Dechlorination of 1,2-dichloroethane catalyzed by Pt–Cu/C: unraveling the role of each metal

Lalith S. Vadlamannati, Vladimir I. Kovalchuk and Julie L. d'Itri *

Department of Chemical Engineering, University of Pittsburgh, Pittsburgh, PA 15261, USA
E-mail: jditri@pitt.edu

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The effect of Pt–Cu/C catalyst composition on the activity and selectivity in the reaction of 1,2-dichloroethane dechlorination in a H_2-containing atmosphere has been investigated. For monometallic Pt catalysts and those with Cu/Pt atomic ratio $\leqslant 1$, the reaction products are almost entirely ethane and monochloroethane. However, increasing the Cu/Pt ratio increases the selectivity towards ethylene. Approximately 90% selectivity towards ethylene is obtained for catalysts with Cu/Pt ratio $\geqslant 9$. Monometallic Cu/C produce only ethylene, but the activity is two orders of magnitude lower than that of other catalysts studied. With time on stream during the initial 2–30 h there is a continuous increase in selectivity towards ethylene at the expense of ethane. This behavior was rationalized in terms of equilibration of bimetallic particle surface composition exposed to the reaction mixture.

Keywords: hydrogen-assisted dechlorination, 1,2-dichloroethane, ethylene, carbon, platinum, copper

1. Introduction

Noble metal catalysts are active for a wide variety of reactions such as dehydrogenation [1], hydrogenolysis [2], hydrodechlorination [3,4], etc. Among the noble metals Pt and Pd have the lowest activity towards ethane hydrogenolysis [5] and Pt exhibits the highest activity towards carbon–halogen bond fission [3,6]. In the hydrodechlorination reaction it is speculated that the noble metal participate in a catalytic cycle in which the metal surface is chlorinated by the chlorinated molecule and then chlorine is removed from the surface via reduction by hydrogen adatoms [6,7]. However, the high reactivity of hydrogen adatoms on noble metals results in hydrodechlorination of chlorohydrocarbons to form paraffins. For example, the main product of ethylchloride hydrodechlorination catalyzed by Pt or Pd was ethane. In contrast, with nickel and iron, ethylene was formed during the same reaction [6].

Addition of a second metal to a noble metal has been shown to alter its catalytic behavior significantly [5,8,9]. Electronic properties of each metal component may change because of alloying, resulting in different catalytic behavior. In addition, dilution of one metal by another during alloying also effects catalytic properties due to a change in the geometry of active sites [10]. Such chemistry of bimetallic catalysts manifests itself in changes in adsorption energetics of reactants and reaction products resulting in higher activity [11,12] or suppression of side reactions resulting in higher selectivity [12–14].

Even though there is a considerable amount of literature available on the dehydrogenation reactions catalyzed by bimetallic catalysts, there is a deficiency of information concerning dechlorination reaction catalyzed by bimetallic catalysts [15–17]. Of particular interest is the idea that various metals could catalyze the formation of olefins and coupling products from chlorinated hydrocarbons. This paper addresses the effect of bimetallic catalyst composition on the activity and selectivity towards the dechlorination of 1,2-dichloroethane. A series of carbon-supported bimetallic Pt–Cu catalysts was chosen for the present investigation. A kinetic study, wherein the atomic ratio of Pt and Cu in the catalyst has been varied in order to understand its effect on the dechlorination reaction chemistry, is reported in this work.

2. Experimental

2.1. Catalyst preparation and characterization

Activated carbon BPL F3, 6–16 mesh, (Calgon Carbon Corporation) was crushed and sieved; a fraction of 24–60 mesh (1400 m^2/g surface area; 2.4 nm average pore diameter, BET data) was used as a support. The support was then co-impregnated with aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ (Alfa, 99.9%) and $CuCl_2 \cdot 2H_2O$ (MCB Manufacturing Chemists, Inc., 99.5%). The material was allowed to equilibrate overnight before drying at ambient temperature and pressure for 24 h. It was then dried at 100 °C for 2 h in vacuum (~25 Torr). The catalyst nomenclature is defined according to the Pt to Cu ratio. For example, a catalyst with Pt to Cu ratio of 1 : 3 is referred to as Pt1Cu3.

