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Effect of catalyst pre-reduction temperature on the reaction of 1,2-dichloroethane and H₂ catalyzed by SiO₂-supported PtCu bimetallics

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ABSTRACT

A combination of reaction kinetics experiments, temperature-programmed investigations and FTIR CO adsorption studies were used to understand the effect of catalyst pretreatment on the reaction of 1,2-dichloroethane and H₂ catalyzed by SiO₂ supported PtCu bimetallics prepared from metal chloride precursors. Higher initial and steady-state selectivities towards ethylene were obtained for catalysts with a Cu to Pt atomic ratio of 1, 2, and 3 after pre-reduction at 220 °C than after pre-reduction at 500 °C. For catalysts with a Cu to Pt atomic ratio of 4 and 5, the initial ethylene selectivity was higher after the 220 °C pre-reduction, but the steady-state ethylene selectivities were essentially the same. Based on the catalyst characterization results, the low temperature pre-reduction yields supported particles with Pt-rich cores covered with Cu-rich layers that are still well-chlorinated, whereas the high temperature pre-reduction yields particles both more metallic and with surfaces richer in Pt. The factors governing the evolution of the catalysts during the two different pretreatments are discussed as well as the impact catalyst pretreatment has on the macroscopic performance behavior.

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1. Introduction

Catalysis by bimetallics continues to be an active field of research. Combinations of a Group VIII metal, such as Pt, and a Group IB metal, such as Cu, have been extensively studied using reactions such as reforming, hydrogenation, and hydrogenolysis [1–4]. The role of the Group IB metal in altering the catalytic performance has been attributed to an electronic effect that modifies the Group VIII metal reaction sites [5–7], to an alteration in the geometric size of the Group VIII metal reaction sites [4–7], and to participation as an active site for one or more elementary reaction steps of the overall reaction [6,8,9].

For the reaction of 1,2-dichloroethane and H_2 catalyzed by PtCu bimetallics, it has been suggested that Cu participants as an active site for the formation of ethylene, as the selectivity towards ethylene increases at the expense of ethane when the concentration of Cu atoms is increased [10–15]. In mechanistic terms, it is proposed that at sufficiently high surface concentrations of Cu, the ensembles of Pt are smaller than the size required to catalyze the dissociative adsorption of the 1,2-dichloroethane, but still large enough to dissociate H_2 and provide by spillover the H atoms that react with Cl to regenerate the Cu sites [10]. The dissociative adsorption of the 1,2-dichloroethane then occurs on the large surface ensembles of Cu atoms, forming an ethyl surface species and two surface Cl species.

Unlike on Pt, the ethyl species on Cu is unstable and readily rearranges to ethylene. And again unlike on Pt, the interaction strength of ethylene with Cu is very weak and thus the ethylene desorbs without undergoing further reaction. In short, by forcing the 1,2dichloroethane to react on Cu, the strongly adsorbed alkyl species on Pt that ultimately yield ethane are prevented from forming.

This investigation centers on the effect of catalyst pretreatment on the reaction of 1,2-dichloroethane and H₂ catalyzed by Pt–Cu/SiO₂. Of particular interest is the relationship between the pre-reduction temperature and the genesis of catalysts with varying Cu to Pt atomic ratio. Temperature-programmed desorption and reduction experiments were conducted to puzzle out the evolution of the catalysts from impregnation to reaction start, and FTIR spectroscopy of adsorbed CO was used to probe the surface composition of the metal particles. The impact catalyst pretreatment on reaction performance was ascertained through chemical reaction kinetics investigations.

2. Experimental

2.1. Catalysts preparation

Silica powder (Aldrich, 99+%, 60–100 mesh, 300 m²/g, 150 Å) was used as the catalyst support. The silica was calcined in air at 500 °C for 12 h prior to the impregnation of the metal precursors using a 0.1 N HCl aqueous solution of H₂PtCl₆·6H₂O (Alfa, 99.9%) and/or a 0.1 N HCl aqueous solution CuCl₂·2H₂O (MCB Manufacturing Chemist, 99.5%). The concentrations of the metals in the

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impregnating solutions were adjusted to obtain the desired loading of each metal. The Pt content was same (2.7 wt%) for all catalysts that contained it, and the amount of Cu was varied from 0 up to a Pt to Cu atomic ratio of 1:5. As well, a 0.5 wt% Cu catalyst was prepared.

The SiO₂ powder was added to the solution containing the dissolved metal precursors at ambient conditions while stirring continuously, and then the mixture was stirred for 12 h. The impregnated SiO₂ was isolated from the solution by filtration and dried at ambient conditions for 24 h. Subsequently, it was dried for 12 h at 100 °C under a static vacuum (~25 Torr). The resulting materials were stored until use in vessels maintained at the same partial pressure of H₂O to eliminate variations in the properties and performance of the catalysts attributable to aging phenomena [11].

2.2. Chemical kinetics study

The kinetics experiments were conducted in a stainless-steel flow reaction system operated under conditions that made the differential reactor assumption valid. The reactor consisted of a quartz tube (10 mm i.d.) in which the catalyst was supported on a quartz frit. The pretreatment gases and gaseous reactants were metered by mass flow controllers (5850E, Brooks) and were mixed prior entering the reactor. The 1,2-dichloroethane was metered into the system by flowing He through a saturator containing the liquid reactant at $0(\pm 1)^{\circ}$ C. The saturator temperature was maintained by a recirculating cooling system (RTE-111, Neslab). A blank experiment showed zero conversion for the system without catalyst.

The amount of the catalyst used in an experiment ranged between 50 and 300 mg so that the steady-state conversion for all the bimetallic catalysts was comparable (between 1.5 and 3%). The conversions were sufficiently low and limited to a narrow enough range that the reported differences in the product selectivity distributions cannot be attributed to differences in conversion levels at the points of comparison.

