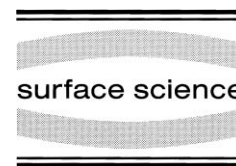




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BOC-MP study on the mechanism of partial oxidation of CH₃OH to HCHO over a silver surface and the promoting effect of halogen to the catalyst

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Abstract

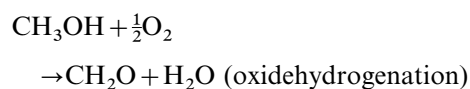
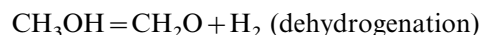
The mechanism of partial oxidation of methanol to formaldehyde over a silver surface and the promoting halogen to the catalyst have been systematically analyzed by the BOC-MP model. The analysis showed that the oxidehydrogenation of methanol to formaldehyde is preferable to the direct dehydrogenation pathway. The promoting effect of halogen to the catalyst has also been interpreted. The modifying atom could not only control the concentration of surface atomic oxygen (not too high), but also promotes the replenishing of surface atomic oxygen and maintains its concentration, to some extent, during the processing of the reaction. Thus, it could increase both the catalytic activity and the selectivity to the formation of formaldehyde. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Bromine; Chemisorption; Chlorine; Iodine; Model of surface chemical reaction; Semi-empirical models and model calculation; Silver catalyst

1. Introduction

The partial oxidation of methanol to formaldehyde over a silver surface is a very important industrial process, and the improvement of the catalysts results in great economic benefits. The study of this reaction mechanism provides useful information for the design of catalysts. The mechanism of this reaction, thus, has been extensively studied and several different mechanisms have been proposed [1–4]. It is regarded that the reaction includes two kinds of processes, i.e. dehydro-

genation of methanol and oxidehydrogenation of methanol:



At the present time, there is still a degree of controversy on the mechanism [1–4]. In the early 1970s, it was reported [5] that the catalytic activity and selectivity of silver catalyst modified by halogen (such as Cl, Br, I) was higher than that of the unmodified silver catalyst. Our recent experimental study [6] also showed that the addition of iodine to silver catalyst would improve both its catalytic

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activity and selectivity. However, there are still no systematic theoretical work which studies the mechanism or interprets the function of the introducing halogen.

In the present study, the mechanism of the studied catalytic reaction and the promoting effect of halogen is analyzed by the bond order conservation Morse potential (BOC-MP) model. For comparison, the reaction on the surface modified by sulfur is also analyzed in a similar way. The BOC-MP method, which was proposed by Evgeny Shustorovich [7–9], is an analytic model based on a few well-defined assumptions and was proven to be a very powerful tool to deal with the problems of chemisorption and heterogeneous catalysis.

2. Calculation detail

The surface we study here is Ag(111) and the halogen-modified surface is presented in Fig. 1. The coverage of pre-adsorbed atoms (halogen or other atoms) on the silver surface is assumed to be 1/10 according to our experiment [6]. Here, we simply introduce the method to calculate the chemisorption heats of species on the modified surface. The BOC-MP formalism can be found in the literature [7–9].

For a modified-surface, the heats of atomic chemisorption could be calculated in a similar way as in Ref. [10]:

If Q_{A-M} is the two-center M–A (metal–adsor-

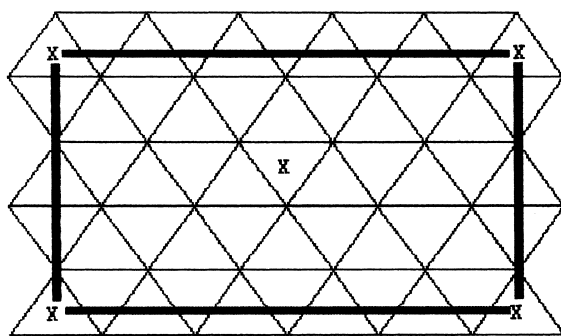


Fig. 1. The model for the modified silver surface.

