УДК 546

Hydrogen-Assisted 1,2-Dichloroethane Dechlorination Catalyzed by Pt-Cu/SiO$_2$: Insights into the Nature of Ethylene-Selective Active Sites

**Dmitry V. Kazachkin, David R. Luebke,
Vladimir I. Kovalchuk* and Julie L. d'Itri**
*Department of Chemical Engineering, University of Pittsburgh,
Pittsburgh, Pennsylvania 15261 [1]*

Differently pretreated silica-supported Pt, Cu, and Pt-Cu catalysts with Cu to Pt atomic ratio of 1 to 6 have been investigated by a combination of reaction kinetics and FTIR spectroscopic studies in order to understand the factors that control the selectivity toward ethylene and ethane in the CH$_2$ClCH$_2$Cl+H$_2$ reaction. Carbon monoxide adsorption was used to probe the electronic modification of Pt and Cu as well as the nature of ethylene-selective active sites. It was shown that there is a very limited, if any, electronic interaction between Pt and Cu in the bimetallic catalysts reduced at 493 K. However, the Pt-Cu catalysts, for which no dipole-dipole coupling shift was observed in the IR spectra of adsorbed CO suggesting extremely small Pt ensembles on the catalyst surface, demonstrated high ethylene selectivity in the 1,2-dichloroethane dechlorination. Electronic interactions between Pt and Cu have been discovered for the Pt-Cu/SiO$_2$ catalysts reduced at 773 K. The interactions manifested themselves by a higher stability of Cu^0-CO adsorption complexes in vacuum and by an increase in intensity of the Pt-CO band in the FTIR spectra upon evacuation of CO from the gas phase suggesting the formation of Pt-Cu solid solutions. The higher temperature reduction resulted in the dipole-dipole coupling shift of 6 to 19 cm^{-1} in the FTIR spectra of adsorbed CO. The initial ethylene selectivity of the catalysts was inversely proportional to the dipole-dipole coupling shift. The observations are consistent with the idea that the nature of the Pt-Cu species, viz., alloy particles as opposed to Cu/Pt overlayers, does not control the reaction selectivity, which is a function of the Pt ensemble size on the surface of Pt-Cu moieties.

Keywords: hydrogen-assisted dechlorination, 1,2-dichlorothane, ethylene, Pt-Cu catalysts, infrared spectroscopy, singleton frequency, dipole-dipole coupling.

Introduction

It has been discovered a decade ago that a combination of Pt or Pd with another metal deposited on a solid support catalyzes hydrodechlorination of vicinal dichloroalkanes such as 1,2-dichloroethane and 1,2-dichloropropane toward the formation of the corresponding alkene, viz., ethylene or propylene [1-3]. Such a chemistry looks surprising because any catalyst that activates H$_2$ should also hydrogenate the product olefin. As chloroalkanes are common environmental pollutants and alkenes

---

have a greater commodity value than alkanes, this chemistry has drawn a continuous interest of researchers [4-17]. It is referred in literature as to hydrogen-assisted dechlorination as opposed to classic hydrodechlorination when alkane and HCl form from 1,2-dichloroalkane and H_2 [18].

Among different noble and non-noble metal combinations, the Pt-Cu system has been studied the most thoroughly [1, 2, 4, 11, 12, 15, 17]. The main question addressed in these publications was about the role of Pt and Cu in the conversion of 1,2-dichloroethane. Based on the experimental evidence, it was concluded that even though the electronic state of Pt and Cu in the supported bimetallic catalysts is modified as compared to the corresponding monometallic catalysts this modification is not a key factor in controlling the catalyst selectivity toward ethylene [4, 12]. Instead, the kinetics performance depends on the size of Pt ensembles in the Cu matrix. The catalysts with relatively large Pt ensembles that exhibited a dipole-dipole coupling shift in the spectra of adsorbed CO catalyzed the $CH_2ClCH_2Cl+H_2$ reaction toward ethane, whereas the catalysts that did not show dipole-dipole coupling shift in the spectra of adsorbed CO were highly selective toward ethylene. Nevertheless, some aspects of this chemistry still remain undisclosed.

It has been assumed *a priori* that the reduction of supported Pt-Cu catalysts at the temperature as low as 493 K results in the formation of alloy Pt-Cu particles on the support surface [2,4,11,12]. Initially, the concentration of Cu in the alloy Pt-Cu particles was suggested to be low because of the chromatographic separation of the Pt and Cu precursors on the support surface during catalyst preparation and, as a consequence, the ethylene selectivity was low [11]. As the reaction proceeded, additional amounts of Cu alloyed with Pt because of the high mobility of the chloride Cu precursors over the support surface [19] resulting in a continuous increase in the ethylene selectivity

[2,11,12]. However, the suggestion that Pt-Cu solid solutions form during the few hour reduction by H_2 at 493 K is dubious. It has been shown that for a Cu monolayer on the Pt(111) surface there is an energy barrier of ~ 110 kJ mol^{-1} for the interlayer mixing and the noticeable diffusion of Cu adatoms into Pt was observed at the temperatures above 550 K [20-23]. Thus, only Cu overlayers on the surface of Pt particles would form during the few hour catalyst reduction at 493 K. If this is the case, the transient behavior of supported Pt-Cu catalysts in terms of the ethylene selectivity could be explained by the continuous conversion of Cu overlayers to Pt-Cu solid solutions assuming that the latter moieties are ethylene selective in the $CH_2ClCH_2Cl+H_2$ reaction, whereas the former ones are not.

The objectives of the present investigation were to compare the catalytic performance of Cu/Pt overlayer moieties in the $CH_2ClCH_2Cl+H_2$ reaction to that of Pt-Cu solid solutions in the effort to elucidate the factors that control the reaction selectivity. It was assumed that the reduction of Pt-Cu/SiO_2 catalysts at 493 K favors the formation of Cu overlayers on the surface of Pt particles, while the reduction at 773 K ensures the formation of Pt-Cu alloy moieties on the silica surface. The nature of the active sites was probed by the infrared spectroscopy of adsorbed CO. Earlier research has shown that a strong intensity redistribution occurs between the bands of CO adsorbed on adjacent sites of a different nature when the difference between vibrational frequencies of the two types of oscillators is relatively small [24,25]. In application to infrared spectra of CO adsorbed on Pt-Cu catalysts, the redistribution phenomenon results in a suppression in the integral intensity of the Pt-CO band and in an enhancement in that of the Cu-CO one if Cu and Pt sites are located in close vicinity to each other. Thus, removing CO adsorbed on Cu by evacuation should result in an increase in

the integral intensity of the Pt-CO band if Pt and Cu form a solid solution.

The information regarding the geometric and electronic properties of the active site can also be derived from the vibrational frequency of non-interacting CO molecules adsorbed in a linear mode and from the shift of the absorption band maximum that results from dipole-dipole interactions between adjacent CO molecules on the metal surface [26-28]. The vibrational frequency of a CO molecule sufficiently isolated from the other CO molecules that dipole-dipole coupling does not occur, the so-called singleton frequency, depends on the electron density on the atom with which CO forms the adsorption complex. In other words, the singleton frequency depends on the degree to which the *d*-orbitals of the metal atom donate electron density to the unoccupied $2\pi^*$-orbital of the adsorbed CO molecule and the degree to which the 5σ-orbital of the adsorbed CO donates electron density to the metal atom. Thus, the singleton frequency characterizes the electronic state of the adsorption site [29]. The dipole-dipole shift at saturation coverage characterizes the size of an ensemble consisting of the same metal atoms, as it is determined by the number of the adjacent vibrating dipoles [30].

Experimental

Catalysts preparation and routine characterization

The catalysts were prepared by pore volume impregnation of SiO_2 (Aldrich, 99+%, 60-100 mesh, 300 m^2 g^{-1}, average pore diameter, 150 Å) with a 0.1 N aqueous HCl solution containing $H_2PtCl_6 \cdot 6H_2O$ (Alfa, 99.9%) or $CuCl_2 \cdot 2H_2O$ (MCB Manufacturing Chemists, 99.5%) or a mixture of $H_2PtCl_6 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$. The concentrations of the metal precursors in the impregnating solution were adjusted to obtain a metal loading of 2.7% Pt and 0.5% Cu for the monometallic catalysts. For the bimetallic Pt-Cu catalysts, the concentration of the Pt precursor in the impregnating solutions was essentially the same as in case of the monometallic Pt catalyst, but the corresponding amount of $CuCl_2 \cdot 2H_2O$ was added to the solution to obtain the desired Cu to Pt atomic ratio.

After impregnation the materials were allowed to equilibrate overnight before drying at ambient temperature and pressure for 24 h and then at 373 K for 2 h in vacuum (~25 Torr). To eliminate possible chromatographic separation [31] of Pt and Cu ions on the surface of silica, the dry materials were repeatedly impregnated with distilled water in the amount of 20% of the H_2O volume required to reach the incipient wetness point. Prior to use, the "wet" samples were stored in tightly closed vials. The catalysts compositions are shown in Table 1. The catalyst nomenclature is defined according to the Pt to Cu atomic ratio. For example, a catalyst with Pt to Cu atomic ratio of 1:3 is referred to as Pt1Cu3 (Table 1).

The carbon monoxide chemisorption measurements were conducted with a volumetric sorption analyzer (Micromeritics, ASAP 2010 Chemi) to determine the fraction of Pt atoms exposed. The procedure is described in detail elsewhere [2]. The measurements were performed at 308 K, and the adsorption stoichiometry, CO/$Pt_{surface}$, was assumed to be equal to 1. Prior to measurements, the catalyst was exposed to flowing He (Praxair, 99.999%, 30 ml min^{-1}) while it was heated from ambient temperature to 403 K at the rate of 5 K min^{-1} and then held at 403 K for 1.5 h. Then the gas stream was switched to H_2 (Praxair, 99.999%, 30 ml min^{-1}). Next, the catalyst was heated from 403 K to the reduction temperature (493 or 773 K) at the rate of 5 K min^{-1} and held at this temperature for 2 h. After reduction, the catalysts was evacuated at the reduction temperature for 1.5 h and cooled to

Table 1. Composition and catalytic performance of Pt-Cu/SiO$_2$ catalysts reduced at 493 and 773 K in the reaction of 1,2-dichloroethane (DCE) dechlorination[a]

Catalyst	Catalyst Composition	T_{red}, K[b]	Conversion, % (Initial[c]/Steady-State)	Selectivity, mol.% (Initial[c]/Steady-State)			Activity, μmol_{DCE} g$_{cat}^{-1}$ s^{-1}	TOF[d], s^{-1}
				C$_2$H$_4$	C$_2$H$_6$	C$_2$H$_5$Cl		
Pt	2.7%Pt	493	17.7/4.0	0/0	93/89	7/11	4.8	0.13
		773	10.8/3.1	0/0	90/92	10/8	4.8	0.13
PtCu1	2.8%Pt+0.9%Cu	493	1.7/1.6	54/55	46/45	0/0	1.8	0.96
		773	2.4/2.0	0/3	95/93	5/4	1.9	0.68
PtCu2	2.7%Pt+1.8%Cu	493	1.9/1.6	89/77	11/23	0/0	1.1	1.1
		773	2.6/2.3	6/42	94/58	0/0	1.6	0.76
PtCu3	2.7%Pt+2.7%Cu	493	2.5/2.4	98/95	2/5	0/0	1.2	1.4
		773	2.3/2.0	20/85	80/15	0/0	1.4	1.1
PtCu4	2.7%Pt+3.5%Cu	493	2.1/1.9	99/96	1/4	0/0	1.3	2.3
		773	2.9/1.5	15/98	85/2	0/0	1.3	1.5
PtCu5	2.7%Pt+4.2%Cu	493	2.6/3.1	100/95	0/5	0/0	1.4	1.7
		773	1.7/1.6	38/97	62/3	0/0	1.6	2.0
PtCu6	2.6%Pt+5.1%Cu	493	1.2/2.1	100/96	0/4	0/0	1.0	1.9
		773	1.7/1.5	85/97	15/3	0/0	1.1	2.3
Cu	0.5%Cu	493	0.008/0.016	100/100	0/0	0/0	0.003	n/a[e]
		773	0.18/0.025	100/100	0/0	0/0	0.0008	n/a[e]

[a]Reaction conditions: $T = 473$ K; $P = 1$ atm (7,000 ppm 1,2-C$_2$H$_4$Cl$_2$, 35,000 ppm H$_2$, balance He). [b]Catalyst reduction temperature. [c]In 1 hour on stream. [d]Turnover frequency. [e]Not applicable.

the measurement temperature. The fraction of exposed Cu atoms was not measured.

