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Be₁₂O₁₂ Nano-cage as a Promising Catalyst for CO₂ Hydrogenation

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An efficient conversion of CO₂ into valuable fuels and chemicals has been hotly pursued recently. Here, for the first time, we have explored a series of M₁₂X₁₂ nano-cages (M = B, Al, Be, Mg; X = N, P, O) for catalysis of CO₂ to HCOOH. Two steps are identified in the hydrogenation process, namely, H₂ activation to 2H*, and then 2H* transfer to CO₂ forming HCOOH, where the barriers of two H* transfer are lower than that of the H₂ activation reaction. Among the studied cages, Be₁₂O₁₂ is found to have the lowest barrier in the whole reaction process, showing two kinds of reaction mechanisms for 2H* (simultaneous transfer and a step-wise transfer with a quite low barrier). Moreover, the H₂ activation energy barrier can be further reduced by introducing Al, Ga, Li, and Na to B₁₂N₁₂ cage. This study would provide some new ideas for the design of efficient cluster catalysts for CO₂ reduction.

The energy crisis and greenhouse effect caused by the emission of carbon dioxide (CO₂) are the two serious global problems at the present day and even remain in the next 50 years¹, which stimulated the current research interest in efficient conversion of CO₂ into valuable fuels and chemicals²⁻⁴. However, due to the negative adiabatic electron affinity (EA) and large ionization potential (IP), the CO₂ molecule is thermodynamically stable and kinetically inert, thus making the conversion difficult under normal conditions⁵. To overcome these challenges, we need to understand the basic chemical processes of the conversion and seek for highly efficient, cost-effective, and environmentally sound catalysts. Since formic acid (FA) has been widely used as a medium for hydrogen storage and an industrial chemical, catalytic hydrogenation of CO₂ to FA becomes one of the most common and promising way to utilize CO₂.

Recently, systems containing frustrated Lewis pairs (FLPs) have been found as effective catalysts for H₂ activation⁶⁻⁸, CO₂ reduction⁹⁻¹¹ and hydrogenation¹²⁻¹⁴ for the production of C1 fuels. As we know that a FLP contains both Lewis acid and base centers, and the most common active Lewis pairs are B/N, B/P, Al/N and Al/P. Furthermore, a cationic Lewis acid component has also been extended to silicon^{15,16}, carbon¹⁷, in ref. 9 and even the transition-metal (Zr^{18,19} and Ti²⁰) complexes, while the Lewis base component has been extended to O⁹, carbenes²¹, ethers²², ketones²³, and sulfides²⁴. The reduction of CO₂ via FLPs usually consists of two major steps: hydrogen activation and hydrogen transfer to CO₂, where a hydrogen molecule is first split into a proton (H⁺) and a hydride (H⁻), and then CO₂ is reduced via a concerted or sequential transfer of H⁺ and H⁻ to CO₂. By theoretical calculations, Liu *et al.* found a relationship between these two steps, i.e. a stronger FLP results in a lower energy barrier for H₂ activation, but in a higher energy barrier for H transfer¹².

Inspired by the mechanism of CO₂ hydrogenation by FLPs, here we raise a question: whether the clusters consisting of the active element for FLPs such as B/N, B/P, Al/N and Al/P etc. could act as catalysts for H₂ splitting and CO₂ further hydrogenation?

In the past few years, experiment and theoretical research efforts have been devoted to (XY)_n (M = B, Al, Be, Mg; X = N, P, O) nanostructures such as nanocages, nanohorns, nanotubes, and nanowires²⁵⁻²⁹. Theoretical studies found that the fullerene-like cages (XY)₁₂ with *Th* symmetry were the most stable geometry^{30,31}. Moreover, B₁₂N₁₂ has been synthesized and detected by laser desorption time-of-flight mass spectrometry³². Al-, Ga-doped³³ and Li-, Na- decorated³⁴ stable B₁₂N₁₂ clusters have been also theoretically studied. In addition, previous studies indicated that BN³⁵, AlN^{36,37} and BeO^{38,39} clusters can absorb H₂ molecularly due to the polar bond between B and N, Al and N, Be and O with different electron affinities. Moreover BN clusters can also capture CO₂⁴⁰⁻⁴². In fact, the most special point for cluster catalysis is that the addition or removal of a single atom can have a substantial influence on the activity and selectivity of reaction, which provides us the basis for converting