Table 1

The values of h in Eq. (1) for different adsorption sites

Adsorption site	Top	Bridge	Hollow
h	$1/(2-1/n)^a$	$3/[4(2-1/n)]$	$1/n$

^a n is the number of nearest metal atoms interacting with an adsorbate on a given surface.

bate) bond energy, it can be assumed that

$$Q_{A-M} = hQ_A, \quad (1)$$

where Q_A is the heat of atomic chemisorption on a given surface, h is a parameter related to the adsorption site of species on the surface. The values of h are listed in Table 1.

It could be simply assumed that the adsorption heat of modifying atom X on the surface is:

$$Q_X = rQ_A, \quad (2)$$

where r is a coefficient. According to the BOC-MP assumptions, the interaction of A–M–X could be described as:

$$-E = (1/n)rQ_A(2Z - Z^2) + hQ_A(1 - Z^2), \quad (3)$$

where Z is the bond order of X–M. Then, the equilibrium value of $Z = Z_0$ (for $dE/dZ = 0$)

$$Z_0 = (1 + nh/r)^{-1}. \quad (4)$$

Thus, the heats of atomic chemisorption on the X-modified surface could be written as:

$$Q_{A-M(X)} = Q_A h [1 - (1 + nh/r)^{-2}]. \quad (5)$$

If A is a molecule, it could be assumed that its heat of chemisorption is the same in all adsorption sites, since it shows a very weak dependence on n [10]. For the $\eta^1\mu_n$ adsorption mode of a molecule,

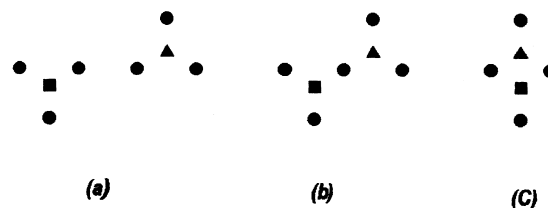


Fig. 2. Some possible structures of adsorption of species on a X modified silver surface: ●, silver; ▲, modifying atom x; and ■, other adsorbate.

Table 2
The number of different adsorption sites in a Ag_{20}X_2 unit

Adsorption site	(0) ^(a)	(1) ^(b)	(2) ^(c)
On-top	14	6	—
Bridge	30	24	6
Hollow	14	18	6

(a),(b),(c) relate to the situation presented in Fig. 2. 0,1,2 is the number of sharing metal atoms (or vertex) of the M–X unit and M-species unit.

h could be assigned as 1, 1/2 and 1/ n for its on-top, bridge, and hollow coordination. The $Q_{\text{A-M(X)}}$ could be calculated in the same way (Eq. (5)).

According to Fig. 2, the number of different adsorption sites in a Ag_{20}X_2 unit is listed in Table 2, and the calculation method for the chemisorption heats is given in Table 3.

3. Result and discussion

3.1. Heats of chemisorption

In the BOC-MP formalism, only a few quantities, namely the heats of atomic chemisorption (Q_{A} or Q_{B}) and several constants—bonding energies (D), structural (n) and numerical (coefficient)—are needed to calculate the heats of chemisorption on metal surface [8], so that the heats of atomic chemisorption should be known at first. In our present study, the experimental value for the heats of atomic chemisorption of oxygen (Q_{O}) and sulfur (Q_{S}) on Ag(111) surface are 80 kcal/mol [11] and 84 kcal/mol [7]. The value for Q_{Cl} , Q_{Br} , Q_{I} , could be estimated by $D(\text{MA})$

[12, 13].

$$D(\text{MA}) = \{-1/y\Delta H_{\text{f}}(\text{MxAy}) + \Delta H_{\text{f}}[\text{A}(\text{g})]\}, \quad (6)$$

where $D(\text{MA})$ is the total bond energy of atom A to the metal surface, $\Delta H_{\text{f}}(\text{MxAy})$ and $\Delta H_{\text{f}}[\text{A}(\text{g})]$ are the formation enthalpy of compound MxAy and A(g). The value of $D(\text{Ag-Cl})$, $D(\text{Ag-Br})$, and $D(\text{Ag-I})$ calculated by Eq. (6) are 60, 50 and 40 kcal/mol, respectively. It was reported [14] that the value of Q_{Cl} is estimated as 53 kcal/mol. So, it is reasonable to qualitatively estimate Q_{Br} and Q_{I} as 43 and 33 kcal/mol, respectively.