The catalyst temperature was controlled to ± 1 °C using a temperature controller (CN2011, Omega) connected to K-type thermocouple (Omega) placed in a quartz pocket that was in direct contact with the catalyst bed. The reaction products were analyzed by on-line GC (HP 5890). The GC was equipped with 3 m 60/80 Porapak Q packed column (Supelco) and flame ionization detector with a detection limit of <0.2 ppm for all chlorocarbons and hydrocarbons involved in this study.

After a catalyst sample was loaded into reactor, it was pretreated prior to the start of the reaction. To begin, it was heated in He (30 mL/min, PraxAir, 99.999%) from room temperature to 130 °C at $5 \,^{\circ}$ C/min and then held in the flowing He at 130 $\,^{\circ}$ C for 1.5 h. Next, the flowing gas was switched from the He to 10% H₂/Ar (30 mL/min). For the samples identified as low temperature pretreated catalysts, the temperature was increased at 5 °C/min to 220 °C, then held at 220 °C for 2 h in the 10% H₂/Ar flow before cooling to the reaction temperature of 200 °C where the gas flow was switch to He for 0.5 h to purge the system prior to starting the reaction. For the samples identified as high temperature pretreated catalysts, the temperature was increased from 130 to 500 °C at 5 °C/min in the 10% H_2/Ar flow then held at 500 °C for 2 h in the 10% H_2/Ar flow before cooling to the reaction temperature of 200 °C where the gas flow was switch to He for 0.5 h to purge the system prior to starting the reaction. Comparable pretreatment routines were used in the volumetric sorption studies and the FTIR investigations.

The reaction was conducted at 200 °C and atmospheric pressure. The reaction mixture consisted of 7000 ppm of 1,2-dichloroethane (Fisher Scientific, 99.8+%), 36,000 ppm H₂, and the balance He. The total flow-rate was 41 mL/min. The reaction was run for approximately 40 h, a time sufficient to achieve steady-state performance. For every kinetics experiment a new sample of catalyst was loaded into reactor and pretreated as specified before reaction.

2.3. Temperature programmed desorption (TPD) and reduction (TPR) investigations

An FTIR cell and instrument (described below) were used to conduct temperature programmed studies with the as prepared catalysts in order to puzzle out the surface chemistry that occurred during pretreatment. A wafer of sample was prepared as described above and then placed in the holder of the cell, which then was evacuated at 10^{-6} Torr for 2 h at room temperature before being sealed off. The wafer temperature was then increased from room temperature to $130 \,^{\circ}$ C at 5 $^{\circ}$ C/min as FTIR spectra of the gas phase in the cell were collected. The wafer temperature was maintained at $130 \,^{\circ}$ C for 1 h before the cell was opened to vacuum and evacuated for 0.5 h. Evacuation of the cell was continued as the wafer was cooled to room temperature in order to begin the temperature programmed reduction experiment.

Two different series of temperature-programmed reduction studies were conducted: one to determine type and stability metal precursor species formed during impregnation and subsequent treatments and another to determine the relative fraction of Cl and other types of ligands that remained after the low temperature pretreatment procedure used for the kinetics investigations. For the first TPR series, 600 Torr of H₂ (99.99%, PennOxygen) was admitted to the evacuated cell containing wafer that underwent the TPD and subsequent treatment. The wafer was heated from room temperature to 500° C at a rate of 5° C/min while FTIR spectra of the gas phase in the cell were collected.

For the other series of TPR experiments, a different treatment was used on the wafer following the TPD and subsequent treatment at 130 °C that lasted for 1.5 h. Instead of cooling to room temperature while continuing to evacuate, a flow of 10% H₂/Ar was sent through the cell as the wafer was heated at 5 °C/min to 220 °C and then maintained at 220 °C for 2 h. Next, the temperature was decreased to 200 °C, after which the H₂/Ar flow was stopped and the cell was evacuated for 0.5 h. The cell was filled with 600 Torr of H₂ and the TPR experiment was begun. The spectra of the gas phase in the cell were collected as the wafer was heated from 200 to 500 °C at 5 °C/min.

2.4. CO adsorption FTIR spectroscopy characterization

The infrared spectra were recorded using a Research Series II FTIR spectrometer (Mattson) equipped with a liquid N₂ cooled MCT detector (Judson Technologies). The spectra were measured in the range of 400 to 4000 cm⁻¹ with resolution of 4 cm⁻¹. For each spectrum 64 scans were collected and averaged. Sample preparation consisted of pressing a powdered catalyst at 800 atm for 1 min into a wafer with a density of 20–30 mg/cm², and the collected spectra were normalized on a per unit wafer density basis. The wafer was balanced in a quartz sample holder in a 0.5 L vacuum cell with NaCl windows and a 12 cm optical path length. The cell operated in the temperature range from 20 to 500 °C, and it was equipped with grease-free glass stopcocks (Ace Glass) connected to gas inlet/outlet ports and a vacuum port with a turbo-molecular pump (Leibold, 2000 L/sec).

The wafer was pretreated in the cell first by evacuation at 10^{-6} Torr while the temperature was increased at 5 °C/min from room temperature to 130 °C and then holding at 130 °C for 1.5 h. Afterwards a 30 mL/min flow of 10% H₂/Ar (Airgas, 99.99%) was sent through the cell, and the temperature was further increased at 5 °C/min from 130 to 220 °C. The temperature was maintained at 220 °C for 2 h before cooling at 5 °C/min to 200 °C. Then, the flow of 10% H₂/Ar was stopped and the cell was evacuated at 10⁻⁶ Torr for

Table 1

Initial and steady-state selectivity distributions for the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min) catalyzed by SiO₂-support PtCu bimetallics pre-reduced at 220 °C and at 500 °C.

	220°C			500°C		
	C_2H_4	C_2H_6	C ₂ H ₅ Cl	C_2H_4	C_2H_6	C ₂ H ₅ Cl
Pt	0/0	93/89	7/11	0/0	90/92	10/8
PtCu1	54/55	46/45	0/0	0/3	95/96	5/1
PtCu2	89/77	11/23	0/0	6/42	94/58	0/0
PtCu3	98/95	2/5	0/0	20/85	80/15	0/0
PtCu4	99/96	1/4	0/0	15/98	85/2	0/0
PtCu5	100/95	0/5	0/0	38/96	62/4	0/0
Cu	100/0	0/0	0/0	100/0	0/0	0/0

0.5 h. The evacuation was continued as the wafer was cooled from $200 \,^{\circ}$ C to room temperature during a time period of 0.5 h.