BET and chemisorption measurements were carried out using a volumetric sorption analyzer ASAP 2010 and ASAP 2010 Chemi (Micromeritics®). The metal–adsorbate ra-

* To whom correspondence should be addressed.

tio was determined from the irreversibly adsorbed CO, H_2 or O_2. The adsorption stoichiometry was assumed to be equal to 1 for CO and 2 for both H_2 and O_2. For each catalyst CO, H_2, O_2 chemisorption and titration of adsorbed oxygen with H_2 (HT) were performed on the same sample at 35 °C. Prior to measurement, the catalyst was reduced at 300 °C for 2 h and at 350 °C for 1 h in H_2 flow. This was followed by evacuation for 1.5 h at 350 °C. Then the catalyst was cooled, CO chemisorption was performed and the catalyst was reduced at 350 °C for 1 h and evacuated for 1.5 h at the same temperature. Next, H_2 chemisorption was conducted after which the catalyst was again evacuated at 350 °C for 1.5 h. This was followed by O_2 chemisorption, evacuation at 35 °C for 1 h and H_2 titration.

2.2. Catalytic experiments

The dechlorination of CH_2ClCH_2Cl was carried out at atmospheric 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 catalyst temperature was measured and controlled with an accuracy of ±1 °C using a temperature controller (Omega model CN2011). Reactants were metered using mass flow controllers (Brooks Instruments model 5850E) and mixed prior to entering the reactor.

Liquid CH_2ClCH_2Cl was maintained at 0 °C and metered into the reaction system via a saturator using He as the carrier gas. Saturation was confirmed by varying the flowrate of helium through the saturator and quantifying the CH_2ClCH_2Cl in the gas phase by a gas chromatograph (GC). The reactor effluent was analyzed by on-line GC and, when necessary, GC/MS to identify the reaction products. The GC (Varian 3300 series) was equipped with a 10 ft 60/80 Carbopack B/5% Fluorocol packed column (Supelco) and a flame ionization detector (FID) capable of detecting concentrations >1 ppm for chlorocarbons and hydrocarbons. The on-line HP GC/MS system consisted of a HP 5890 series II plus GC (also equipped with a Fluorocol column) connected to a HP 5972 mass-selective detector. Hydrogen chloride, a reaction product was detected by GC/MS but not quantified.

Prior to reaction, the catalyst was dried in flowing He (30 ml/min) while it was heated from 303 to 403 K at the rate of 3.3 K/min and then held at 403 K for 60 min. Next, the gas stream was switched to a reducing mixture of H_2 (10 ml/min) and He (50 ml/min) and the catalyst was heated from 403 to 493 K at a rate of 4 K/min and held at 493 K for 90 min. The catalyst was then cooled in He (50 ml/min) to the desired reaction temperature.

For a standard dechlorination reaction, 0.1 g of the catalyst was used and the total flow of the reactant mixture was 41 ml/min consisting of CH_2ClCH_2Cl (7,000 ppm), H_2 (36,600 ppm) and He as the balance. The reaction temperature was maintained at 473 K until steady state was achieved. Steady state was defined as a change in conversion of less than 0.2% and a change in product selectivities of less than 1% in a 5 h TOS. In order to compare selectivities, the weight of each bimetallic catalyst was adjusted to maintain the conversion at comparable levels (4–5%). However, for Cu/C the conversion could not be raised beyond 1%, even with 200 mg of catalyst and a total reactant flow of only 3 ml/min.

In all experiments the conversion of reactants was maintained below 5%. It was demonstrated in a special experiment that there is a linear relationship between conversion and space velocity for CH_2ClCH_2Cl dechlorination over Pt–Cu/C at conversions between 0 and 6%, suggesting the absence of transport limitation.

