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STUDY ON CHEMISORPTION OF H_2, O_2, CO AND C_2H_4 ON Pt-Ag/SiO_2 CATALYSTS BY MICROCALORIMETRY AND FTIR

L. Li[1,2]*, X. Wang*[1]*, J. Shen*[3]*, L. Zhou*[1] *and T. Zhang*[1,2*]

[1]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
[2]Graduate School of Chinese Academy of Sciences, Beijing 100039, China
[3]Department of Chemistry, Nanjing University, Nanjing 210093, China

Adsorption microcalorimetry has been employed to study the interaction of ethylene with the reduced and oxidized Pt-Ag/SiO_2 catalysts with different Ag contents to elucidate the modified effect of Ag towards the hydrocarbon processing on platinum catalysts. In addition, microcalorimetric adsorption of H_2, O_2, CO and FTIR of CO adsorption were conducted to investigate the influence of Ag on the surface structure of Pt catalyst. It is found from the microcalorimetric results of H_2 and O_2 adsorption that the addition of Ag to Pt/SiO_2 leads to the enrichment of Ag on the catalyst surface which decreases the size of Pt surface ensembles of Pt-Ag/SiO_2 catalysts. The microcalorimetry and FTIR of CO adsorption indicates that there still exist sites for linear and bridged CO adsorption on the surface of platinum catalysts simultaneously although Ag was incorporated into Pt/SiO_2. The ethylene microcalorimetric results show that the decrease of ensemble size of Pt surface sites suppresses the formation of dissociative species (ethylidyne) upon the chemisorption of C_2H_4 on Pt-Ag/SiO_2. The differential heat *vs.* uptake plots for C_2H_4 adsorption on the oxygen-preadsorbed Pt/SiO_2 and Pt-Ag/SiO_2 catalysts suggest that the incorporation of Ag to Pt/SiO_2 could decrease the ability for the oxidation of C_2H_4.

Keywords: *chemisorption, differential heat, microcalorimetry, Pt-Ag/SiO_2*

Introduction

Platinum catalysts have been widely used in the chemical and petrochemical industries for hydrocarbon processing reactions such as hydrogenation, dehydrogenation, oxidation, isomerization, aromatization and hydrogenolysis [1, 2]. Compared to catalysts containing only Pt, the formation of alloys or bimetallic clusters can dramatically improve selectivity and stability of many reactions for hydrocarbon conversion [3, 4]. IB group metals often serve as inert or less active components to modify the catalytic behavior of Pt. This modification often causes the change in the surface structure of Pt catalyst, thereby changing the adsorption energies of hydrocarbon on Pt catalyst, which is an important parameter related to the activity and selectivity of Pt catalyst for hydrocarbon conversion reaction [5]. Microcalorimetry is an effective method to study this interaction between hydrocarbon and catalyst surface from the energetic point of view [6].

Ag has been extensively used to catalyze the oxidation of ethylene [7]. However, few of papers has been found to investigate the modification effect of Ag towards the surface structure of Pt and the corresponding chemisorption change of hydrocarbon on the Pt-Ag/SiO_2 catalyst up to now.

In the present paper, ethylene was used as probe molecule and microcalorimetry was employed to study the adsorption and activation of ethylene on reduced and oxidized Pt-Ag/SiO_2 catalyst. This could be essential in constructing general reaction mechanism for the reactions involving the adsorption of olefins. In addition, the microcalorimetric adsorption of H_2, O_2, CO and FTIR of CO adsorption on Pt/SiO_2 and Pt-Ag/SiO_2 were conducted to investigate the effect of Ag on the surface structure of Pt catalyst.

Experimental

Catalyst preparation

The catalysts were prepared by the incipient wetness impregnation method [8]. The SiO_2 support (400 $m^2\ g^{-1}$, 15–30 mesh) was provided by Qingdao Ocean Chemical Company. The precursors used for preparing Pt/SiO_2 and Ag/SiO_2 were 5% acetic acid (AR) solution of the $H_2PtCl_6 \cdot 6H_2O$ (AR) and $AgNO_3$ (AR). The Pt-Ag/SiO_2 catalysts were prepared by impregnating the required amount of acetic acid (AR) solution of the $H_2PtCl_6 \cdot 2H_2O$ (AR) and $AgNO_3$ (AR) successively. The impregnated sample was dried at room temperature for 12 h and further dried at 393 K overnight. Finally, the dried sample was heated in O_2 at 573 K for 3 h. The loading of Pt in Pt/SiO_2 and Pt-Ag/SiO_2 catalysts was 3% and the atomic ratios of Pt and Ag were 1:1 and 1:3 in Pt-Ag/SiO_2 catalysts. The loading of Ag in Ag/SiO_2 was 5%.