After pretreating the wafer, a background spectrum was recorded. The 10 Torr of CO was admitted to the cell, and after 15 min a spectrum was recorded. The cell was evacuated for 15 min, and then another spectrum was recorded. The wafer was then subjected to the high temperature pretreatment. Specifically, a flow of the 10% H₂/Ar (30 mL/min) was admitted to the cell and the wafer was heated at 5 °C/min from room temperature to 500 °C, and then held at 500 °C for 2 h before the temperature was decreased to 200 °C at 5 °C/min. The 10% H₂/Ar flow was then stopped, and the cell was evacuated for 0.5 h. Afterwards, the evacuation was continued as the wafer was cooled from 200 °C to room temperature during a time period of 0.5 h. Finally, the CO adsorption FTIR experiments were repeated with this high temperature pretreated catalyst.

2.5. Chemisorption measurements

The samples were characterized by CO chemisorptions measurements using a volumetric sorption analyzer (Micromeritics, ASAP 2010). The results were used to calculate the per cent Pt atoms exposed for each catalyst, as described elsewhere [12].

Not surprisingly the monometallic catalyst had the highest percent Pt atoms exposed: 27% for both the low temperature and high temperature pretreated samples. For the bimetallic catalysts pretreated at high temperature, increasing the Cu content decreased the per cent Pt atoms exposed, a trend that has been reported in earlier published investigations [12,13]. Specifically, the catalysts with Cu/Pt atomic ratios of 1,2,3,4, and 5 had per cent Pt metal atoms exposed of 1.95, 1.53, 0.88, 0.64, and 0.58%, respectively. For the bimetallic catalysts pretreated at low temperature, the total volume of chemisorbed CO was below the detection limit of the instrument, which is not surprising given that the low temperature pretreatment only partially reduced the metal precursor species to lesser chlorinated species. However, the CO adsorption FTIR results for the bimetallic catalysts pretreated at low temperature do indicate the presence of surface Pt atoms metallic in character, albeit far fewer in concentration as when the bimetallic catalysts were reduced at high temperature.

3. Results

3.1. Chemical kinetics investigations

The initial and steady-state selectivity behavior for the catalysts in the reaction of H_2 and 1,2-DCE are summarized in Table 1, both after low temperature and high temperature pretreatment, and the time on stream behavior is provided in Figs. 1–7. Of primary interest is the behavior of the bimetallic catalysts. However, the results for the Pt and the Cu catalysts have been included as points of reference.

The Pt catalyst was the most active catalyst, converting approximately 4.75 μ mol/s/g_{cat} of reactant regardless of the pre-reduction treatment, and selectively formed ethane as the major product with monochloroethane (11% or less) as the only other product (Fig. 1). The Cu catalyst was the least active catalyst, roughly a factor of 100 less active than the Pt catalyst, and it was 100% selective towards ethylene at all time on stream after both the low temperature and the high temperature pretreatments (Fig. 2). For both monometallic catalysts the pre-reduction temperature had little effect on the product selectivity.

For the bimetallic catalysts the steady state activities were all in the range of $1-2 \mu mol/s/g_{cat}$ regardless of the pre-reduction temperature. And in contrast to the monometallic catalysts, the product selectivity was more affected by the pre-reduction temperature. For the PtCu1 catalyst pretreated at low temperature, the initial ethylene selectivity was 54%, with ethane as the only other product. The selectivity increased by 1% to 55% during the 40 h reaction (Fig. 3A). However with the PtCu1 catalyst pretreated at high temperature, the initial ethylene selectivity was zero and increased with time on stream to a steady-state level of 3% (Fig. 3B). The ethane selectivity was initially 95% and increased during the length of the reaction to 96%. Plus, the PtCu1 catalyst pretreated at high temperature was the only bimetallic catalyst to form monochloroethane (MCE). There was 5% MCE in the effluent of the first sample taken on-stream and then it appeared again roughly 10 h later and increased to 1% by the end of the reaction.



Fig. 1. Time on stream behavior of Pt/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): □ – Ethane, \triangledown – Monochloroethane.



Fig. 2. Time on stream behavior of Cu/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): \bigcirc – Ethylene.



Fig. 3. Time on stream behavior of PtCu1/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): ○ – Ethylene, □ – Ethane, ▽ - Monochloroethane.

For the PtCu2 catalyst pretreated at low temperature, the initial ethylene selectivity was 89%, and ethane was the only other reaction product (Fig. 4A). During the course of the reaction, the ethylene selectivity decreased to 77%, which was mirrored by a corresponding increase in the selectivity towards ethane. However, after the PtCu2 catalyst was pretreated at high temperature, the initial ethylene selectivity was only 6%. The other 94% of the product stream was ethane (Fig. 4B). The ethylene selectivity increased to 42% at the expense of ethane during the first 20 h time on stream and then stayed essentially constant for the remainder of the 40 h reaction. For the PtCu3 catalyst pretreated at low temperature, the initial ethylene selectivity was 98%, and again ethane was the only other reaction product (Fig. 5A). The ethylene selectivity decreased during the course of the 40 h reaction to 95% as the ethane selectivity increased to 5%. However, with the PtCu3 catalyst pretreated at high temperature, the initial ethylene selectivity was only 20% and the rest of the product stream was ethane (Fig. 5B). By the second time the effluent stream was sampled, less than an hour later, the ethylene selectivity had increased to more than 70% at the expense of ethane. And thereafter the ethylene selectivity continued to



Fig. 4. Time on stream behavior of PtCu2/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): ○ -Ethylene, □ - Ethane.



Fig. 5. Time on stream behavior of PtCu3/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): \bigcirc – Ethylene, \square – Ethane.



