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Relationship between adsorption properties of Pt–Cu/SiO_2 catalysts and their catalytic performance for selective hydrodechlorination of 1,2-dichloroethane to ethylene

Lin Li[a], Xiaodong Wang[a,*], Aiqin Wang[a], Jianyi Shen[b], Tao Zhang[a,**]

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China*
[b] *Department of Chemistry, Nanjing University, Nanjing 210093, PR China*

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ABSTRACT

Microcalorimetric adsorption technique was employed to study the interaction of the reactants and product in the 1,2-dichloroethane hydrodechlorination over Pt/SiO_2, Cu/SiO_2 and Pt–Cu/SiO_2 catalysts in order to understand the high selectivity towards C_2H_4 on the Pt/SiO_2 catalyst modified by Cu. When the adsorption properties of the reactants and product on bimetallic catalysts were compared with those on monometallic counterparts, significant differences in the strength and number of adsorption sites concerning the reactants and product were evidenced. The adsorption properties of the bimetallic catalysts could be attributed to the change in Pt surface structure modified by Cu, studied by the microcalorimetry and FTIR of CO adsorption. Relating the adsorption properties with high ethylene selectivity on bimetallic catalysts, we inferred that high ethylene selectivity on bimetallic catalysts could be attributed to the moderate adsorption and activation of reactants and product. This work gave the direct evidence of high C_2H_4 selectivity in 1,2-dichloroethane hydrodechlorination reaction on the Pt–Cu/SiO_2 catalysts from the energetic point of view.

1. Introduction

There is an increasing demand for developing new routes to convert chlorocarbons of industrial byproducts into more useful or environmentally benign ones. Hydrodechlorination of chlorinated organics is a particularly attractive alternative compared with incineration of wastes from the chlorine industry from both the economical and environmental point of view [1]. A technologically relevant example is the hydrodechlorination of 1,2-dichloroethane over noble metal catalysts to produce ethane [2]. However, it is more desired to produce ethylene instead of ethane from 1,2-dichloroethane. To this end, bimetallic catalysts composed of metals from Groups VIII and IB show great potential [3–17]. Specifically, supported Pt–Cu bimetallic catalysts were reported to catalyze the hydrodechlorination of 1,2-dichloroethane to ethylene with the selectivity close to 100% when the Cu contents in Pt–Cu catalysts increased [5–7]. For example, a SiO_2 supported Cu catalyst exhibited hardly any conversion of 1,2-dichloroethane, while Pt/SiO_2 showed 82.8% C_2H_6 selectivity with no C_2H_4 selectivity and 17.2% C_2H_5Cl selectivity. With the increasing Cu/Pt ratios from 1:1 to 9:1 on PtCu/SiO_2 catalysts, the C_2H_6 selectivity decreased from 82.8 to 3.8%, while C_2H_4 selectivity increased from 0 to 96.2% [7].

It is well documented that the electronic and geometric modification of Group VIII metals by Group IB metals can bring significant changes in catalytic performance compared to those of the individual components. Several studies have been devoted to addressing the possible reasons for high ethylene selectivity on Pt–Cu bimetallic catalysts [5,7,18]. A very recent work about dendrimer-derived Pt–Cu/SiO_2 catalysts for hydrodechlorination of 1,2-dichloroethane showed that electronic modification of Pt by Cu hardly existed [18]. The papers by d'Itri and coworkers [5,7] demonstrated that there existed electronic modification in Pt–Cu/SiO_2 catalysts; however, it did not impact the catalyst's selectivity patterns. Most likely, the authors speculated that high ethylene selectivity resulted from a decreased energy of ethylene adsorption on the Pt–Cu catalysts. However, a direct experimental evidence is still missing.

The heat evolved when a reactive molecule contacts the surface of a catalyst is related to the energy of the bonds formed between the adsorbed species and the catalyst and hence to the nature of the bonds and to the chemical reactivity of the surface. For example, if a molecule adsorbs too strongly, the catalyst surface becomes covered with the species which prevents subsequent adsorption of other molecule. Similarly, if a molecule adsorbs too weakly, it does

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[*] Corresponding author at: State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, PR China. Tel.: +86 411 84379680; fax: +86 411 84685940.
[**] Corresponding author. Tel.: +86 411 84379015; fax: +86 411 84691570.
E-mail addresses: xdwang@dicp.ac.cn (X. Wang), taozhang@dicp.ac.cn (T. Zhang).

