Computational insights into the catalytic role of the functional groups in Hydrogenation of CO_2 with Manganese Complexes: A DFT study

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ABSTRACT

The replacement of noble metals in homogeneous catalysts for the current CO_2 hydrogenation reaction with 3d transition metals (Fe, Co, Ni and Mn), with lower costs, have attracted a great attention of many research groups to the interconversion of chemical and electrical energy, like CO_2 and H_2. Inspired by that motivation, catalysts containing transition metals need to be investigated and designed ideally based on the deep level of knowledge of the molecular structure, the chemical bonding between ligands and metals, and the state of electronic ergonomics related to this configuration. In this study, several Mn (I) complexes with monoophosphine ligands (PN ligands) were investigated in the hydrogenation reaction of CO_2. The results calculated by density functional theory show that the chemical bonding nature of the NH group and the functional groups associated with N can affect the structure, charge density and catalytic capacity which is a direct link to the CO_2 hydrogenation reaction mechanism. Finally, the results obtained from clarifying the role of N-H bonds in the design of the catalyst stabilize the anion format in the H_2 separation process. The calculation of density functional theory is performed using ORCA quantum calculation software.

Introduction

The recent global developments, industrialization, and modernization has led to the higher demanding of energy and productions of more and more CO_2. The sustainability of fossil fuels and the uncontrolled escalation of CO_2 level therefore becomes a major concern of this century[1]. Thus, the conversion of CO_2 into a carbon-based fuel (HCOOH[2], CH_3OH[1], CH_4[3]) attracts a lot of attention since the CO is a potential precursor in various industry processes. It is expected that the development of a catalyst for the CO_2 reduction is a promising approach for the interconversion of chemical and electrical energy. In recent years, a lot of progress has been made for the development of cheap and environ- mental friendly catalytic pathway for the hydrogenation of carbon dioxide into formic acid.[4]

Until now, several transition metals based homogeneous catalysts have been experimentally and theoretically investigated for CO_2 hydrogenation[5]. Attractively, catalytic processes employing gaseous H_2 as the reductant has the advantage of operating waste-free, and thus are inherently more efficient and environmentally benign compared to the stoichiometric processes employing such reducing

agents as lithium aluminium hydride and sodium borohydride currently ruling the pharmaceutical industry. Historically catalytic systems for the reduction of carboxylic acid derivatives were based on noble metals (e.g. Ru, Os, and Ir), As matter of fact of, the processes of catalytic hydrogenation employing precious metal catalysts shows many desirable characteristics. The first advantage is that contribution to process cost from the catalysts is very low, because catalyst loadings is as low as 0.0001 mol% of total mass. Hence, these reactions are inexpensive to run, with simple purifications and excellent economy. However, there are a lot of processes that can be optimized to this level of performance with a precious metal catalyst, but the hydrogenation processes require considerably higher catalyst loadings. With a catalyst that is expensive on a per-gram basis, process costs turn out to be very high, which are further increased by the purification getting more complex, since for most products <5 ppm of Ir, Rh, or Ir impurities are required. Earth-abundant metal catalysts based on more abundant sources, could be several times cheaper to produce than precious metal systems, and hence offer opportunities to operate a wide range of catalytic hydrogenations. Thus, inexpensive and earth abundant transition metals based (Fe, Co, Ni, and Mn) catalysts have been receiving more attention from the scientific community. Beller and co-workers have been reported a series of iron and cobalt complexes using tetraphos ligand; out of which Co complexes show more catalytic activity compared to the Fe complexes[6]. After that several other earth abundant transition-metals based catalysts have been investigated for CO2 hydrogenation reaction. Nevertheless, the activities of these complexes are very low compared to the noble-metal based complexes. So, several computational and experimental groups have been engaged in understanding the detailed mechanism for CO_2 hydrogenation reactions, which may be a crucial step in terms of designing non-noble transition metal based homogeneous catalysts for efficient CO_2 hydrogenation reactiona. Due to its high natural abundance and excellent biocompatibility, manganese is considered an attractive metal for fine-chemical and pharmaceutical applications as the low toxicity renders quantitative removal of catalytic residues superfluous. Consequently, increased focus of the scientific community has culminated in exceptionally rapid development of a series of highly active Mn- catalysts capable of efficiently reducing particularly challenging carbonyl substrates such as carboxylic acid esters and nitriles [12,13]. Further