Carbon monoxide uptakes of Pt-Cu/SiO$_2$ catalysts reduced at 493 K were too small for precise volumetric measurements; thus, Pt dispersions of these catalysts were calculated as follows:

$$D_{(Pt-Cu)} = D_{Pt} \times [I_{(CO/Pt-Cu)} / I_{(CO/Pt)}],$$

where $D_{(Pt-Cu)}$ – Pt dispersion of a Pt-Cu/SiO$_2$ catalyst reduced at 493 K; D_{Pt} – dispersion of Pt in the 2.7%Pt/SiO$_2$ reduced at 493 K measured volumetrically; $I_{(CO/Pt-Cu)}$ – integral intensity of the absorption bands in the IR spectra of CO irreversibly adsorbed on Pt in the Pt-Cu/SiO$_2$ catalyst reduced at 493 K; $I_{(CO/Pt)}$ – integral intensity of the absorption bands in the IR spectra of CO irreversibly adsorbed on Pt in the 2.7%Pt/SiO$_2$ catalyst reduced at 493 K.

Kinetics experiments

The dechlorination of CH$_2$ClCH$_2$Cl was conducted at ambient pressure in a stainless-steel flow reaction system connected to a quartz microreactor (10 mm i.d.) in which the catalyst was supported on a quartz frit. The reactor zone containing the catalyst was heated by an electric furnace. The temperature of the catalyst was measured and controlled with an accuracy of ± 1 K with a temperature controller (Omega, model CN2011). Gaseous reactants were metered with mass flow controllers (Brooks, 5850E) and mixed prior to entering the reactor. The liquid CH$_2$ClCH$_2$Cl (Sigma-Aldrich, 99.8%) was maintained at 273 K and metered into the reaction system via a saturator; He was the carrier gas. Saturation was confirmed by varying the flow rate of He through the saturator and quantifying the CH$_2$ClCH$_2$Cl in the gas phase by a gas chromatograph (GC) (Varian 3300 series).

The effluent from the reactor was analyzed on-line by GC. The GC was equipped with a 3

m 60/80 Porapak Q packed column (Supelco) and a flame ionization detector capable of detecting concentrations > 1 ppm for all chlorocarbons and hydrocarbons involved in this study. Hydrogen chloride, a reaction product, was not quantified.

Prior to reaction, the catalyst was exposed to flowing He (Praxair, 99.999%, 30 ml min^{-1}) while it was heated from the ambient temperature to 403 K at the rate of 5 K min^{-1} and then held at 403 K for 1.5 h (the drying step). Then the gas stream was switched to a 10% H$_2$/Ar mixture (Airgas, 99.99%, 30 ml min^{-1}). Next, the catalyst was heated from 403 K to the reduction temperature (493 or 773 K) at the rate of 5 K min^{-1} and held at this temperature for 2 h (the reduction step). The catalyst was then cooled in He (30 ml min^{-1}) to the reaction temperature and the He flow was switched to the reactant mixture.

For a typical dechlorination reaction, 0.1 g of catalyst was used and the total flow of the reactant mixture through the reactor was 41 ml min^{-1}. The flow consisted of 7,000 ppm of CH$_2$ClCH$_2$Cl, 36,000 ppm of H$_2$, and He (balance). The reaction temperature was 473 K. The reaction was run for 40 h or longer until steady-state performance with respect to activity was achieved. Steady state was defined as a change in conversion of less than 0.2% within a 10 h interval. In order to compare selectivities, the weight of the each bimetallic catalyst was adjusted to maintain the steady-state conversion at comparable levels (1 to 3%). However, for Cu/SiO$_2$ the conversion could not be raised beyond 0.03% even with 0.3 g of catalyst.

FTIR spectroscopic investigation of CO adsorption

Infrared spectra were recorded with a Research Series II FTIR spectrometer (Mattson) equipped with a liquid N$_2$ cooled MCT detector (Judson Technologies) and an IR cell used in previous research [32]. The cell volume was

200 cm³, and the light path-length was 12 cm. The cell was equipped with glass stopcocks (Ace Glass Inc.) connected to gas inlet/outlet ports. The spectra of adsorbed CO were measured with a resolution of 4 cm⁻¹. To obtain a satisfactory signal to noise ratio, 64 scans were accumulated per spectrum.

The infrared spectra were collected in the transmission mode, which mandates the use of thin wafers of catalyst. Such self-supporting catalyst wafers (~20 mg cm⁻² thick) were prepared by powdering the catalyst in an agate mortar and then pressing the powder at 830 atm for 3 min. Subsequently, the wafers were mounted into the IR cell, evacuated at room temperature for 15 min, heated to 403 K at 5 K min⁻¹, evacuated at 403 K for 1.5 h, heated to 493 K at 5 K min⁻¹ in a 5% H_2/Ar mixture flowing at 30 ml min⁻¹, and held at 493 K for 2 h while the gas mixture continued to flow. Finally, the temperature was lowered to 473 K, the gas phase was evacuated to a pressure of ≤10⁻⁶ Torr, and the wafer was allowed to cool down to ambient temperature under continuous evacuation.

After the CO adsorption experiments described below were performed, the catalyst wafer was evacuated at ambient temperature for 15 min, heated to 773 K at 5 K min⁻¹ in a 5% H_2/Ar mixture flowing at 30 ml min⁻¹, and held at 773 K for 2 h under the same gas mixture flow. Then the temperature was lowered to 473 K, the gas phase was evacuated to a pressure of ≤10⁻⁶ Torr, and the wafer was allowed to cool down to ambient temperature under continuous evacuation. After this pretreatment, another set of CO adsorption experiments was conducted.

The frequency shift that results from dipole-dipole coupling and the singleton frequencies of CO adsorbed on the catalyst were measured by the isotopic dilution method [29,33] using mixtures of different compositions of $^{12}C^{16}O$ (Praxair, 99.99+%) with $^{13}C^{18}O$ (Isotec, 99+%

^{13}C, 95+% ^{18}O). Initially, the pretreated catalyst wafer was exposed to $^{12}C^{16}O$ for 15 min at room temperature and an equilibrium pressure of 10 Torr. Then, the gaseous $^{12}C^{16}O$ was evacuated, and a mixture of $^{13}C^{18}O+^{12}C^{16}O$ of known composition (10 Torr) was admitted to the IR cell. After 15 min the spectrum of adsorbed CO in the presence of the gas phase was recorded. Then, the gaseous CO was evacuated for 15 min, and the spectrum of adsorbed CO was recorded in the absence of gas phase. By repeating this procedure while systematically varying the composition of the isotopic mixture, the spectra of adsorbed CO as a function of $^{13}C^{18}O+^{12}C^{16}O$ mixture composition were determined. Similar to the procedure described elsewhere [24,34], the singleton frequencies, $v_{Pt}(^{12}C^{16}O)$, for the Pt-$^{12}C^{16}O$ linear complexes were determined from the spectra of the adsorbed $^{13}C^{18}O+^{12}C^{16}O$ mixtures with very low $^{13}C^{18}O$ concentrations by increasing the frequency of the Pt-$^{13}C^{18}O$ absorption band by 100 cm⁻¹, a difference between vibrational frequencies of $^{13}C^{18}O$ and $^{12}C^{16}O$ molecules [35]. The dipole-dipole shifts, $\Delta v_{Pt}(^{12}C^{16}O)$, were determined as the difference between the frequency of the Pt-$^{12}C^{16}O$ absorption band in the spectra of $^{13}C^{18}O+^{12}C^{16}O$ mixtures with very low $^{13}C^{18}O$ concentrations and the Pt-$^{12}C^{16}O$ band singleton frequency.

Temperature programmed desorption (TPD) and reduction (TPR)

The TPD and TPR experiments were carried out in the IR cell described above. In all experiments, 0.02-0.05 g catalyst wafers were used.

Prior to the TPD experiment, the wafer was evacuated at ambient temperature for 2 h. Then the cell was disconnected from the vacuum pump by means of a valve and the wafer temperature was increased from ambient temperature to 403 K at a rate of 4 K min⁻¹ while FTIR spectra of gas phase in the cell were recorded every 2-5 min.

Temperature-programmed reduction experiments were conducted according to two different protocols. According to the first protocol, the catalyst wafer after the TPD experiment was evacuated at 403 K for 1.5 h and cooled to room temperature under continuous evacuation. Then 600 Torr of H_2 were admitted to the IR cell and the wafer was heated to 773 K at a rate of 4 K min^{-1} while the composition of the gas phase in the IR cell was monitored with FTIR.

According to the second TPR protocol, a fresh catalyst wafer was reduced in the IR cell at 493 K for 1.5 h similar to the procedure described in the previous section. Then, the temperature was lowered to 473 K and the cell was evacuated for 0.5 h. Next, 600 Torr of H_2 was admitted to the IR cell and the temperature was increased to 773 K at a rate of 4 K min^{-1}. During the heating, FTIR spectra of gas phase in the cell were recorded every 2-5 min.

Results

Dispersion measurements

The dispersion of Pt in the monometallic 2.7%Pt/SiO_2 catalyst was essentially independent of the catalyst reduction temperature. The fractions of Pt atoms exposed determined by volumetric measurements of irreversibly adsorbed CO were 27 and 26.5% after the reduction at 493 and 773 K, respectively (Fig. 1). Addition of Cu to Pt resulted in a dramatic decrease in the apparent Pt dispersion of bimetallic catalysts reduced at both temperatures. The fraction of Pt atoms exposed of the PtCu1/SiO_2 reduced at 773 K was approximately 2%, and the fraction of surface Pt atoms in Pt-Cu/SiO_2 catalysts gradually decreased further as the Cu to Pt ratio increased to reach 0.4% for the PtCu6/SiO_2 (Fig. 1). This trend is consistent with the results reported elsewhere [2, 13, 36].