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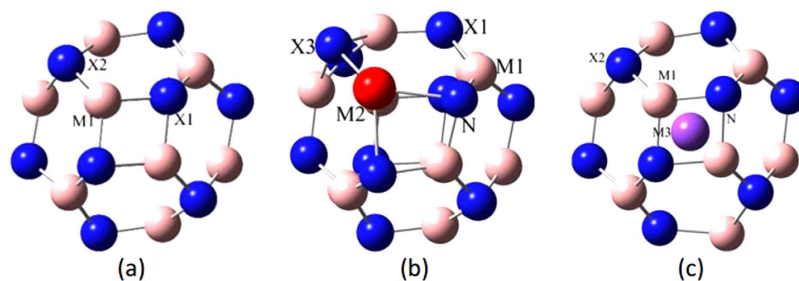


Figure 1. Geometry sketches. (a) MX clusters (M1 = B, Al, Be, Mg; X = N, P or O); (b) $\text{AlB}_{11}\text{N}_{12}$ and $\text{GaB}_{11}\text{N}_{12}$ ($\text{M}_2 = \text{Al}, \text{Ga}$); (c) $\text{LiB}_{12}\text{N}_{12}$ and $\text{NaB}_{12}\text{N}_{12}$ ($\text{M}_3 = \text{Li}, \text{Na}$).

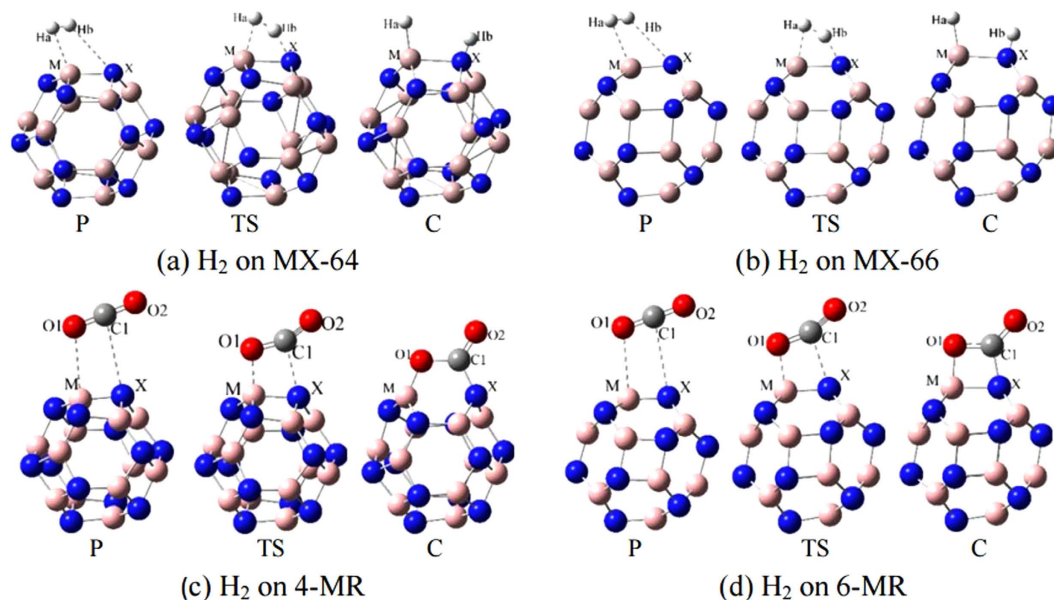


Figure 2. Geometry sketches for H_2 and CO_2 physisorption (P), chemisorption (C) and the transition states (TS) in MX-64 and MX-66 configurations.

CO_2 to different products with different efficiencies by introducing different atoms to the cluster surface or inside the cluster with more flexibilities and diversities. Based on these points, in the present work we systematically study H_2 dissociation (2H^*) and CO_2 hydrogenation using $\text{M}_{12}\text{X}_{12}$ ($\text{M} = \text{B}, \text{Al}, \text{Be}, \text{Mg}$; $\text{X} = \text{N}, \text{P}, \text{O}$) cage clusters, and explore the involved mechanisms.