3. Results

3.1. Characterization

The results of chemisorption measurements of carbon-supported monometallic Pt, Cu and bimetallic PtCu catalysts, as well as of pure support are listed in table 1. The main feature of these results is the negligible hydrogen uptake. Similar observations were reported by Krishnakutty and Vannice, who found that for carbon-supported Pd the equilibrium hydrogen coverage was significantly

Table 1
Irreversible gas uptakes and apparent dispersions of (Pt + Cu)/C catalysts.

Catalyst composition (wt%)	Pt/Cu (at. ratio)	Uptake (μmol/g_{cat})				Apparent dispersion (%)			
		CO	H_2	O_2	H_2 (HT)	CO/Pt_t	H/Pt_t	$O/(Pt+Cu)_t$	H/Pt_t (HT)
Support	–	0	0	3.0	0	–	–	–	–
0.49Pt	∞	6.8	0.2	9.0	8.5	26.5	1.7	70.5	66.4
0.49Pt + 0.05Cu	3:1	10.0	0.2	10.8	6.9	39.8	1.4	65.7	64.1
0.49Pt + 0.16Cu	1:1	13.2	0.5	13.0	8.0	52.4	4.0	51.8	50.7
0.49Pt + 0.32Cu	1:2	10.9	0.5	23.6	4.7	43.6	3.9	62.6	37.8
0.49Pt + 0.48Cu	1:3	10.4	0.3	23.5	3.2	41.5	2.5	46.8	25.5
0.48Pt + 0.95Cu	1:6	11.0	0.4	23.3	1.9	44.8	3.0	26.8	15.4
0.47Pt + 1.40Cu	1:9	12.1	0.6	26.5	0.9	49.1	5.0	21.7	7.2
0.46Pt + 2.80Cu	1:18	10.7	0.4	28.1	0.7	45.2	3.6	12.1	5.9
0.49Cu	0	0	0	22.4	0	–	–	56.9	–
1.92Cu	0	0	0	29.7	0	–	–	19.6	–

Table 2
Steady-state kinetics parameters of (Pt + Cu)/C catalysts for the hydrodechlorination of 1,2-dichloroethane.

Catalyst	Time on stream for steady state (h)	Conversion (%)	Selectivity (mol%)			Activity ($mol\,min^{-1}\,g_{cat}^{-1}$)
			C_2H_4	C_2H_6	C_2H_5Cl	
Pt	14	4.0	6	92	2	1.7
Pt1Cu1	24	4.4	3	95	2	6.6
Pt1Cu2	61	4.4	67	33	0	2.5
Pt1Cu3	67	4.3	77	23	0	5.1
Pt1Cu6	81	4.1	81	19	0	2.2
Pt1Cu9	23	5.0	87	13	0	2.5
Pt1Cu18	22	4.5	87	13	0	2.4
Cu	16	0.6	100	0		0.03

lower compared to Pd supported on oxides [18]. The CO/Pt ratios were similar for all bimetallic catalysts and substantially higher than that for the monometallic Pt/C catalyst (table 1). Both Pt and Cu chemisorbed O_2 and the uptake of oxygen increased with increasing Cu/Pt ratio, viz. increased loading. However, the O/(Pt + Cu) ratios decreased with increasing metal loading reflecting a general trend in dispersion. It is worth noting that pure support also adsorbed oxygen irreversibly. The uptake of oxygen on the carbon support was negligible related to total carbon surface area, but significant compared to O_2 uptakes of the catalysts (table 1). The results of hydrogen titration (table 1) do not correlate with those of CO chemisorption; H/Pt_t ratios decreased with increasing Cu/Pt atomic ratio. It is important to note that Cu is incapable of reducing adsorbed oxygen at 35 °C.

