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On the Origin of the Different Performance of Iron and Manganese Monocations in Catalyzing the Nitrous Oxide Reduction by Carbon Oxide

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The potential energy profiles for the Fe^+- and Mn^+-assisted reduction of N_2O by CO were studied at the B3LYP density functional level in order to get the differences in the reaction mechanisms determining the efficiency of iron and the inactivity of manganese as ionic catalysts. Both ground and excited states of cations were taken into account in view of a possible participation of the highest multiplicities to the reduction process. Results indicated that a spin inversion occurs in the rate-determining step of iron ion-catalyzed reaction that improves the performance of the cation. However, also in the absence of the two-state reactivity phenomenon, contrary to manganese ion, iron is active in catalyzing the reaction.

Introduction

Reactions catalyzed by transition metal cations have attracted great interest in view of their applications in industrial processes.[1] The role of these species can be decisive for a reaction and often consists in accelerating the process favoring the opening of a channel at lower energy that can be also symmetry forbidden.

In the year 2005, some metal cations (M^+) were recognized as possible catalysts for oxygen-atom transport in the reduction reaction of N_2O by CO.[2,3]

On the basis of a previously suggested two-step mechanism[4] (see Scheme 1), in which atomic cations work as shuttles that transfer the oxygen from the donor (N_2O) to the acceptor (CO) molecule, Bohme et al.[2,3] hypothesized that the catalytic activity of these cations was to be attributed to a general thermodynamic requirement. This requires that the cation oxygen affinity values fall in an energetic window ranging from N_2 to CO oxygen affinities.

Scheme 1

$$1)\ M^+ + N_2O \rightarrow MO^+ + N_2$$

$$2)\ MO^+ + CO \rightarrow M^+ + CO_2$$

However, among the 26 cations potentially able to catalyze the reaction, only 10 were proven to be efficient at room temperature. The failure of the remaining species either in the formation of MO^+ or in its reduction by CO was ascribed to the kinetic nature and in some cases to the difficulties inherent in spin-forbidden reaction paths.

Iron(I) and manganese(I) were found to belong to catalytically active and non-active category of cations, respectively.

The potential energy profile for the Fe^+ (^6D)-catalyzed reduction of N_2O by CO was computed by the same authors[3] using the density functional hybrid B3LYP/6-311+G(d) protocol aiming to elucidate the work mechanism of an ionic catalyst.

In fact, the recent progress in computational chemistry showed that many theoretical first principle methods can be particularly useful for the chemical and physical characterization of the species involved in these reactions, especially as experimental results are difficult to obtain.

A good combination of the method and of the basis set is mandatory to reproduce accurately both thermodynamic and kinetic data.

In this work, we have revisited the reaction path proposed previously for Fe^+ (^6D). The novelty of our investigation

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lies in introducing the energetic profile for the first excited state (^{4}F) in view of a possible spin inversion during the reaction. This phenomenon occurs quite frequently when transition metal cations are involved in a reaction.[5−8] Furthermore, with the aim to explain the different behavior of Fe^+ and Mn^+ cations, we performed computations also for the manganese (^{7}S)- and (^{5}D)-catalyzed reactions for which no suggestion about the action mechanism was previously proposed.

The present work represents a part of a systematic study on the different performance that metal cations exhibit in activating N_2O and other greenhouse molecules. In particular, we chose Fe^+ and Mn^+ because, although their electronic configuration is different by one electron, they show opposite catalytic activity in the N_2O reduction process.

Computational Details

All computations were performed at the B3LYP[9−10] level of theory using the Gaussian 03/DFT code.[11]

The 6-311+G(d) basis set[12−14] was chosen to describe nonmetal atoms.

DZVP (opt) and DZVP (d) (opt) sets of Chiodo et al.,[15] built up to improve the reliability of density functional B3LYP method in the prediction of transition metal ion ground- and excited-state ordering and splitting,[16] were chosen to describe Fe^+ and Mn^+ cations, respectively.

Zero point energy (ZPE) corrections, derived from vibrational analysis, were included in all relative energy values.

