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Density functional theory calculations and 2D $^1$H-2C HETCOR solid state NMR spectroscopy prove that CO$_2$ can probe, by its own reactivity, different types of N-donor surface ligands on SBA15-supported Zr$^{IV}$ hydrides: $[[\equiv\text{Si-O}](\equiv\text{Si-N=})\text{[Zr]}\text{H}]$ and $[[\equiv\text{Si-NH}](\equiv\text{Si-X})\text{[Zr]}\text{H}]$ (X= O or NH). Moreover, $[[\equiv\text{Si-O}](\equiv\text{Si-N=})\text{[Zr]}\text{H}]$ activates CO$_2$ more efficiently than the other complexes and leads to a carbamato Zr formate.

CO$_2$ activation and reduction for alternative energy source has received wide attention. A variety of metal hydrides have been already tested for the CO$_2$ insertion and activation. In certain cases, modeling studies have given important insight how these reactions occur and what factors are essential to determine the selectivity and efficiency.

Recently, amine-modified SBA15 surfaces with either silanol/silylamine, $[[\equiv\text{Si-OH}(\equiv\text{Si-NH})]]$ or bis-silylamine, $[[\equiv\text{SiNH}_2]]$ pairs (named as [N,O] and [N,N], respectively) have demonstrated a potential role as new chelating ligands in surface organometallic chemistry (SOMC). Interestingly, their use as N-donor surface ligands allow the isolation of species defined as putative in molecular chemistry. Thus, the design of π bond between the transition metal and the N-donor surface ligands is achieved through the hydrogen treatment of a bipoal silylamiido-silyloxo bis-neopentyl zirconium 1 (Scheme 1). This reaction was not observed with bipoal bis-silylamido bis-neopentyl zirconium 2. As reported earlier, the formation of different hydride complexes 1a-c and 2a-c (Scheme 1) were confirmed by advance solid state NMR and FTIR spectroscopy. However, the unambiguous identification of 1b, whose homogenous counterpart has been reported to be only putative, was not achieved. Herein, we demonstrated a combined experimental and computation study utilizing CO$_2$ to support the formation of those zirconium hydride species supported on N-donor SBA15.

The reactivity of CO$_2$ on zirconium hydride supported on unmodified silica was studied first by our group. The synthesis of either $[[\equiv\text{SiO}_2]\text{[Zr]}\text{H}]$, tripodal zirconium monohydride or $[[\equiv\text{SiO}_2]\text{[Zr]}\text{H}_2]$ bipoal zirconium bis-hydride were not possible due to surface heterogeneity resulting from heat treatment. The main product was the tripodal zirconium monohydride $[[\equiv\text{SiO}_2]\text{[Zr]}\text{H}]$, (80%). The work was followed by a more recent computational study. The main difference of the current work with all previous works is the presence of [N,O] and [N,N] isolated chelating pairs in close vicinity which allows the formation of a chelated metal with π bond between transition metal and the N-donors surface ligands (Scheme 1). The CO$_2$ insertion may take place on the zirconium bis-hydride, 1a and 2a as shown in scheme 2. In this case, the insertion of two molecules of CO$_2$ in two different Zr-H bonds is possible. The PES diagram (Fig.1) is drawn assuming energy of “naked” complex as 0.00 kcal.mol$^{-1}$. The coordination energy for the first CO$_2$ molecule is 1.9 and 2.8 kcal.mol$^{-1}$ for 1a (red profile) and 2a (blue profile), respectively. The first insertion barrier is about 6.0 kcal.mol$^{-1}$ for both, 1a and 2a.

Scheme 1: Synthesis of Zr hydrides supported on [N,O] and [N,N] SBA15.  

Scheme 2: CO$_2$ insertion into zirconium bis-hydride 1a and 2a yielding to zirconium bis-formate 3a and 4a respectively.
However the products, P1 are stabilized with respect to the starting hydride complexes by a factor of 30.2 and 28.5 kcal/mol$^{-1}$ for 1a and 2a, respectively. The insertion of the second CO$_2$ molecule to the remaining zirconium hydride is slightly energy consuming. The barrier is 12.3 and 9.8 kcal/mol$^{-1}$ for 1a and 2a, respectively. The overall process is highly exergonic and the bis-formate, P2 adducts are 52.7 and 50.5 kcal/mol$^{-1}$ more stable than the starting complexes, 1a and 2a. Furthermore, we have explored the CO$_2$ insertion possibilities to [(Si-O-)[Si-N=]Zr=H] complex 1b through the Zr-H and/or Zr=N bond. Two pathways may occur (Fig. S1, see ESI). The green path shows a first CO$_2$ insertion into the Zr-H σ bond and a second into the Zr=N imido π bond while the blue path shows the insertion into Zr=N bond followed by an insertion into Zr-H bond. There was no dramatic difference between the two paths. At first the insertion of coordinated CO$_2$ into the Zr-H bond (R⇒P1) (TS1) barrier was 6.9 kcal/mol$^{-1}$ (Fig.1) while the insertion of CO$_2$ into the Zr=N bond (R⇒P1') (TS1') barrier was 8.7 kcal/mol$^{-1}$. However the P1 and P1' stabilities exhibit significant difference, (P1*= -33.5 and P1'*= -20.6 kcal/mol$^{-1}$) with respect to the starting complex. Indeed, the green path is preferred and the first CO$_2$ insertion takes place at the Zr-H σ bond in 1b. The coordination of the second molecule of CO$_2$ will further stabilize the overall system and its insertion barrier (P1⇒P2) (TS2) is 3.6 kcal/mol$^{-1}$. At the same time the insertion barrier of CO$_2$ to P1' (P1'⇒P2) (TS2') via blue path is found as 6.0 kcal/mol$^{-1}$. The difference between the two pathways P1⇒P2 and P1'⇒P2 is small but the P1⇒P2 pathway is preferred because of thermodynamic stability of P1 with respect to P1'.