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not compete with other molecule and remain on the surface long enough for surface reaction to take place. Therefore, an intermediate chemisorption strength is necessary for high catalytic reactivity and selectivity.

The purpose of the present work is to study the adsorption and activation of reactants and product on mono- and bimetallic catalysts by employing microcalorimetry so as to elucidate the relationship between adsorption properties of Pt–Cu/SiO_2 catalysts and their catalytic performance for selective hydrodechlorination of 1,2-dichloroethane to ethylene. In addition, the microcalorimetry and FTIR of CO adsorption are conducted to characterize the surface structure of Pt/SiO_2 modified by Cu.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by impregnation method. The support is SiO_2 (BET: 400 m^2/g, 15–30 mesh). The precursor for preparing Pt/SiO_2 and Cu/SiO_2 is 5% acetic acid (AR) solution of $H_2PtCl_6\cdot 6H_2O$ (AR) and $CuCl_2$ (AR). The content of Pt in Pt/SiO_2 and Pt–Cu/SiO_2 catalysts is 3% and the atomic ratios of Pt to Cu in Pt–Cu/SiO_2 catalysts are fixed at 1:1 and 1:3, respectively. The content of Cu in Cu/SiO_2 is 5%. In a preparation, a required amount precursor was impregnated on the SiO_2 support. The impregnated samples were dried at room temperature for 12 h and at 393 K overnight. The dried samples were heated in O_2 at 573 K for 3 h.

2.2. Microcalorimetry

Microcalorimetric measurement was performed by using a BT2.15 heat-flux calorimeter (France, Seteram) at 313 K. Briefly, the calorimeter was connected to a gas-handling and a volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement ($\pm 0.5 \times 10^{-4}$ Torr). The maximum apparent leak rate of the volumetric system was 10^{-6} Torr/min in a system volume of approximately 80 cm^{-3}. The ultimate dynamic vacuum of the system was ca. 10^{-7} Torr.

The procedures for microcalorimetric adsorption have been described in detail elsewhere [19]. First, the sample was heated to 673 K in 4 h and held at this temperature for 4 h in a special treatment cell using a dynamic high pure H_2 (99.999%) atmosphere. After being reduced, the sample was evacuated for 2 h at 673 K, then transferred to a side-armed Pyrex and sealed in a Pyrex capsule. The capsule can minimize the possible contamination in the high vacuum system in the course of thermal equilibrium (6–8 h) with the calorimeter. After thermal equilibrium was reached, the capsule was broken by a vacuum feedthrough and 'fresh' catalyst was exposed. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of probe molecules onto the sample until it became saturated (5–6 Torr). Specially, liquid 1,2-dichloroethane (AR) was purified firstly by freeze/pump/thaw cycles with liquid nitrogen, and then the saturation steam of liquid 1,2-dichloroethane was introduced for microcalorimetric measurement. The differential heat versus adsorbate uptake plots and adsorption isotherms can be obtained simultaneously after a typical microcalorimetric experiment.

2.3. Infrared spectroscopy

Catalyst samples (~10 mg) were pressed into self-supporting wafers and loaded into a quartz IR cell equipped with CaF_2 windows, where they were reduced and evacuated using the same procedure as for microcalorimetric adsorption measurements. Next, the IR cell was placed in the chamber of the infrared spectrometer (Bruker EQUINOX 55) and connected to a high-vacuum and gas-handling system. After the desired vacuum was reached, the spectrum for the clean sample was collected. Then, some CO was dosed onto the wafers with 3 Torr CO in the gas phase. Subsequently, a spectrum of the sample plus adsorbate and gas phase CO was collected. The background of the catalysts and gas phase CO were subtracted to obtain the IR spectrum of adsorbed CO on the catalysts. Infrared spectra were collected in the absorbance mode with a resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Surface structural characterization of the catalysts