Fig. 6. Time on stream behavior of $PtCu4/SiO_2$ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H_2 (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): \bigcirc – Ethylene, \square – Ethane.

increase at the expense of ethane to 85% after $40\,h$ time on stream.

For the PtCu4 catalyst pretreated at low temperature, the initial ethylene selectivity was 99% and the ethane selectivity was 1% (Fig. 6A). The ethylene selectivity decreased to 96% during the course of the 40 h reaction, while the ethane selectivity correspondingly increased to 4%. With the PtCu4 catalyst pretreated at high temperature, the initial ethylene selectivity was only 15%, the other 85% of the product stream was ethane (Fig. 6B). By the time the second sampling of the effluent stream was made, roughly an hour later, the ethylene selectivity was 92% and the ethane selectivity was 8%. Thereafter, the ethylene selectivity increased at the expense of ethane to 98% by the end of the 40 h reaction.

For the PtCu5 catalyst pretreated at low temperature, the initial ethylene selectivity was 100% and remained essentially constant (Fig. 7A). However, with the PtCu5 catalyst pretreated at high temperature, the initial ethylene selectivity was only 38%, with ethane comprising the other 62% of the product stream (Fig. 7B). By the



Fig. 7. Time on stream behavior of PtCu5/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B) in the reaction of 1,2-dichloroethane (7000 ppm) and H₂ (35,000 ppm) in He at 200 °C (total flow rate 41 mL/min): \bigcirc – Ethylene, \square – Ethane.



Fig. 8. FTIR spectra of room temperature CO adsorption on Pt/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B).

second sampling of the product stream, roughly an hour later, the ethylene selectivity had increased to 83% at the expense of ethane. And thereafter the ethylene selectivity continued to increase to 96% at the expense of ethane by the end of the 40 h reaction time.

3.2. Temperature programmed desorption (TPD) and reduction (TPR) investigations

It must be acknowledged that the rate of species evolution measured during temperature-programmed investigations with powdered catalysts such as the type conducted for this work depend on many parameters including the geometry of the system, the mass of sample, and the extent to which the powdered material has been compacted during waferization [14]. Thus, the results presented herein emphasize the qualitative behavior and the relative trends, as opposed to asserting an undue level of quantitative detail given the scope of this research investigation.

For all of the as prepared catalysts, both H_2O and HCl evolved during the temperature-programmed desorption experiment. The desorption of H_2O started at roughly 70 °C, whereas the start of HCl desorption was roughly 100–110 °C for the Pt and bimetallic samples and 120 °C for the monometallic Cu sample.

Gas-phase H₂O and HCl also formed with all of the catalysts during the room temperature to 500 °C TPR after the 130 °C in vacuum treatment. The formation of H₂O occurred over the entire temperature range with all of the catalysts. The formation of HCl occurred at the lowest temperature with the Pt catalyst, roughly 85 °C, and was essentially complete before 150 °C. It formed at the highest temperature with the Cu catalyst, starting at roughly 180 °C and evolving at one rate to the temperature of 225 °C and then continuing from 225 °C to 280 °C at a different rate. The results for the bimetallic catalysts were in between those of Pt and Cu. The formation of HCl started roughly at 130 °C at one rate to the temperature of 160 °C and then continued at a different rate from 160 °C to 225 °C. Carbon monoxide also formed during the TPR, most likely from the decomposition of surface carbonate species, at roughly 250 °C with Pt and the bimetallics and at 280 °C with the Cu catalyst.

For the 200–500 °C TPR experiments conducted after reduction at 220 °C in 10% H_2/Ar , the formation of HCl occurred with all of the catalysts. The onset temperature was roughly 300 °C or more and the amount of HCl formed was approximately 6 times greater with the bimetallics and Cu catalyst than with the Pt catalyst. Water and CO were also formed during the TPR.

3.3. FTIR CO adsorption spectroscopy investigations

3.3.1. Monometallic catalysts

The spectra for CO adsorption on the Pt catalyst are shown in Fig. 8 and are provided as a basis of comparison for the spectra of the five bimetallic catalysts. After both the low temperature and the high temperature pre-reduction, exposure of the Pt catalyst to 10 Torr of CO resulted in the appearance of two spectral bands. The positions of these bands were 2077 and $1834 \,\mathrm{cm^{-1}}$ for the low temperature sample (Fig. 8A) and 2075 and $1768 \,\mathrm{cm^{-1}}$ for the high temperature sample (Fig. 8B). The assignments of these vibrational bands are well established. The high frequency band ($2075-2077 \,\mathrm{cm^{-1}}$) is attributed to CO linearly adsorbed on a Pt atom [10,12,15-17], and the low frequency band ($1768-1835 \,\mathrm{cm^{-1}}$) is attributed to CO with two and three fold coordination to Pt atoms [15,16]. The evacuation of the gas phase for 15 min resulted in band shifts of less than $10 \,\mathrm{cm^{-1}}$ to lower frequency band, which is indicative of a small change in the coverage of CO due to the strong CO–Pt interaction.

The adsorption of CO on Cu (not shown) has also been studied by infrared spectroscopy. The band positions (excluding zeolite systems) have been found to fall in different regions for each metal oxidation state: $Cu^0 - 2110 \text{ cm}^{-1}$ and lower, $Cu^{1+} - 2110$ to 2140 cm^{-1} , and $Cu^{2+} - 2145 \text{ cm}^{-1}$ and above [18]. These ranges are considered typical for Cu species of oxides and on oxide supports. The interaction strength of CO with Cu^0 and with Cu^{2+} is very weak, to the extent that such adsorption complexes are unstable at room temperature in the absence of a CO partial pressure. The $CO-Cu^{1+}$ interaction is comparably stronger, and thus more robust evacuation conditions are required for the CO to desorbs. Most importantly, the lack of stability of CO adsorbed on Cu species as compared to CO adsorbed on Pt allows the adsorption bands for the bimetallic catalysts to be readily classified by metal type, as described below.