Transition states were confirmed, applying the intrinsic reaction coordinated (IRC) procedure implemented in the Gaussian 03 package.[17,18]

Table 1. Theoretical and Experimental Oxygen Affinity Values (kcal/mol)

compound	OA (theor)	OA (exptl)
N_2	40.12	39.95 ± 0.02[a]
CO	126.34	127.30 ± 0.02[a]
Fe^+	70.99	80.00 ± 1.40[b]
Mn^+	57.68	68.00 ± 3.00[b]

[a] From ref 20. [b] From ref 21a,b.

The calculation method STABLE,[19,20] which ensures the wavefunction to be tested during optimization, was used everywhere.

The lowest energy electronic state for all species was searched using the ALTER[11] keyword.

NBO analysis[21] was performed to rationalize the metal ion−ligand bond type occurring in the species where the cations with different multiplicity are involved.

Results and Discussion

Preliminary computations indicated that the ground electronic states ^{6}D ($3d^64s^1$) for Fe^+ and ^{7}S ($3d^54s^1$) for Mn^+,[22] are separated from the first excited states ^{4}F ($3d^7$) and ^{5}D ($3d^6$) by 12.0 and 36.8 kcal/mol, respectively. Although the differences with experimental gap values (5.8 kcal/mol for iron and 41.7 kcal/mol for manganese) are not small,[22] the basis set used here for metal ions reproduces the correct order of electronic spin states. This is not usually expected in density functional computations since most of the traditional basis sets reverse the stability of the electronic states (for example, the 6-311+G(d) set predicts the quartet as ground state for Fe^+) or give worse splitting values.[22]

The experimental oxygen affinities[23,24] for the two considered cations and for N_2 and CO molecules were reproduced at B3LYP level in order to verify the congruity with the above-mentioned thermodynamic requirements (see Table 1). The values that we have obtained for cations appear underestimated by about 10 kcal/mol. This happens often in DFT computations, especially when transition metal ions are considered. However, the relative oxygen affinity values are well reproduced, and in any case, the absolute values also meet the thermodynamic criterion.

The exothermicity in terms of ΔH_0 for the N_2O reduction by CO was computed to be 86.2 kcal/mol (experimental value is 87.0 kcal/mol[23]). We have estimated that in the absence of any catalyst, the reaction needs an activation energy of 47.6 kcal/mol, which is in agreement with a previous literature value of 47.2 kcal/mol.[3]

The Fe^+-catalyzed process follows the mechanism illustrated in Figure 1a. Stationary points on energetic paths and