The surface properties of the catalysts are characterized by combining adsorption microcalorimetry and infrared spectroscopy of adsorbed CO. Fig. 1 shows the results of microcalorimetric measurements of CO adsorption on Pt/SiO_2, Cu/SiO_2 and Pt–Cu/SiO_2 catalysts. The initial heat of CO adsorption on Pt/SiO_2 is 136 kJ/mol, which is consistent with the value reported on other Pt/SiO_2 catalysts [20]. The differential heat versus CO uptake on Pt/SiO_2 remains almost constant at 130 kJ/mol up to 50 μmol/g and then decreases until a saturation uptake of ca. 70 μmol/g is reached. Much lower than those on Pt, the initial heat and saturation uptake of CO adsorption on Cu/SiO_2 are only 80 kJ/mol and 9 μmol/g. With the introduction of Cu to Pt/SiO_2, both the heat and CO uptake are greatly lowered. For example, the initial heat of CO adsorption on Pt–Cu(1:1)/SiO_2 is only 118 kJ/mol and it decreases slowly with the increase in uptake up to about 20 μmol/g. The differential heat of CO adsorption on Pt–Cu(1:3)/SiO_2 decreases quickly from the initial heat of 110 kJ/mol without any plateau and the saturation uptake is only 9 μmol/g. Apparently, the presence of Cu dramatically alters the CO adsorption properties of Pt catalyst.

Fig. 2 presents IR spectra for CO adsorption on the Pt/SiO_2, Cu/SiO_2 and Pt–Cu/SiO_2 catalysts at room temperature. The bands near 2055 and 1822 cm^{-1} for Pt/SiO_2 are linear and bridged adsorbed CO on Pt, respectively [21]. The initial heat for the linear and bridged adsorbed CO on Pt, were calculated to be 206 and 94 kJ/mol, respectively [22]. The measured initial heat (136 kJ/mol) on Pt/SiO_2 in Fig. 1 is lower than that for linear species and higher than that for bridged species, suggesting that the differential heat measured for CO adsorption on Pt/SiO_2 catalyst could be the average heat produced by the formation of both bridged and linear CO species on Pt sites. The adsorption of CO on the Cu/SiO_2 shows a major IR band at 2128 cm^{-1}, which can be assigned to linearly bonded CO on Cu [23]. With the addition of Cu to Pt/SiO_2, three

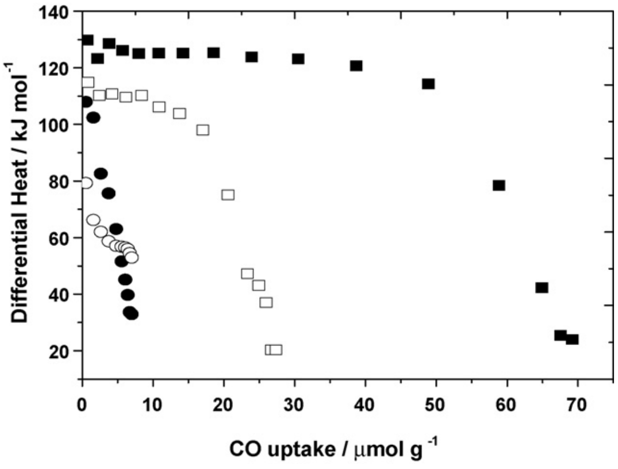

Fig. 1. Differential heat vs. adsorbate uptake for CO adsorption on 3% Pt/SiO_2 (■), Pt–Cu(1:1)/SiO_2 (□), Pt–Cu(1:3)/SiO_2 (●) and 5% Cu/SiO_2 (○) at room temperature.

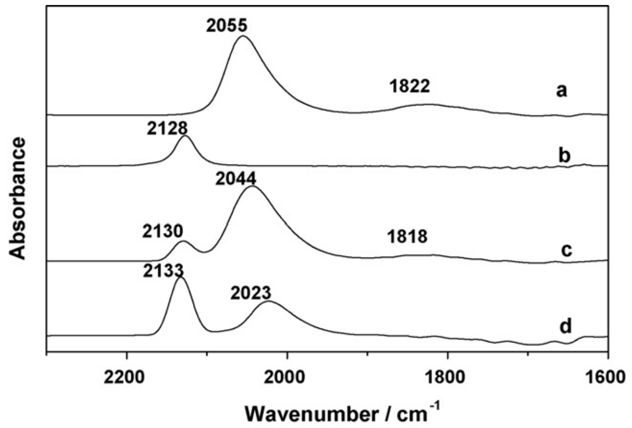

Fig. 2. Infrared spectra for CO adsorption on (a) 3% Pt/SiO_2, (b) 5% Cu/SiO_2, (c) Pt–Cu(1:1)/SiO_2 and (d) Pt–Cu(1:3)/SiO_2 with 3 Torr CO in the gas phase at room temperature.