From the heats of atomic chemisorption, the heats of chemisorption of species on a clean or modified surface are calculated and listed in Table 4. The corresponding adsorption mode of η^2 -intermediate species on silver surface are sketched in Fig. 3.

From the calculated results in Table 4, the following conclusions could be obtained.

- (1) The heats of chemisorption of species on modified silver surfaces are less than those on a clean silver surface. The magnitude of these chemisorption heats decrease in the order of $\text{I} > \text{Br} > \text{Cl} > \text{O} > \text{S}$ for the modifying (or pre-adsorbed) atoms.
- (2) With the coverage of $\theta_{\text{X}} = 1/10$ of the modifying atom X (X = O, S, Cl, Br, I), the preferable adsorption site of atoms or radicals is still the hollow site, while the preferable adsorption site of molecules is the on-top site. So, in Table 4, only the heats of chemisorption of molecules in the on-top site are listed.

3.2. Activation barrier

According to the experimental proposed mechanism [1–4] the activation barriers for the possible

Table 3
The calculation method for the chemisorption heat

Adsorption site	(0) ^a	(1)	(2)
On-top	$Q_{\text{A}}h^b$ (14/20) ^c	$Q_{\text{A-M(X)}}$ (6/20)	
Bridge	$2Q_{\text{A}}h$ (30/60)	$Q_{\text{A}}h + Q_{\text{A-M(X)}}$ (24/60)	$2Q_{\text{A-M(X)}}$ (6/60)
Hollow	$3Q_{\text{A}}h$ (14/38)	$2Q_{\text{A}}h + Q_{\text{A-M(X)}}$ (18/38)	$Q_{\text{A}}h + 2Q_{\text{A-M(X)}}$ (6/38)

^aSame as in Table 2.

^bThe value of h is different for different sites; see Table 1.

^cThe ratio of the relevant site in the total similar sites.

Table 4
Bond energies (D) in the gas phase and heats of chemisorption (Q) of species on clean or modified surface^a

