Ab initio study of the isocyanate surface complex over silica and alumina

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Abstract

Ab initio calculations have been performed to study the stability of isocyanate complex (NCO) over silica and alumina surfaces. Mulliken and natural bond population analysis methods have been used in order to analyze charge distributions and the direction of charge transfer processes. The results indicate that the NCO group adsorbs linearly and perpendicularly to both surfaces; namely, on top site over silica and on bridge site over alumina. It was observed that the charge transfer from the oxygen lone pairs of NCO to the N–C antibonds produces a weakening of N–C link. This phenomenon is more important over alumina, yielding to an easier NCO decomposition over the surface of this oxide. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isocyanate; Silica; Alumina; Ab initio; Cluster model

1. Introduction

New government regulations require that vehicles emit less NO_x, CO and hydrocarbons, transforming them to NO_2, CO_2 and H_2O. In automobile catalytic converters, CO and nitrogen oxides react over metal support catalysts. The oxygen used to oxidize CO to CO_2 is supplied by O_2, as well as by the NO reduction to N_2. Then, the NO + CO reaction plays an important role in the removal of pollutants [1–3].

Recently an increasing interest was focused on the presence of intermediate species other than monoatomic N, O or non-dissociated CO. In particular, the formation of isocyanate complex (NCO) as a product of NO + CO reaction has been observed on Pt/SiO_2, Rh/SiO_2 and Rh/Al_2O_3 catalysts, and Ni, Cu and Pt in zeolites [4–8]. The NCO complex is formed on the metal and migrates to the support [4,8]. For this reason, it is believed that this complex could act as a spectator species, i.e. not playing a central role in the overall $2 NO + 2 CO \Rightarrow N_2 + 2 CO_2$ reaction. However, NCO can react with water to yield ammonia and can be the source of the formation of HCN, a dangerous gas which can also act as a catalyst poison [8].

Solymosi et al. studied the adsorption of NCO, using HNCO as a source of this complex, over several oxides usually acting as supports. These authors discovered that NCO is very stable on silica but it decomposes easily on titania and zirconia. They established that the NCO stability decreases in the following order: $SiO_2 > Al_2O_3 > MgO > Cr_2O_3 > TiO_2$ [8].

The goal of this work is to study comparatively the stability of NCO group adsorbed over silica and alumina model clusters employing an ab initio method. The natural bond orbital (NBO) and Mulliken

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population analysis were used to explain the mentioned stability from an electronic point of view.

2. Model

The molecular orbital calculations have been performed using the unrestricted Hartree–Fock (UHF) method as implemented in the software package Gaussian 98 [9] with minimal multiplicity. The HF method provides reasonable results in full geometry optimization [10]. The alumina surface was represented by cutting the hexagonal unit of ideal α-alumina in such a way that Al and O ions are exposed one below the other [11]. A similar procedure was applied with the surface of silica for which the ideal β-cristobalite structure was used with the Si–O–Si angles having 180° [12]. For both oxides, the terminal oxygen atoms were saturated with hydrogens. This is a well-known procedure to embed the cluster and eliminate spurious effects due to dangling bonds of unsaturated oxygen atoms [13–15]. Thus, the clusters representing the oxide surfaces can be designed by $Si_4O_3(OH)_9$ and $Al_4O_3(OH)_6$. In Fig. 1 schematic pictures of these clusters are given. The geometric structure of both oxides was fixed throughout the calculation. In particular, the Si–O and Al–O distances were set to 1.61 and 1.84 Å values, respectively [12,16]. The height,

orientation, internal angles and distances of the isocyanate complex have been fully optimized.

The molecular orbitals were expanded with the 6-31G atomic basis set, which has shown in the past to be an adequate election to give good energies and molecular conformations for molecules of oxides in comparison with the 3-21G basis set [17,18]. The quadratically convergent self consistent field (SCF) formalism based on the method of Bacsckay [19] was applied. For the geometry optimization, the Berny algorithm that employs internal coordinates [20] was used.

Electron delocalization interactions were studied employing the NBO approach [21]. Within this approach, localized orbitals correspond either to occupied orbitals (core, bonds and lone pairs) and unoccupied orbitals (antibonds and Rydberg orbitals). Their respective occupation numbers are given by the density-matrix element as calculated in the NBO basis. Since the Fock matrix is not diagonal in the NBO basis, it is also possible to evaluate by means of second order perturbation theory, the delocalization energy, $\Delta E^{(2)}$, associated to the charge delocalization from an occupied orbital to an unoccupied orbital [22].