3.3.2. Bimetallic catalysts

For the PtCu1 catalyst pre-reduced at low temperature, exposure to 10 Torr of CO resulted in the appearance of two vibrational bands: one at 2137 cm⁻¹ and the other at 2036 cm⁻¹ (Fig. 9A). The intensity of the band at 2137 cm⁻¹ decreased by 70% after 0.5 min of evacuation and to the baseline after evacuation for 15 min. The intensity of the 2036 cm⁻¹ band changed little during the evacuation, based on peak height, but the band maximum shifted to 2044 cm⁻¹. After pre-reduction at high temperature, exposure to 10Torr of CO resulted in the appearance of three spectral features: a band at 2125 cm⁻¹, a convoluted band at 2052 cm⁻¹, and a broad band at 1753 cm⁻¹ (Fig. 9B). The intensity of the 2125 cm⁻¹ band decreased by 4% after 0.5 min evacuation, whereas the band at 2052 cm⁻¹ increased 7% in intensity. After 15 min evacuation, the intensity of the 2125 cm⁻¹ had decreased to 30% of its original size and the intensity of the 2052 cm⁻¹ had increased to 133% of its original size. It should also be noted that the shape of the band at $2052 \, \text{cm}^{-1}$ became more symmetric after evacuation of



Fig. 9. FTIR spectra of room temperature CO adsorption on PtCu1/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B).



Fig. 10. FTIR spectra of room temperature CO adsorption on PtCu2/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B).

the gas phase. The broad band at 1753 cm⁻¹ remained essentially unchanged during the evacuation procedure.

For the PtCu2 catalyst pre-reduced at low temperature, exposure to 10 Torr of CO resulted in the appearance of two bands: 2137 and 2033 cm⁻¹ (Fig. 10A). The intensity of the band at 2137 cm⁻¹ decreased by 74% after 0.5 min of evacuation and to the base-line after evacuation for 15 min. The intensity of the 2033 cm⁻¹ band changed little during the evacuation, but the band maximum shifted 2038 cm⁻¹. After pre-reduction at high temperature, exposure to 10 Torr CO resulted in a band at 2129 cm⁻¹ and a band at 2050 cm⁻¹ that had a shoulder feature at 2018 cm⁻¹ (Fig. 10B). The intensity of the 2129 cm⁻¹ band decreased by 35% after 0.5 min

evacuation, whereas the band at 2050 cm^{-1} increased by 17%. After 15 min evacuation, the intensity of the 2125 cm^{-1} had decreased to 16% of its original size and the intensity of the 2050 cm^{-1} had increased to146% of its original size. The prominence of the low frequency shoulder feature also decreased with evacuation time.

For the PtCu3 catalyst pretreated at low temperature, exposure to 10 Torr of CO resulted in the appearance of two bands: 2139 and 2029 cm⁻¹ (Fig. 11A). After evacuation for 0.5 min, the intensity of the high frequency band decreased by 66% and the resulting band showed maxima at 2150 and 2135 cm⁻¹. After 15 min of evacuation the band intensity had decreased to the baseline. However, the low frequency band intensity was stable to evacuation, based



Fig. 11. FTIR spectra of room temperature CO adsorption on PtCu3/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B).



Fig. 12. FTIR spectra of room temperature CO adsorption on PtCu4/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B).



Fig. 13. FTIR spectra of room temperature CO adsorption on PtCu5/SiO₂ pre-reduced at 220 °C (A) and 500 °C (B).

on peak height, but the band position shifted from $2029 \,\mathrm{cm}^{-1}$ to $2042 \,\mathrm{cm}^{-1}$. After pre-reduction at high temperature, exposure to 10 Torr CO resulted in a high frequency band at $2123 \,\mathrm{cm}^{-1}$ and a low frequency band at $2042 \,\mathrm{cm}^{-1}$ with shoulder feature at $2015 \,\mathrm{cm}^{-1}$ (Fig. 11B). The intensity of the high frequency band decreased by 22% after 0.5 min evacuation, whereas the band at $2038 \,\mathrm{cm}^{-1}$ increased by 16%. After 15 min evacuation, the intensity of the 2123 cm⁻¹ had decreased to 33% of its original size and the intensity of the 2038 cm⁻¹ had increased to 157% of its original size. The prominence of the low frequency shoulder feature also decreased with evacuation time.

For the PtCu4 catalyst pretreated at low temperature, exposure to 10 Torr of CO resulted in the appearance of two bands: 2140 and 2031 cm⁻¹ (Fig. 12A). After evacuation for 0.5 min, the intensity of the high frequency band decreased by 77% and the resulting band showed maxima at 2150 and 2135 cm⁻¹. After 15 min of evacuation the band intensity had decreased to the baseline. The low frequency band intensity was stable to evacuation, but the band position shifted from 2031 cm⁻¹ to 2038 cm⁻¹. After pre-reduction at high temperature, exposure to 10 Torr CO resulted in a high frequency band at 2127 cm^{-1} and a low frequency band at 2038 cm^{-1} with shoulder feature at 2016 cm⁻¹ (Fig. 12B). The intensity of the high frequency band decreased by 28% after 0.5 min evacuation, whereas the band at 2038 cm⁻¹ increased by 24%. After 15 min evacuation, the intensity of the 2127 cm^{-1} had decreased to 20%of its original size and the intensity of the 2038 cm⁻¹ had increased to 183% of its original size. The prominence of the low frequency shoulder feature also decreased with evacuation time.

For the PtCu5 catalyst pretreated at low temperature, exposure to 10 Torr of CO resulted in the appearance of two bands: 2142 and 2029 cm⁻¹ (Fig. 13A). After evacuation for 0.5 min, the intensity of the high frequency band decreased by 77% and the resulting band showed maxima at 2150 and 2133 cm⁻¹. After 15 min of evacuation the band intensity had decreased to the baseline. However, the low frequency band intensity was essentially stable to evacuation, but the band position shifted from 2029 cm^{-1} to 2036 cm^{-1} . After pre-reduction at high temperature, exposure to 10 Torr CO resulted in a high frequency band at 2125 cm⁻¹ and a low frequency band at 2044 cm^{-1} with shoulder feature at 2015 cm^{-1} (Fig. 13B). The intensity of the high frequency band decreased by 28% after 0.5 min evacuation, whereas the band at 2044 cm⁻¹ increased by 22%. After 15 min evacuation, the high frequency band intensity had decreased to 16% of its original size and the intensity of the low frequency band (2044 cm⁻¹) had increased to 181% of its original size. The prominence of the low frequency shoulder feature also decreased with evacuation time.