bands at 1818, 2044 and 2130 cm^{-1} appear in the spectrum for the adsorption of CO on Pt–Cu(1:1)/SiO_2. The bands at 1818 and 2044 cm^{-1} can be assigned to linearly bonded and bridged-bonded CO on Pt, while the band at 2130 cm^{-1} is attributed to CO on Cu. This result indicates that some of Cu atoms are exposed on the surface of Pt–Cu(1:1)/SiO_2, decreasing the heat of CO adsorption on the catalyst because of lower adsorption heat of CO on Cu. With the further increase in Cu contents, the Pt sites on Pt–Cu(1:3)/SiO_2 for bridged adsorption disappear and the intensity ratio of linearly bonded CO on Cu and Pt increases greatly, indicating that the catalyst surface is mainly composed of Cu sites, and therefore the adsorption heat is close to that of CO on Cu/SiO_2. In addition, it is noteworthy that the intensity of the band of CO adsorbed on Cu sites in spectrum (d) for the Pt–Cu(1:3)/SiO_2 is greater than that in spectrum (b) for the Cu/SiO_2, demonstrating that the dispersion of Cu is enhanced by the presence of Pt in Pt–Cu(1:3)/SiO_2 catalyst.

3.2. The interaction of reactants and product with the catalysts

The general reaction mechanism for 1,2-dichloroethane hydrodechlorination catalyzed by metal catalysts could be expressed as follows [5,7,8,11,13–14,24]:

$$Cl–CH_2–CH_2–Cl + 3M \rightarrow 2M–Cl + M–C_2H_4 \quad (1)$$

$$2M–Cl + H_2 \rightarrow 2M + 2HCl \quad (2)$$

$$M–C_2H_4 \leftrightarrow M + C_2H_4 \quad (3)$$

$$M–C_2H_4 + H_2 \rightarrow M + C_2H_6 \quad (4)$$

M: metal active sites.

It is suggested that with the adsorption of 1,2-dichloroethane on catalyst, chlorine atoms were abstracted by the surface metal atoms with the formation of adsorbed chlorine, which then are removed as HCl by reacting with adsorbed hydrogen. The adsorbed ethylene either desorbs into the gas phase or reacts with adsorbed H atoms to form ethane.

3.2.1. Adsorption of 1,2-dichloroethane

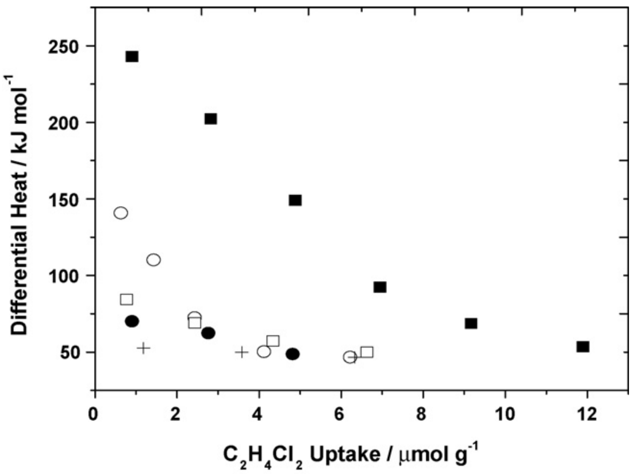

Fig. 3. Differential heat vs. adsorbate uptake for $C_2H_4Cl_2$ adsorption on 3% Pt/SiO_2 (■), Pt–Cu(1:1)/SiO_2 (□), Pt–Cu(1:3)/SiO_2 (●), 5% Cu/SiO_2 (○) and SiO_2 (+)at room temperature.

