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Theoretical study of catalytic reduction of CO_2 with H_2O by BOC-MP method

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ABSTRACT

Bond-Order Conservation-Morse Potential (BOC-MP) method is used to carry out the calculation on the CO2+ H2O system. One of the best catalysts for methanol synthesis in catalytic reduction of CO2 with H2O is Cu/ZnO/Al2O3 whose surface is supported by with some amount of Pd or Ga. Reduction of CO2 with H2O on Cu will result in methanol formation; while on Ni will lead to methane formation. In the mechanism of methanol synthesis from CO2+ H2O on Cu, the formate (HCOO) hydrogenation step is rate-determining step and in the mechanism of methane synthesis on Ni, carbon hydrogenation is rate-determining step. The kinetic of each proposed mechanism is investigated.

Keywords: Reduction of CO2; BOC-MP; Catalyst; Methanol

INTRODUCTION

The large-scale emission of carbon dioxide into the atmosphere is one of the most serious and dangerous problems upon the earth, especially with regard to the devastating consequences of the greenhouse effect [1]. The reduction and/or fixation of carbon dioxide can be said to be one of the most important areas of research in today chemistry, not only for solving the many urgent problems resulting from the pollution of the global environment but also for finding ways to maintain vital carbon resources[2].

GOALS

The goals of the present work are:

(1) Designing two catalysts for the process of CO_2 reduction through a thermal reaction.(experimental-theoretical)

(2) Suggesting the reaction pathways for the synthesis of methanol and methane from CO_2

(3) Investigating the kinetic of the assumed reaction.

METHOD

In the BOC-MP method (Bond-Order Conservation-Morse Potential) the total bonds between the adsorbate and its underlying adsorbent atom(s) is conserved and the bond energy is assumed to follow the Morse potential model. The optimization of the energy of the adsorbed ensemble, adsorbate and its underlying surface atom(s), is achieved by a variational method [3]. The details of calculations can be found in the original literatures [3, 4, 5].

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Within the BOC-MP framework, in the zero coverage limits, the heats, qAB, of adsorption of molecules and molecular fragments are calculated. The experimental values of qA (heat of adsorption of atom) are known for H and O but not for C. For carbon we have assumed the values of qC=120 and 171 kcal/mol for Cu(111) and Ni(111) respectively, based on an extrapolation of values of qC for a periodic series of transition metals. Table 1 lists the experimental values of qAB, qA and qCO as well as the calculated values of qAB and the total bond energies, DAB+qAB, for chemisorbed species thought to be involved in all of the reaction occurring on Cu(111) and Ni(111)[6, 7].

The BOC-MP method also permits calculation of activation barriers, ΔE, for elementary processes such as dissociation, recombination and disproportionation [8, 9].

The resulting equations used in the calculations of the heats of adsorptions are given below without going into the details of derivations. Firstly, the heat of atomic adsorption of A on an n-fold surface site forming Mn-A is

$$q_A = q_{0A}[2-(1/n)] \qquad (1)$$

where q0A is the two center bond energy. For a mono-coordinated(η1) admolecule AB with A end down, M-A-B, three caces have been distinguished. If AB is strongly bonded on to the surface and retains its localized unpaired electrons in the case of adsorption of free radicals , one has

$$q_{AB}=q_A^2/(q_A+D_{AB}) \qquad (2)$$

where DAB is the gas phase bond dissociation energy of AB. On the other hand if AB is weekly bonded on to the surface as in the case of the adsorption of closed shell molecules, one arrives at

$$q_{AB}= q_{0A}^2/(q_{0A}+D_{AB}) \qquad (3)$$

In the intermediate situation the average of the above values is employed

$$q_{AB}=0.5\{[q_A^2/(q_A+D_{AB})]+[q_{0A}/(q_{0A}+D_{AB})]\}. \qquad (4)$$

So far as kinetics of the processes are concerned, the activation energies of adsorptions, surface reactions and desorptions can also be related to the q and D values[2]. The activation energy, EAB,g, of the dissociation of AB impinging on the surface is given by

$$E_{AB,g}^* =0.5[D_{AB}+(q_A q_B)/(q_A +q_B) -q_{AB} -q_A-q_B] \qquad (5)$$

while the dissociation of the adsorbed AB species occurs with the activation energy of

$$E_{AB,s}^* =0.5[D_{AB}+(q_A q_B)/(q_A +q_B) +q_{AB} -q_A-q_B]. \qquad (6)$$

Concerning the recombination of chemisorbed A and B entities, the activation energy of the desorptive recombination is

$$E_r = E_f - \Delta H \qquad (7)$$

where Ef is either EAB,g* or EAB,s* and ΔH , the enthalpy change in the reaction, is obtained from

$$\Delta H = -\Sigma[(q + D)_{Pi} - (q +D)] \qquad (8)$$

where Pi and Ri refers to the products and reactants respectively. The details of the derivation can be found in the original literature[6,7].