Results and Discussions

Geometry structures. For $\text{M}_{12}\text{X}_{12}$ type cluster with T_h symmetry as $\text{B}_{12}\text{N}_{12}$, $\text{Al}_{12}\text{N}_{12}$, $\text{B}_{12}\text{P}_{12}$, $\text{Al}_{12}\text{P}_{12}$, $\text{Be}_{12}\text{O}_{12}$ and $\text{Mg}_{12}\text{O}_{12}$, they all consist of eight 6-membered rings (6-MR) and six 4-membered rings (4-MR), as was shown on Fig. 1(a). To improve the binding with CO_2 and H_2 , Al, Ga [Fig. 1(b)] and Li, Na [Fig. 1(c)] are introduced to $\text{B}_{12}\text{N}_{12}$ cage, the geometry parameters can be found in Table S1 of Supporting Information, where there are two types of M-X bonds: the bond shared by two 6-MRs (labelled MX-66), and the other one shared between a 4-MR and 6-MR (labelled MX-64), the former is longer than the latter for all studied nano-cages.

H_2 and CO_2 Activation. In order to determine the configuration with the lowest energy for H_2 and CO_2 adsorption on the surface of the cluster, a number of different initial structures have been used for optimization. The results of stable $\text{H}_2/\text{M}_{12}\text{X}_{12}$, $\text{CO}_2/\text{M}_{12}\text{X}_{12}$ complexes as well as their corresponding transition state (TS) structures are shown in Fig. 2. For the convenience of discussions, we distinguish the physisorption (P) from the chemical functionalization (C) for the molecules on the cages. As seen from Fig. 2, in the process of physisorption, H_2 and CO_2 molecules are weakly adsorbed on the clusters with minor changes in geometry. While in the chemical adsorption, H_2 is dissociated forming 2H^* and CO_2 is chemically activated forming CO_2^* . The corresponding geometry parameters as well as their TSs are shown in Tables S2 and S3, and the interaction energies of H_2 and CO_2 physisorption and chemical adsorption are given in Table S4 of Supporting Information.

The activation energies of H_2 on MX-64 and MX-66 are labeled as ΔG_1^H and ΔG_2^H , respectively, while the activation energies of CO_2 on MX-64 and MX-66 are labeled as ΔG_1^C and ΔG_2^C respectively. The energy barriers

Clusters	B ₁₂ N ₁₂	Al ₁₂ N ₁₂	B ₁₂ P ₁₂	Al ₁₂ P ₁₂	Be ₁₂ O ₁₂	Mg ₁₂ O ₁₂	LiB ₁₂ N ₁₂	NaB ₁₂ N ₁₂	AlB ₁₁ N ₁₂	GaB ₁₁ N ₁₂
ΔG_1^H	1.19	0.61	0.74	1.25	1.04	0.31	0.99	0.90	0.76	0.83
ΔG_2^H	1.27	0.68	1.06	1.46	1.33	0.73	1.09	0.92	0.84	0.94
ΔG_1^C	0.56	0.12	1.11	0.61	0.44	0.04	0.56	0.50	0.39	0.46
ΔG_2^C	0.51	0.11	1.06	0.63	0.47	0.03	0.33	0.26	0.36	0.43

Table 1. Gibbs energy barrier for H₂ (ΔG^H), and CO₂ activation (ΔG^C), All values are in eV.

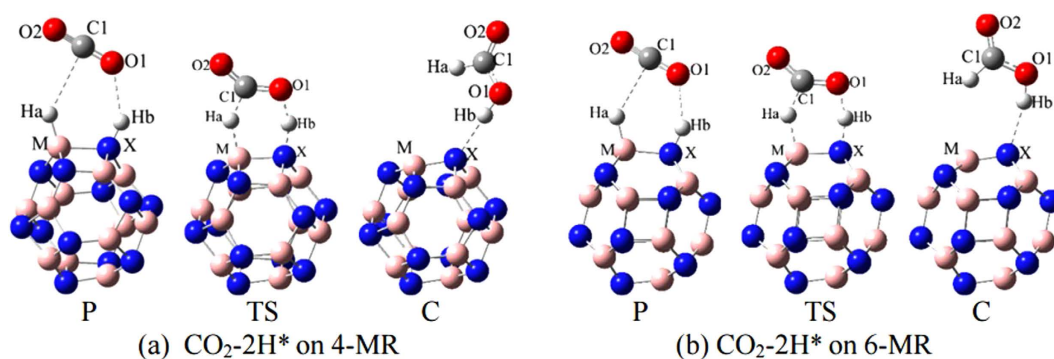


Figure 3. Geometry sketches for 2H* transfer from MX cluster to CO₂ in physisorption (P), chemisorption (C) and the transition states (TS) on MX-64 (a) and MX-66 (b) of the MX-2H* clusters.