Species	D^b	Site	Q					
			Clean	X=O	X=S	X=Cl	X=Br	X=I
O	—	T	48.0	46.2	46.0	47.0	47.2	47.5
		B	72.0	68.1	67.9	69.7	70.2	70.8
		H	80.0 ^c	74.7	74.5	76.7	77.4	78.2
H	—	T	31.2	29.2	29.1	30.0	30.3	30.6
		B	46.8	42.8	42.6	44.2	44.8	45.4
		H	52.0 ^c	47.0	46.8	48.5	49.2	49.9
C	—	T	72.0	70.4	70.3	71.2	71.4	71.6
		B	108.0	104.5	104.2	106.0	106.6	107.1
		H	120.0 ^d	114.9	114.6	117.0	117.8	118.5
OH	102.0	T	33.0	31.0	30.9	31.9	32.1	32.4
		B	49.5	45.5	45.3	46.9	47.5	48.1
		H	55.0 ^e	49.9	49.7	51.5	52.2	53.0
CH ₃ O	383.0	T	22.8	20.8	20.7	21.5	21.8	22.1
		B	34.2	30.4	30.2	31.6	32.1	32.6
		H	38.0 ^f	33.4	33.3	34.6	35.2	35.8
OOH	165.0	T	20.8	24.9	24.8	25.6	25.9	26.2
		B	38.4	36.4	36.2	37.7	38.2	38.8
		H	44.8	40.0	39.8	41.3	42.0	42.7
CH ₃	293.0	T	14.2	13.6	13.6	13.9	14.0	14.1
		B	22.4	21.3	21.2	21.8	22.0	22.1
		H	25.6	24.0	23.9	24.7	24.9	25.2
CH ₃ OH	487.0	T	9.5	8.0	7.9	8.3	8.5	8.7
CH ₂ OH ^g	393.0	T	8.9	7.4	7.4	7.7	7.9	8.1
H ₂ CO	361.0	T	10.2	8.6	8.6	9.0	9.2	9.4
HCO ^g	274.0	T	9.6	8.0	8.0	8.4	8.6	8.8
CO ^c	257.0	T	6.5	5.2	5.2	5.5	5.6	5.7
CO ₂	384.0	—	3.2	3.0	3.0	3.1	3.1	3.2
HCOOH	481.0	—	13.2	12.3	12.2	12.7	12.8	12.9
HCOO	384.0	—	39.0	34.8	34.6	36.4	36.9	37.6
H ₂ COO	385.0	—	53.0	47.6	47.4	49.7	50.4	51.2
H ₃ COO	428.0	—	65.1	58.9	58.6	61.2	62.0	63.0
OCH ₂ HO	434.0	—	65.2	59.1	58.8	61.4	62.2	63.1
O ₂	119.0	—	9.5 ^h	8.8	8.7	9.1	9.2	9.3

^aAll bond energies and heats of chemisorption in kcal/mol, X is the modifying atom.

^bRefs [15,16].

^cExperimental value, Ref. [11].

^dRef. [8].

^eRef. [17].

^fRef. [18].

^gAdsorbed via oxygen.

^hExperimental value is 9.2 kcal/mol⁻¹, Ref. [19].

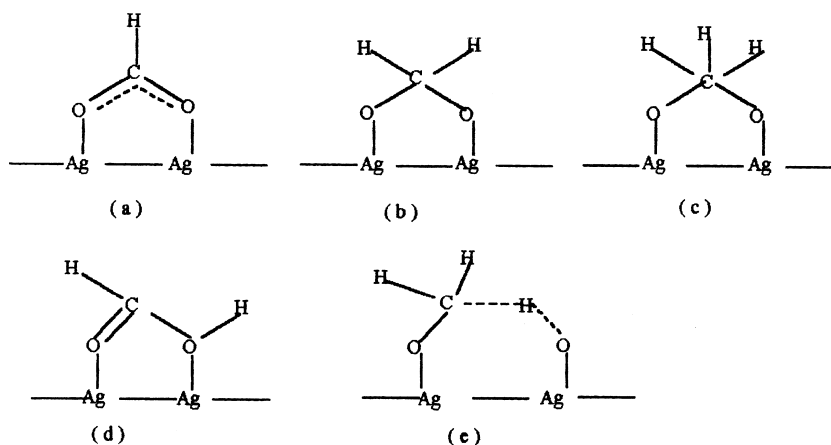
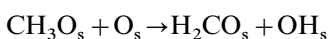
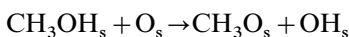
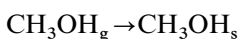
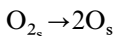
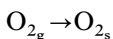


Fig. 3. Adsorption mode of η^2 -intermediate species on a silver surface.

elementary reactions on clean or modified silver surfaces have been calculated and listed in Table 5.