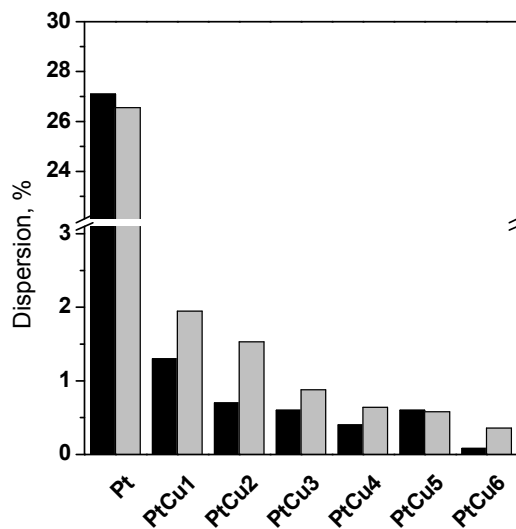For bimetallic Pt-Cu/SiO_2 catalysts reduced at 493 K, the amounts of CO adsorbed irreversibly

Fig. 1. Dispersions of Pt/SiO_2 and Pt-Cu/SiO_2 catalysts reduced at 493 (black bars) and 773 K (gray bars). Platinum dispersions of Pt/SiO_2 reduced at both temperatures and Pt-Cu/SiO_2 reduced at 773 K were determined volumetrically from the irreversibly adsorbed CO whereas Pt dispersions of Pt-Cu/SiO_2 reduced at 493 K were calculated based on volumetric and FTIR measurements

were too small to be measured reliably with the ASAP 201 Chemi Micromeritics instrument. Thus, the Pt dispersions of these catalysts were calculated using results of volumetric and FTIR measurements (see Experimental section). According to the calculations, the Pt dispersion of the PtCu1/SiO_2 was only 1.3% and the dispersion decreased as the Cu to Pt ratio increased, so that the fraction of Pt atoms exposed of the PtCu6/SiO_2 was 0.4% (Fig. 1). It is worth noting that Pt dispersions calculated with FTIR data can be used as an estimate only because the extinction coefficients for CO adsorbed on Pt in mono- and bimetallic catalysts might be quite different.

Kinetics experiments

The kinetics results for the catalysts reduced at 493 and 773 K are shown in Table 1. The Pt/SiO_2 permanently deactivated as the 1,2-dichloroethane conversion decreased by a factor of 3 to 4 during the first 50 hours on stream. In contrast, the

conversion for the Pt-Cu catalysts decreased only slightly during the first 1-2 hours on stream and remained essentially constant thereafter. However, the 1,2-dichloroethane conversion for the Cu/SiO_2 reduced at 773 K decreased by an order of magnitude during the first 80 hours on stream, whereas the conversion for the same catalyst reduced at 493 K was increasing with time on stream to exceed the initial conversion by a factor of 2 at steady-state (Table 1).

The Pt/SiO_2 exhibited the highest catalytic activity on per mass of catalyst basis; the activities of the $Pt-Cu/SiO_2$ were lower by a factor of 3-5. The bimetallic catalysts with the Cu to Pt ratio greater than 1 did not show a clear dependence of catalytic activity on Cu loading. The activity of Cu/SiO_2 was negligible. The Pt/SiO_2 had the turnover frequency (TOF) of 0.13 s^{-1}, being the lowest one among Pt-containing catalysts. Upon addition of copper, the TOFs of bimetallic catalysts increased to exceed that of the Pt/SiO_2 by an order of magnitude. It is worth noting, that the TOFs of the $Pt-Cu/SiO_2$ reduced at 493 K were close to those of the catalysts reduced at 773 K (Table 1).

The product selectivities for the Pt/SiO_2 and Cu/SiO_2 catalysts did not depend on the reduction temperatures and were also independent of time on stream. The latter catalyst was 100% selective toward ethylene, while the former one catalyzed 1,2-dichloroethane dechlorination to form approximately 90% of ethane and 10% of monochloroethane (Table 1). However, the selectivities for the Pt-Cu catalysts were a function of reduction temperature and time on stream as well as a function of catalyst composition.

The characteristic features of the bimetallic catalysts were catalyzing the $CH_2ClCH_2Cl + H_2$ reaction toward the formation of C_2H_4 and the absence of monochloroethane among the reaction products (Table 1). The initial selectivity for the $PtCu1/SiO_2$ reduced at 493 K toward C_2H_4 was

54% and it did not change with time on stream. For the $PtCu2/SiO_2$ reduced at 493 K, the initial C_2H_4 selectivity was 89%. The selectivity decreased with time on stream to drop to 77% in 65 h. The initial ethylene selectivities for the other Pt-Cu catalysts reduced at 493 K were close or equal to 100% and decreased to 95-97% at steady-state.

The $PtCu1/SiO_2$ reduced at 773 K exhibited no ethylene selectivity initially and this selectivity increased to only 3% in 40 h on stream when the catalyst reached the steady state. Even though the other Pt-Cu catalysts reduced at 773 K showed initial ethylene selectivities, they were much lower than those for the catalysts reduced at 493 K (Table 1). However, ethylene selectivities increased with time on stream, and the steady state selectivity figures for the catalysts with Cu to Pt atomic ratio greater than 3 were virtually the same as those for the catalysts reduced at 493 K (Table 1).

Temperature programmed desorption (TPD) and reduction (TPR)

The TPD and TPR experiments were conducted with Pt/SiO_2, $PtCu1/SiO_2$, $PtCu3/SiO_2$, $PtCu6/SiO_2$, and Cu/SiO_2 catalysts. The objective of the TPD experiments was to elucidate chemical processes occurring during the drying step of the catalyst treatment prior to the kinetics testing. Temperature programmed desorption experiments demonstrated that all catalyst samples start releasing H_2O at ~340 K (not shown). The onset of the HCl evolution by the Pt and PtCu samples was observed at ~370 K whereas the monometallic Cu sample started releasing HCl at ~390 K (not shown). The evolution of H_2O and HCl would have been an indication of the decomposition of Cu and Pt hydroxides/hydroxychlorides, which may form during catalyst preparation and/or storage [19]. Another source of water could be a temperature stimulated desorption of H_2O that was not

removed by a prolonged sample evacuation at room temperature prior to the TPD experiments.

The TPR experiments were performed to probe the reducibility of the bimetallic Pt-Cu and the corresponding monometallic catalysts. During the heating in hydrogen of a 2.7%Pt/SiO$_2$ wafer dried in vacuum at 403 K, the onset of the HCl formation was observed at ~360 K (not shown). This temperature is consistent with that of the Pt chlorides reduction reported elsewhere [19]. Only trace amounts of HCl were evolved by the catalyst wafer above 420 K whereas the H$_2$O evolution was observed in the whole temperature range of the TPR experiments (not shown). Probably, the water released because of temperature stimulated desorption of strongly bound H$_2$O as well as because of dehydroxylation of the SiO$_2$ surface. In addition, the evolution of trace amounts of CO and CH$_4$ was detected with the onset of the formation at ~520 and ~570 K, respectively (not shown). The emerging of CO was assigned to the decomposition of carbonate-carboxylate species formed from the metal chlorides during the catalyst preparation/storage while the appearance of CH$_4$ was attributed to the Pt-catalyzed hydrogenation of these species and/or CO.

In the TPR experiment with a 0.5%Cu/SiO$_2$ wafer, hydrogen chloride evolution began at ~440 K. The IR-TPR profile for the HCl evolution had two different slopes in the range of 450-490 and 490-550 K (not shown). These slopes were attributed to the reduction of Cu(II) to Cu(I) and Cu(I) to Cu(0), respectively [37,38]. Similar to the TPD experiment with Pt/SiO$_2$, the Cu/SiO$_2$ wafer released water in the whole temperature range of the experiment. The onset of CO evolution was observed at ~550 K. No CH$_4$ formation was detected for the Cu/SiO$_2$.

The TPR of PtCu1/SiO$_2$, PtCu3/SiO$_2$ and PtCu6/SiO$_2$ bimetallic samples showed the onset of HCl formation at ~400 K. At 520 K CO became

detectable in the gas phase. A continuous increase in the water concentration in the gas phase was observed throughout the whole temperature range for all bimetallic samples. Similar to the Cu/SiO$_2$, no CH$_4$ was detected in the TPD experiments with the bimetallic Pt-Cu catalysts.

The TPR experiments with the catalysts preliminary reduced at 493 K for 2 h showed that the reduction of the Pt and Cu compounds on the silica surface does not occur completely. For the Pt/SiO$_2$, H$_2$O and HCl along with CH$_4$ were detected in the gas phase at 570 K (not shown). However, the amount of HCl released was approximately 100 times less then that for the wafer without preliminary reduction. This suggests that after reduction at 493 K the Pt/SiO$_2$ catalyst holds ~1% of the initial Cl content. Hydrogen chloride, H$_2$O, and CO were also detected in the gas phase during the TPR experiments with the reduced at 493 K Cu/SiO$_2$ and bimetallic Pt-Cu wafers, with the HCl amounts being 6 times greater in comparison with the pre-reduced Pt/SiO$_2$. No product in the gas phase was detected in the TPD experiments with Pt, Cu, and Pt-Cu catalyst wafers pre-reduced at 773K.

FTIR spectroscopy of adsorbed CO

For the Pt/SiO$_2$ catalyst reduced at 493 K, the addition of $^{12}C^{16}O$ at room temperature to the IR cell resulted in the IR bands at 1835 and 2077 cm^{-1} (Fig. 2A). These bands are assigned to CO adsorbed on metallic Pt in the bridging and linear forms, respectively [39,40]. When the gas phase was removed by evacuation, the intensity of both bands decreased by approximately 10% and peak maxima shifted to 1815 and 2069 cm^{-1}. Room temperature adsorption of $^{12}C^{16}O$ on the Pt/SiO$_2$ catalyst reduced at 773 K resulted in the bands at 1764 and 2075 cm^{-1} (Fig. 2B). Evacuation of the gas phase decreased the band intensity for the linear CO mode by less than 10% and shifted the band position to 2071 cm^{-1} whereas the band
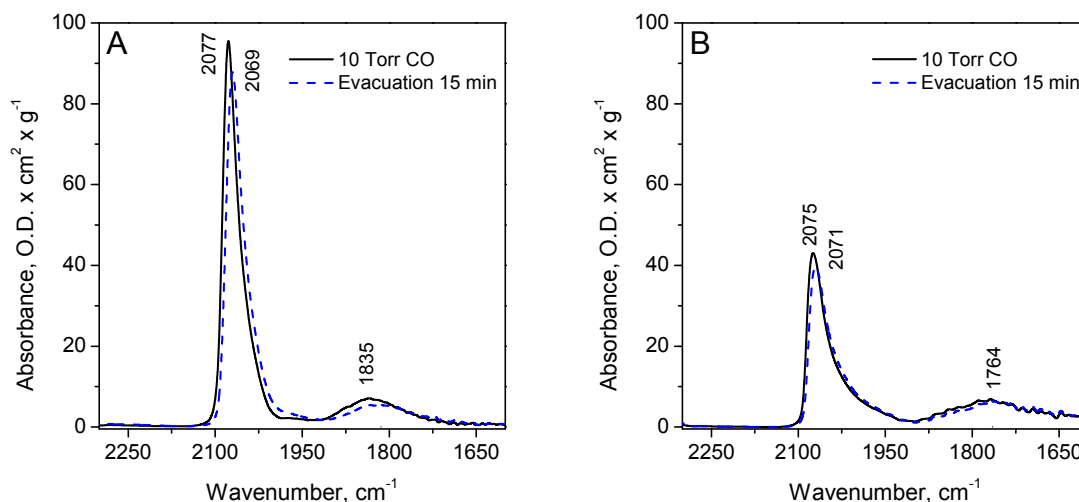
Fig. 2. IR spectra of $^{12}C^{16}O$ adsorbed on Pt/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase
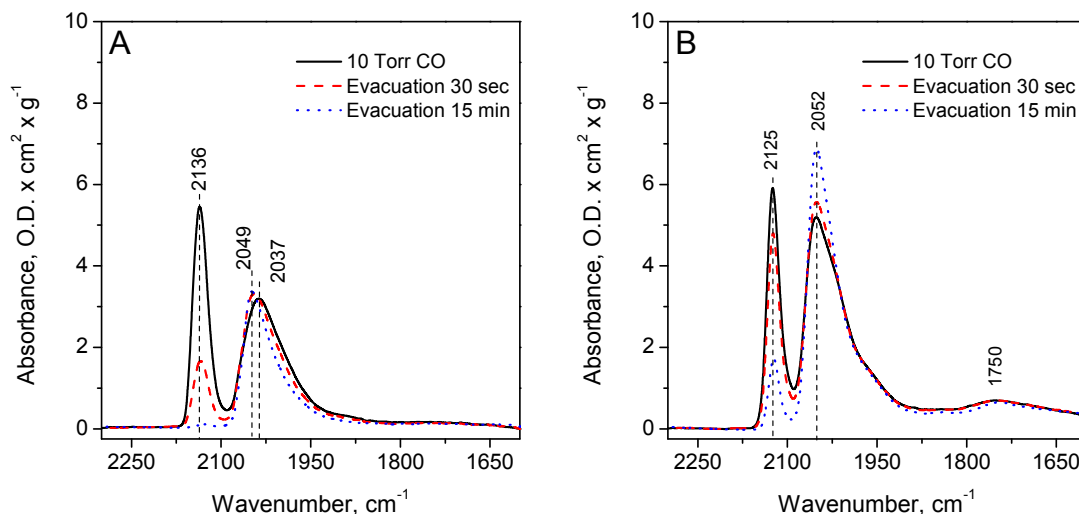