improvement has been made via ligand modification. Traditionally a robust assignment of the coordination geometry of transition-metal complexes requires an understanding of both the position of the ligands and the nature of the chemical bonding. So, motivated by these studies, a series of bidentate aminophosphine (PN) based bifunctional Mn (I) complexes (Fig 1) were studied. for CO_2 hydrogenation. The Mn-PN complex has been investigated theoretically and their potential and remarkable characters were also discussed.

Experimental

All density functional theory (DFT) calculations were performed using the BP86 functional and the def2-TZVP basis set as implemented in Orca 4.2 program[7]. Our preliminary studies on homogeneously-catalyzed processes have evidenced the high accuracy and predictive power of this methodology for various homogeneously catalysis. The numerical thresholds were systematically increased using the TightSCF, Grid4 and FinalGrid5 options. All the studied structures are verified with no imaginary frequencies.
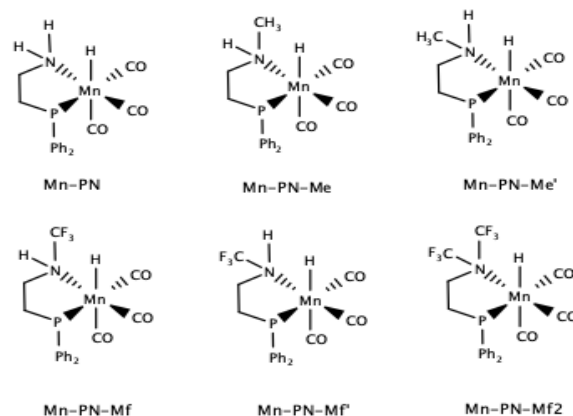

Fig 1: The modelled bidentate aminophosphine ligands based Mn (I) complexes for CO_2 hydrogenation reaction

Results and discussion

Molecular structures of catalytic Mn complexes

Here, six catalysts of the CO2 hydrogenation reaction are studied, their names and structures are illustrated in Fig 1. These Mn complexes are modeled by changing the number of the σ-donor and π-acceptor binding with the N atom of the ligands. In these complexes, CO is a strong π- acceptor ligand, while CH_3 and CF_3 is a strong σ-donor (or poor π- acceptor) functional groups. Complex 1 (Figure 1, Mn-PN) has one bidentate aminophosphine (PN) group, three CO

(two equatorials, one axial) and one hydrogen atom. One of the H in the PN ligand of complex 1 is substituted by a CH_3 to model complex 2 and complex 3 (Figure 1, Mn-PN-Me and Mn-PN-Me'), and then CF_3 to model complex 3 (Mn-PN-Mf and Mn-PN-Mf'). The CO ligand is chosen as an axial ligand as CO has a large trans effect compared to the hydride ligand. For comparison, we have compared obtained results with the complex Mn-P. As being investigated by Dubois[8], the axial Mn-H bond can facilitate the hydride transfer mechanism. In the Mn-PN, the N-H functionality plays a crucial role in facilitating hydrogenation reaction via formation/cleavage of the N-H bond. In details, Dub et al. suggest that the N-H bond is not formed in ketone hydrogenation rather involved in stabilizing the oxy-anion(−O-) inter- mediate via a strong hydrogen-bonding interaction (N-H···O) and such oxy-anion intermediate further leads to the heterolytic H_2 cleavage. Therefore, N-H bond helps in stabilization the oxy-anion inter- mediate, this oxy-anion further initiates the heterolytic H_2 cleavage. Thus, to understand the role of the N-H functionality, the hydrogen atoms were substituted by methyl (-Me) groups to model six Manganese complexes as shown in Fig 1.