By analyzing the activation barriers listed in Table 5, it could be concluded that the preferable pathway of partial oxidation of methanol is as follows:



From the proposed mechanism above, it can be inferred that the direct dehydrogenation of methanol is more difficult than the oxidehydrogenation of methanol. In addition, from the schematic pathway of the desorption of formaldehyde and its complete oxidation sketched in Fig. 4, it can be seen that the main products of partial oxidation of methanol are HCHO and CO_2 on the surface of low coverage of atomic oxygen (here $\theta_{\text{O}}=1/10$). The desorption of HCHO ($E_a=8.6$ kcal/mol) is easier than its complete oxidation ($E_a=10.4$ or 10.7 kcal/mol). Almost no CO could be found in the products, since CO is easy to be oxidized by surface OH species ($E_a=0$), while it is difficult to be desorbed ($E_a=5.2$ kcal/mol).

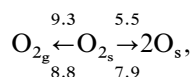
Meanwhile, the calculation also showed that the

surface atomic oxygen is very important for the partial or complete oxidation. All these calculation results are in agreement with experiments [6].

In order to investigate the modifying effect of the halogen atoms, the activation barriers of reactions occurring on modified silver surfaces have been calculated and the coverage of modifying atom on the surface have been assumed to be $1/10$.

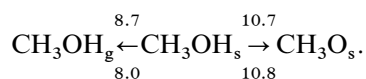
Comparing the reactions occurring on oxygen pre-adsorbed surfaces ($\theta_{\text{O}}=1/10$) with those happened on iodine pre-adsorbed surfaces ($\theta_{\text{I}}=1/10$), the promoting effect of iodine to the silver catalyst could be summarized as follows.

- (1) The promoting effect to the formation of the surface atomic oxygen:



where the value above the arrow is the energy barrier in kcal/mol of reaction on $1/10$ oxygen pre-adsorbed silver surface, and that below the arrow is the energy barrier of reaction on $1/10$ iodine pre-adsorbed silver surface.

- (2) The promoting effect to the formation of the surface methoxide:



- (3) The promoting effect to the direct dehy-

Table 5
 Energetics of possible elementary steps of the oxidation of methanol to formaldehyde over clean or modified silver surface^a