for H₂ activation (ΔG^H) are calculated as the Gibbs energy difference between the TS^H (the TS for H₂ activation) and the initial state of H₂ adsorption:

$$\Delta G^H = G_{TS}^H - G_p^H \quad (1)$$

Similarly, the energy barriers for the CO₂ activation (ΔG^C) are calculated as the Gibbs energy difference between the TS^C (the TS for CO₂ activation) and the initial state of CO₂ adsorption:

$$\Delta G^C = G_{TS}^C - G_p^C \quad (2)$$

The calculated results are listed in Table 1, and typical structures with H₂ and CO₂ either in physisorption, or chemisorption as well as their transition states are given in the Fig. 2. All the Gibbs energy barrier for H₂ activation on MX-64 are all lower than which of the MX-66. When the activation barrier is overcome, H₂ can be dissociated generating hydridic (Ha) and protic (Hb) hydrogens.

Instead for CO₂ activation, the Gibbs energy barrier on MX-64 are all higher than that of the MX-66 except for Al₁₂P₁₂ and Be₁₂O₁₂ clusters. The activation barriers of CO₂ are lower than that of H₂ for the studied systems except for B₁₂P₁₂. The Al, Ga doped and Li, Na decorated B₁₂N₁₂ cages have lower activation energy barriers for H₂ and CO₂ than those of the pristine B₁₂N₁₂. This illustrates that the doping with Al and Ga as well as decoration with Li and Na can increase the activity of B₁₂N₁₂ cluster.

To clarify the effect of H₂ and CO₂ adsorptions on the electronic structures of nano-cages, natural bond orbital (NBO) analyses are performed and the results are listed in Table S5, from which one can see that upon the adsorption, charges on the cages are redistributed due to the geometry change and charge transfer. For example, in all the cases CO₂ received electrons from cages resulting in the activation. The charges on M sites in all clusters are decreased upon the H₂ adsorption, while increased upon the CO₂ adsorption.

The different behaviors in H₂ activation on MX-64 and MX-66 are due to the different activities between them. As seen from Table S5, more charges are on M and X sites in MX-64 than those in MX-66, which makes the former more active with a lower H₂ activation barrier as compared with the latter one.

2H* transfer mechanism. Two reaction pathways for CO₂ hydrogenation on Lewis pair moiety have been identified, one involves the physisorbed CO₂ reacting with the chemisorbed 2H*, and the other one involves the physisorbed H₂ reacting with CO₂*. For the latter, the reaction barrier for hydrogenation of the activated CO₂* is usually very high as found by Ye¹² (2.65 eV in UiO-66-P-BF₂ catalyst) and by us (2.84 eV for MX-64 and 2.97 eV for MX-66 of B₁₂N₁₂), and this pathway leads to the formation of chemisorbed HCO and OH ([HCO + OH]*) instead of HCOOH as shown in Supporting Information (Fig. S1). Consequently, in the following discussions, we only focused on the first pathway for HCOOH formation.

According to the first pathway, CO₂ is firstly physisorbed on MX-2H*(P), and then forms HCOOH (C) via the transition state (TS) (Fig. 3). For B₁₂N₁₂ nano cage, the reaction barrier for H₂ activation on MX-64 (1.19 eV) is lower than that on MX-66 (1.27 eV), while the 2H* transfer barrier on MX-64 (1.28 eV) is higher than that on MX-66 (1.19 eV). The IRC calculations show that the hydride and protons are transferred to CO₂ simultaneously.

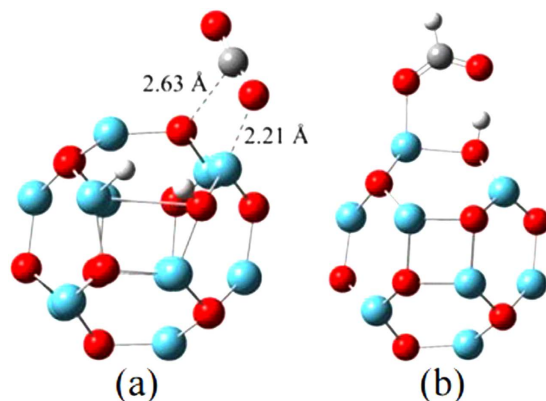


Figure 4. (a) Physisorption of CO₂ on Mg₁₂O₁₂-2H*[•]; (b) HCOOH on Mg₁₂O₁₂-2H*[•]. (The jade-blue sphere representing Mg atom, red sphere representing O atom, gray sphere representing C atom and white sphere representing H, respectively).