Similarly, the CO$_2$ insertions into the other zirconium monohydrides (1c and 2c) take place via the reaction described in scheme 3. The activation processes were analysed over potential energy surface. The CO$_2$ coordination energy ΔG for the tripodal zirconium monohydride [N,O,O] 1c (red profile) and [N,N,O] 2c (blue profile) is found as 4.7 and 3.6 kcal/mol$^{-1}$, respectively, including entropic corrections (Fig. 2A). The CO$_2$ insertion into Zr-H bonds occurs through a four-centered (TS) with a barrier of 10.1 and 9.4 kcal/mol$^{-1}$ for 1c and 2c, respectively.

The tripodal [N,O,O] coordinated Zr-H (1c + CO$_2$, Fig. 2B) seems to be more electronegative as the distance of Zr-O is slightly lower, 2.34 Å than that of [N,N,O] supported Zr-H (2c + CO$_2$, Fig 2C), 2.39 Å. The overall CO$_2$ insertion process into Zr-H is an exergonic process (in terms of free energy). The CO$_2$ adduct for 1c and 2c was -28.0 and -27.6 kcal/mol$^{-1}$, respectively more stable than the starting material.

![Fig-1: PES diagram for CO$_2$ insertion 1a (red) and 2a (blue) and 1b (green). TS = Transition state.](image)

![Fig-2: (A) PES diagram for CO$_2$ insertion over tripodal zirconium monohydride, 1c (red) and 2c (blue) and their respective first TS geometries (B) and (C).](image)

A close look at the transition state geometries (Fig-S2, ESI) for CO$_2$ insertion at 1a and 2a indicates that, geometries are very similar for the complexes 1a and 2a but the interatomic distances between anchoring N and O of 1a is 3.0 Å and bond (N-Zr-O) angle is 98 ° while in 2a the anchoring N and N distance is 3.5 Å and bond (N-Zr-N) angle is 115 °. Moreover, the comparison of the insertion barrier of CO$_2$ into Zr-H σ bond in 1a and 1b (Fig. 1 and S1) indicates clearly that the presence of Zr=N bond facilitates the CO$_2$ insertion into Zr-H bond. The same conclusion arises by comparing the insertion barrier of Zr-H σ bond in case of 1c and 1b (Fig.2 and Fig.S1).

The natural bonding orbital (NBO) analysis was also performed for the reactant, TS and product involved in CO$_2$ insertion for different complexes. The zirconium is an 8-electron d-system. The charge transfer from ligand to metal as well as the positive charge density on the metal play important role for the CO$_2$ insertion. The Zr centre has a positive density along the reaction coordinates as presented in Table S1. Among 1a, 2a and 1b for reactant “R”, the highest positive density/least charge transfer is associated with 1b which apparently facilitates the CO$_2$ insertion. Complexes 1c and 2c have only one CO$_2$ insertion possibility. Even though the positive density is high there is no significant effect in the TS on the positive density which remains the same as in the reactant. However in the case of 1b there is a significant effect on the positive density at TS2 (from 1.89 to 2.17 e). In this way, the Δq for R to P2 are respectively 0.40, 0.44, 0.37, 0.26 and 0.27 for complexes 1a, 2a, 1b, 1c and 2c. After charge analysis it is interesting to see via the molecular orbital diagram, how this charge transfer affects and what atomic orbitals are involved in the frontier orbitals of molecule. We have thus analysed the first transition states in the three most active cases (1a, 2a and 1b); the details are presented in Fig. 3. In case of 1a the highest occupied molecular orbital (HOMO) of TS1 consists mainly of Zr-H bond, out of which the Zr contribution is 32% while the H
contributing is 67.8%. The transferring H behaves like free radical hydrogen and 100% contributing to HOMO, at the same time minor contribution exhibited from antibonding (A) Zr-O orbital. The HOMO distribution for bonding (B), non-bonding (NB) and anti-bonding (A) is 0.71, 0.17 and 0.11 as mentioned in Fig. 3.