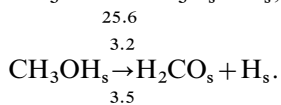
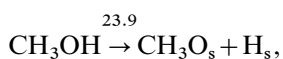
Reaction		Clean	X=O	X=S	X=Cl	X=Br	X=I
CH ₃ OH _g →CH ₃ OH _s	ΔH	-9.5	-8.0	-7.9	-8.3	-8.5	-8.7
	ΔE_f	0	0	0	0	0	0
	ΔE_r	9.5	8.0	7.9	8.3	8.5	8.7
CH ₃ OH _s →CH ₃ O _s +H _s	ΔH	23.5	31.6	31.8	29.2	28.1	27.0
	ΔE_f	23.5	31.6	31.8	29.2	28.1	27.0
	ΔE_r	0	0	0	0	0	0
CH ₃ OH _s +O _s →CH ₃ O _s +OH _s	ΔH	-1.5	1.4	1.4	0.9	0.5	0.1
	ΔE_f	10.5	10.7	10.7	10.8	10.8	10.7
	ΔE_r	12.0	9.3	9.3	9.9	10.3	10.6
CH ₃ OH _s →CH ₃ _s +OH _s	ΔH	20.9	26.1	26.3	24.1	23.4	22.5
	ΔE_f	20.9	26.1	26.3	24.1	23.4	22.5
	ΔE_r	0	0	0	0	0	0
CH ₃ OH _s +O _s →CH ₃ _s +OOH _s	ΔH	48.1	47.7	47.7	48.0	48.0	48.0
	ΔE_f	48.1	47.7	47.7	48.0	48.0	48.0
	ΔE_r	0	0	0	0	0	0
CH ₃ OH _s →CH ₂ OH _s +H _s	ΔH	42.6	47.6	47.7	46.1	45.4	44.7
	ΔE_f	42.6	47.6	47.7	46.1	45.4	44.7
	ΔE_r	0	0	0	0	0	0
CH ₃ OH _s +O _s →CH ₂ OH _s +OH _s	ΔH	17.6	17.4	17.3	17.8	17.8	17.8
	ΔE_f	17.6	17.4	17.3	17.8	17.8	17.8
	ΔE_r	0	0	0	0	0	0
CH ₃ O _s +O _s →OCH ₂ HO _s	ΔH	1.8	-2.0	-2.0	-1.1	-0.6	-0.1
	ΔE_f	13.8	10.5	10.5	11.4	11.8	12.2
	ΔE_r	12.0	12.5	12.5	12.5	12.4	12.3
CH ₃ O _s +O _s →H ₃ COO _s	ΔH	7.9	4.2	4.2	5.1	5.6	6.0
	ΔE_f	16.8	13.6	13.6	14.5	14.9	15.3
	ΔE_r	8.9	9.4	9.4	9.4	9.3	9.3
CH ₃ O _s →H ₂ CO _s +OH _s	ΔH	-2.2	-0.2	-0.1	-0.9	-1.2	-1.5
	ΔE_f	3.2	3.5	3.6	3.3	3.3	3.2
	ΔE_r	5.4	3.7	3.7	4.2	4.5	4.7
CH ₃ O _s +O _s →H ₂ CO _s +OH _s	ΔH	-27.0	-30.4	-30.5	-29.2	-28.8	-28.4
	ΔE_f	0	0	0	0	0	0
	ΔE_r	27.0	30.4	30.5	29.2	28.8	28.4
H ₂ CO _s →H ₂ CO _g	ΔH	10.2	8.6	8.6	9.0	9.2	9.4
	ΔE_f	10.2	8.6	8.6	9.0	9.2	9.4
	ΔE_r	0	0	0	0	0	0
H ₂ CO _s +O _s →H ₂ COO _s	ΔH	13.2	11.7	11.7	12.0	12.2	12.4
	ΔE_f	13.2	11.7	11.7	12.0	12.2	12.4
	ΔE_r	0	0	0	0	0	0
H ₂ CO _s →HCO _s +H _s	ΔH	35.6	40.6	40.8	39.1	38.4	37.7
	ΔE_f	35.6	40.6	40.8	39.1	38.4	37.7
	ΔE_r	0	0	0	0	0	0
H ₂ CO _s +O _s →HCO _s +OH _s	ΔH	10.6	10.4	10.4	10.8	10.8	10.8
	ΔE_f	10.6	10.4	10.4	10.8	10.8	10.8
	ΔE_r	0	0	0	0	0	0
H ₂ COO _s →HCOO _s +H _s	ΔH	-37.0	-33.2	-33.0	-34.2	-34.7	-35.3
	ΔE_f	0	0	0	0	0	0
	ΔE_r	37.0	33.2	33.0	34.2	34.7	35.3
H ₂ COO _s +O _s →HCOO _s +OH _s	ΔH	-62.0	-63.4	-63.4	-62.5	-62.3	-62.2
	ΔE_f	0	0	0	0	0	0
	ΔE_r	62.0	63.4	63.4	62.5	62.3	62.2
HCOO _s +O _s →CO ₂ _s +H _s	ΔH	-16.2	-15.2	-15.2	-15.2	-15.4	-15.5
	ΔE_f	0	0	0	0	0	0

Table 5 (continued)