Clusters	B ₁₂ N ₁₂	Al ₁₂ N ₁₂	B ₁₂ P ₁₂	Al ₁₂ P ₁₂	Be ₁₂ O ₁₂	LiB ₁₂ N ₁₂	NaB ₁₂ N ₁₂	AlB ₁₁ N ₁₂	GaB ₁₁ N ₁₂
ΔG_1^{HT}	1.45	1.43	2.02	1.41	0.45	2.16	1.75	2.05	2.25
ΔG_2^{HT}	1.40	1.36	1.91	1.47	0.24	1.49	1.51	1.89	2.06

Table 2. Gibbs energy barrier for H₂ transfer (ΔG^{HT}) to form HCOOH, all values are in eV.

In other words, the H transfer step is essentially the donation of a hydride and a proton from the ion-pair products to CO₂ via a concerted mechanism. Tables S6 and S7 list the corresponding geometry parameters, transition states, and interaction energies for CO₂ and HCOOH.

When attempting to bind CO₂ with Mg₁₂O₁₂-2H* in a way shown in Fig. 3(P), we cannot find any stable structures from our calculations. While CO₂ can directly bond at Mg and O sites (as shown in Fig. 4a) with a stronger binding energy of -0.5 eV (Table S4). Similarly, when introducing HCOOH to Mg₁₂O₁₂ shown in Fig. 3(C), one H atom of HCOOH was taken away by the O atom in Mg₁₂O₁₂ nano-cage (Fig. 4b). This suggests that Mg₁₂O₁₂ is not competent to be the catalyst for CO₂ hydrogenation to HCOOH.

The activation energies of H₂ transfer on MX-64 and MX-66 are labeled as ΔG_1^{HT} and ΔG_2^{HT} and respectively. The energy barriers for H₂ activation (ΔG^{HT}) are calculated as the Gibbs energy difference between the TS^{HT} (the TS for H₂ transfer) and the initial state of CO₂ the physisorbed on MX-2H*:

$$\Delta G^{HT} = G_{TS}^{HT} - G_p^{HT} \quad (3)$$

The corresponding activation energies for H₂ transfer are listed in Table 2, where one can see that the activation energies of H transfer are all higher than 1.0 eV, except for Be₁₂O₁₂ cage. Just the opposite to the H₂ activation process in Table 1, all the Gibbs energy barriers for 2H* transfer on MX-64 are all higher than that of MX-66.

Based on the overall consideration of H₂ activation and 2H* transfer barriers as listed in Tables 1 and 2, one can find that introducing Al, Ga, Li, and Na to B₁₂N₁₂ cage has definitely decreased the H₂ activation energy barrier but increased the 2H transfer energy as compared to the pristine B₁₂N₁₂.

In order to be more intuitive, a potential energy surfaces of the reaction pathway are shown in Fig. 5 showing a balance between H₂ activation and H transfer. Thus, the interaction between the cluster and H₂ is extremely important, the stronger catalyst with more strength to activate the hydrogen molecule would promote a faster hydrogen activation process. On the other hand, a stronger catalyst has more strength to keep the hydrogen, thus would slow down the hydrogen transfer process. This is in accordance with the general Sabatier principle⁴³.

To understand the trend of protonation activation barriers for the studied nanocages, we analyze the charges on C site of CO₂. In the free standing state, C carries 1.069 e. When CO₂ is adsorbed with MX-66 configuration on B₁₂N₁₂-2H*, NaB₁₂N₁₂-2H* and LiB₁₂N₁₂-2H*, the charges increase to 1.086, 1.084, and 1.087 e, respectively. The increased charges on C site make it more active to easily bind H with smaller barriers. The similar mechanism can also be applied to other cages.

2H* transfer one by one with stepwise mechanism. When checking the overall the activation energy barrier of H₂ activation and transfer (seen from Tables 1 and 2), one can find that many clusters such as Al₁₂N₁₂, NaB₁₂N₁₂ and AlB₁₁N₁₂ etc. have lower H₂ activation but higher 2H* transfer barriers. To search for a lower barrier of H transfer, the other mechanism needs to be investigated further. We find that a new stepwise mechanism exists for CO₂ hydrogenation only on Be₁₂O₁₂ cage as shown in Fig. 6.