Fig. 3. IR spectra of $^{12}C^{16}O$ adsorbed on PtCu1/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase

intensity and position for the bridging CO mode remained invariable (Fig. 2B).

When 10 Torr CO was present in the gas phase, the spectrum of CO adsorbed on the PtCu1/SiO$_2$ catalysts reduced at 493 K consisted of the bands at 2037 and 2136 cm^{-1} (Fig. 3A). Bands in the range of 2030-2050 cm^{-1} have been previously assigned to $^{12}C^{16}O$ adsorbed linearly on Pt atoms embedded into the Cu matrix [33,41,42], whereas the band at 2136 cm^{-1} is attributed to $^{12}C^{16}O$ adsorbed on metallic Cu

[33,42-44]. The 2136 cm^{-1} band is asymmetric and can be fitted to two Gaussian peaks with maxima at 2142 cm^{-1} and 2131 cm^{-1}. Thus, it is reasonable to suggest that there are two kinds of Cu(0) sites. Evacuation of the $^{12}C^{16}O$ at room temperature for 15 min resulted in the disappearance of the high frequency band at 2136 cm^{-1} and in the shift of the 2037 cm^{-1} band to 2049 cm^{-1} with an insignificant increase in the absolute intensity (Fig. 3A). However, the integral intensity of the band did
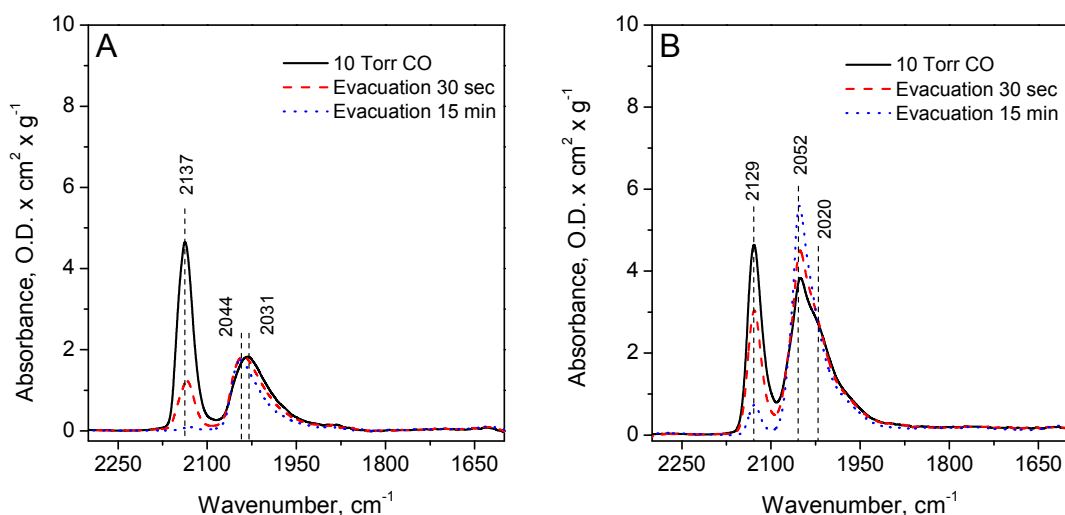
Fig. 4. IR spectra of $^{12}C^{16}O$ adsorbed on PtCu2/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase

not change. The disappearance of the band at 2136 cm^{-1} upon room temperature evacuation highlights thermal instability of the complexes of CO with Cu(0) [33, 42-44].

Exposure of the PtCu1/SiO$_2$ catalysts reduced at 773 K to 10 Torr CO resulted in a spectrum with the band of CO adsorbed on metallic Cu at 2125 cm^{-1} and in the bands of CO adsorbed on metallic Pt in the linear and bridging modes at 2051 and 1750 cm^{-1}, respectively (Fig. 3B). When gas-phase CO was removed by evacuation, the intensity of the high-frequency band decreased significantly and shifted to 2123 cm^{-1}, while the band of linear Pt-CO complexes increased in integral intensity by approximately 40% and shifted to 2052 cm^{-1}.

The spectrum of PtCu2/SiO$_2$ reduced at 493 K consisted of the band of Cu-CO complexes at 2137 cm^{-1} and that of linear Pt-CO complexes at 2031 cm^{-1} when 10 Torr CO were present in the gas phase (Fig. 4A). Evacuation for 15 min resulted in a virtual disappearance of the high frequency band and in a shift of the low frequency band to 2044 cm^{-1} with insignificant decrease in integral intensity.

When the PtCu2/SiO$_2$ catalyst wafer was reduced at 773 K, the bands at 2129 and 2050 cm^{-1}

because of linear CO complexes with metallic Cu and Pt sites appeared in the spectrum in the presence of 10 Torr CO in the gas phase. In addition, the low frequency band had a distinct shoulder at 2020 cm^{-1} (Fig. 4B). Room temperature evacuation caused a sharp decrease in intensity of the 2129 cm^{-1} band and its shift to 2127 cm^{-1}. As well, the band at 2050 cm^{-1} showed a considerable increase in intensity encompassing thereby the shoulder at 2020 cm^{-1} and shifted to 2052 cm^{-1}.

The assignment of the 2020 cm^{-1} band is ambiguous. The low frequency peak of the two bands observed in the region of 2030-2045 cm^{-1} in the spectra of CO adsorbed on silica-supported cluster-derived Pt-Cu catalysts was assigned to a bridging or semi-bridging mode between Pt and Cu [45]. It has been reported also that CO adsorption on a Cu/Al$_2$O$_3$ reduced at 173-550 K and the CO pressure of 75 Torr resulted in a band in the 2000-2010 cm^{-1} spectral region assigned to bridged species [43,46]. However, these assignments are questionable because the spectral region where bridged Pt [39,40] and Cu [47,48] carbonyls are detected is well below 1900 cm^{-1}. In addition, bridged carbonyls on Cu were observed only at low temperatures and
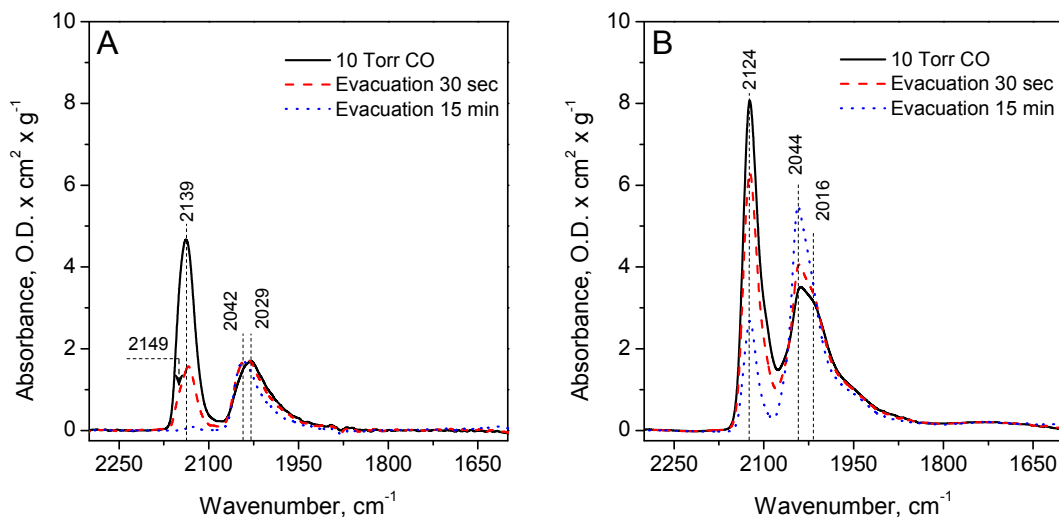
Fig. 5. IR spectra of $^{12}C^{16}O$ adsorbed on PtCu3/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase

Fig. 6. IR spectra of $^{12}C^{16}O$ adsorbed on PtCu4/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase

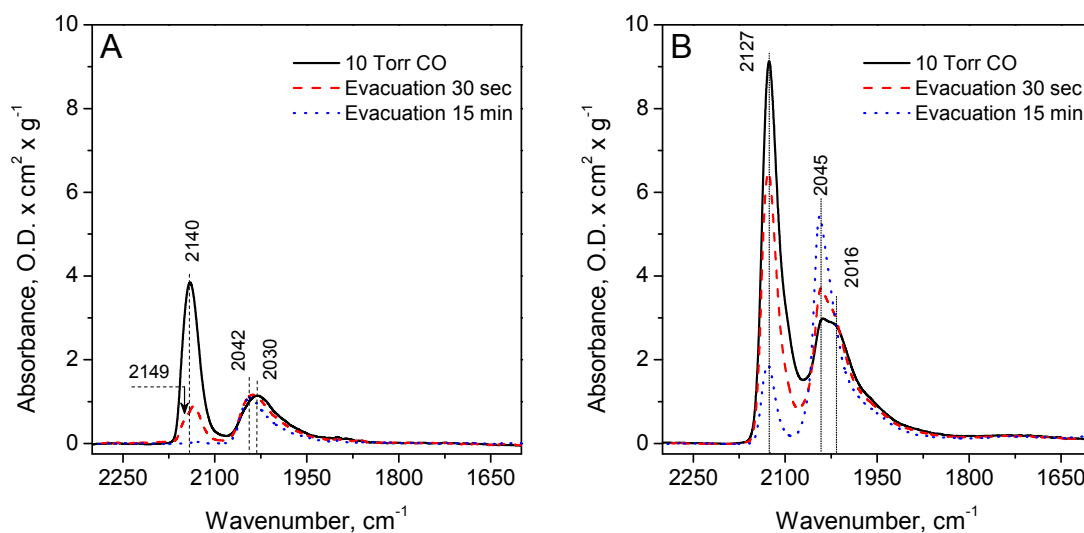high coverages [47-49]. In another investigation, a stable in vacuum band at 2018 cm^{-1} developed after exposure of a reduced Cu/SiO$_2$ to CO was assigned to linear Cu^0-CO adsorption complexes formed with low coordinated Cu atoms [50]. Nevertheless, the nature of this band requires further investigation. It is worth noting that the band at approximately 2020 cm^{-1} was present also in the spectrum of CO adsorbed on the PtCu1/

SiO$_2$ reduced at 773 K but much less pronounced (Fig. 3B).