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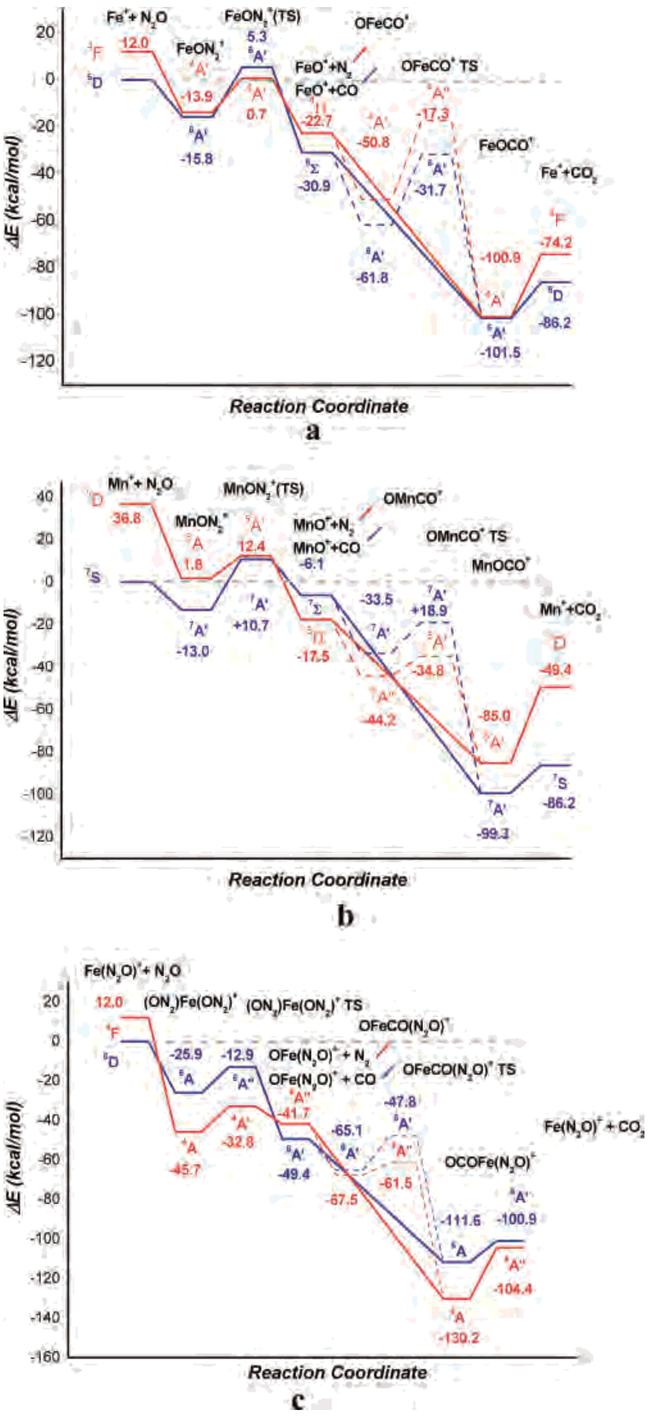

Figure 1. Potential energy profiles for the Fe^+- and Mn^+-catalyzed reduction of N_2O by CO with (a, b) the participation of only one N_2O molecule, (c) the participation of two N_2O molecules. Blue and red solid lines refer to the ground and excited states of cations, respectively. Dashed lines indicate alternative reaction channels. Blue and red arrows designate incoming and leaving molecule, respectively.

their dimensions, absolute energy values, and ZPE corrections are collected in the Supporting Information for all species.

After the coordination of the N_2O molecule by Fe^+ in its ^6D and ^4F electronic states, the $^6A'$ and $^4A'$ $FeON_2^+$ adducts, lying at 15.8 and 13.9 kcal/mol below the reactants asymptote, are formed.

For both multiplicities, the NBO analysis indicates that in the $FeON_2^+$ species, oxygen atom, and iron cation are covalently bound. A charge transfer of 0.3 and 0.5|e| occurs from ligand to metal ion, for sextet and quartet, respectively.

The FeO^+ oxide in the sextet ($^6\Sigma^+$) and quartet ($^4\Pi$) spin states is generated from $FeON_2^+$ through the transition state (TS) that lies at 21.1 and 13.2 kcal/mol, respectively. In both cases, the imaginary frequency of 751 (for sextet) and 849 cm^{-1} (for quartet) corresponds to the stretching vibrational mode that preludes to the breaking of the N−O bond.

FeO^+ oxides retain the covalent character of the iron ion−ligand bond with a charge transfer of about 0.5|e| for both high- and low-spin states.

From this point onward, two alternative reaction channels are possible. Depending on its electronic state, $^6\Sigma^+$ or $^4\Pi$, FeO^+ oxide reacts with CO giving rise to the $^6A'$ or $^4A'$ linear $OFeCO^+$ minima that lie 30.9 and 20.5 kcal/mol below the energy of the new reactants ($FeO^+ + CO$). Our results indicate that these last species evolve into the $^6A'$ and $^4A'$ $FeOCO^+$ through two transition states having corresponding multiplicity before reaching the Fe^+ (^6D) or Fe^+ (^4F) and CO_2 products. Barriers to overcome are of 30.1 and 33.5 kcal/mol, respectively. $FeOCO^+$ minima appear to be decidedly more stable than $OFeCO^+$ species (of 39.7 kcal/mol in the case of the $^6A''$sextet and of 50.1 kcal/mol in the case of the $^4A'$ quartet) and allow to obtain products with a barrierless process.