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* Author for correspondence: taozhang@dicp.ac.cn

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Microcalorimetry

Microcalorimetric measurement was performed by using a BT2.15 heat-flux calorimeter. Briefly, the calorimeter was connected to a gas handling and a volumetric system employing MKS Baratron Capacitance Manometers for precision pressure measurement ($\pm0.5\times10^{-4}$ Torr). The maximum apparent leak rate of the volumetric system was 10^{-6} Torr min^{-1} 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 [9]. Briefly, 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 could minimize the possible contamination in the high vacuum system during the 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). The differential heat *vs.* adsorbate uptake plots and adsorption isothermals could be obtained simultaneously after a typical microcalorimetric experiment.

Infrared Spectroscopy

Catalyst samples 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 measurement. Next, the IR cell was placed in the chamber of the infrared spectrometer (Bruck 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. Next, an amount of CO was dosed onto the wafer with 3 Torr CO in the gas phase. Subsequently, a spectrum of the sample plus adsorbate and gas phase CO was collected. The spectrum minus the IR spectra of sample and gas phase CO to obtain spectrum of adsorbate. Infrared spectra were collected in the absorbance mode with a resolution of 2 cm^{-1}.

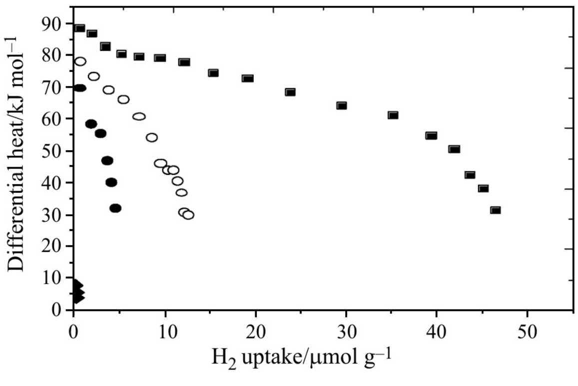

Fig. 1 Differential heat *vs.* adsorbate uptake for H_2 adsorption at room temperature on ■ – 3% Pt/SiO_2, ○ – Pt-Ag(1:1)/SiO_2, ● – Pt-Ag(1:3)/SiO_2 , ◆ – 5% Ag/SiO_2

Results and discussion

Figure 1 shows the differential heat *vs.* uptake plots for the adsorption of H_2 on Pt/SiO_2 and Pt-Ag/SiO_2 (the adsorption of H_2, CO, O_2 and C_2H_4 on SiO_2 can be negligible). The initial heat of H_2 adsorption on 3% Pt/SiO_2 catalyst is 88 kJ mol^{-1}, which is consistent with the value of 90 kJ mol^{-1} reported for Pt powder [10]. The differential heat of H_2 adsorption on Pt/SiO_2 decreases with increasing H_2 uptake due probably to adsorption on weaker sites and/or possible lateral interaction between adsorption species. The Pt dispersion is 61%, which is calculated from the H_2 chemisorption amount with the differential heat greater than 40 kJ mol^{-1} on Pt/SiO_2. The average diameter of Pt particles, calculated by H_2 dispersion [11], is about 1.78 nm. It indicates that Pt is well dispersed on the SiO_2 support. It can be seen from Fig. 1 that the adsorption of H_2 on Ag/SiO_2 can be negligible in our experiment condition. The initial heats of H_2 adsorption on Pt-Ag(1:1)/SiO_2 and Pt-Ag(1:3)/SiO_2 are 78 and 70 kJ mol^{-1}, which are lower than that on Pt/SiO_2, suggesting that the addition of Ag to Pt/SiO_2 reduces the strong adsorption sites of H_2 on Pt/SiO_2 catalyst. In addition, the H_2 saturation uptakes on Pt-Ag(1:1)/SiO_2 and Pt-Ag(1:3)/SiO_2 are lowered to 12 and 4.5 μmol g^{-1}, respectively, which indicates the addition of Ag to Pt/SiO_2 suppresses the dissociative adsorption of H_2 on Pt/SiO_2.