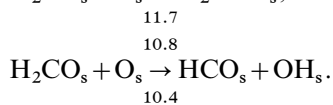
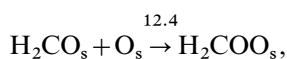
Reaction		Clean	X=O	X=S	X=Cl	X=Br	X=I
$\text{HCOOS} + \text{O}_s \rightarrow \text{CO}_2 + \text{OH}_s$	ΔE_r	16.2	16.2	15.2	15.2	15.4	15.5
	ΔH	-41.2	-45.4	-45.6	-43.5	-43.0	-42.4
	ΔE_r	0	0	0	0	0	0
$\text{HCOO}_s + \text{H}_s \rightarrow \text{HCOOH}_s$	ΔE_r	41.2	45.4	45.6	43.5	43.0	42.4
	ΔH	-19.2	-27.5	-27.8	-24.8	-23.7	-22.4
	ΔE_r	1.5	0	0	0	0	0
$\text{HCOO}_s + \text{OH}_s \rightarrow \text{HCOOH}_s + \text{O}_s$	ΔE_r	20.7	27.5	27.8	24.8	23.7	22.4
	ΔH	5.8	2.7	2.6	3.5	3.9	4.5
	ΔE_r	8.6	6.6	6.5	7.2	7.4	7.8
$\text{HCO}_s \rightarrow \text{CO}_s + \text{H}_s$	ΔE_r	2.8	3.9	3.9	3.7	3.5	3.3
	ΔH	-31.9	-27.2	-27.0	-28.6	-29.2	-29.8
	ΔE_r	0	0	0	0	0	0
$\text{HCO}_s + \text{O}_s \rightarrow \text{CO}_s + \text{OH}_s$	ΔE_r	31.9	27.2	27.0	28.6	29.2	29.8
	ΔH	-56.9	-57.4	-57.4	-56.9	-56.8	-56.7
	ΔE_r	0	0	0	0	0	0
$\text{HCO}_s + \text{O}_s \rightarrow \text{HCOO}_s$	ΔE_r	56.9	57.4	57.4	56.9	56.8	56.7
	ΔH	-59.4	-62.1	-62.1	-61.3	-60.9	-60.6
	ΔE_r	0	0	0	0	0	0
$\text{CO}_s + \text{OH}_s \rightarrow \text{CO}_2 + \text{H}_s$	ΔE_r	59.4	62.1	62.1	61.3	60.9	60.6
	ΔH	-18.7	-19.9	-19.9	-19.6	-19.5	-19.4
	ΔE_r	0	0	0	0	0	0
$\text{CO}_s + \text{O}_s \rightarrow \text{CO}_2$	ΔE_r	18.7	19.9	19.9	19.6	19.5	19.4
	ΔH	-43.7	-50.1	-50.3	-47.9	-47.1	-46.3
	ΔE_r	6.0	4.9	4.9	5.1	5.2	5.3
$\text{CO}_s \rightarrow \text{CO}_g$	ΔE_r	49.7	55.0	55.2	53.0	52.3	51.6
	ΔH	6.5	5.2	5.2	5.5	5.6	5.7
	ΔE_r	6.5	5.2	5.2	5.5	5.6	5.7
$\text{CO}_2 \rightarrow \text{CO}_2g$	ΔE_r	0	0	0	0	0	0
	ΔH	3.2	3.0	3.0	3.1	3.1	3.2
	ΔE_r	3.2	3.0	3.0	3.1	3.1	3.2
$\text{O}_2g \rightarrow \text{O}_2s$	ΔE_r	0	0	0	0	0	0
	ΔH	-9.5	-8.8	-8.7	-9.1	-9.2	-9.3
	ΔE_r	0	0	0	0	0	0
$\text{O}_2s \rightarrow 2\text{O}_s$	ΔE_r	9.5	8.8	8.7	9.1	9.2	9.3
	ΔH	-31.5	-21.6	-21.3	-25.3	-26.6	-28.1
	ΔE_r	4.3	7.9	8.0	6.5	6.0	5.5
	ΔE_r	35.8	29.5	29.3	31.8	32.7	33.6

^a ΔH is the reaction enthalpy difference, ΔE_r is the energy barrier of reaction, ΔE_r is the energy barrier of the reverse reaction.

drogenation of methanol:



oxidation of methanol:



(4) The promoting effect to inhibit the complete

Among the four aspects of the promoting effect

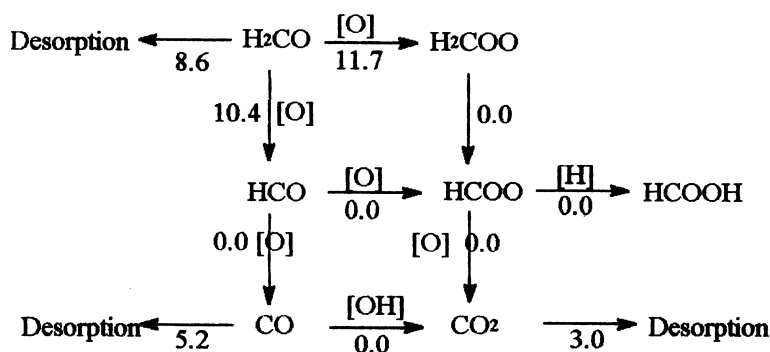


Fig. 4. Scheme of the desorption of formaldehyde and its complete oxidation.

of iodine to the silver catalyst, the first is the most important. The addition of iodine to the catalyst serves a dual effect. On the one hand, the iodine atom could be adsorbed on the silver surface [20] and occupy some surface sites, so that the concentration of surface atomic oxygen will be lowered and controlled. It reduces the complete oxidation of methanol. On the other hand, during the processing of the reaction, the surface atomic oxygen on the halogen modified silver surface could be replenished faster ($E_{a(\text{dissociation of O}_2)} = 5.5 \text{ kcal/mol}$) than that on the unmodified silver surface ($E_{a(\text{dissociation of O}_2)} = 7.9 \text{ kcal/mol}$). In this way, the concentration of surface atomic oxygen on the iodine modified surface could be more easily replenished. The former effect makes the iodine-modified silver surface bear higher selectivity, and the latter improves the activity of the catalyst. By the same analysis, it was found that Cl and Br have the similar promoting effect as iodine, while S has the contrary effect. The addition of S to the silver catalyst, therefore, contaminates the catalyst.

According to the BOC-MP formalism and the calculation details presented in Section 2, it is clear that the heat of atomic chemisorption (Q_A) is a principal factor to determine the property of the modifying atom. In this catalysis system, halogen atoms (Cl, Br, I) have the smaller heat of chemisorption than that of the oxygen atom, while the sulfur atom has the greater one. Although concrete conditions should be analyzed concretely, the discussions above indicate as follows. In a metal catalysis system, if a certain adsorbed atom is an

important factor relating to the catalytic activity and selectivity of the catalyst, a potential promoting atom should have a smaller heat of chemisorption than that of the adsorbed atom. In this way, the promoting atom could not only control the concentration of the adsorbed atom (not too high), but also promotes the replenishing of the adsorbed atom and maintains its concentration, to some extent, during the processing of the catalytic reaction.

4. Conclusion

The mechanism of partial oxidation of methanol to formaldehyde over a silver surface and the promoting effect of halogen to the catalysts have been successfully analyzed by the BOC-MP method. In summary, the results are as follows:

- (1) The heats of chemisorption of species on modified silver surfaces are less than those on a clean silver surface. The magnitude of these heats of chemisorption decrease in the order corresponding to the modifying (or pre-adsorbed) atoms of $\text{I} > \text{Br} > \text{Cl} > \text{O} > \text{S}$.
- (2) The oxidehydrogenation of methanol to formaldehyde is preferable to the direct dehydrogenation pathway.
- (3) The promoting effect of halogen to the catalyst could be explained as its dual effect, the modifying atom could not only control the concentration of surface atomic oxygen (not too high), but also promote the replenishing of surface atomic oxygen with the processing of

the reaction. Thus, it could increase both the catalytic activity and the selectivity to the formation of formaldehyde.

- (4) If a surface atom is important to both the catalytic activity and selectivity in a metal catalysis system, a potential promoting atom should have a smaller heat of atomic chemisorption on the catalysts surface than that of the surface atom.

The present work also confirmed that the simple BOC-MP model is a powerful and useful tool to investigate the catalytic reaction on the micro-level.

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