The concept of overlap population (OP) from the Mulliken population analysis was used to study the bond strength between two atoms.
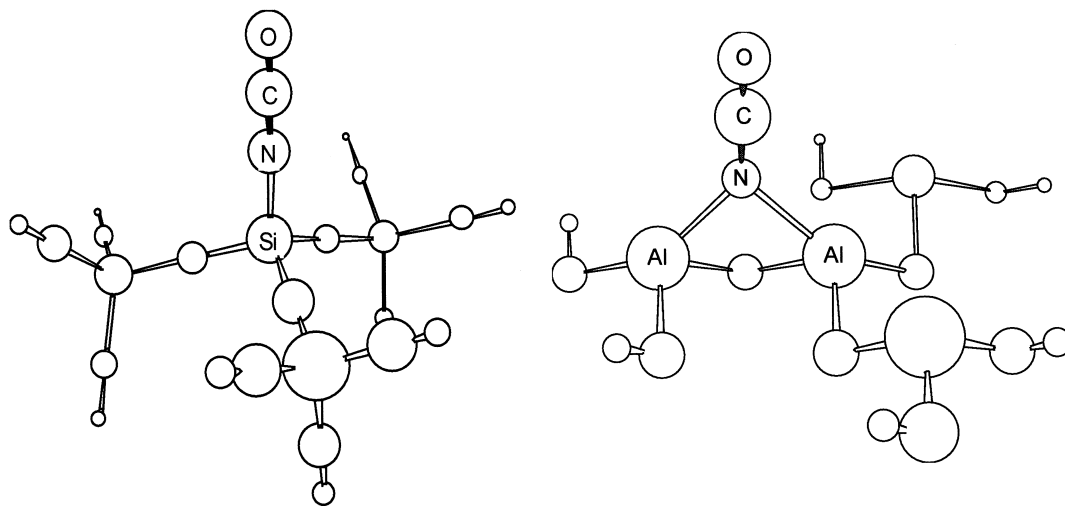

Fig. 1. Schematic representation of the NCO group adsorbed over silica (left) and alumina (right) cluster models.

3. Results and discussion

In Table 1, the main geometric, electronic and vibrational parameters of NCO adsorption over silica, alumina and HNCO in gas phase are shown. Over silica NCO coordinates more favorably with only one Si, while on alumina NCO prefers to be linked forming a bridge between two Al. Imposing the on top geometry is not a stable situation; thus, deriving to the two-fold geometry. The results indicate that the isocyanate group adsorbs linearly and perpendicularly to the oxide surfaces in both cases. Regarding the geometry, the most significant difference is observed in the N–C distance: 1.218 Å on alumina and 1.179 Å on silica. The last value is similar to that obtained for HNCO. The C–O distance is somewhat shorter on alumina. Besides, the N–Al distance is longer than the N–Si distance. The OP values of C–O bond are very similar although slightly lower for free HNCO.

Table 1
Geometric parameters (distances d in Å, and angles in °), Mulliken net charges Q (in electron units), overlap populations (OP) and frequencies ν (in cm^{-1}) of asymmetric stretching vibration[a]

	SiO$_2$	Al$_2$O$_3$	HNCO
d(T–N)[b] (Å)	1.729	2.060	0.979
d(N–C)	1.179	1.218	1.176
d(C–O)	1.178	1.159	1.179
(T–N–C)[b] (°)	180.0	135.5	153.9
(N–C–O)	180.0	178.7	175.7
Q(T)[b] (e$^-$)	+2.503	+1.594	+0.438
Q(N)	−0.771	−1.021	−0.678
Q(C)	+0.625	+0.755	+0.752
Q(O)	−0.509	−0.398	−0.512
Q(NCO)	−0.655	−0.664	−0.438
OP(T–N)[b]	0.351	0.110	0.660
OP(N–C)	1.442	1.104	1.151
OP(C–O)	1.041	1.089	1.014
ν (cm^{-1})			
Calculated[c]	2208	2067	2201
Experimental[d]	2300	2255	2274

[a] Multiplicities for NCO/SiO$_2$, NCO/Al$_2$O$_3$ and HNCO are 1, 2 and 1, respectively.
[b] T = Si, Al or H.
[c] Scaled according to the empirical factor of 0.8929, as suggested in [9].
[d] From [8].