The IR spectra of CO adsorbed on the PtCu3/SiO$_2$, PtCu4/SiO$_2$, PtCu5/SiO$_2$, and PtCu6/SiO$_2$ reduced at 493 and 773 K are shown in Fig. 5-8. For each of the catalyst reduced at 493 K, the spectrum recorded in the presence of gas phase consisted of the bands of linear Cu-CO and Pt-CO complexes at 2139-2144 and 2029-2030 cm^{-1},
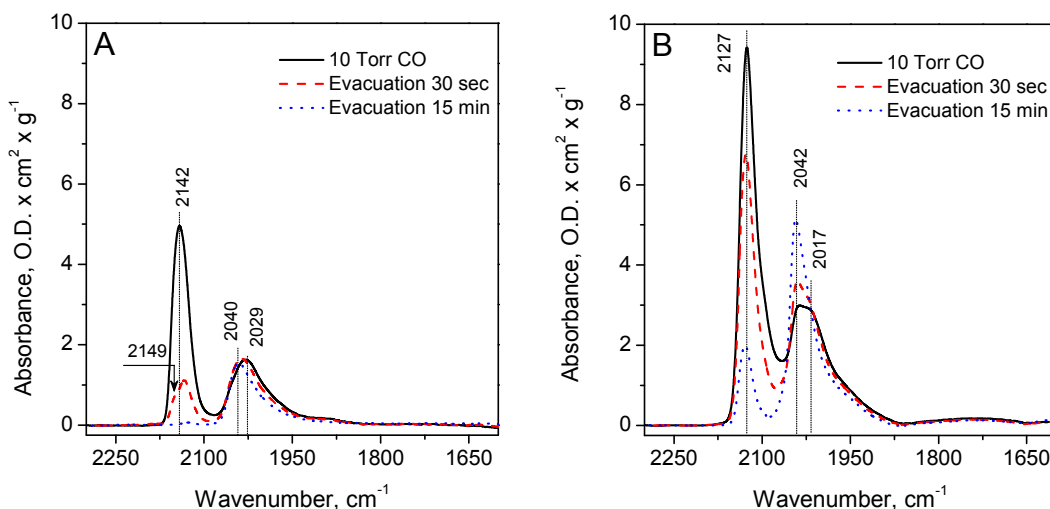
Fig. 7. IR spectra of $^{12}C^{16}O$ adsorbed on PtCu5/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase
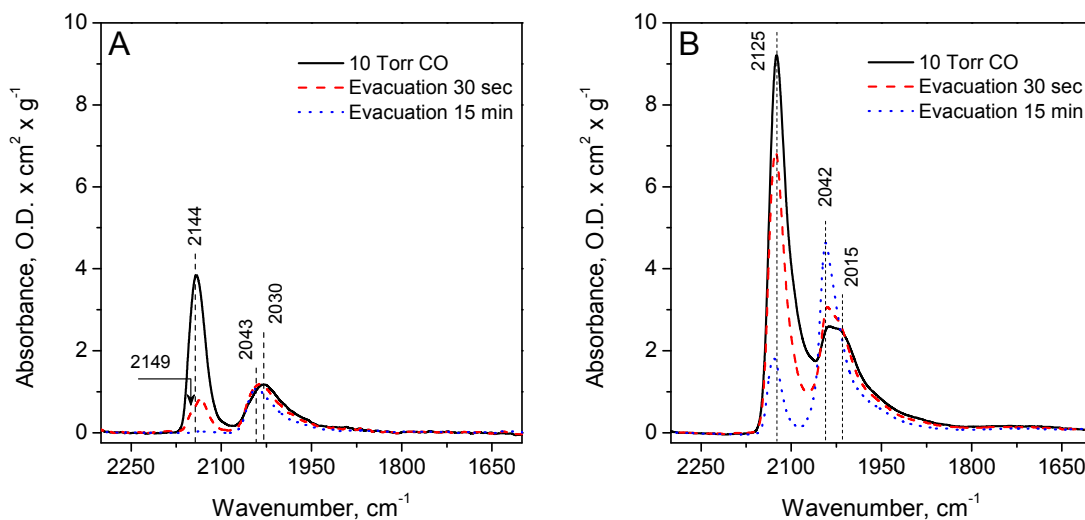

Fig. 8. IR spectra of $^{12}C^{16}O$ adsorbed on PtCu6/SiO$_2$ reduced at 493 (A) and 773 K (B) in the presence and in the absence of the gas phase

respectively (Fig. 5A-8A). The high frequency band is asymmetric and split into two poorly resolved bands at 2149 and 2132-2134 cm^{-1} resulting from 30 second evacuation. After 15 min evacuation of the gas phase, the Cu-CO band disappeared while the band of Pt-CO experienced a blue shit by 11-13 cm^{-1} with the intensities remaining essentially invariable (Fig. 5A-8A).

For the catalysts reduced at 773 K, there were three bands in the spectra at 2124-2127,

2036-2038, and 2015-2017 cm^{-1}, respectively, when CO was present in the gas phase. The latter band manifested itself as a low-frequency shoulder of the 2036-2038 cm^{-1} band (Fig. 5B-8B). Evacuation of the gas phase caused a sharp decrease of the Cu-CO band in intensity but it did not disappear as it was observed for the reduction temperature of 493 K. Evacuation did not result in a shift of the band position either. However, 15 min evacuation affected both the intensity

— 315 —

Table 2. Singleton frequencies and dipole-dipole coupling shifts of the $^{12}C^{16}O$ complexes with Pt[a] for the silica-supported Pt and Pt-Cu catalysts reduced at 493 and 773 K

Catalyst	$\nu_{Pt}(^{12}C^{16}O)$[b], cm^{-1}		$\Delta\nu_{Pt}(^{12}C^{16}O)$[c], cm^{-1}	
	T_{red} = 493 K	T_{red} = 773 K	T_{red} = 493 K	T_{red} = 773 K
Pt	2035	2032	42	37
PtCu1	2042	2032	7	19
PtCu2	2042	2035	1	10
PtCu3	2041	2034	0	10
PtCu4	2043	2035	0	8
PtCu5	2040	2037	0	7
PtCu6	2040	2037	0	6

[a] In the absence of the gas-phase CO. [b] Singleton frequency. [c] Dipole-dipole coupling shift.

and the position of the Pt-CO band. It shifted to the higher wavenumbers by 4-6 cm^{-1} with a two-fold increase in intensity. This increase worsened the resolution of the 2036-2038 cm^{-1} band and its shoulder at 2015-2017 cm^{-1}, but an asymmetry of the shifted band at 2042-2045 cm^{-1} suggested that the band at 2015-2017 cm^{-1} was still present in the spectra (Fig. 5B-8B).

Singleton frequencies and dipole-dipole shifts of the $^{12}C^{16}O$ complexes with Pt in silica-supported Pt and Pt-Cu catalysts are listed in Table 2. The spectra of the $^{12}C^{16}O+^{13}C^{18}O$ isotopic mixtures used for the measurements of these characteristics of the CO adsorbed are not shown. The singleton frequency of Pt-$^{12}C^{16}O$ complexes for the Pt/SiO$_2$ reduced at 493 K was 2035 cm^{-1}. It was 5-8 cm^{-1} greater for the Pt-Cu catalysts, but there was no correlation between the singleton frequency and the Cu to Pt atomic ratio (Table 1). For the Pt/SiO$_2$ and PtCu1/SiO$_2$ reduced at 773 K, the singleton frequency was 2032 cm^{-1}. The frequency increased with an increase in the Cu to Pt atomic ratio, but the trend was very weak. The difference between singleton frequencies for Pt/SiO$_2$ and PtCu6/SiO$_2$ was 5 cm^{-1} only (Table 2). The singleton frequencies for the bimetallic catalysts reduced at 773 K were 3-10 cm^{-1} lower than those for the catalysts reduced at 493 K.

The dipole-dipole shift for the Pt/SiO$_2$ reduced at 493 K was 42 cm^{-1}. It reduced to 7 cm^{-1} for the PtCu1/SiO$_2$ and remained virtually zero for the other bimetallic catalysts (Table 2). While the dipole-dipole shift for the Pt/SiO$_2$ reduced at 773 K was close to that for the catalyst reduced at 493 K, the shifts for the Pt-Cu catalysts reduced at 773 K exceeded those for the bimetallic catalysts reduced at 493 K. The shift was 19 cm^{-1} for the PtCu1/SiO$_2$ and it decreased gradually as the Cu to Pt atomic ratio increased to reach 6 cm^{-1} for the PtCu6/SiO$_2$ (Table 2).

Discussion

The present investigation provides evidence that active sites of different nature form on the surface of the silica support for the Pt-Cu/SiO$_2$ catalysts reduced at 493 and 773 K. The FTIR spectroscopy results of adsorbed CO presented in this work are consistent with the formation of surface particles of Pt-Cu solid solutions after the reduction at 773 K and with the formation of Cu overlayers on the surface of Pt particles after the catalyst reduction at 493 K.

Even though the Pt-Cu/SiO$_2$ catalysts were repeatedly impregnated with distilled water to eliminate possible chromatographic separation [31] of Pt and Cu ions during the first impregnation of the support with aqueous solutions of H$_2$PtCl$_6$

and $CuCl_2$, the Pt and Cu chlorides may still be separated on the silica surface. Because both Pt and Cu chlorides/oxychlorides are relatively stable in an inert atmosphere and migrate readily over the surface of oxide and carbon supports at higher temperatures [19,51], the drying of the Pt-Cu/SiO_2 catalysts in He flow at 403 K (see Experimental section) would lead to a redistribution of Pt and Cu chloride moieties on the support by surface diffusion. As Pt chlorides are thermally unstable at temperatures above 370 K [52] it is expected that some Pt chlorides will decompose to the Pt metal. The Pt metal sites could serve as a trap for the mobile $CuCl_x$ moieties by catalyzing dissociation of Cu-Cl bonds on the Pt surface. The driving force of this process is the energy of cohesion between Pt and Cu [53]. Thus, after the drying step of the Pt-Cu/SiO_2 catalyst pretreatment, the metal-containing moieties on the support surface would consist of microcrystals of partially decomposed Pt chlorides encompassed by $CuCl_x$ species. Of course, a fraction of Cu chlorides may crystallize apart of Pt-containing moieties.

Both thermodynamics and kinetics favor the reduction of platinum chlorides by H_2 to the metallic state [19,31]. Hence, at higher temperatures the life time of Pt chloride moieties in the presence of H_2 is not expected to be long. Copper chlorides are more stable and need higher temperature or longer time at lower temperature to be reduced to the metal. Indeed, according to the TPD/TPR results, in monometallic catalysts the reduction of Pt starts at 360 K, while reduction of Cu chlorides requires the temperature of 440 K. In the presence of platinum, copper chloride should also reduce rapidly. Silica supports favor hydrogen spillover [19], and there would not be a shortage of dissociated H in close proximity to the $CuCl_x$ moieties even if Pt clusters, the source of dissociated H, are quite distant. However, the TPR results show that the reduction of Pt-Cu/SiO_2 catalysts starts at 400 K, 40 K higher than the

temperature of the Pt/SiO_2 reduction. This fact provides an indirect support to the suggestion that in the Pt-Cu/SiO_2 catalysts, after the drying step, microcrystals of partially decomposed Pt chlorides are covered by $CuCl_x$ moieties. If this is the case, molecular hydrogen has to diffuse through the $CuCl_x$ layer to be activated on the Pt sites. If the H_2 diffusion is slower than the kinetics of the Pt and Cu chloride reduction by dissociated hydrogen, the onset temperature of the Pt-Cu/SiO_2 catalysts reduction will be higher than that of the Pt/SiO_2 reduction.