4. Discussion

The kinetics results of this investigation show that the prereduction temperature affects the performance of the catalysts – significantly for the bimetallic catalysts with the lowest Cu to Pt atomic ratio and not so much for those with the highest ratio. The question of why will be addressed first through the proposal of descriptive models for the evolution of the catalysts during the low temperature pretreatment and during the high temperature pretreatment. Then, the salient trends and features of the reaction kinetics will be discussed in the context of the catalysts that result from the two different pretreatments.

4.1. Evolution of bimetallic catalysts pre-reduced at low temperature

The temperature-programmed desorption results show that during the initial drying step both HCl and H₂O evolve, indicating the formation of chlorides, hydroxychlorides, and oxychlorides of the metals on the support surface [19]. Based on the temperature-programmed reduction results, some fraction of these species most likely contain both types of metals, as the temperature range in which HCl forms during TPR with the bimetallic catalysts (130–225 °C) is in between that for the Pt catalyst (85–150 °C) and the Cu catalyst (180–280 °C), both of which are in good agreement with reported literature values [19–23]. As well, the lack of HCl formation in the 85–130 °C range argues against the formation of a significant separate Pt phase during the drying step [24]. However, the possibility of Cu only species cannot be excluded, and indeed seems likely with the catalysts having the highest Cu to Pt atomic ratios.

From the start of the low temperature pre-reduction to its end, the metal containing entities converts only from more chlorinated to less chlorinated, not to zero valent metal. This is evident from the formation of HCl during the TPR conducted after the low temperature pre-reduction step. As well, the formation of particles with highly chlorinated surfaces may be inferred from the FTIR CO adsorption results (Figs. 9A-13A) and the assessment of the most viable assignment for the high frequency absorption band at 2137–42 cm⁻¹. The band is too unstable under evacuation conditions to be attributed to a CO-Pt adsorption complex, and the band position is too high in frequency to assign to CO adsorbed on Cu⁰ (2110 cm⁻¹ and below [18]). And although the frequency is in the range for CO adsorbed on Cu⁺¹ of non-zeolitic oxide moieties and materials (2110–2140 cm⁻¹ [18]), the lack of stability of the band in the absence of gas-phase CO is inconsistent with the relatively strong interaction between CO and Cu⁺¹. However, both the band position and lack of stability under evacuation conditions fit with an assignment of CO adsorbed on CuCl, which has a reported frequency of 2134–36 cm⁻¹ and an adsorption enthalpy low enough that the adsorption behavior is reversible at 373 K [25]. Further, the positions of the two peak maxima $(2150 \,\mathrm{cm}^{-1})$ and 2133-35 cm⁻¹) that are clearly identifiable with the three high Cu content catalysts after 0.5 min evacuation agree surprising well with assignments reported for CO adsorbed on disordered CuCl films (2144 and 2125 cm⁻¹) [25]. Highly chlorinated particle surfaces also serve to explain the negligible volume of CO uptake in the chemisorption measurements with these catalysts.

In putting forth a model describing the series of steps that occur during the low temperature reduction with H₂, a primary point to consider is the temperature used was low enough that the reduction of the dried precursor species occurred slowly and not to completion during the allotted time period. As well, prior investigations have shown that both platinum and copper chloride moieties/clusters are mobile on oxide supports in this same temperature range [23,26,27]. Thus, following an initial step in which HCl and H₂O evolve as the precursor species formed during the drying stage are reduced to metal chloride moieties, surface diffusion of chlorinated species becomes a factor in the supported bimetallic particle assembly process.

Platinum-chlorine bonds reduce more readily than copper-chlorine bonds, based on the TPR results herein and in the literature, so atoms and/or clusters of Pt with metallic character should form more readily than their Cu counterparts. In essence, in this step the support becomes decorated with metal sites consisting mostly of Pt atoms, as the other chloride moieties diffuse about surface and any remaining precursor species undergo the initial partial reduction to form the mobile intermediates. These newly formed Pt sites are participants in the next evolutionary step. They catalyze the dissociation of H_2 and thus serve as stationary sources of H atoms. Mobile species that diffuse to these site are provide with the H atoms necessary to hydrogenate their metal–chlorine bonds, and by this process particle growth occurs one layer after another. Of course, it is also possible that H atoms formed on the Pt sites spillover to the support and surface diffuse to react with some metal chloride or other precursor species. However, regardless of the net direction of diffusion, the faster rate of platinum-chlorine bond hydrogenation, as compared to the hydrogenation of copper–chlorine bonds, drives the growth of particles with Pt-rich cores and outer layers rich in Cu. Based on the FTIR results, CuCl is present at the outer most layers.

The above description is consistent a prior investigation of supported RuCu bimetallics that showed using metal chloride precursors, rather than metal nitrates, favored the formation of bimetallic particles having surfaces covered by Cu [28]. While the aforementioned kinetics pathway involving mobile surface species most likely controls the assembly process that occurs during the low temperature reduction, it should also be noted that thermodynamics favors formation of particles with surfaces enriched in Cu. Indeed, vacuum conditions alone are sufficient to induce some surface segregation of Cu [29,30], as Cu has a lower solid–vapor surface free energy than Pt [31]. And more pronounced surface enrichment in Cu is driven by adsorbed Cl [32–34].

