental importance: in this spirit, the cooperative employment of experimental and theoretical studies can be very helpful to elucidate the main features of such complex systems.

References

- [1] C.L. Edwards, U.S. Patent 4,721,816 (1988).
- [2] C.L. Edwards, U.S. Patent 4,721,817 (1988).
- [3] K.L. Matheson, P.A. Schwab, Proc. of 3rd CESIO Int. Surfactants World Congr. and Exhibition, London, 1991, p. 291.
- [4] M. Di Serio, P. Iengo, R. Gobetto, S. Bruni, E. Santacesaria, *J. Mol. Catal. A: Chem.* 112 (1996) 235.
- [5] F. Babou, B. Bigot, P. Sautet, *J. Phys. Chem.* 97 (1993) 11501.
- [6] K. Arata, M. Hino, *Appl. Catal.* 59 (1990) 205.
- [7] N.A. Benesi, *J. Phys. Chem.* 61 (1957) 970.
- [8] K. Arata, *Adv. Catal.* 37 (1990) 165.
- [9] M.J.S. Dewar, W. Thiel, *J. Am. Chem. Soc.* 99 (1977) 4899.
- [10] M.J.S. Dewar, E.G. Zebisch, E.F. Healye, J.J.P. Stewart, *J. Am. Chem. Soc.* 107 (1985) 3902.
- [11] J.J.P. Stewart, *J. Comput. Chem.* 10 (1989) 209, J.J.P. Stewart, MOPAC 6.00: QCPE No. 438.
- [12] R.H. Cayton, M.H. Chisholm, E.R. Davidson, V.F. DiStasi, P. Du, J.C. Huffman, *Inorg. Chem.* 30 (1991) 1020.
- [13] M.F. Guest, P. Sherwood, GAMESS, an ab initio program, The Daresbury Laboratory, Warrington.
- [14] M.W. Schmidt, K.K. Baldrige, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.J. Jensen, S. Koseki, M. Matsunaga, K.A. Nguyen, S. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, *J. Comput. Chem.* 14 (1993) 1347.
- [15] J.S. Binkley, J.A. Pople, W.J. Hehre, *J. Am. Chem. Soc.* (1980) 102, 939.
- [16] M.S. Gordon, J.S. Binkley, J.A. Pople, W.J. Pietro, W.J. Hehre, *J. Am. Chem. Soc.* 104 (1982) 2797.
- [17] R.J. Hogdson, *Prog. Inorg. Chem.* 19 (1975) 1973.
- [18] B. Peri, *J. Phys. Chem.* 69 (1965) 211.
- [19] H. Kawakami, S. Hoshida, *J. Chem. Soc., Faraday Trans. 2* 82 (1986) 1385.
- [20] R.L. Kuczkowsky, R.D. Suenram, F.J. Lovas, *J. Am. Chem. Soc.* 103 (1981) 2561.
- [21] M. Misono, T. Okuhara, *Chemtech*, November (1993) 23.
- [22] T.K. Cheung, B.C. Gates, *Chemtech*, September (1997) 28.
- [23] M. Hino, PhD thesis, Hokkaido Univ., 1982.
- [24] M. Di Serio, P. Iengo, G. Vairo, E. Santacesaria, *J. Surf. Deter.* 1 (1998) 83.
- [25] P. Iengo, M. Di Serio, A. Sorrentino, V. Solinas, E. Santacesaria, *Appl. Catal. A: General* 167 (1998) 85.
- [26] O. Saur, M. Bensitel, A.B. Mohammed Saad, J.C. Lavalley, Carl P. Tripp, B.A. Marrow, *J. Catal.* 99 (1986) 104.
- [27] C. Morterra, G. Cerrato, C. Emanuel, V. Bolis, *J. Catal.* 142 (1993) 349.
- [28] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, G. Strukul, *J. Catal.* 149 (1994) 181.