RESULTS AND DISCUSSIONS

As mentioned, the best catalyst for methanol synthesis in catalytic reduction of CO2 with H2O is Cu/ZnO/Al2O3 along with some amount of Pd or Ga on its surface. Not only these metals give special stability to the catalyst but also active the reduced Cu, subsequently an increase will occur in active sites on the surface. On the other hand, molecules of hydrogen will break on the mentioned metals. This will make hydrogen, as a more available and easier reagent.

Table 1. Heats of chemisorption (q) and total bond energies (D) in the gas-phase and the sum of q and D on Cu(111) and Ni(111)

Species	D	Cu(111)		Ni(111)	
	(kcal/mol)	q	q+D	q	q+D
H	--	56	56	63	63
O	--	103	103	115	115
C	--	120	120	171	171
CO	257	12	269	27	284
CO_2	384	5	389	6	390
HCO	274	27	301	50	324
H_2CO	361	16	377	20	381
H_3CO	383	55	438	65	448
CH_3OH	487	15	502	18	505
HCOO	384	59	443	35	419
OH	102	52	154	61	163
H_2O	220	14	234	17	237
H_2	104	5	109	7	111

The BOC-MP calculations clearly project that CO_2 undergoes hydrogenation to methanol much more readily than CO on Cu, because of the low activation barrier to form $HCOO_{(s)}$ and the fact that the pathway from this intermediate to $H_2CO_{(s)}$ is energetically more favorable than that involving the hydrogenation of $CO_{(s)}$. So far the mechanism of CO_2 hydrogenation on Cu(111) proceed via the formate ($HCOO_{(s)}$) formation. Therefore the mechanism of CO_2 reduction on Cu may be suggested as follows:

$$H_{2(g)} \xrightleftharpoons[E_{a(-1)}=15]{\Delta H=-8,\,E_{a(1)}=7} 2H_{(s)}$$

$$CO_{2(g)} \xrightleftharpoons[E_{a(-2)}=5]{\Delta H=-5,\,E_{a(2)}=0} CO_{2(s)}$$

$$CO_{2(s)}+H_{(s)} \xrightleftharpoons[E_{a(-3)}=2]{\Delta H=2,\,E_{a(3)}=4} HCOO_{(s)}$$

$$HCOO_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(-4)}=0]{\Delta H=19,\,E_{a(4)}=19} H_2CO_{(s)}+O_{(s)}$$

$$H_2CO_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(5)}=9]{\Delta H=-5,\,E_{a(5)}=4} H_3CO_{(s)}$$

$$H_3CO_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(-6)}=18]{\Delta H=-8,\,E_{a(6)}} H_3COH_{(s)}$$

$$H_3COH_{(s)} \xrightleftharpoons[E_{a(-7)}=0]{\Delta H=15,\,E_{a(7)}=15} H_3COH_{(g)}$$

Regarding the above data, the rate determining step in the formate route to methanol projected to be the hydrogenation of formate group.

Direct verification of our calculations of q and Ea is limited by the scarcity of the appropriate experimental data. The available data for q are presented in table 2 and those for ΔE, in the table3.

Table 2. Comparing calculated and experimental heats of adsorption,q.

Ad-species	Surface	q(kcal/mol)		
		Calc.	Exp.	Ref
H_2O	Cu(111)	14	14	[10]
			11-13	[11]
	Pd(111)	10	10	[12]
CH_3OH	Cu(111)	15	17	[10]
CO_2	Cu(111)	5	4-5	[13]

Table 3. Comparing calculated and experimental ΔE

Reaction	Surface	ΔE (kcal/mol)		
		Calc.	Exp.	Ref.
$H_{2g} \longrightarrow 2H$	Cu(111)	7	5	[3]
$H_2O_s \longrightarrow H_s + OH_s$	Cu(111)	26	27	[14]
$O_s + H_s \longrightarrow OH_s$	Cu(111)	21	22	[15]
$CO_s + O_s \longrightarrow CO_{2g}$	Pd(111)	24	25	[14]
$CH_3O \longrightarrow H_2CO + H_s$	Cu(111)	25	24	[16]
$OH_s + CO_s \longrightarrow HCOO_s$	Rh(100)	10	8	[17]