There exists the miscibility gap in solid solution of Pt and Ag [5]. Furthermore, the heat of sublimation for Ag is lower than that for Pt. Therefore, Ag could segregate to the surface of bimetallic catalyst in the course of preparation [12]. Monte Carlo simulation of supported Pt-Ag catalyst [13] has demonstrated that Ag segregates to the surface of the supported Pt-Ag catalyst and tends to occupy the lowest coordinated sites, which leads to the decrease of ensemble size of Pt surface sites on Pt-Ag/SiO_2 catalysts. The decrease in ensemble size of Pt surface sites means that not only the threefold Pt hollow sites which are the most stable sites for hydrogen adsorption, but also the sites for H_2 adsorbing dissociatively could be decreased. This is the possible reason why the addition of Ag causes the decrease in the initial heat and saturation uptake of H_2 adsorption on Pt/SiO_2.

The differential heat *vs.* uptake plots for O_2 adsorption on Pt/SiO_2, Ag/SiO_2 and Pt-Ag/SiO_2 catalysts are shown in Fig. 2. The initial heat of O_2 adsorption on Pt/SiO_2 is as high as 350 kJ mol^{-1} and the differential heat remains almost constant at 330 kJ mol^{-1} with the increase in O_2 uptake up to almost 25 μmol g^{-1}. The adsorption plateau of differential heat *vs.* O_2 uptake is probably due to the very high adsorption strength between Pt and O, which restricts the surface mobility of O on Pt/SiO_2. As a result, the measured differential heat of O_2 adsorption on Pt/SiO_2 is the random mean value [6] of each dose. In spite of the absence of H_2 adsorption on the reduced Ag/SiO_2, O_2 adsorption on Ag/SiO_2 produces the initial heat of 285 kJ mol^{-1} and uptake of 6 μmol g^{-1}. Furthermore, it is found that the differential heat and saturation uptake of O_2 adsorption on Pt-Ag/SiO_2 catalysts are higher than those on Ag/SiO_2 and lower than those on Pt/SiO_2, suggesting that O_2 could adsorb on Pt and Ag sites on the surface of Pt-Ag/SiO_2 catalysts simultaneously.

The O/H ratios can be calculated from the ratio of O_2 and H_2 saturation uptakes shown in Figs 1 and 2. The O/H ratio of Pt/SiO_2 is 0.8 while O/H ratios of Pt-Ag(1:1)/SiO_2 and Pt-Ag(1:3)/SiO_2 reach 1.8 and 3.5, respectively. It can be seen that the O/H ratio increases with the Ag contents in Pt-Ag/SiO_2 catalysts. This is clearly indicative of the enrichment of Ag on the surface of Pt-Ag/SiO_2 catalysts.

Figure 3 shows the results of microcalorimetric measurement of CO adsorption on Pt/SiO_2 and Pt-Ag/SiO_2 catalysts. CO adsorption on Pt/SiO_2 produces an initial heat of 136 kJ mol^{-1}, which is in agreement with the reported value of 142 kJ mol^{-1} for other Pt/SiO_2 catalyst [14], and a differential heat plateau *vs.* CO uptake up to almost 50 μmol g^{-1}. In our experiment, the adsorption of CO on Ag/SiO_2 is hardly detected. As compared with H_2 adsorption on Pt-Ag/SiO_2, the adsorption of CO on Pt-Ag/SiO_2 catalysts exhibits greatly different behavior. An initial heat produced upon the adsorption of CO on Pt-Ag/SiO_2 is close to that on Pt/SiO_2, while the initial heat of H_2 adsorption on Pt-Ag/SiO_2 is lower than that on Pt/SiO_2. In addition, the differential heat of CO adsorption *vs.* uptake on Pt-Ag/SiO_2 exhibits a plateau as compared to the gradual decrease of differential heat of H_2 adsorption on Pt-Ag/SiO_2 with increasing H_2 uptake. This behavior of CO adsorption on Pt-Ag/SiO_2 will be discussed below according to the results of FTIR.