Thus, the reduction of the Pt-Cu/SiO_2 catalysts at 493 K will result in the metallic particles consisted of the Pt core covered with multilayers of Cu along with the particles of metallic Cu consistent with the two peaks for the Cu-bonded CO in the IR spectra (Fig. 3A-8B). Alloying of Cu and Pt is not expected because of high energy barrier for the diffusion of Cu into Pt [20]. Previous studies showed that alloy formation takes place after annealing Cu/Pt overlayers to the temperatures above 550 K [20,21,54]. It is worth noting that alloying between Pt and Cu in Pt-Cu/C catalysts reduced at 493 K was not detected by HRTEM even though catalytic properties of Cu and Pt were significantly modified [55].

The suggestion about the formation of multilayers of Cu over Pt particles is supported by the results of the IR investigation of adsorbed CO. A low stability of the Cu-CO adsorption complexes in vacuum (Fig. 3A-8A) similar to that of pure Cu [33,42-44] is consistent with a very weak, if any, electronic modification of Cu; hence, alloying of Pt-Cu does not take place. On the other hand, a very small dipole-dipole coupling shift of the Pt-CO band for the PtCu1/SiO_2 and the absence of it for the other Pt-Cu catalysts (Table 2) along with a very low apparent Pt dispersion suggest that Pt in the catalysts reduced at 493 K is blocked by Cu. A blue shift of Cu-CO bands by 45-50 cm^{-1} for the Pt-Cu/SiO_2

as compared to silica- and alumina-supported Cu [33,42] can be explained by electron withdrawal effect of the residual Cl (see TPR results) as well as by the roughness of the Cu surface due to a relatively low catalyst reduction temperature. It was shown previously that the frequencies of CO adsorbed on "smooth" Cu(100) and Cu(111) single crystals are lower than those on "rough" Cu(211) and Cu(311) [56].

Removing the CO adsorbed on Cu of the Pt-Cu/SiO$_2$ catalysts reduced at 493 K by evacuation does not result in a change in integral intensity of the Pt-CO band (Fig. 3A-8A) suggesting that there are limited, if any, electronic interactions between Pt and Cu [24,25,53,57,58]. However, a possibility of some electronic interaction between Pt and Cu is inferred from a blue shift of the Pt-CO band by 11-13 cm^{-1} when the CO adsorbed on Cu sites was removed (Fig. 3A-8A). Similar shifts were observed for CO on Pt(111) surfaces covered with 0.12-0.29 monolayer of Cu after the CO adsorbed on Cu was removed, but the shift was only two wavenumbers [57]. Much greater shift of 22 cm^{-1} was reported for reduced at 873 K Pt-Cu/Al$_2$O$_3$ catalysts [58]. The shift was explained in terms of electronic modification of Pt and Cu under assumptions that CO adsorption on Cu results in an electron transfer from CO to Cu and that alloying Cu and Pt increases the population of the Pt(d) orbitals. Such explanation is hardly valid. It has been shown that CO adsorption on Cu(100) produces a shift of +0.5 eV in the Cu(3d) and Cu(2p$_{3/2}$) levels [59] indicating electron transfer from Cu to CO. As well, according to the UPS and XPS results reported elsewhere [54], electron transfer from Pt to Cu takes place when Cu deposited on the Pt(111) migrates into Pt(111) to form surface alloys (*vide infra*). Hence, it is very difficult, if possible at all, to explain the CO frequency shift observed (Fig. 3A-8A) within simple models of molecular orbital theory. This effect requires further investigation.

The singleton frequencies of Pt-CO complexes for the reduced at 493 K Pt-Cu/SiO$_2$ catalysts do not allow one to make an insightful conclusion about the electronic modification of Pt. The frequencies for the bimetallic catalysts are greater that that for the Pt/SiO$_2$, but the difference is 5-8 cm^{-1} only (Table 2). This difference could be attributed to an electron withdrawal effect of chlorine atoms rather than to an electronic modification of Pt by Cu, as the TPD/TPR results show that after the reduction at 493 K the Pt-Cu/SiO$_2$ catalysts retain 6 times as much Cl as the Pt/SiO$_2$.

The formation of alloy Pt-Cu particles in the catalysts reduced at 773 K is evident from the spectra of CO adsorbed on Pt. Evacuation of CO from the gas phase over the catalyst wafers results in a sharp decrease in intensity of the Cu-CO absorption band and in a significant increase in intensity of the Pt-CO band (Fig. 2B-7B). Similar intensity redistribution was observed in infrared reflection absorption spectra of CO adsorbed on ultrathin Cu films supported on Pt(111) and has been assigned to the formation of heteronuclear metal-metal bonds [53,57]. An increase in intensity of the Pt-CO absorption band after the gas-phase CO is removed by evacuation was also reported for the Pt-Cu/Al$_2$O$_3$ catalysts reduced at 873 K [58]. Thus, the intensity redistribution between the Cu-CO and Pt-CO bands observed in the present investigation is consistent with the formation of Pt-Cu moieties in which Pt and Cu atoms are in an intimate contact, namely, with the formation of Pt-Cu alloys.

The formation of alloy Pt-Cu particles for the Pt-Cu/SiO$_2$ catalysts reduced at 773 K is also evident from the analyses of the spectra of CO adsorbed on Cu. There is a single absorption band with a maximum at 2124-2129 cm^{-1}, independent of CO surface coverage (Fig. 3B-8B). This frequency is ~30 cm^{-1} higher than that for CO linearly adsorbed on metallic Cu supported

on alumina [33] or silica [42]. Even though CO adsorption complexes with Cu(0) decompose readily in vacuum [33, 42-44] and the band at 2124-2129 cm^{-1} does not disappear during 15 min evacuation (Fig. 3B-8B), it cannot be assigned to stable in vacuum at room temperature complexes of CO with Cu$^+$ ions [43,44,46,50]. Indeed, if copper in the Pt-Cu/SiO$_2$ catalysts reduces to the metallic state at 493 K (*vide supra*), it should definitely reduce at 773 K, the temperature that is 280 K higher. Thus, the increased stability of the Cu^0-CO complexes in vacuum is due to the peculiarities of electronic interactions between Cu and Pt in Pt-Cu alloys.

The results of UPS and XPS investigations of surface alloys formed after migration of Cu multilayer into Pt(111) indicate electron transfer from Pt to Cu [54,60-62]. Theoretical calculations with a cluster model showed that electronic interactions between Pt and Cu result in a Cu(s,p) → Pt charge transfer accompanied by Pt → Cu(d) and Cu(s,p) → Cu(d) electron transfers [63]. Thus, electronically modified surface Cu atoms of Pt-Cu surface alloys should bind CO stronger than the surface of bulk Cu due to an increased donation of the electron density from the d-orbitals of Cu to the 2π*-orbital of CO adsorbed. Indeed, the temperature of CO desorption from a Cu monolayer deposited on Pt(111) is ~70 K higher than that from Cu(111) [53, 61]. This change in the desorption temperature corresponds to an enhancement of ~20 kJ mol^{-1} in the strength of the Cu-CO bond [61,64]. The fact that an enhancement in the stability of the Cu-CO adsorption complexes does not result in a red shift in the C-O stretch frequency for Pt-Cu/SiO$_2$ catalysts (Fig. 3B-8B) as compared to that for supported Cu [33,42] is not surprising. A blue shift in the C-O stretch frequency resulting from an increase in π-backdonation was reported elsewhere for fractional monolayer coverages of Cu over Pt(111) [53,57]. It has been concluded

that C-O stretch frequency is more sensitive to the charge on the metal to which the molecule is bonded than to the electron population of the CO 2π-orbitals [53,57].

The electronic state of Pt alloyed with Cu is also modified. For example, the CO desorption temperature from Pt in Pt-Cu surface alloys is decreased by as much as 100 K as compared to pure Pt [20]. This is indicative of the Pt(d) → Cu electron transfer. The increase in the CO singleton frequencies for the reduced at 773 K Pt-Cu/SiO$_2$ catalysts (Table 2) is consistent with a reduction in the Pt(5d) population. However, the effect is very weak. The maximum difference between the singleton frequencies of Pt/SiO$_2$ and Pt-Cu/SiO$_2$ does not exceed 5 cm^{-1} (Table 2). It might be due to the fact that, according to previous theoretical studies, CO vibrational shifts on metals and metal oxides depend not only on the extent of π-backdonation, but also on the interaction between the CO dipole momentum and the charge on the metal center and on the repulsion arising when the CO molecule stretches in the presence of the rigid surface to which it is bound (the so-called Wall effect) [65, 66].

Even though IR spectra of CO adsorbed on Pt provide little to no information about the electronic modification of Pt in the Pt-Cu/SiO$_2$ catalysts for both reduction temperatures, important information can be derived from the dipole-dipole coupling shifts of the Pt-CO complex frequency (Table 2). The shift allows one to judge on the relative sizes of Pt ensembles on the surface of Pt-Cu moieties [30]. The dipole-dipole coupling shift is absent for the reduced at 493 K Pt-Cu/SiO$_2$ catalysts with Cu to Pt atomic ratio greater than 1 (Table 2). The absence of dipole-dipole coupling suggests that Pt is blocked by Cu almost completely, and the exposed Pt consists of very small ensembles, maybe even of isolated Pt atoms. At higher reduction temperatures the rate of the Cu overlayer diffusion into Pt increases

and, as a consequence, the concentration of Cu on the surface of Pt-Cu moieties decreases while that of Pt increases. In addition, hydrogen in the gas phase favors an enrichment of the Pt-Cu surface in Pt. The driving force for this chemistry to occur is the different energies of H adsorption on Pt and Cu [67]. The heats of H_2 chemisorption on Pt and Cu are 109 and 34 kJ mol^{-1}, respectively [19]. The enrichment in Pt results in a relatively large dipole-dipole coupling shifts of the Pt-CO band for the Pt-Cu/SiO$_2$ catalysts reduced at 773 K (Table 2).

Characteristic feature of the catalytic performance of the reduced at 493 K Pt-Cu/SiO$_2$ catalysts that do not exhibit dipole-dipole coupling of CO adsorbed on Pt is the high initial selectivity toward ethylene in the $CH_2ClCH_2Cl + H_2$ reaction (Table 1). The initial ethylene selectivity of the catalysts reduced at 773 K is much lower and this selectivity is inversely proportional to the dipole-dipole coupling of CO adsorbed on Pt (Table 1) or, in the other words, to the size of Pt ensembles on the surface of Pt-Cu moieties. Thus, the results of the present investigation are consistent with the suggestion that the extent of electronic modification of Pt and Cu does not control the ethylene selectivity of the catalysts in the hydrogen-assisted dechlorination of 1,2-dichloroethane. Instead, the size of Pt ensembles plays a crucial role for the ethylene selectivity. It has been shown that isolated Pt atoms do not bind ethylene, the primary product of 1,2-dichloroethane dechlorination, strongly favoring thereby its desorption rather than hydrogenation toward ethane [18].