According to the reaction mechanism mentioned above and DFT results [25], the adsorption and activation of 1,2-dichloroethane mainly proceeded via the bond formation between Cl and metal. Thus, the adsorption of 1,2-dichloroethane under our experiment condition can give the information of the interaction of metal–Cl bond on different catalysts. The differential heat versus uptake for 1,2-dichloroethane adsorption on Pt/SiO_2, Cu/SiO_2 and Pt–Cu/SiO_2 catalysts and SiO_2 at room temperature are shown in Fig. 3. The initial heat of 1,2-dichloroethane adsorption on SiO_2 is about 53 kJ/mol, which could be attributed to the interaction of 1,2-dichloroethane with surface OH– groups on SiO_2 because a negative IR band at 3744 cm^{-1}, which can be assigned to OH– vibration of the surface silica appeared upon the introduction of 1,2-dichloroethane (not shown for the sake of brevity). Much higher than those on the support, the initial heat and saturation uptake for the adsorption of 1,2-dichloroethane on Pt/SiO_2 are 250 kJ/mol and 12 μmol/g, respectively, suggesting that a very strong interaction exists between Pt active sites and 1,2-dichloroethane. The initial heat and saturation uptake of 1,2-dichloroethane adsorption on Cu/SiO_2 are close to 150 kJ/mol and 6 μmol/g. The higher initial heat than that on the SiO_2 support implies that Cu–Cl bond is strong, in agreement with the report that Cl can remain adsorbed on Cu(1 1 0) even up to 750 K [26].

Interestingly, the initial heats of 1,2-dichloroethane adsorption on Pt–Cu/SiO_2 catalysts are only about 70 kJ/mol though both Pt/SiO_2 and Cu/SiO_2 exhibit much higher heats, suggesting that the addition of Cu to Pt/SiO_2 significantly decreased the strong interaction of 1,2-dichloroethane with bimetallic catalyst surface. The adsorption and activation of 1,2-dichloroethane on metal catalysts may be a structure sensitive or size-demanding elementary step [5,24]. Both the dilution of Pt by Cu and the dispersion of Cu by Pt can decrease the surface ensemble of Pt or Cu, which could affect the adsorption and activation of 1,2-dichloroethane, leading to the lower adsorption strength of 1,2-dichloroethane finally.

3.2.2. Adsorption of H_2

H_2 is important for removing chlorine from the catalyst surface via reduction in the reaction course of 1,2-dichloroethane hydrodechlorination [5–14,24]. Thus, it is worthwhile to study the adsorption and activation of H_2 on Pt/SiO_2, Cu/SiO_2 and Pt–Cu/SiO_2 catalysts. The microcalorimetric measurements of H_2 adsorption are shown in Fig. 4. The initial heat and saturation uptake of H_2 adsorption on the 3% Pt/SiO_2 catalyst are 88 kJ/mol and 45 μmol/g, while the corresponding values on the 5% Cu/SiO_2 is only 54 kJ/mol and 2 μmol/g. Much higher adsorption heat and uptake on Pt/SiO_2 than those on Cu/SiO_2 imply that H_2 can easily adsorb and activate on Pt surface. This result is in agreement with the report that H_2 can dissociate readily on Pt [27] while H_2 adsorption on Cu is an activated process [28]. It can be visualized that the introduction of Cu to Pt/SiO_2 changes the initial heat and saturation uptake of H_2 adsorption on Pt catalysts. The corresponding values are 81 kJ/mol and

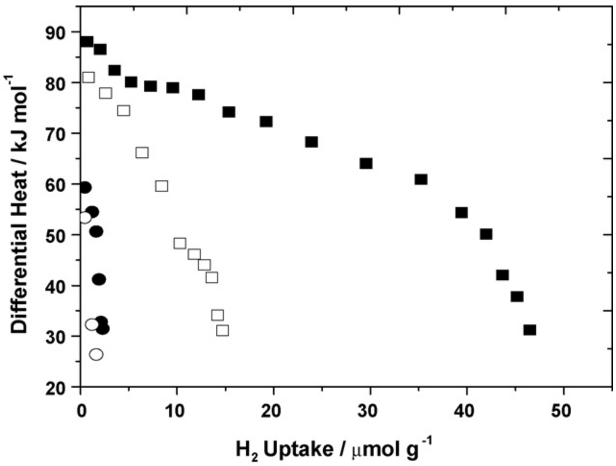

Fig. 4. Differential heat vs. adsorbate uptake for H_2 adsorption on 3% Pt/SiO_2 (■), Pt–Cu(1:1)/SiO_2 (□), Pt–Cu(1:3)/SiO_2 (●) and 5% Cu/SiO_2 (○) at room temperature.