Thus, these chemisorption data illustrate that a more detailed investigation is required before quantitative dispersion changes are discussed, but a qualitative picture of the relative dispersion can be obtained. For example, from O/(Pt + Cu) ratios it is clear that the mean size of bimetallic particles on the surface decreases as metal loading increases, while the fraction of Pt atoms exposed remains essentially the same as Pt dilutes with Cu. As the main goal of this paper is to understand the selectivity issue, TOFs of the catalysts studied are not addressed in section 4. Dispersion measurement of these Pt–Cu/C catalysts will be, however, the subject of a forthcoming work.

3.2. Kinetic experiments

Both monometallic Pt/C, Cu/C and bimetallic Pt–Cu/C catalysts were active for dechlorination of 1,2-dichloroethane. All catalysts containing Pt had a similar steady-state activity (∼2–7 $\mu mol\,min^{-1}\,g_{cat}^{-1}$) while Cu/C was about two orders of magnitude less active (table 2). The conversion for each catalyst dropped during the first 0.5 h of reaction (a decrease ranging from 4 to 10%) after which it decreased at a rate of ∼0.1% every 5 h (figures 1–3). The Pt1Cu1 exhibited the highest activity (6.6 $\mu mol\,min^{-1}\,g_{cat}^{-1}$) among all the bimetallics.

Increasing the Cu content in the catalyst resulted in an increase in the steady-state selectivity towards ethylene (table 2). For monometallic Pt/C, the major product was

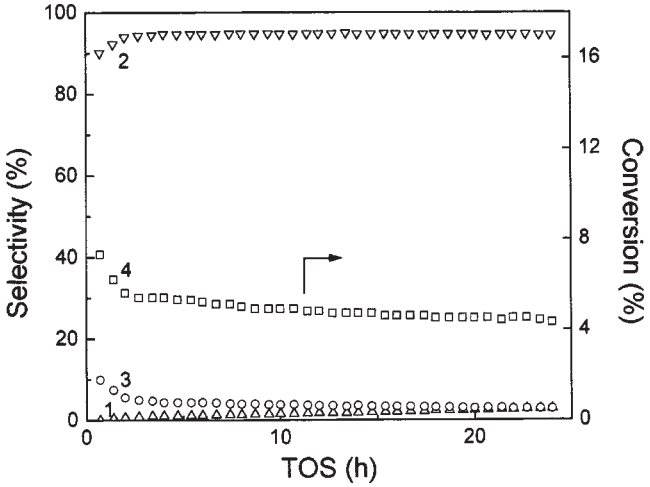

Figure 1. Selectivity vs. time on stream for Pt1Cu1 at 200 °C, 1 – ethylene, 2 – ethane, 3 – chloroethane, 4 – conversion.

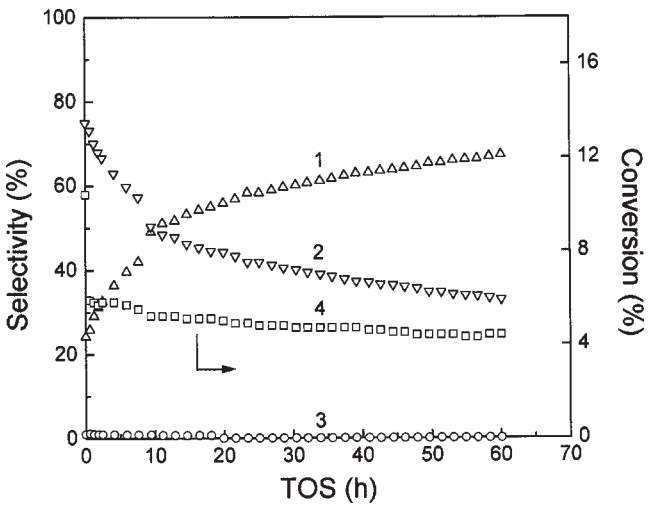

Figure 2. Selectivity vs. time on stream for Pt1Cu2 at 200 °C, 1 – ethylene, 2 – ethane, 3 – chloroethane, 4 – conversion.