Concerning the calculated Mulliken net charges, we can observe that in the three cases, the N and O atoms have negative charge while that of the C atom is positive. In particular, the N charge on alumina is very large. This observation can be related to a particular charge transfer mechanism as it will be outlined later. The net charge for the NCO group is higher when it is adsorbed over the oxide surfaces.

The shorter N–C distance over silica is presumptively an indication of a stronger N–C bond. This can be verified looking at the overlap population values. Indeed, the overlap population for silica is significantly higher than that for alumina (1.442 against 1.104) and still for the isocyanic acid, showing that the N–C bond strength is higher in the first case.

The NCO decomposition reaction over a catalytic site can be expressed as [23]

$$2T\text{–}NCO \Rightarrow N_2 + 2CO + 2T, \quad T = Si \text{ or } Al$$

and requires as an obvious intermediate step, the N–C breaking. In such a way, the stability of this group must be related to N–C bond strength. Hence, taking into account the precedent considerations, the NCO decomposition is more probable over alumina than on silica because the N–C bond is weaker in the first case.

Regarding the frequencies, the asymmetric stretch of isocyanate, which is the most intensive of the bands, has been calculated. Infrared studies show that the position of this band depends on the nature of the support and it decreases as the stability decreases, i.e. in the sequence SiO$_2$ > Al$_2$O$_3$ > MgO > Cr$_2$O$_3$ > TiO$_2$ [8].

Looking at the calculated values, it can be observed that all of them are underestimated with respect to the experiments, although the order SiO$_2$ > HNCO > Al$_2$O$_3$ is the correct one. However, the relative differences are not so well represented. In particular, the HNCO and SiO$_2$ frequencies are very close. Complementary calculations performed using the PM3 semiempirical method [24] give 2292, 2255 and 2267 cm^{-1} values for SiO$_2$, Al$_2$O$_3$ and HNCO, respectively, in good agreement with the experimental results. This improvement could be due to the inclusion of some degree of electron correlation effects in the last method.

Looking the overlap population corresponding to T–N bonds for T = H, Si or Al in Table 1, we notice that the different OP's are in the following order:
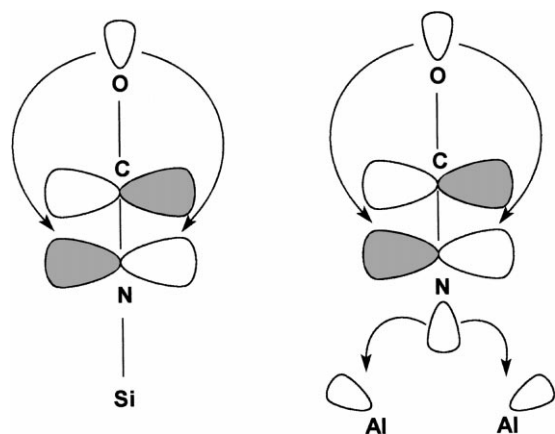
Fig. 2. Qualitative depiction of the charge transfer process $n(O) \rightarrow (N–C)^*$ when NCO adsorbs over silica (left) and alumina (right). The charge transfer process $n(N) \rightarrow n^*(Al)$ is also shown.

Table 2
Natural charges Q (in electron units) and orbital occupations (Occ[a])

	SiO$_2$	Al$_2$O$_3$	HNCO
$Q(T)^b$ (e$^-$)	+2.680	+1.902	+0.480
$Q(N)$	−1.074	−1.173	−0.844
$Q(C)$	+1.042	+0.999	+0.994
$Q(O)$	−0.631	−0.565	−0.630
$Q(NCO)$	−0.663	−0.739	−0.480
Occ (N–C)	5.95	5.84	5.98
Occ (C–O)	2.00	1.96	1.99
Occ $n(O)$	5.34	5.08	5.32
Occ (N–C)*	0.64	0.76	0.65
Occ (C–O)*	0.01	0.24	0.05
$n(O) \rightarrow (N–C)^*$ (kcal/mol)	397.27	571.97	409.67
$n(N) \rightarrow n^*(Al)$	–	51.26	–

[a] Lone pairs are indicated with 'n'. The notation $n(O) \rightarrow (N–C)^*$ designs the charge transfer process from the oxygen lone pairs of NCO to the antibonds N–C. Delocalization energies are in kcal/mol.