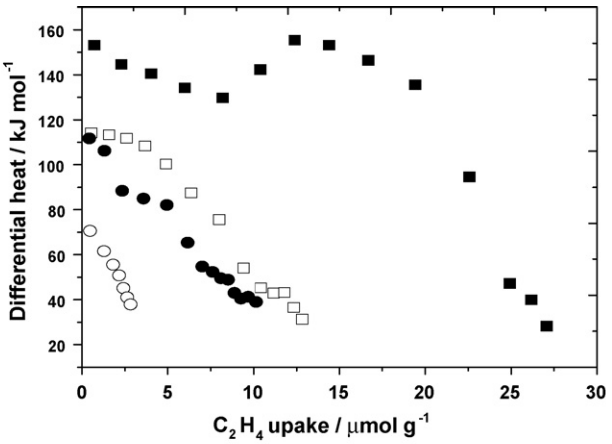

Fig. 5. Differential heat vs. adsorbate uptake for C_2H_4 adsorption on 3% Pt/SiO_2 (■), Pt–Cu(1:1)/SiO_2 (□), Pt–Cu(1:3)/SiO_2 (●) and 5% Cu/SiO_2 (○) at room temperature.

15 μmol/g for Pt–Cu(1:1)/SiO_2, and further decrease to 60 kJ/mol and 4 μmol/g when the Cu/Pt atomic ratio in Pt–Cu/SiO_2 catalyst reaches 3. These results indicate that the adsorption and activation of H_2 on Pt catalysts is suppressed significantly with the addition of Cu.

The adsorption of reactants on the surface of catalysts is the starting point of a heterogeneous catalysis process; therefore, plays a primary role in determining the chemical reactivity of the surface of catalyst. As for the Pt and Cu catalysts, the high adsorption heat of 1,2-dichloroethane implies that strength of M–Cl bond (M: Pt or Cu) are strong. Much higher adsorption heat and uptakes of H_2 adsorption on Pt than on Cu implies that H_2 can dissociate on the surface of Pt very easily. Therefore, though the adsorption strength of H_2 is lower than that of 1,2-dichloroethane on Pt catalyst, H_2 could readily dissociate on Pt to facilitate the removal of adsorbed Cl according to the reaction mechanism, while H_2 cannot compete with the strongly adsorbed Cl on Cu/SiO_2, leading to the poisoning of the active sites finally. The addition of Cu to Pt catalysts significantly suppresses the adsorption heat of 1,2-dichloroethane, implying that the strength of metal–Cl bond become weaker on Pt–Cu bimetallic catalysts. Importantly, the adsorption heats of H_2 is equivalent to that of 1,2-dichloroethane, suggesting that H_2 can competitively adsorb on the bimetallic catalysts to facilitate the removal of the adsorbed Cl, and enable the progress of the dechlorination reaction.

3.2.3. *Adsorption of C_2H_4*

Ethylene is one of the products of 1,2-dichloroethane hydrodechlorination reaction. The species formed upon the adsorption of ethylene could be similar to the intermediate of hydrodechlorination reaction. Therefore, it is necessary to obtain the information about the species and strength of ethylene adsorption on Pt/SiO_2, Cu/SiO_2 and Pt–Cu/SiO_2 catalysts. The microcalorimetric results are shown in Fig. 5. Ethylene adsorption on Pt/SiO_2 at room temperature produces an initial heat of 157 kJ/mol, which is in agreement with 160 kJ/mol on Pt powder [29] and 150 kJ/mol on Pt film [30]. The differential heat decreases to a value about 130 kJ/mol as the first 8 μmol/g of ethylene adsorb. At higher coverages, however, the differential heat apparently increases and then decreases at higher coverages until the surface becomes saturated with a total ethylene uptakes of 27 μmol/g. Vibrational spectroscopies have been used to identify the nature of surface species formed upon adsorption and/or reaction of hydrocarbon with supported metal catalysts [31,32]. It has been observed that ethylene adsorption on Pt catalyst above room temperature produced mainly ethylidyne species and dissociative H [31]. Therefore, the apparent maximum shown in the calorimetric plot of Pt/SiO_2 is caused by the evolution of gas ethane produced from the reaction of ethylene with surface hydrogen atoms that were formed at lower coverages from the dissociative adsorption of ethylene. This result implies that in hydrodechlorination reaction, the possible intermediate on Pt catalyst could exist mainly as ethylidyne, in favor of the formation of ethane (self-hydrogenation reaction). Ethylene adsorption on Cu/SiO_2 produces an initial heat of only 70 kJ/mol, which can be attributed to weak π species formed upon ethylene adsorption on Cu [31].