ethane (selectivity ∼92%) while the second major product was ethylene (selectivity ∼6%); the selectivity towards chloroethane was less than 2%. Ethane and chloroethane were also the major products with the Pt1Cu1 catalyst – ethane having a selectivity ∼95% and chloroethane ∼2%. However, with a Cu content above the 1 : 1 Pt–Cu ratio, the

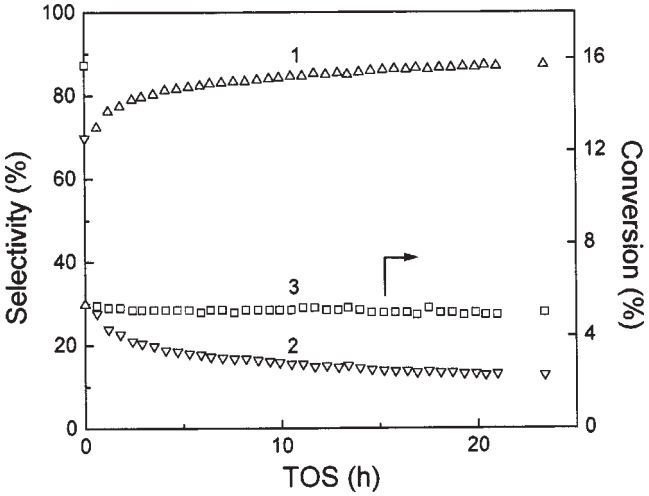

Figure 3. Selectivity vs. time on stream for Pt1Cu9 at 200 °C, 1 – ethylene, 2 – ethane, 3 – conversion.

selectivity towards ethylene increased considerably. The selectivity towards ethylene for Pt1Cu2, Pt1Cu3, Pt1Cu6, Pt1Cu9 and Pt1Cu18 catalysts increased from 67% with Pt1Cu2 to 87% with Pt1Cu18 (table 2). Thus, there is a marked difference in the selectivity of the monometallic Pt, bimetallic Pt1Cu1, and catalysts with higher Cu content.

Although for all catalysts conversion changed less than 0.1% during 5 h on stream, the changes in selectivity were more pronounced before steady state was achieved. As shown in figure 1 for Pt1Cu1 the selectivity towards ethylene, ethane and chloroethane changed by only 4% during the course of the reaction. However, the selectivity towards ethane and ethylene changed dramatically with time on stream (TOS) for Pt1Cu2, Pt1Cu3 and Pt1Cu6 catalysts. Figure 2 represents the typical dependence of selectivity as a function of TOS for these samples. Initially, the catalysts exhibited a much higher selectivity towards ethane than towards ethylene, but at steady state the selectivity patterns are reversed. There was an initial sharp rise in selectivity towards ethylene from 29 to 82% at early (first 5 h) TOS with the Pt1Cu9 catalyst after which it reached a steady-state (15 h TOS) selectivity to ethylene of approximately 87% (figure 3). For the Pt1Cu18 a similar behavior was observed as the Pt1Cu9, viz. a sharp rise in selectivity towards ethylene in the first 5 h and a long period (20 h) during which the selectivity increased by about 2%. No significant change in selectivity towards products with TOS was observed for the monometallic Pt and Cu.

4. Discussion

4.1. Chemical kinetics

Addition of a second metal to a noble metal alters catalytic activity and selectivity significantly in a number of hydrocarbon reactions (H–D exchange, hydrogenolysis, dehydrogenation) [10]. Such results are commonly interpreted in terms of changes in the electronic properties of active sites or changes in the geometry of the site [10]. However, only a few investigations have provided insight into the reaction mechanism, viz. how the second metal changes absolute and relative rates of elementary reaction steps [11,12,19]. This, of course, is the most challenging aspect of obtaining the molecular level understanding of the surface chemistry associated with bimetallic catalysts.