The CO_2 hydrogenation mechanism was proposed by Singh Rawat[9]. Singh's work proposed classical Noyori mechanism for ketone hydrogenation where hydride and proton transfer take place from the M-H and N-H bond, respectively. The works here focus on the characters of N- H and Mn- H bonds in the two aforementioned mechanisms in which the N-H functionality of the PN ligand shows a metal–ligand cooperation (MLC) mechanism for CO2 hydrogenation or not. Rather than that, the N-H functionality can work as a chemically innocent ligand for stabilizing the formate anion via N-H···O hydrogen bonding. In our optimized structures, the charge distributions on N and Mn varied significantly from two N-H bonding to none of them while the bond lengths remain the same. The charge on the Mn atom is negative because the interactions that stabilize these complexes involve delocalization of charge from the lone pairs of the NH into the orbitals of the metal. The lower the metal charge the more likely the delocalization shifts. Here the aromatic PN ligands-based complexes were expected to show higher catalytic activity due to the chemical nature of the PN ligand. Note that the PNP ligand contributes through the metal–ligand cooperation (MLC) mechanism via aromatization/dearomatization of the ligand. In this case, the dearomatization of PNP initiates the heterolytic H_2 cleavage.

In Mn-PN-Me' and Mn-PN-Me, the polarization of Mn-H and N-H, in which Mn and N atoms carried the negative charge while the H atom has the positive charge, in the optimized structures, suggested that the Mn-H bond tends to be hydridic, whereas the N-H bond tends to be protonic. The polarized Mn-H and N-H bonds then favors the hydrogen bonding interactions. Therefore, the extent of hydrogen bonding interactions is very important for the stabilization of formate anion, which further facilitate the heterolytic H2 cleavage and lowers the overall barrier. Since the bond lengths stay the same, there is no spatial effect from substituting the H with the CH_3 or CF_3 group. Therefore, Mn-PN-Me' and Me-PN-Mf' can take part in the metal-ligand cooperation mechanism for CO_2 hydrogenation. Additionally, the polarity of the Mn-H and N-H bonding increase the probability of the formation of N-H..O and M-H...C along the reaction's process bond. Therefore, the formation of Mn−H...CO_2 is more favorable when both the equatorial ligands (CO) are strong π-acceptors, in other word, when the charge on Mn get highest. The bonds actively participate in the reaction mechanism as proposed by Noyori for asymmetric hydrogenation reaction. Hence, the formation/cleavage of M-H and N-H bonds is very important for hydride/proton transfer related catalytic hydrogenation reactions. On the other hand, in some cases, the N-H functionality does not participate directly in the reaction but helps in stabilizing the important intermediates.

Table 1: The summary of the optimized bond length and charges distribution on the Mn and N atoms in the studied molecules

Structures	Charge on N	Charge on Mn	N-H (A°)	Mn-H (A°)
Mn-PN	-0.3360	-0.3084	1.018	1.592
Mn-PN-Me	-0.1525	-0.2021	1.018	1.592
Mn-PN-Me'	-0.1437	-0.1737	1.018	1.592
Mn-PN-Mf	-0.1945	-0.3748	1.027	1.599
Mn-PN-Mf'	-0.2039	-0.0951	1.026	1.586
Mn-PN-Mf2	-0.1892	-0.1537	0.000	1.592

Role of non-innocent and innocent ligand

This part of the paper is devoted to study the underlying reason behind the very large free energy barrier for the classical Noyori type hydrogenation mechanism for the CO2 hydrogenation process. Therefore, the molecular orbitals and structural parameters were explicitly analyzed. The results are summarized in Fig 2 and Table 2 as they show different chemical nature of N-H functionality within PN ligand.