By following this reaction mechanism, the first H transfer is a rate-limiting step-with an activation energy of 0.22 eV on MX-64 bond (red line on Fig. 6) and 0.36 eV on the MX-66 bond (blue line on Fig. 6), In contrast, the 2H* transfer activation on MX-64 and MX-66 bonds is 0.45 eV and 0.24 eV, respectively. Then, we can conclude

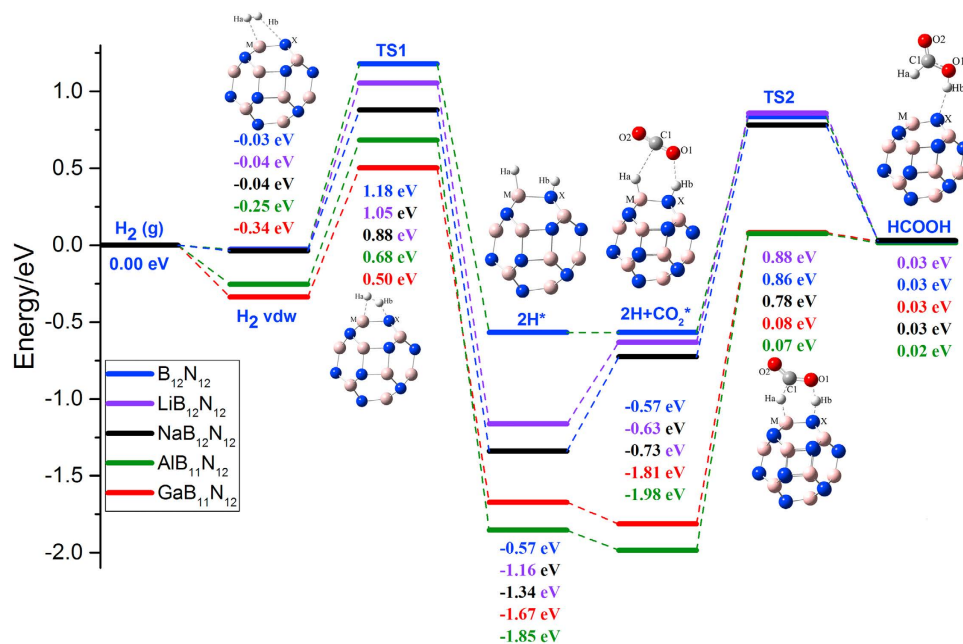


Figure 5. Relative potential energy surfaces for H_2 activation and $2H^*$ transfer pathway in Al, Ga doped, Li, Na decorated $B_{12}N_{12}$ and pristine $B_{12}N_{12}$ with Mx-66 bond as example.

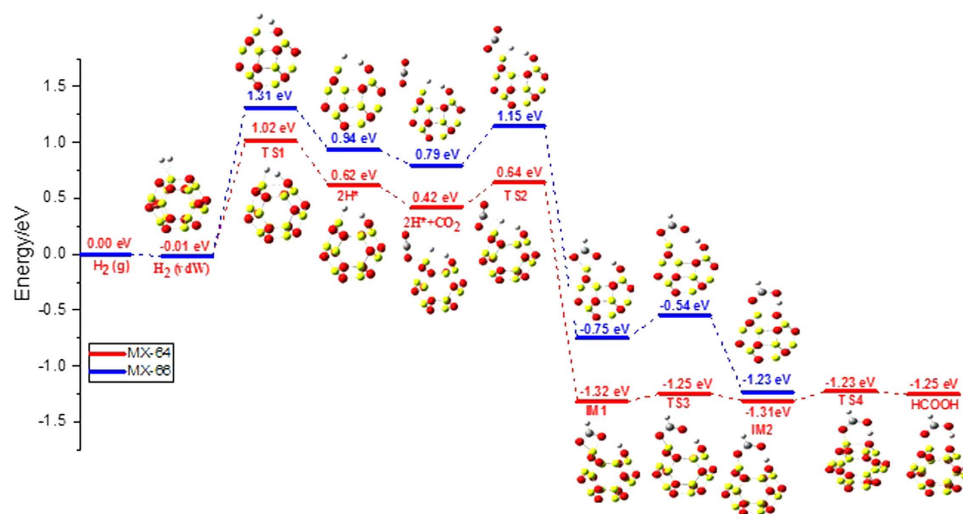


Figure 6. Relative potential energy surfaces for H_2 activation and H^* stepwise transfer pathway on Mx-64 (redline) and Mx-66 (blue line) bond for $Be_{12}O_{12}$. (The yellow sphere representing Be atom, red sphere representing O atom, gray sphere representing C atom and white sphere representing H, respectively).

that $2H^*$ simultaneously transfer to CO_2 on MX-66 bond has lower activation energy than that of the one H transfer stepwise, but on MX-64 bond the situation is opposite.