Most interestingly, the present investigation has demonstrated that bimetallic PtCu catalysts, which are highly selective towards ethylene, exhibit activity approximately the same as that of the Pt/C catalyst which is less selective (table 2). The fraction of Pt atoms exposed in the bimetallic PtCu catalysts is even higher than in monometallic Pt/C (table 1). Thus, one must visualize why 1,2-dichloroethane does not react on the Pt sites in PtCu catalysts to form ethane. Classical hydrogenation chemistry would suggest that the ethylene precursor should react with surface H atoms to produce ethane [20].

Because Pt/C readily dechlorinates 1,2-dichloroethane to form ethane, it is reasonable to suggest that the reactant adsorbs on Pt sites, C–Cl bond scission occurs, and then hydrogenation of the surface alkyl fragment readily takes place. Therefore, the lower selectivity of bimetallic catalysts towards ethane infers that C–Cl bond cleavage is significantly suppressed on the Pt sites in PtCu catalysts with Cu/Pt atomic ratio $\geqslant 2$. The reason for this might lie in the structure sensitivity of C–Cl bond hydrogenolysis, which has been suggested by several authors [7,21,22]. The suppressed selectivity of PtCu catalysts towards ethane can be visualized in terms of dilution of Pt by Cu. Hydrogenolysis of a C–Cl bond may require larger Pt ensembles and the addition of Cu decreases the number of sufficiently large Pt islands suitable for the bond scission.

The changes in selectivity with time on stream are also consistent with the idea presented above. Although the bimetallic catalysts were prepared by co-impregnation of the carbon support with aqueous solution of H_2PtCl_6 and $CuCl_2$, mixed crystallites probably do not form during drying. Bimetallic complexes of Pt^{IV} and Cu^{II} have not been previously identified [23,24] and crystal lattice parameters of H_2PtCl_6 and $CuCl_2$ are quite different [25]. It is, therefore, likely that these salts crystallize separately and low temperature reduction (at 220 °C) with H_2 for 1.5 h (see section 2) results in the formation of monometallic Pt and Cu particles together with bimetallic particles with low concentration of either Pt or Cu. It is not expected that the thermodynamically favored PtCu particles form, because surface migration of metal atoms followed by alloying is slow at low temperatures [8]. Thus, catalytic behavior of bimetallic catalysts at the start of the reaction is determined by two types of particles: one with a high Pt concentration which produces ethane as a main product of 1,2-dichloroethane dechlorination and another with a high Cu concentration which produces ethylene. With increasing time on stream the system equilibrates slowly resulting in statistical distribution of both Pt and Cu in bimetallic particles and an increase in the selectivity towards ethylene at the expense

of ethane. Therefore, formation of a surface alloy of Pt and Cu appears to be a key feature of this chemistry.

One must also consider the change in selectivity with time on stream assuming that extensive alloying does indeed occur during the preparation and pretreatment. In this case, the composition of bimetallic particles/surfaces change as the dechlorination reaction proceeds. The driving force for this chemistry is the different energies of H and Cl adsorption on Pt and Cu. The heats of H_2 chemisorption on Pt and Cu are 109 and 34 $kJ\,mol^{-1}$, respectively [26]. In addition, adsorption of H_2 on Cu is an activated process [27], whereas H_2 readily dissociates on Pt [26]. Thus, it is possible that the surface of PtCu particles is enriched with Pt during the pretreatment with H_2. This would result in a high initial selectivity towards ethane. A similar enrichment of the surface due to the strong interaction between the group VIII metal atom and H was observed in the case of Ni–Au alloy [28].

The energy of Cl adsorption on Cu cannot be determined directly from thermodesorption data because chlorine adsorbed on Cu desorbs as CuCl [29]. However, the fact that a CuCl compound forms suggest that the Cu–Cl bond energy on the Cu surface is probably closer to that for stoichiometric CuCl which is 86 kcal/mol. The activation energy for Cl desorption from Pt is only 47.5 kcal/mol for a (111) surface [30] and 59.5 kcal/mol for a (110) surface [31]. From the above data it appears as if Cl has a greater affinity for Cu compared to Pt. So as the reaction proceeds, one could expect that the Cl adatoms induce the enrichment of the bimetallic surface with Cu. This results in an increase in the selectivity towards ethylene.