However, surprisingly, we have found that, irrespective of multiplicity, the $FeOCO^+$ can be directly obtained when CO moves close to FeO^+ oxide from the oxygen side (second channel). In any case, this fact does not influence the reaction path. The rate-determining step is, in fact, the formation of oxide that occurs before obtaining of $FeOCO^+$ species.

Analyzing the geometrical features of $FeOCO^+$ systems in both multiplicities, the Fe^+−O distance is sufficiently long (2.36 and 2.03 Å for sextet and quartet, respectively) to allow an easy removal of CO_2. On the other hand, C−O bond lengths (of 1.17 Å) are already short enough to support the formation of a carbon dioxide molecule.

As can be noted, the iron ion−ligand bond lengths vary with the multiplicity of cation. In particular, the Fe−O bond is more frequently characterized by a covalent contribution, while the Fe−C interaction is essentially of electrostatic nature. The $FeOCO^+$ species represents the only case in which we find a purely electrostatic Fe−O bond. The separation between the two involved centers in this adduct is particularly large in the sextet state of the cation due to the presence of an electron in the 4s orbital, which is much more diffuse than the d orbitals.

In agreement with a selected-ion flow tube (SIFT) experimental study,[25] in which it is suggested that the O-atom abstraction from FeO^+ by CO is a reaction that is exothermic by more than 40.0 kcal/mol, we found that the process occurs with a heat development of 55.3 kcal/mol.

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The presence of two crossings between the reaction profiles at different multiplicity, immediately before and after the first TS, indicates that the phenomenon termed two-state reactivity (TSR), which usually involves participation of spin inversion in the rate-determining step,[26−29] occurs. Because of a double spin inversion, the process ultimately follows the sextet minimum energetic path characterized by only one barrier of 16.4 kcal/mol for the formation of FeO^+ oxide.

However, in a gas-phase experiment, the intermediates do not lose all of their energy. Thus, the relevant barrier is not that of the bottom of the well, but rather that from the reactants. Hence, the rate-limiting barrier in the iron-catalyzed reaction is more properly equal to 0.7 kcal/mol.

Despite the very similar aspect of the path, the mechanism of Mn^+-catalyzed reaction (see Figure 1b) proposes significant new results. Two successive crossings between the ground septet and excited quintet profiles, occurring after the first $MnON_2^+$ and the second $OMnCO^+$ transition state (or before the formation of $MnOCO^+$ adduct if we refer to the alternative channel), allow the reaction to start and finish with the same multiplicity. The geometrical parameters of the species involved in the two energetic paths of manganese ion are given in the Supporting Information.

As in the case of iron-mediated reaction, after the MnO^+ formation, the path stretches below the reactants asymptote.

The most substantial difference in the Mn^+-catalyzed process concerns the height of the barrier for the oxide formation. The first intermediate $MnON_2^+$ ($^7A'$) allows an energetic gain of 13.0 kcal/mol, but as can be noted by Figure 1b, another 10.7 kcal/mol are necessary to overcome the next transition state in which the removal of N_2 molecule begins (imaginary stretching frequency is 688. cm^{-1}).

As it is well known from the Arrhenius formula for the evaluation of kinetics, a difference of about 10 kcal/mol between two barriers implies that rates change by several orders of magnitude. Thus, it is quite clear why, at room temperature, Fe^+ can be considered active and Mn^+ not.

The major difficulty of forming the MnO^+ with respect the FeO^+ oxide can be explained through the NBO analysis of the $MnON_2^+$ precursor. Contrary to the iron ion case, in this species the Mn−O bond is described as a purely electrostatic interaction. The natural charge on cation after the N_2O coordination is practically equal to 1. This means that the oxygen atom is still integral with nitrogen, and the breaking of the O−N bond is consequently less easy than in the $FeON_2^+$ adduct.

The differences in the bond lengths between metal cation and ligand in the various species with different multiplicity depend, also in this case, on the different orbital occupation. The NBO analysis for other minima on the path shows that Mn−O and Mn−C bonds are always ionic. Again, the interactions are weaker in all cases in which the cation has the spin electronic state of a septet because of the presence of an electron in the more diffuse 4s orbital.