Figure 4 presents IR spectra for CO adsorption on the Pt/SiO_2 and Pt-Ag/SiO_2 catalysts at room temperature. The bands near 2055 and 1822 cm^{-1} in curve A are

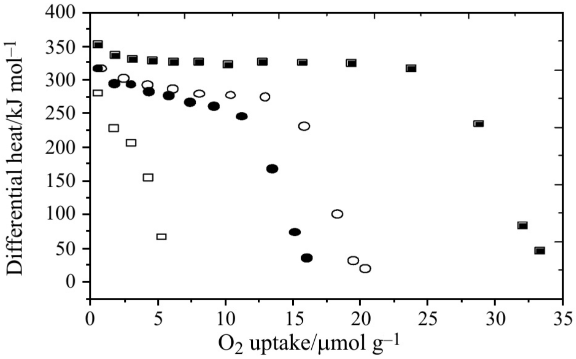

Fig. 2 Differential heat *vs.* adsorbate uptake for O_2 adsorption at room temperature on ■ – 3% Pt/SiO_2, ○ – Pt-Ag(1:1)/SiO_2, ● – Pt-Ag(1:3)/SiO_2 , □ – 5% Ag/SiO_2

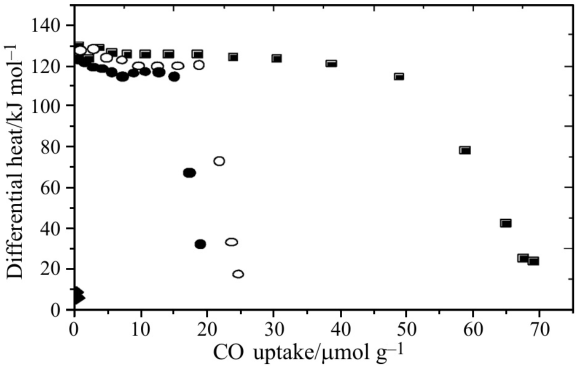

Fig. 3 Differential heat *vs.* adsorbate uptake for CO adsorption at room temperature on ■ – 3% Pt/SiO_2, ○ – Pt-Ag(1:1)/SiO_2, ● – Pt-Ag(1:3)/SiO_2 , ◆ – 5% Ag/SiO_2

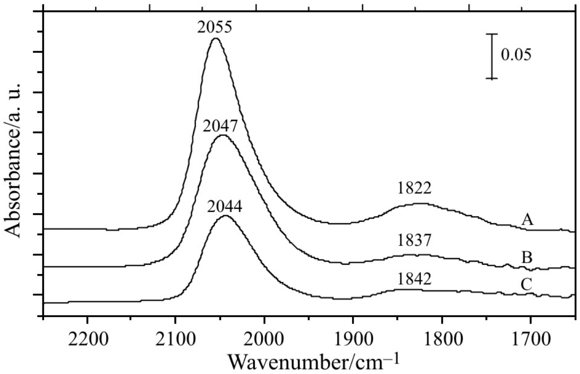

Fig. 4 Infrared spectra for CO adsorption at room temperature on A – 3% Pt/SiO_2, B – Pt-Ag(1:1)/SiO_2, C –Pt-Ag(1:3)/SiO_2

from CO molecular adsorption on linear and bridged sites of Pt atoms [15]. The initial adsorption heat for the linear and bridged species of CO on supported Pt catalyst, were calculated by the AEIR method [16], are 206 and 94 kJ mol^{-1}, respectively. The measured initial heat (136 kJ mol^{-1}) of CO adsorption on Pt/SiO_2 in Fig. 3 is lower than that for linear species and higher than that for bridged species, suggesting that the differential heat for CO adsorption on the Pt/SiO_2 catalyst could be the average heat produced by the formation of both bridged and linear CO species on Pt sites. This average adsorption heat leads to the differential heat remaining constant up to 50 μmol g^{-1} for CO adsorption on Pt/SiO_2 (Fig. 3). Curve B and C in Fig. 4 show the bridged and linear species of CO adsorption on Pt sites also simultaneously exist on $Pt\text{-}Ag/SiO_2$ catalysts though the band intensity decreases, indicating that the average adsorption heat also appears during the process of CO adsorption on $Pt\text{-}Ag/SiO_2$ catalysts. Therefore, the similar initial heat of CO adsorption on $Pt\text{-}Ag/SiO_2$ as that on Pt/SiO_2, and the adsorption heat plateau *vs.* CO uptake on $Pt\text{-}Ag/SiO_2$ can be attributed to the average heat produced for the adsorption of CO on linear and bridged sites of Pt atoms on the $Pt\text{-}Ag/SiO_2$ surface. The microcalorimetry and FTIR of CO adsorption indicate that there still exist linear and bridged active sites of CO adsorption on the surface of Pt catalysts simultaneously although Ag was incorporated into Pt/SiO_2.