Using the assumed mechanism and steady state approximation the following rate equation for reduction of CO2 on Cu(111) can be resulted.

$$Rate_{CH_3OH}=\frac{k_4K_3K_2K_1}{\left[1+(K_1P_{H_2})^{1/2}+K_1P_{CO_2}\right]^2}P_{H_2}P_{CO_2}$$

$$If \quad 1+(K_1P_{H2})^{1/2} >> (K_1P_{CO2}$$

$$\longrightarrow \quad Rate = k_4K_3K_2\ P_{CO2}$$

$$k = k_4K_3K_2$$

$$\longrightarrow E_{app} = E_{forward\ 4} + \Delta H_3 + \Delta H_2 = 16 kcal/mole$$

On the other hand, methanol is not formed by the hydrogenation of CO2 and CO on Ni, but methane formation is projected. The methane formation proceeds via the carbon species formation. Because the activation barrier of carbon species formation is much lower than that of formate and/or formyl species formation. Regarding the results of our calculations, we may assume the mechanism of CO2 reduction on Ni as follows:

$$H_{2(g)} \xrightleftharpoons[E_{a(-1)}=23]{\Delta H=-23,\,E_{a(1)}=0} 2H_{(s)}$$

$$CO_{2(s)} \xrightleftharpoons[E_{a(-2)}=15]{\Delta H=-8,\,E_{a(2)}=7} CO_{(s)}+O_{(s)}$$

$$CO_{(g)} \xrightleftharpoons[E_{a(-3)}=35]{\Delta H=-29,\,E_{a(3)}=6} C_{(s)}+O_{(s)}$$

$$C_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(-4)}=5]{\Delta H=37,\,E_{a(4)}=42} CH_{(s)}$$

$$CH_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(-5)}=23]{\Delta H=-6,\,E_{a(5)}=17} CH_{2(s)}$$

$$CH_{2(s)}+H_{(s)} \xrightleftharpoons[E_{a(-6)}=24]{\Delta H=-8,\,E_{a(6)}=16} CH_{3(s)}$$

$$CH_{3(s)}+H_{(s)} \xrightleftharpoons[E_{a(-7)}=14]{\Delta H=0,\,E_{a(7)}=14} CH_{4(s)}$$

$$CH_{4(s)} \xrightleftharpoons[E_{a(-8)}=0]{\Delta H=6,\,E_{a(8)}=6} CH_{4(g)}$$

$$O_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(-9)}=22]{\Delta H=-2,\,E_{a(9)}=20} OH_{(s)}$$

$$OH_{(s)}+H_{(s)} \xrightleftharpoons[E_{a(-10)}=21]{\Delta H=-11,\,E_{a(10)}=10} H_2O_{(s)}$$

$$H_2O_{(s)} \xrightleftharpoons[E_{a(-11)}=0]{\Delta H=17,\,E_{a(11)}=17} H_2O_{(g)}$$

In the above mechanism, the rate-determining step is the hydrogenation of CH(s) species. Using the assumed mechanism and steady state approximation, one can conclude the following rate equation for reduction of CO2 on Ni(111).

$$Rate_{CH_4} = \frac{k_4 K_{H_2} K_{CO_2}}{K_8 K_9 K_{10} P_{H_2O}\left[1+(K_{H_2}P_{H_2})^{1/2}+P_{CO}P_{CO_2}\right]} P_{H_2} P_{CO}$$

$$If\ [1+(K_{H2}P_{H2})^{1/2}] >> P_{CO}P_{CO2} \longrightarrow E_{app} = 0$$

The same rate law is reported in several experimental works. [8,9]

CONCLUSION

On the basis of this work, the best catalyst for methanol synthesis in catalytic reduction of CO2 is Cu/ZnO/Al2O3 along with some amount of Pd or Ga is supported on its surface.

The reduction of CO_2 with water onCu will result in methanol formation, while on Ni it will cause methane formation. In the mechanism of methanol synthesis from CO2 on Cu, formate hydrogenation (HCOO) is rate-determining step and in the mechanism of methane synthesis on Ni, carbon hydrogenation is rate- determining step.

Investigating the kinetic of proposed mechanism, we deduced that the reaction of methanol formation in reduction of CO2 with H2O on Cu is first order with respect to each of hydrogen and carbon dioxide concentration and appearance activation energy for this process is about 16 kcal/mol.

On the basis of value of Eapp for Ni, the Ni is the best methanation catalyst.

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