For practical applications of an efficient catalyst, both the H_2 activation and transfer barriers should be comparable or lower than 1 eV^{44} . Among all systems studied here, $Be_{12}O_{12}$ is the most promising catalyst, where the H_2 activation barrier is close to 1 eV (1.04 eV) on MX-64 bond, and the following H^* transfer barriers are all lower than 1 eV , (0.45 eV by the $2H^*$ simultaneously transfer mechanism, while 0.22 eV by the H^* stepwise transfer mechanism). Therefore, the reaction pathway on $Be_{12}O_{12}$ MX-64 bond has the lowest barrier based on the overall consideration of the H_2 activation (1.04 eV) and H^* stepwise transfer (0.22 eV).

Conclusions

In summary, based on the DFT and MP2 calculations, a series $M_{12}X_{12}$ nano-cages have been studied for activating H_2 and CO_2 to form HCOOH. The hydrogenation process mainly consists of H_2 activation to $2H^*$, and then $2H^*$ further transfer to CO_2 forming a HCOOH molecule. Two kinds of H^* transfer mechanisms are found: one involves $2H^*$ simultaneous transfer, and the other is a stepwise H^* transfer to CO_2 . The two mechanisms result

in the same product HCOOH. Moreover, Al, Ga doped and Li, Na decorated $B_{12}N_{12}$ cages have lower H_2 activation energy barriers, but higher $2H^*$ transfer activation barriers than that of the pristine $B_{12}N_{12}$. For practical applications, in order to have an efficient catalyst to reduce CO_2 , we should search for a catalyst that has a balance between the energy barriers for H_2 activation and the H transferring. Among all the systems studied here, $Be_{12}O_{12}$ is found to be the most promising catalyst, its reaction pathway on MX-64 bond has the lowest barriers (1.04 eV for H_2 activation and 0.22 eV for H^* transferring). This conclusion would motivate experimental work in the future.

Methods

Since many theoretical calculations have demonstrated that different DFT functions (e.g. B97D, ω -B97X-D, and M06-2X) and basis sets (e.g. 6-31 G*, 6-31 + G**) led to very similar results for the systems only containing main group elements for H_2 activations^{7,8,11}. In this work, all the geometry optimizations are performed at the M06-2X/6-31 + G** level as implemented in Gaussian 09 package⁴⁵. Solvent effects are taken into account by using the polarizable continuum model (PCM) with toluene as a solvent. The highly parameterized, empirical exchange correlation functional, M06-2X, developed by Zhao and Truhlar, was shown to better describe the main-group thermochemistry and kinetics than other density functionals such as B3LYP⁴⁶. Moreover, this hybrid density M06-2X functional has been previously proved to have a good reliability in computing molecular binding energies of H_2 and CO_2 on FLPs⁴⁷. Frequency calculations are carried out at the same level to characterize the nature of the stationary points along the reaction coordinates. No imaginary frequencies were found for the local minima, and one and only one imaginary frequency was found for the transition state. The Natural Bond Orbital (NBO 3.1) program⁴⁸, was used to calculate the natural charges at the M06-2X/6-31 + G** level of theory. The thermal contributions at room temperature (298.15 K) including the specific free energies were obtained from a harmonic analysis, and accurate electronic energies were obtained from frequency calculations using Møller-Plesset second-order perturbation theory (MP2)^{49,50} with the cc-pVTZ triple- ζ quality basis^{51,52}. Using the optimized geometries and starting from the TS, intrinsic reaction coordinate (IRC) calculations are performed to verify the true connection of the reactants, the transition states and the products for both H_2 , CO_2 activation and H transfer processes.

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Author Contributions

H.Z. carried out the theoretical calculations and wrote the manuscript. G.Z. and Y.L. analyzed the reaction mechanism. Q.S., H.S. and S.C. designed the study.

Additional Information

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