However, neither the particle growth process nor the Cl-induced surface enrichment in Cu results in the complete exclusion of Pt atoms from the surface of the particles, as evidenced by the CO adsorption FTIR spectra that show a band at 2029–36 cm⁻¹ (Figs. 9A-13A). This band is stable to evacuation and is assigned to CO linearly adsorbed on Pt atoms with nearest neighbor surface atoms of Cu [35–38]. The roughly 40 cm⁻¹ lower frequency compared to that of CO linearly adsorbed on the Pt catalyst (2075–77 cm⁻¹) is a results of the decrease in the CO dipole–dipole coupling that occurs when the surface ensembles of Pt are large and the coverage of CO is high [39,40]. That some Pt atoms are always at the surface of the bimetallic particles is not surprising given the presence of H₂ in the gas phase and the stronger adsorbate-metal interaction of hydrogen with Pt [41-43] than Cu [44,45]. Indeed, in the absence of Cl with H₂ present an enrichment of the surface in Pt would be expected [46].

4.2. Evolution of bimetallic catalysts pretreated at high temperature

In contrast to the low temperature reduction pretreatment step, the high temperature reduction at 500 °C is sufficient to remove the majority of the Cl. This is evident from the TPR results of this investigation and others showing that HCl formation ceases by 300 °C, even for monometallic Cu catalysts [20-22]. It is also reflected in the FTIR band position for CO adsorbed on the Cu species of the bimetallic catalysts (Figs. 9B-13B). At 2123-29 cm⁻¹, the band is approximately 10 cm⁻¹ lower in frequency than the band assigned to CO adsorbed on CuCl after the low temperature pre-reduction. It is also more stable under evacuation conditions - albeit certainly less stable than bands associated with CO adsorbed on Pt species. Although the frequency range is typical for CO adsorbed on Cu⁺¹, the fact that the band intensity decreases under evacuation conditions and the reduction temperature was sufficiently high to reduce Cu⁺¹ species are two reasons cited in the past to preclude an assignment of CO on Cu⁺¹ [10]. However, attributing the band to CO adsorbed on Cu⁰ requires an accounting for a position well about the typical range of 2110 cm⁻¹ and below [18]. One viable option is an electronic modification by neighboring Pt atoms that increases the CO-Cu⁰ interaction strength, as XPS and UPS investigations have shown a Cu core-level binding shift of -0.5 eV for Cu overlayered

on Pt foil [47]. The FTIR results do provide evidence that the Cu atoms are in atomic closeness with Pt atoms. First, the shoulder band at 2015–18 cm⁻¹ is associated with CO bridged between a Pt and a Cu [48]. And second, the intensity increase in the CO–Pt band during evacuation is indicative of an energy intensity redistribution effect [49].

In putting forth a description of the series of events that occur during the high temperature reduction, a reasonable starting point for consideration is that all of the steps described for the low temperature reduction occur and then some more. The point of experimental departure occurs at 220 °C, where the temperature is further increased to 500 °C and then held there for 2 h. Thus, instead of 2 h at 220 °C during which the hydrogenation rate slows while remaining metal chloride species move about and assemble, hydrogenation of Cl continues to near completion as the temperature advances towards 500 °C. Based on the TPR results, the majority of chlorine has been removed by the time the temperature reaches 300 °C. Progressively, there is less Cl driving Cu to the surface, and the effects of an ongoing thermal treatment in a partial pressure of hydrogen become important. Adsorbed hydrogen induces surface enrichment in Pt [50-52]. The end result, therefore, is supported particles that are both more surface rich in Pt and more metallic than their low temperature reduced counterparts. The difference in the two is particularly apparent from the spectra of CO adsorption on PtCu1 (Fig. 9). The characteristic broad band for CO bound to two and three Pt atoms $(1750-1860 \text{ cm}^{-1})$ is present after the high temperature pre-reduction – a reflection of the large surface ensembles of Pt atoms, whereas the same band is absent after the low temperature pre-reduction. As well, the intensity of the linearly adsorbed CO-Pt (2038–52 cm⁻¹) is larger after the high temperature pre-reduction than after the low.

Not surprisingly, increasing the amount of Cu relative to Pt at the impregnation stage places a limit on the amount of Pt that may segregate to the surface. This is demonstrated by the increase in the intensity of the FTIR band for CO on Cu $(2123-29 \text{ cm}^{-1})$ relative to the band for CO on Pt $(2036-52 \text{ cm}^{-1})$ as a function of increasing Cu to Pt atomic ratio in the catalyst (Figs. 9B–13B).

4.3. Impact of catalyst pretreatment on catalyst performance

The kinetics results show that the catalyst pretreatment has the most impact on the bimetallic catalysts with the least amount of Cu. With Pt1Cu1, Pt1Cu2, and Pt1Cu3 the ethylene selectivity is higher after low temperature pre-reduction at all time on stream than after the high temperature pretreatment. The difference is the largest with Pt1Cu1 and the smallest with Pt1Cu3, as increasing the Cu content increases the ethylene selectivity for both the low and high temperature pretreated catalysts. With the PtCu4 and PtCu5 catalysts, the ethylene selectivity is only higher after low temperature reduction during the first hour or so of time on stream. Thereafter the selectivity is approximately the same, in the 90+% range.

As discussed above, the use of metal chloride precursors and a low pre-reduction temperature results in supported particles with a preferential concentration of Pt in the core and Cu at the outer surface, and surface layers better described as a metal chloride than zero valent metal. In comparison, the supported particles have surfaces enriched in Pt after the high temperature pre-reduction. This difference is most apparent with the PtCu1 catalyst, which has Pt ensembles large and numerous enough after the high temperature pre-reduction to exhibit a FTIR absorption band for CO adsorbed with two-fold and three fold coordination to Pt atoms. This catalyst exhibited essentially the same product selectivity as monometallic Pt. Its low temperature pre-reduced counterpart, with less Pt at the surface, yielded more ethylene than ethane. And by increasing the amount of Cu at the surface by increasing the Cu to Pt atomic ratio used for the synthesis, the selectivity towards ethylene is increased at the expense of ethane.