The formation and transformation of carbon-carbon double bond are often involved in the hydrocarbon processing reaction and the corresponding surface species may be similar to those formed upon the adsorption of ethylene on the catalysts. So ethylene is often used as probe molecule to study the interaction between hydrocarbon and catalyst. Figure 5 shows the results of microcalorimetric measurement of ethylene adsorption on Pt/SiO_2 and $Pt\text{-}Ag/SiO_2$ catalysts at room temperature. Ethylene adsorption on Pt/SiO_2 at room temperature produces an initial heat of 157 kJ mol^{-1}, which is agreement with 160 kJ mol^{-1} on Pt powder [10] and 150 kJ mol^{-1} on Pt film [17]. An apparent maximum appears in the plots of differential heat *vs.* uptake on Pt/SiO_2. Vibrational spectroscopies have been used to identify the nature of surface species formed upon adsorption and/or reaction of hydrocarbon with supported metal catalysts [18, 19]. It has been observed that ethylene adsorption on Pt catalyst at room temperature produced mainly ethylidyne species and dissociative H [20]. So the apparent maximum in the plot can be caused by the evolution of gas ethane produced from the reaction of ethylene with surface hydrogen atoms [10], as shown in following equations:

$$C_2H_4+2Pt \rightarrow Pt{\equiv}CCH_3+Pt{-}H$$

$$2Pt{-}H+C_2H_4 \rightarrow C_2H_6\uparrow+2Pt$$

In our experiment, the adsorption of ethylene on reduced Ag/SiO_2 can also be negligible. It can be seen from Fig. 5 that the initial heat of ethylene adsorption on Pt/SiO_2 is lowered with the addition of Ag to Pt/SiO_2 and the apparent maximum is suppressed in the plot of differential heat *vs.* uptake. This is indicative of the decrease of ethylidyne adsorption species on the $Pt\text{-}Ag/SiO_2$ catalysts. Generally, the formation of ethylidyne species requires a 3-fold site composed of adjacent metal Pt atoms [21]. Therefore, it implies that the addition of Ag to Pt/SiO_2 decreases the 3-fold Pt hollow sites on the catalyst surface, and Ag plays an important role in decreasing the size of Pt surface ensembles. The literature [4] reports that hydrogenolysis, isomerization and coking reactions proceed on large ensembles of surface Pt sites while only small ensembles of surface Pt sites are necessary for dehydrogenation reaction. Therefore, the ethylene microcalorimetric results indicate that the addition of Ag to Pt/SiO_2 could be a useful way to adjust the selectivity and stability of Pt/SiO_2 for the hydrocarbon conversion reaction.

Oxygen is necessary for catalyzing ethylene to ethylene oxide [7]. So it is worthwhile to study the interaction between ethylene and the oxygen species on the surface of catalyst. In this paper, the microcalorimetric experiment for ethylene adsorption on oxygen-preadsorbed Pt/SiO_2, Ag/SiO_2 and $Pt\text{-}Ag/SiO_2$ catalysts are conducted and the results are shown in Fig. 6. It can be noted that ethylene adsorption on oxygen-preadsorbed Pt/SiO_2 catalyst produces a very high initial heat of 440 kJ mol^{-1}, suggesting serious oxidation of C_2H_4 on oxidized Pt/SiO_2 at room tem-