[b] T = Si, Al or H.

0.660 (H–N) > 0.351 (Si–N) > 0.220 (Al–N), after normalizing the OP (Al–N) to take into account the number of bonds for the bridge site. Evidently the Al–N bond is less covalent than the Si–N and H–N ones. This points out the possibility of an important contribution of ionic nature in the Al–N bond. Indeed, notwithstanding the observation that the complete NCO group has nearly the same net charge in silica or alumina, in the last case there is a significant electron drift of ∼0.3e from the oxygen atom to the nitrogen atom, which remains negatively charged facing the positive Al ions. This charge transfer process is illustrated in Fig. 2.

These electronic structure properties can be studied from an alternative point of view. In Table 2, the principal parameters of the NBO analysis extracted from the previous molecular orbital calculations are summarized. The NBO analysis for T–NCO reveals the main features of its electronic structure: single C–O bond, triple N–C bond, the corresponding antibonds and the three oxygen lone pairs. Besides, the N atom has a lone pair only over alumina (like the NCO$^-$ ion). The magnitude of individual atomic net charges for N, C and O is somewhat greater than that calculated through the Mulliken population analysis, but they also show that an important O $\rightarrow$ N electron drift is present in alumina in comparison with silica, supporting the idea that an important ionic bond has been formed between N and Al. This charge comes

fundamentally from the O lone pairs (see Fig. 2), as it can be deduced noting that its population is 0.26 units lower in alumina than in silica. This fact can contribute to the important increase of 0.12 units in the N–C antibonding population. On the other hand the N–C bond population decreases by 0.11 units. The last two results are in agreement with the fact that the N–C bond has become weaker in alumina. The $n(O) \rightarrow (N–C)^*$ parameter of NBO is notably greater in alumina than in silica. Another interesting observation is the greater (C–O)* occupation (by 0.23 units). It would indicate a weaker CO bond; nevertheless, as Table 1 shows the C–O distance is somewhat shorter, likely due to a lower electron–electron repulsion accompanying the above commented oxygen lone pairs depopulation.

It is instructive to relate these results with the electronic properties of bulk alumina. The α-Al$_2$O$_3$ ideal periodic structure can be constructed using as an elemental unit a triangular prism with a central Al atom, surrounded by six O atoms, three of them at 1.84 Å and the other three at 1.98 Å [16]. A NBO analysis performed on a small cluster with this same geometry shows the presence of three strong O–Al covalent bonds and three ionic O–Al bonds, respectively. In our model of the alumina surface, the exposed Al atoms can be considered as saturated in its covalence, remaining intact its ionic bond forming ability, as in

the case when the isocyanate group adsorbs at bridge between two Al atoms. Noticeably in bulk alumina a non-negligible $n(O) \rightarrow n^*(Al)$ electron transfer is observed between the atoms participating in the ionic bond. Similarly, a non-negligible $n(N) \rightarrow n^*(Al)$ electron transfer is present when the isocyanate group is adsorbed.

The electronic structure of the HNCO molecule, when compared with those of NCO over SiO_2 or Al_2O_3, reveals that the internal N–C or C–O bonds behave similarly to the case of silica (see Table 2). The associated interatomic distances are also very close as it can be verified looking at Table 1. On the other hand, the main difference is evidenced in the N charge, which is $\sim 0.2e$ lower than over SiO_2 or Al_2O_3, making the H–N bond significantly more covalent than the Si–N or the Al–N.

4. Conclusions

The present ab initio cluster model calculations indicate that the NCO group adsorbs preferentially on top site over silica and on bridge site over alumina, in an end-on orientation. The N atom is linked directly to the cationic species. The N–C bond is longer and weaker on alumina, enhancing its decomposition to N_2 and CO. This property can be explained by means of an electron population analysis of the molecular orbitals, revealing that a greater charge transfer $n(O) \rightarrow (N–C)^*$ is present over alumina. As a consequence, an important ionic bond is formed between N and Al. On the other hand, a lone pair on the N atom participates in a charge transfer to the nearest Al atom. These results are in agreement with the experimental evidence of an easier NCO decomposition over alumina in comparison with silica.

Acknowledgements

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