Because metal cations during the experiment[2,3] are subjected to a fixed N_2O flow, it should be a concrete possibility that they can coordinate more than one molecule of nitrous oxide, as can be inferred from the proven presence of FeO^+-$(N_2O)_{1,2,3}$ species[2,3].

Since in the first part of this work we have ascertained that Mn^+ does not have a catalytic role, we have considered that it would be interesting to examine the effect of an additional N_2O ligand only on the Fe^+ path.

The coordination chemistry of this cation in the presence of two N_2O molecules was carefully studied to individuate the lowest energy stationary points on the ground and excited profiles that we reported in Figure 1c.

Fe^+, in the electronic spin state of quartet (^4F), reacts with the two molecules of nitrous oxide, giving rise to the asymmetric ^4A $(ON_2)Fe(ON_2)^+$ adduct that is more stable by about 20 kcal/mol than the analogous species ^6A obtained from the cation in its ground state. Through the transition states, which lie at 12.95 kcal/mol for sextet ($^6A'$) and 12.88 kcal/mol for quartet ($^4A'$) above the corresponding minima, the reaction leads to the $^6A'$ and $^4A''$ OFe $(N_2O)^+$ oxides. After two spin inversions testified by the crossings occurring between the two different energetic profiles, this last species appears to be more stable in the sextet state $^6A'$ rather than in the quartet $^4A''$.

Computations indicated that, also in this case, two energy channels exist for both electronic states. In fact, adding CO to the previous oxides, the $OFeCO(N_2O)^+$ adducts can be formed that evolve into the $OCOFe(N_2O)^+$ after the clearing of the respective barriers. Products are obtained in a barrierless process, as in the case examined before.

The reaction between the $^6A'$ and $^4A''$ $OFe(N_2O)^+$ and CO can also occur when carbon oxide interacts on the oxygen side. The ^6A and ^4A $OCOFe(N_2O)^+$ systems lie 111.6 and 130.2 kcal/mol below the reactants energy.

Furthermore, when the two energetic profiles at different multiplicity do cross, a new stability inversion between the electronic spin states of the species occurs.

Since carbon dioxide is already practically formed and the Fe−O distance is quite long, $^6A''$ or $^4A''$ $Fe(N_2O)^+$ and CO_2 products are easily obtained in a step without a barrier.

The next removal of nitrous oxide from iron ion, to regenerate catalyst, lets the overall process begin and terminate with the same multiplicity of sextet despite the presence of crossings. These phenomena are, however, important in delineating the most favorable path.

Considering that the whole path lies below the reactant asymptote, the reaction appears to be thermodynamically and kinetically highly favored.

Preliminary computations were performed, taking into account the effect of the coordination of a third N_2O molecule by Fe^+. Our calculations showed that the only stable sextet species $Fe(N_2O)_3^+$ has a geometry not suitable for the course of the reaction. Indeed, all of the three ligands are coordinated to the cation from the nitrogen side, and a transition structure necessary to convert this species into a reactive form was

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not found. This let us suppose that species having higher coordination around the iron ion should not participate in the catalytic event.

Conclusions

On the basis of our computational results, we can suggest that the crucial step in such a process is the formation of MO^+ or $MO(N_2O)^+$ oxides since their next reduction by CO occurs in a barrierless process.

For the two metal cations, MO^+ generation entails a different energetic expense, which is higher for manganese ion by about 10. kcal/mol.

For iron, the participation by a spin inversion in the rate-determining step reroutes the reaction to the temporarily most favorable quartet path to go back then, once and for all, to the sextet energetic profile.

The spin inversion occurring in the case of manganese is irrelevant for the reaction kinetics.

Both metal cations let the whole process follow a symmetry-allowed mechanism.

The coordination of a second nitrous oxide molecule by the iron cation has a significant effect on the reaction kinetic aspects, suggesting a path in which the barriers are only “fictitious” obstacles.

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Supporting Information Available: SCF energies, ZPE corrections, and geometrical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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