Furthermore, we have investigated the underlying reason behind the stable for the classical Noyori type hydrogenation mechanism for CO_2 hydrogenation. To understand this, we have analyzed the molecular orbitals, the final Gibbs energies and structural parameters (**Error! Reference source not found.**) of all Mn-containing molecules as they show different chemical nature of N-H bond functionality within PN ligand. Since all molecules are stable, based on the delocalization of both the HOMO and LUMO of each molecule the frontier molecular orbitals of these complexes (Table 2) suggest that HOMO (-5.163 eV) of Mn-PN-Mf is the most stabilized followed by HOMO in Mn-PN-Me and HOMO in Mn-PN. . The rest of the Mn complexes could be excluded since the orientation of the two N-H and Mn-H bond do not favor the mechanism of CO_2 hydrogenation. This is very much consistent with their position in the proposed reaction mechanism. In case of Mn-PN-Me, the lone pair of N atom is interacting with the Mn, which leads to a Mn-N bond length of 2.167 Å i.e. shorter compared to that in Mn-PN-Mf (2.222 Å). The reason is because the CF_3 group has stabilized the N-H bond while the effect is much weaker with the presence of CH_3 group. Such localization of lone pair on N atom destabilizes the HOMO, which in turn destabilizes the N-H bond.

Table 2: The molecular orbital of the Mn complexes

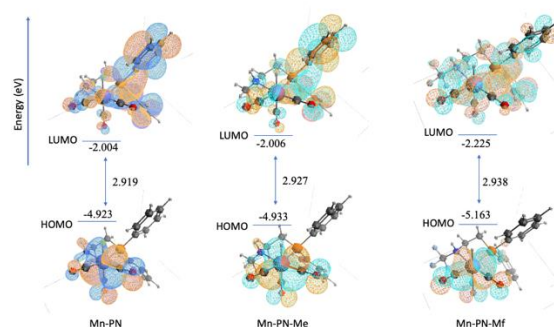| The structures	HOMO (eV)	LUMO (eV)	ΔE(eV)
Mn-PN	-4.923	-2.004	2.919
Mn-PN-Me	-4.933	-2.006	2.927
Mn-PN-Me'	-4.933	-1.995	2.938
Mn-PN-Mf	-5.163	-2.225	2.938
Mn-PN-Mf'	-5.182	-2.172	3.010
Mn-PN-Mf2	-5.281	-2.637	2.644

Fig 2: The molecular orbital of three Mn complexes, Mn-PN, Mn-PN-Me, Mn-PN-Mf

Remarkably, the results show the innocent nature of N-H bond favors CO2 hydrogenation reaction compared to the non-innocent nature of N-H. Here, the innocent nature of N-H bond probably originates hydrogen-bonding interactions, which plays a important role in the stabilization of the intermediate in Singh' proposed mechanism [ref] through metal ligand participation. However, such hydrogen-bonding interactions are less in Mn-PN-Me' as the N-H group is directed opposite to the formate anion. Therefore, the extent of hydrogen bonding interactions is very important for the stabilization of intermediates with the formate anion, which further favors the heterolytic H2 cleavage and lowers the overall barrier. The obtained results suggest that the chemically innocent nature of the N-H functionality is very important over the chemically non-innocent nature of N-H functionality for CO_2 hydrogenation reaction.

Conclusion

In summary, a detailed investigation of the potential catalyst for the CO_2 hydrogenation reaction is carried out on the Mn-based complexes by changing the ratio of the π-acceptor character of the ligands (CO, CH_3 and CF_3). Detailed complexes' structures have been analyzed to show that Mn complexes can be promising catalysts for CO2 the hydrogenation reaction and the reaction thermodynamics are very much comparable with the previous theoretical studies. Therefore, chemical nature of N-H functionality is very important for the stabilization of formate anion which further favors heterolytic CO_2 hydrogenation. Thus, the conducted DFT calculations and results are expected to be instrumental in designing bifunctional ligand-based catalysts for CO_2 hydrogenation reactions

Acknowledgments

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