As the $CH_2ClCH_2Cl + H_2$ reaction proceeds, the ethylene selectivity of the reduced at 493 K Pt-Cu/SiO$_2$ catalysts with Cu to Pt atomic ratio greater than 1 decreases whereas that of the catalysts reduced at 773 K increases (Table 1). Such catalytic performance is explained by the equilibration of the catalysts' surface with the reactants and products. Hydrogen and ethylene have a greater heat of adsorption on Pt [19] favoring an enrichment of the bimetallic surface in Pt; Cl atoms, the product of 1,2-dichloroethane dissociation, have greater affinity for Cu when compared to Pt [68-70] favoring a surface enrichment in Cu. Thus, the transient performance of the Pt-Cu/SiO$_2$ catalysts in terms of the ethylene selectivity infers that the average size of Pt ensembles when the equilibrium between the catalysts and the reaction mixture is reached is intermediate between the sizes of the Pt ensembles in the catalysts reduced at 493 and 773 K.

The steady-state turnover frequencies (TOFs) of Pt-Cu/SiO$_2$ catalysts in the CH_2ClCH_2Cl + H_2 reaction are approximately one order of magnitude greater than those of Pt/SiO$_2$, being virtually independent of the Cu loading and the reduction temperature (Table 1). The difference in catalytic activity between bimetallic Pt-Cu and monometallic Pt catalysts is approximately the same as the difference between the rates of stoichiometric dechlorination of 1,2-dichloroethane over silica-supported Cu and Pt [71]. These observations are consistent with the hypothesis that for Pt-Cu/SiO$_2$ catalysts 1,2-dichloroethane dissociate on Cu sites to form ethylene and adsorbed Cl atoms. As hydrogen dissociative adsorption on Cu is an activated process with a relatively low adsorption energy, the concentration of H atoms on the Cu surface would be low [19]. Thus, monometallic Cu/SiO$_2$ catalyst possesses very low activity in the reaction under consideration (Table 1) as the surface Cl can not be removed easily due to a lack of surface hydrogen. Therefore a noble metal is needed to provide an abundant source of dissociated hydrogen which upon spilling over from Pt sites reduces surface CuCl species followed by HCl desorption. The independence of the activity of the Pt-Cu/SiO$_2$ catalysts on per surface Pt atom

basis on Cu loading (Table 1) suggests that the rate-determining step of the $CH_2ClCH_2Cl + H_2$ reaction is H diffusion from Pt to Cu sites or reduction of surface CuCl species rather than the dissociation of the first C-Cl bond of the 1,2-dichloroethane as it has been proposed elsewhere [7] for Pd-Ag/SiO$_2$ catalysts.

Conclusion

The results of the present investigation suggest that the different temperature of the Pt-Cu/SiO$_2$ catalysts reduction results in the formation of different active sites on the surface of the silica support. The characteristic features of the active sites of the catalysts reduced at 493 K are a very weak, if any, electronic interaction between Pt and Cu and the absence of the dipole-dipole coupling shift of the linear Pt-CO band in the IR spectra of adsorbed CO. These are consistent with the idea that metallic Cu blocks physically the surface of Pt particles making thereby the size of Pt ensembles exposed very small. Such active sites are 100% selective toward ethylene in the $CH_2ClCH_2Cl + H_2$ reaction.

The alloy Pt-Cu particles form in the catalysts reduced at 773 K. In these particles, there is an electronic interaction between Pt and Cu, which manifests itself by an increased stability of the Cu^0-CO adsorption complexes in vacuum and by an intensity redistribution between Pt-CO and Cu-CO bands in the IR spectra of adsorbed CO. As well, a significant dipole-dipole coupling shift of the linear Pt-CO band suggests relatively large Pt ensembles on the surface of Pt-Cu moieties. Such moieties exhibit relatively low ethylene selectivity in the $CH_2ClCH_2Cl + H_2$ reaction and this selectivity is inversely proportional to the dipole-dipole coupling shift.

Initial ethylene selectivity of the Pt-Cu/SiO$_2$ catalysts reduced at 493 K decreases with the course of the reaction, whereas the initial selectivity of the catalysts reduced at 773 K increases with time on stream. The steady-state ethylene selectivities of the Pt-Cu catalyst with Cu to Pt atomic ratio greater than two reduced at different temperatures are very close suggesting the similar surface composition of the Pt-Cu moieties independent of the reduction temperature. Thus, the nature of the Pt-Cu species formed upon catalyst reduction does not control the reaction selectivity. The selectivity is a function of the composition of the Pt-Cu particle surface, which, in turn, is a result of chemical equilibration between the catalyst and the reaction mixture.

Acknowledgement

References

1. Ito, L. N.; Harley, A. D.; Holbrook, M. T.; Smith, D. D.; Murchison, C. B.; Cisneros, M. D. Catalytic conversion of 1,2-dichloropropane to propylene. WO 9407819, 1994.

2. Vadlamannati, L. S.; Kovalchuk, V. I.; d'Itri, J. L., Dechlorination of 1,2-dichloroethane catalyzed by Pt-Cu/C: unraveling the role of each metal. *Catalysis Letters* **1999,** 58, (4), 173-178.

3. Heinrichs, B.; Delhez, P.; Schoebrechts, J.-P.; Pirard, J.-P., Palladium–Silver Sol-Gel Catalysts for Selective Hydrodechlorination of 1,2-Dichloroethane into Ethylene. *Journal of Catalysis* **1997,** 172, (2), 322-335.

4. Borovkov, V. Y.; Luebke, D. R.; Kovalchuk, V. I.; D'Itri, J. L., Hydrogen-Assisted 1,2-Dichloroethane Dechlorination Catalyzed by Pt-Cu/SiO$_2$: Evidence for Different Functions of Pt and Cu Sites. *Journal of Physical Chemistry B* **2003,** 107, (23), 5568-5574.

5. Srebowata, A.; Stefanowicz-Pieta, I.; Juszczyk, W.; Karpinski, Z., Chlorine removal from 1,2-dichloroethane over Ni/C catalysts *Polish Journal of Chemistry* **2007,** 81, (8), 1521-1529.

6. Srebowata, A.; Juszczyk, W.; Kaszkur, Z.; Karpinski, Z., Hydrodechlorination of 1,2-dichloroethane on active carbon supported palladium-nickel catalysts. *Catalysis Today* **2007,** 124, (1-2), 28-35.

7. Heinrichs, B.; Schoebrechts, J.-P.; Pirard, J.-P., Palladium–Silver Sol–Gel Catalysts for Selective Hydrodechlorination of 1,2-Dichloroethane into Ethylene. III. Kinetics and Reaction Mechanism *Journal of Catalysis* **2001,** 200, (2), 309-320.

8. Srebowata, A.; Juszczyk, W.; Kaszkur, Z.; Sobczak, J. W.; Kepinski, L.; Karpinski, Z., Hydrodechlorination of 1,2-dichloroethane and dichlorodifluoromethane over Ni/C catalysts: The effect of catalyst carbiding. *Applied Catalysis A: General* **2007,** 319, 181-192.

9. Srebowata, A.; Sadowska, M.; Juszczyk, W.; Kaszkur, Z.; Kowalczyk, Z.; Nowosielska, M.; Karpinski, Z., Hydrogen-assisted dechlorination of 1,2-dichloroethane over silica-supported nickel-ruthenium catalysts. *Catalysis Communications* **2006,** 8, (1), 11-15.

10. Lambert, S.; Ferauche, F.; Brasseur, A.; Pirard, J.-P.; Heinrichs, B., Pd-Ag/SiO$_2$ and Pd-Cu/SiO$_2$ cogelled xerogel catalysts for selective hydrodechlorination of 1,2-dichloroethane into ethylene. *Catalysis Today* **2005,** 100, (3-4), 283-289.

11. Luebke, D. R.; Vadlamannati, L. S.; Kovalchuk, V. I.; d'Itri, J. L., Hydrodechlorination of 1,2-dichloroethane catalyzed by Pt-Cu/C: effect of catalyst pretreatment. *Applied Catalysis B: Environmental* **2002,** 35, (3), 211-217.

12. Vadlamannati, L. S.; Luebke, D. R.; Kovalchuk, V. I.; d'Itri, J. L.; Avelino Corma, F. V. M. S. M. a. J. L. G. F., Olefins from chlorocarbons: Reactions of 1,2-dichloroethane catalyzed by Pt-Cu. In *Studies in Surface Science and Catalysis*, Elsevier: 2000; Vol. 130A, pp 233-238.

13. Rhodes, W. D.; Lazar, K.; Kovalchuk, V. I.; d'Itri, J. L., Hydrogen-Assisted 1,2-Dichloroethane Dechlorination Catalyzed by Pt-Sn/SiO$_2$: Effect of the Pt/Sn Atomic Ratio. *Journal of Catalysis* **2002,** 211, (1), 173-182.

14. Rhodes, W. D.; Margitfalvi, J. L.; Borbath, I.; Lazar, K.; Kovalchuk, V. I.; d'Itri, J. L., Hydrogen-assisted 1,2-dichloroethane dechlorination catalyzed by Pt-Sn/SiO$_2$ catalysts of different preparations. *Journal of Catalysis* **2005,** 230, (1), 86-97.

15. Avdeev, V. I.; Kovalchuk, V. I.; Zhidomirov, G. M.; d'Itri, J. L., Ethylene adsorption on the Pt-Cu bimetallic catalysts. Density functional theory cluster study. *Surface Science* **2005,** 583, (1), 46-59.

16. Avdeev, V. I.; Kovalchuk, V. I.; Zhidomirov, G. M.; d'Itri, J. L., Models of active sites in supported Cu metal catalysts in 1,2-dichloroethane dechlorination. DFT analysis. *Journal of Structural Chemistry* **2007,** 48, (Supplement), S160-S170.

17. Avdeev, V. I.; Kovalchuk, V. I.; Zhidomirov, G. M.; d'Itri, J. L., DFT analysis of the mechanism of 1,2-dichloroethane derchlorination on supported Cu-Pt bimetallic catalysts. *Journal of Structural Chemistry* **2007,** 48, (Supplement), S171-S183.

18. Kovalchuk, V. I.; d'Itri, J. L., Catalytic chemistry of chloro- and chlorofluorocarbon dehalogenation: from macroscopic observations to molecular level understanding. *Applied Catalysis A: General* **2004,** 271, (1-2), 13-25.

19. Anderson, J. R., *Structure of Metallic Catalysts*. Academic Press: London, 1975; p 478.

20. Yeates, R. C.; Somorjai, G. A., The growth and alloy formation of copper on the platinum(111) and stepped (553) crystal surfaces; characterization by LEED, AES, and carbon monoxide thermal desorption. *Surface Science* **1983,** 134, (3), 729-744.

21. Paffett, M. T.; Campbell, C. T.; Taylor, T. N.; Srinivasan, S., Copper adsorption on platinum(111) and its effects on chemisorption: a comparison with electrochemistry. *Surface Science* **1985,** 154, (1), 284-302.

22. Leung, L. W. H.; Gregg, T. W.; Goodman, D. W., Electrochemical and ultrahigh vacuum characterization of ultrathin copper films on platinum(111). *Langmuir* **1991,** 7, (12), 3205-3210.

23. Tsay, J. S.; Mangen, T.; Wandelt, K., Kinetic study of the formation of a surface-confined Cu50Pt50 alloy. *Thin Solid Films* **2001,** 397, (1-2), 152-156.