These results support a mechanistic proposal that was put forth in earlier investigations [10,12,13,53]. Namely, that ethane forms by a reaction pathway involving sites containing only Pt atoms. Copper not only inhibits this overall reaction, but is also a site for the conversion of 1,2-dichloroethane to ethylene. Higher surface concentrations of Cu yield higher selectivities of ethylene, because there are fewer Pt sites of sufficient size to catalyze the dissociative adsorption of 1,2-dichloroethane and subsequent steps in forming ethane. Yet, the small ensembles of one or a few Pt atoms still available even at the highest Cu to Pt atomic ratio readily catalyze the dissociative adsorption of H₂ to generate the H atoms necessary to hydrogenate the Cl atoms deposited on Cu. Thus, using a pretreatment that selectively segregates Cu to the surface and increasing the amount of Cu relative to Pt both inhibits the total hydrogenation pathway and promotes the partial hydrogenation catalysis.

A fair question to ask is to what extent the catalyst pretreatment affects the performance of the catalyst with increasing time on stream. The proposed models for the transformations the catalysts undergo as a function of reduction conditions provide a description of the catalysts at the start of the reaction. With a reactant stream containing both a chlorinated molecule and H₂ the relative tug of Cu by chlorine and pull on Pt by hydrogen is determined by the composition of the gas phase. Yet, the conversion as a function of time on stream for all the catalysts is remarkably constant, behavior often used to infer little change in a catalyst with time on stream. But with several catalysts the product selectivity changes appreciably during the first 10 or so hours on stream despite an unremarkable change in conversion. Most notable in this regard is the behavior of the PtCu2 catalyst in comparison to the PtCu1 catalyst.

If only to consider the PtCu1 behavior, it would be tempting to attribute the stability in both selectivity and conversion with time on stream to bimetallic particles more stable than the proposed egg and shell type particles, namely ordered PtCu containing alternating layers of Cu and Pt atoms on (111) planes that is stable below 812 °C [54]. The preferential formation of particles with Pt terminated planes during high temperature reduction and particles with Cu terminated planes during low temperature reduction would account for the difference in selectivity. Yet with PtCu2, which does not form an ordered phase, attributing the change in selectivity with time on stream to reaction gas induced surface enrichment - in Pt after low temperature reduction and in Cu after high temperature reduction – is seemingly at odds with the conversion remaining constant. Indeed, one premise of the dual site model is the dissociative adsorption of 1,2-dichloroethane is forced to occur on copper site by making the ensembles of Pt too small to catalyze the step. In other words, the rate of ethane formation on Pt is faster than the rate of ethylene formation catalyzed by a bimetallic. Thus, there must be more to the story.

One possibility is the ethane and ethylene formation pathways share a common rate-determining step, which would mean the intrinsic activity of the Pt sites in the bimetallic catalysts for one or more steps involved in ethane formation are substantially lower than those of freshly pretreated Pt. In fact, the activity of the Pt sites in the bimetallics is comparable to the activity of the Pt catalysts after several tens of hours time on stream (Fig. 1). As treatment in chlorine is actually used to reverse particle sintering with supported platinum catalysts [26,55,56], the conversion decrease is probably not due to a loss in metal dispersion. However, the metal may be gradually becoming more metal chloride in nature, which is less active for the 1,2-dichloroethane to ethane reaction. And it would not be surprising that the Pt sites in the bimetallics would be more rapidly chlorinated as the TPR results show Cu inhibits the overall chlorine hydrogenation rate in comparison to pure Pt. Thus, one consistent, albeit speculative, accounting for the time on stream behavior of the bimetallic catalysts is that the single site ethane formation pathway and the dual site ethylene formation pathway share a common rate-determining step involving the second half reaction of the catalytic cycle - the hydrogenation of the surface species formed from the dissociative adsorption of 1,2-dichloroethane. Either the formation of hydrogen ad-atoms could be the slow step, or the hydrogenation of chlorine could be rate-determining - assuming the direct and indirect mixed metal effects render it roughly the same from both types of site in the bimetallic. However, selectivity would be governed by the relative rates of a step earlier in the mechanisms of the reactions such as the relative rate of 1,2-dichloroethane dissociative adsorption on Cu and on Pt sites. Thus, changes in the surface composition of the particles induced by the reaction gases during time on stream would change the fraction of reactant converted on each type of site, but not the overall amount of reactant converted.

5. Conclusions

The use of platinum and copper metal chloride precursors and a low pre-reduction temperature (220 °C) yields silica supported particles with platinum-rich cores coated with copper-rich layers that are still well-chlorinated. The first step in the formation of these particles is the reduction of Pt containing moieties, which is then followed by surface diffusion of Cu chloride moieties to the Pt sites where their reduction, at least partial, takes place. The presence of Cl plays a critical role in the evolution of egg and shell type particles as a ligand that facilitates surface mobility of metal moieties and is more difficult to reduce when coordinated to copper than platinum. In contrast, particles that are more metallic and have higher surface concentrations of Pt result from pre-reduction at high temperature (500 °C). Essentially all of the chlorine is hydrogenated before the temperature reaches 500 °C and the continued hydrogen treatment at 500 °C drives H-adsorbate induced surface enrichment in Pt. Increasing the relative amount of copper compared to platinum offsets the enrichment effects.

Ethane, the total hydrogenation product of the reaction between 1,2-dichloroethane and H_2 , forms most readily on the bimetallic catalysts with the lowest Cu to Pt atomic ratio, especially those pre-reduced at high temperature. It is concluded that all reaction steps in the catalytic formation of ethane occur on Pt sites, which are intrinsically less activity than Pt only for one or more step in the overall reaction. The transformation of 1,2-dichloroethane to ethylene involves sites of Cu and hydrogen atoms from platinum sites to react with chlorine. A common rate determining step involving chlorine removal with the bimetallic catalysts could explain the trend of conversion remaining essentially constant as the ethylene to ethane selectivity changes. And both surface enrichment with respect to a specific metal and extent of chlorine oxidation of the metal surface layer driven by the reaction gas composition may account for the time on stream selectivity changes.

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