The evaluation of the diffusion rate of Pt atoms in a Cu matrix on the basis of diffusion coefficients of Cu and Pt in their binary alloy shows that the average displacement of Pt atoms per hour is approximately 0.4 Å at 200 °C [32]. This corresponds to an equilibration time of more than 1,000 h, assuming an average alloy particle size of 3 nm. This time exceeds the transient period of the PtCu catalysts studied ($<$100 h) by more than one order of magnitude. However, it appears reasonable that the equilibration within several tens of atomic layers of the surface is enough for significant change in selectivity. This would take much less time. Thus, the results of the present investigation do not allow a definitive differentiation between the role of alloying and equilibration of surface composition of bimetallic particles in changing the catalyst selectivity during the transient period. Forthcoming spectroscopic work will clarify this issue.

4.2. Influence of Cu content

The relationship between Cu content and the steady-state selectivity patterns allows consideration of another facet of the chemistry. 1,2-dichloroethane undergoes C–Cl bond dissociation on Cu sites resulting in the formation of adsorbed $\cdot CH_2–CH_2\cdot$ species which readily desorb as ethylene. It is reported in literature that C–Cl bond scission in vicinal dichlorohydrocarbons occurs easily on a Cu surface followed by olefin formation even in the absence of hydrogen [29,33]. Work by Koel and coworkers has shown that olefins desorb more rapidly from noble metal surfaces containing a second metal; they also decompose in a lesser extent [34,35]. Heat of ethylene adsorption on supported Pt is lower than on Cu (22–30 kcal/mol [36] and 18 kcal/mol [37], respectively). Thus, if the olefin formation occurs on the Cu site, a lower heat of adsorption of the olefin product allows one to visualize this site as a kind of "molecular launch pad".

As hydrogen adsorption on Cu is an activated process, the concentration of H atoms on the Cu surface is low [1]. Thus, monometallic Cu/C catalyst possesses very low activity in the reaction under consideration (table 2) as surface Cl cannot be removed readily due to a lack of surface hydrogen. A noble metal is needed to provide an abundant source of dissociated hydrogen which upon spilling over from Pt sites reduces surface CuCl species and forms HCl. A similar mechanism was suggested before for 1,2-dichloroethane dechlorination catalyzed by Pd–Ag/SiO_2 sol–gel catalysts [16]. However, more direct evidence from spectroscopic investigations will be the subject of future papers.

5. Conclusion

The effect of Pt–Cu/C catalyst composition on the activity and selectivity in the 1,2-dichloroethane dechlorination reaction has been studied. For monometallic Pt catalysts and those with Cu/Pt atomic ratio $\leqslant$1, the products are almost entirely ethane and monochloroethane. As the Cu/Pt ratio is increased, the selectivity towards ethylene increases and approaches 90% for catalysts with Cu/Pt ratio $\geqslant$9. Monometallic Cu/C produces only ethylene, with the activity being two orders of magnitude lower than for Pt/C and Pt–Cu/C catalysts. The dramatic change in selectivity of 1,2-dichloroethane dechlorination catalyzed by Pt–Cu/C compared to Pt/C is described in terms of C–Cl bond scission on the Cu surface as a critical step in the formation of ethylene. The C–Cl bond scission on the Pt surface results in ethane formation, but this parthway is significantly suppressed by the Pt dilution with Cu. It is hypothesize that C–Cl bond hydrogenolysis requires large Pt ensembles. The increase in selectivity towards ethylene at the expense of ethane during first 20 h of time on stream is rationalized in terms of equilibration of bimetallic particle surface composition exposed to the reaction mixture.

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