Similarly in case of 2a the highest occupied molecular orbital (HOMO) mainly consists of both Zr-H bonds and H contribution is major while Zr contribution is minor. The HOMO distribution for bonding (B), non-bonding (NB) and anti-bonding (A) in 2a is 0.86, 0.10 and 0.03. In the case of 1b HOMO density is mainly centered on the Zr-N bond where Zr contribution is 17.2% whereas the N contribution is 82.7%. The respective HOMO distribution for bonding, non-bonding and anti-bonding is 0.84, 0.12 and 0.02. Based on this observation it appears that the nitrogen modified SBA15 surface perturbs the electron density at the Zr metal centre. The Zr-imido system in 1b should be most active for CO coordination because this ligand leads to the lowest electron density at the metal center.

In order to confirm these theoretical calculations we performed experiments at room temperature and passed $^{13}$CO$_2$ over the materials displaying the different SBA15 supported zirconium hydrides complexes 1a, 1b, 1c and 2a, 2c (Scheme 1). As previously described, $^{29,30}$ zirconium hydride supported on silica reacts quickly with CO$_2$. Interestingly, not only zirconium hydride, but also the silylimido surface ligand 1b reacts with $^{13}$CO$_2$, to yield as expected by modelling, a new [N,O] bound cyclic zirconium formate carbimato complex 3b (Scheme 4) characterized by 2D $^1$H-$^{13}$C HETCOR solid state NMR spectroscopy.

Upon $^{13}$CO$_2$ addition (200 Torr, 2h, at room temperature), zirconium hydrides complexes (grey solid) are instantaneously converted into their zirconium formates analogues (white off solid). This in agreement with the complete disappearance of the proton resonance at 10, 12 and 14 ppm assigned to the different zirconium hydrides (1a, 1b, 1c and 2a, 2c)$^{30}$ and the appearance of a new broad proton signal around 8 ppm in the $^1$H MAS NMR spectra (Fig. S3-S4, ESI). This proton resonance is attributed to the proton of the formate zirconium complexes 3a, 3b, 3c and 4a, 4c (Scheme 2-4). The $^{13}$C MAS experiments revealed more simple patterns: the spectrum of 3a, 3b and 3c exhibited four well-resolved signals at 180.7, 167.7, 161.2 and 55.5 ppm (Fig.4) while the spectrum of materials 4a and 4c shows only three resonances at 181.3, 169.4, and 56.6 (Fig. 5).

Furthermore, the 2D $^{13}$C-$^1$H HETCOR spectrum of 3a, 3b and 3c shows a strong correlation between proton resonances at around 8 ppm in F2 and carbon resonances at 180.7, 167.7 and 161.2 in F1. The signals at 180.7 and 167.7 ppm correspond to the carbonyl group of the monoformate and bis(formate) zirconium, respectively. As described in Scheme 4, 1b contains both a zirconium hydride and a silylimido surface ligands. An imido metal complex, is also known to react swiftly with CO$_2$ to generate a carbimato metal complex$^{29}$. So, upon the reaction with $^{13}$CO$_2$ a new N,O-bound carbimato zirconium-formate complex is generated. The chemical shift depicted at 161.2 ppm can be readily assigned to the carbon corresponding to the carbimato carbon in 3b. As expected, the 2D $^{13}$C-$^1$H HETCOR spectrum of 2a and 2b after reaction with $^{13}$CO$_2$ features only the two signals at 181 and 169 ppm assigned previously to zirconium mono and bis-formate, 4a and 4c respectively. The carbon peak at 55.5 ppm observed for all materials corresponds to a methoxy fragment.$^{29}$

In summary, DFT calculations and experimental data successfully show that the insertion and the activation of CO$_2$ with amine-modified SBA15 supported zirconium hydrides is globally an easy process. CO$_2$ is highly reactive towards supported zirconium hydrides complexes and specifically with that containing a silylimido bond, [(SiSi-O)-(SiSi-N)] [Zr]H 1b. Indeed, in the case of complex 1b, coordination of CO$_2$ results in the stabilisation of the adduct. The first CO$_2$ insertion into Zr-H bond is about 7 kcal/mol$^{1}$ while the
second CO\textsubscript{2} insertion into silylimido bond, N=Zr is about 3.6 kcal.mol\textsuperscript{-1}.

Scheme 4: CO\textsubscript{2} insertion into zirconium imido mono-hydride 1b yields to the carbimato mono-formate 2b.

Fig. 4 (1) \textsuperscript{13}C CP-MAS NMR spectrum of 3a, 3b and 3c and (2) 2D carbon-proton hetero nuclear dipolar correlation (HETCOR) spectrum of 3a, 3b and 3c.

Fig. 5. (1) \textsuperscript{13}C CP-MAS NMR spectrum of 4a and 4c and (2) 2D carbon-proton hetero nuclear dipolar correlation (HETCOR) spectrum of 4a, and 4c.

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