It is worthy to note that the plot of differential heat versus C_2H_4 uptake on the Pt–Cu/SiO_2 catalysts does not show the apparent maximum observed on Pt/SiO_2. Clearly, the addition of Cu suppresses completely the dissociative adsorption species of ethylene on Pt/SiO_2, indicating that the threefold Pt hollow sites [33,34] necessary for the formation of ethylidyne have been decreased significantly on Pt–Cu/SiO_2 catalysts, in agreement with the decreasing ensemble size of Pt surface sites on the bimetallic catalysts. Furthermore, ethylene adsorbs on Pt–Cu/SiO_2 catalysts with an initial heat of about 116 kJ/mol, in agreement with differential heats of 120–136 kJ/mol reported for the adsorption of molecular ethylene on Pt(1 1 0) [35]. These results indicate that in hydrodechlorination reaction, the possible intermediate on Pt–Cu/SiO_2 catalysts could exist as the nondissociative species of ethylene (di-σ or π), decreasing the self-hydrogenation reaction.

The comparison of the initial heats for ethylene adsorption indicates that the incorporation of Cu into Pt/SiO_2 catalysts leads to the decrease in initial heat of ethylene adsorption species from 157 kJ/mol for Pt/SiO_2 to about 116 kJ/mol for Pt–Cu/SiO_2 catalysts. DFT studies also showed that adsorption heat of ethylene on Pt–Cu bimetallic catalysts is lower than that on Pt catalyst [36]. Generally, the temperature (K) for desorption of adsorbed species is usually approximately equal to the four times of adsorption heat (kJ/mol) [37,38]. Thus, at the reaction temperature (473 K) of 1,2-dichloroethane hydrodechlorination [5–7,17], the corresponding temperatures for desorption of the possible intermediate calculated approximately from the initial heat of ethylene adsorption were about 628 K on Pt/SiO_2 and 464 K on Pt–Cu/SiO_2 catalysts, respectively, suggesting that the ethylene adsorption species can adsorb on Pt/SiO_2 catalyst irreversibly while it adsorbs reversibly on Pt–Cu/SiO_2 catalysts. Therefore, in hydrodechlorination reaction, the possible intermediate on Pt–Cu/SiO_2 catalysts could desorb into gas phase as ethylene more easily than hydrogenate to form ethane.

4. Conclusions

The introduction of Cu to Pt/SiO_2 changed the adsorption heat of CO and the adsorption state of CO as evidenced by the techniques of microcalorimetric adsorption and FTIR, suggesting that the addition of Cu to Pt/SiO_2 decreased the ensemble size of surface Pt sites.

The adsorption strengths of 1,2-dichloroethane and H_2 on Pt/SiO_2 catalyst decreased with the introduction of Cu, suggesting that Cu played an important role in moderating adsorption and activation ability for reactants and enabling the progress of the dechlorination reaction. Microcalorimetry of ethylene adsorption indicated that nondissociative species of ethylene could be the intermediate on $Pt–Cu/SiO_2$ catalysts in the hydrodechlorination procedure. Moreover, the introduction of Cu to Pt/SiO_2 catalyst lowered the bonding strength of adsorbed ethylene, causing reversible adsorption of ethylene on $Pt–Cu/SiO_2$ at reaction temperature. Therefore, the adsorbed ethylene could be easily desorbed as ethylene in the dechlorination reaction.

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