24. Borovkov, V. Y.; Kolesnikov, S. P.; Kovalchuk, V. I.; d'ItriJ.L, Probing Adsorption Sites of Silica-Supported Platinum with $^{13}C^{16}O + ^{12}C^{16}O$ and $^{13}C^{18}O + ^{12}C^{16}O$ Mixtures: A Comparative Fourier Transform Infrared Investigation. *Journal of Physical Chemistry B* **2005,** 109, (42), 19772-19778.

25. Persson, B. N. J.; Hoffmann, P. M., Vibrational phase relaxation at surfaces: The role of lateral interaction. *Journal of Electron Spectroscopy and Related Phenomena* **1987,** 45, 215-225.

26. Mahan, G. D.; Lucas, A. A., Collective vibrational modes of adsorbed CO. *Journal of Chemical Physics* **1979,** 68, (4), 1344-1348.

27. Persson, B. N. J.; Liebsch, A., Collective vibrational modes of isotopic mixtures of CO on Cu(111) and Cu(001) *Surface Science* **1981,** 110, (2), 356-368.

28. Persson, B. N. J.; Ryberg, R., Vibrational interaction between molecules adsorbed on a metal surface: The dipole-dipole interaction. *Physical Review B* **1981,** 24, (12), 6954-6970.

29. Hammaker, R. M.; Francis, S. A.; Eischens, R. P., Infrared study of intermolecular interactions for carbon monoxide chemisorbed on platinum. *Spectrochimica Acta* **1965,** 21, (7), 1295-1309.

30. Crossley, A.; King, D. A., Infrared spectra for CO isotopes chemisorbed on Pt (111): Evidence for strong absorbate coupling interactions. *Surface Science* **1977,** 68, 528-538.

31. Ponec, V.; Bond, G. C., *Catalysis by Metals and Alloys*. Elsevier: Amsterdam, 1995; p 734.

32. Deshmukh, S. S.; Borovkov, V. Y.; Kovalchuk, V. I.; d'Itri, J. L., FTIR Spectroscopic and Reaction Kinetics Study of the Interaction of CF_3CFCl_2 with γ-Al_2O_3. *Journal of Physical Chemistry B* **2000,** 104, (6), 1277-1284.

33. Toolenaar, F. J. C. M.; Stoop, F.; Ponec, V., On electronic and geometric effects of alloying. An infrared spectroscopic investigation of the adsorption of carbon monoxide on platinum-copper alloys. *Journal of Catalysis* **1983,** 82, (1), 1-12.

34. Borovkov, V. Y.; Kolesnikov, S. P.; Koval'chuk, V. I.; d'Itri, J. L., The state of metals in the Pt/Al_2O_3 and (Pt-Cu)/Al_2O_3 catalysts as indicated by IR spectroscopy with isotope dilution of $^{12}C^{16}O$ with $^{13}C^{18}O$ molecules. *Russian Chemical Bulletin* **2007,** 56, (5), 863-869.

35. Pinchas, S.; Laulicht, I., *Infrared Spectra of Labelled Compounds*. Academic Press: London - New York, 1971; p 371.

36. Early, K. O.; Rhodes, W. D.; Kovalchuk, V. I.; d'Itri, J. L., Hydrogen-assisted 1,2,3-trichloropropane dechlorination on supported Pt-Sn catalysts. *Applied Catalysis B: Environmental* **2000,** 26, (4), 257-263.

37. Rouco, A. J., TPR study of Al_2O_3- and SiO_2-supported $CuCl_2$ catalysts. *Applied Catalysis, A: General* **1994,** 117, (2), 139-149.

38. Rouco, A. J., *Low-temperature ethylene oxyhydrochlorination: effects of supports and promoters on the mobilities of active species in $CuCl_2$ catalysts*. 1995; Vol. 157, p 380-387.

39. Sheppard, N.; Nguyen, T. T., The vibrational spectra of carbon monoxide chemisorbed on the surfaces of metal catalysts - a suggested scheme of interpretation. *Advances in Infrared and Raman Spectroscopy* **1978,** 5, 67-148.

40. De La Crus, C.; Sheppard, N., An exploration of the surfaces of some Pt/SiO_2 catalysts using CO as an infrared spectroscopic probe. *Spectrochimica Acta* **1994,** 50A, (2), 271-285.

41. Stoop, F.; Toolenaar, J. C. M.; Ponec, V., Geometric and ligand effects in the IR spectra of carbon monoxide adsorbed on a platinum-copper alloy. *Journal of the Chemical Society, Chemical Communications* **1981**, (20), 1024-1025.

42. Toolenaar, F. J. C. M.; Reinalda, D.; Ponec, V., Adsorption of carbon monoxide on platinum-copper alloys. On the possible role of atomic and collective properties of metals in chemisorption: observations by infrared spectroscopy. *Journal of Catalysis* **1980,** 64, (1), 110-115.

43. Dandekar, A.; Vannice, M. A., Determination of the dispersion and surface oxidation states of supported Cu catalysts. *Journal of Catalysis* **1998,** 178, (2), 621-639.

44. Hadjiivanov, K. I.; Kantcheva, M. M.; Klissurski, D. G., IR study of CO adsorption on Cu-ZSM-5 and CuO/SiO_2 catalysts: σ and π components of the Cu^+-CO bond. *Journal of the Chemical Society, Faraday Transactions* **1996,** 92, (22), 4595-4600.

45. Chandler, B. D.; Pignolet, L. H., DRIFTS studies of carbon monoxide coverage on highly dispersed bimetallic Pt-Cu and Pt-Au catalysts. *Catalysis Today* **2001,** 65, (1), 39-50.

46. Dulaurent, O.; Courtois, X.; Perrichon, V.; Bianchi, D., Heats of Adsorption of CO on a Cu/Al_2O_3 Catalyst Using FTIR Spectroscopy at High Temperatures and under Adsorption Equilibrium Conditions. *Journal of Physical Chemistry B* **2000,** 104, (25), 6001-6011.

47. Hayden, B. E.; Kretzschmar, K.; Bradshaw, A. M., An Infrared Spectroscopic Study of CO on Cu(111): The Linear, Bridging and Physisorbed Species. *Surface Science* **1985,** 155, (2-3), 553-566.

48. Raval, R.; Parker, S. F.; Pemble, M. E.; Hollins, P.; Pritchard, J.; Chesters, M. A., FT-RAIRS, EELS and LEED studies of the adsorption of carbon monoxide on copper(111). *Surface Science* **1988,** 203, (3), 353-377.

49. Hollins, P., The influence of surface defects on the infrared spectra of adsorbed species. *Surface Science Reports* **1992,** 16, (2), 51-94.

50. Hadjiivanov, K.; Venkov, T.; Knozinger, H., FTIR spectroscopic study of CO adsorption on Cu/SiO_2: formation of new types of copper carbonyls. *Catalysis Letters* **2001,** 75, (1-2), 55-59.

51. Stevenson, S. A.; Dumesic, J. A.; Baker, R. T. K.; Ruckenstein, E., *Metal-Support Interactions in Catalysis, Synthering, and Redispersion*. Van Nostrand Reinhold Co.: New York, 1987; p 315.

52. Lide, D. R., *CRC Handbook of Chemistry and Physics*. 83rd ed.; CRC Press LLC: Boca Raton, 2002; p 2664.

53. Rodrigues, J. A.; Goodman, D. W., The Nature of the Metal-Metal Bond in Bimetallic Surfaces. *Science* **1992,** 257, (5072), 897-903.

54. Shek, M. L.; Stefan, P. M.; Lindau, I.; Spicer, W. E., Electronic structure of different Pt-Cu surfaces. *Physical Review B* **1983,** 27, (12), 7288-7300.

55. Chakraborty, D.; Kulkarni, P. P.; Kovalchuk, V. I.; d'Itri, J. L., Dehalogenative oligomerization of dichlorodifluoromethane catalyzed by activated carbon-supported Pt–Cu catalysts: effect of Cu to Pt atomic ratio *Catalysis Today* **2004,** 88, (3-4), 169-181.

56. Hollins, P.; Pritchard, J., In *Vibrational spectroscopy of adsorbates*, Willis, R. F.; Agarwal, B. K., Eds. Springer-Verlag: Berlin, 1980; Vol. 15.

57. Rodriguez, J. A.; Truong, C. M.; Goodman, D. W., Infrared Vibrational Studies of CO Adsorption on Cu/Pt(111) and CuPt(111) Surfaces. *Journal of Chemical Physics* **1992,** 96, (10), 7814-7825.

58. Sokolova, N. A.; Barkova, A. P.; Furman, D. B.; Borovkov, V. Y.; Kazansky, V. B., IR-spectroscopic study of the state of Cu and Pt in copper-platinum-alumina catalysts for paraffin dehydrogenation subjected to different reductive and oxidative treatments. *Kinetics and Catalysis (Translation of Kinetika i Kataliz)* **1995,** 36, (3), 434-440.

59. Egelhoff, W. F., Surface electronic structure and screening of 3d-band holes in Cu(100). *Physical Review B* **1984,** 29, (8), 4769-4771.

60. Santra, A. K.; Rao, C. N. R., Interaction of Carbon Monoxide with Bimetallic Overlayers. *Journal of Physical Chemistry* **1994,** 98, (23), 5962-5965.

61. Shek, M. L.; Stefan, P. M.; Lindau, I.; Spicer, W. E., CO chemisorption on Cu adlayers on Pt(111). *Physical Review B* **1983,** 27, (12), 7301-7312.

62. Shek, M. L.; Stefan, P. M.; Lindau, I.; Spicer, W. E., Photoemission study of the adsorption of Cu on Pt(111). *Physical Review B* **1983,** 27, (12), 7277-7287.

63. Rodriguez, J. A.; Kuhn, M., Electronic and Chemical Properties of Ag/Pt(111) and Cu/Pt(111) Surfaces: Importance of Changes in the d Electron Populations. *Journal of Physical Chemistry* **1994,** 98, (44), 11251-11255.

64. Rodrigues, J. A.; Campbell, R. A.; Goodman, D. W., The nature of metal-metal bonding at bimetallic interfaces *Surface Science* **1994,** 307-309, (1), 377-383.

65. Ryberg, R., Infrared Spectroscopy of Molecules Adsorbed on Metal Surfaces. In *Advances in Chemical Physics*, Lawley, K. P., Ed. John Wiley & Sons: Chichester, 1989; Vol. 76, p 1.

66. Pacchioni, G.; Cogliandro, G.; Bagus, P. S., Characterization of oxide surfaces by infrared spectroscopy of adsorbed carbon monoxide: a theoretical investigation of the frequency shift of CO on MgO and NiO. *Surface Science* **1991,** 255, (3), 344-354.

67. Ponec, V., Selectivity in Catalysis by Alloys. *Catalysis Reviews - Science and Engineering* **1975,** 11, (1), 41-70.

68. Yang, M. X.; Sarkar, S.; Bent, B. E.; Bare, S. R.; Holbrook, M. T., Degradation of Multiply-Chlorinated Hydrocarbons on Cu(100). *Langmuir* **1997,** 13, (2), 229-242.

69. Erley, W., Chlorine adsorption on the (111) faces of Pd and Pt. *Surface Science* **1980,** 94, (2-3), 281-292.

70. Erley, W., Chlorine adsorption on the (110) faces of Ni, Pd and Pt *Surface Science* **1982,** 114, (1), 47-64.

71. Anju, Y.; Mochida, I.; Yamamoto, H.; Kato, A.; Seiyama, T., The Dehalogenation of Haloalkanes on SiO_2-supported Metals. *Bulletin of the Chemical Society of Japan* **1972,** 45, (8), 2319-2323.