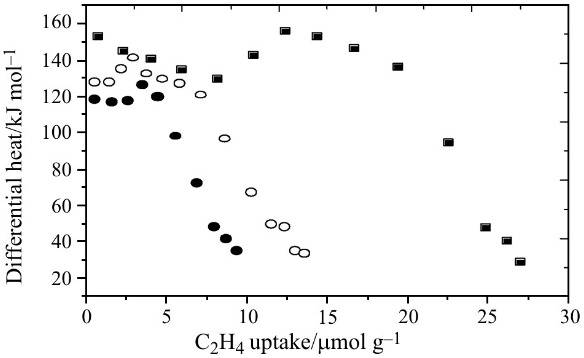

Fig. 5 Differential heat *vs.* adsorbate uptake for C_2H_4 adsorption at room temperature on ■ – 3% Pt/SiO_2, ○ – $Pt\text{-}Ag(1:1)/SiO_2$, ● – $Pt\text{-}Ag(1:3)/SiO_2$

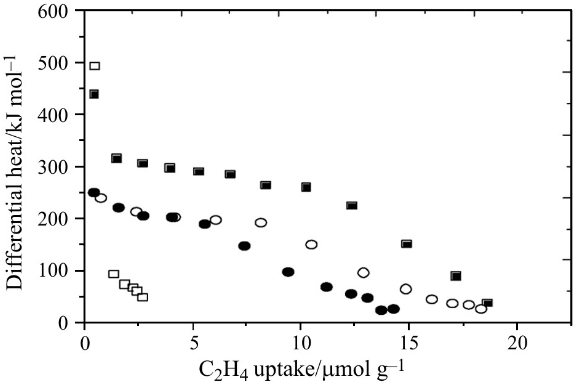

Fig. 6 Differential heat *vs.* adsorbate uptake for C_2H_4 adsorption at room temperature on oxygen-preadsorbed ■ – 3% Pt/SiO_2, ○ – $Pt\text{-}Ag(1:1)/SiO_2$, ● – $Pt\text{-}Ag(1:3)/SiO_2$, □ – 5% Ag/SiO_2

perature. Interestingly, ethylene adsorption on oxygen-preadsorbed Ag/SiO_2 catalyst produces an even higher initial heat of 490 kJ mol^{-1}, and the differential heat of adsorption drops quickly to about 100 kJ mol^{-1} with increasing C_2H_4 uptake, which indicates that ethylene could mainly adsorb on oxidized Ag/SiO_2 catalyst molecularly and only a small fraction is seriously oxidized. It is noteworthy that the initial heats of ethylene adsorption on oxygen-preadsorbed Pt-Ag/SiO_2 catalysts are about 250 kJ mol^{-1}, which is much lower than that on Pt/SiO_2 and Ag/SiO_2 with preadsorption oxygen, suggesting that the too high oxidation ability of Pt/SiO_2 catalyst is significantly lowered by the presence of Ag. The microcalorimetric results of ethylene adsorption on pre-oxidized catalysts also indicate that the incorporation of Ag into the Pt/SiO_2 catalysts can decrease the serious oxidation of olefins.

Conclusions

The differential heats *vs.* H_2 uptake on Pt/SiO_2 and Pt-Ag/SiO_2 show that the dramatic decrease in initial heat and saturation uptake for H_2 adsorption on Pt-Ag/SiO_2 catalysts is due to the decrease in ensemble size of Pt surface sites with the addition of Ag into Pt/SiO_2. Comparison of the chemisorption of O_2 and H_2 on Pt-Ag/SiO_2 catalysts with different Ag contents elucidates the enrichment of Ag on the bimetallic catalysts surface. A similar initial heat and adsorption plateau produced with the adsorption of CO on Pt/SiO_2 and Pt-Ag/SiO_2 indicate that coexistence of linear and bridged active sites of Pt for CO adsorption on Pt-Ag/SiO_2 catalysts. The chemisorption of C_2H_4 on Pt catalysts shows the incorporation of Ag into Pt/SiO_2 suppresses the dissociative adsorption species of ethylene, which can be beneficial to the selectivity and stability of Pt catalysts in hydrocarbon conversion reaction. Correspondingly, C_2H_4 adsorption on oxygen-preadsorbed catalysts clearly shows that the serious oxidation activity of hydrocarbon on Pt/SiO_2 is suppressed by the presence of Ag.

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