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Hydrogen-assisted dechlorination of 1,2-dichloroethane on active carbon supported palladium–copper catalysts

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ABSTRACT

A series of active carbon supported palladium–copper catalysts with varying amounts of both metal components and overall metal loading 2 wt.%, prepared by incipient wetness impregnation were characterized by temperature programmed reduction (TPR), hydrogen chemisorption, temperature programmed (palladium) hydride decomposition (TPHD), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). TPHD and XRD studies indicated that the bimetallic Pd–Cu/C catalysts exhibited a considerable degree of alloying. Pd/C, Cu/C and Pd–Cu/C catalysts were investigated in the hydrodechlorination (HdCl) of 1,2-dichloroethane in the gas phase at a relatively low reaction temperature (210–230 °C). All catalysts showed fair stability with time on stream (up to ~15 h). The Pd/C and Pd-rich Pd–Cu catalysts essentially retained their initial activity while the bimetallic samples with higher Cu content exhibited some deactivation at the initial stage of reaction. Cu-rich bimetallic samples exhibited the highest selectivities toward ethene (desired reaction product), >90%. For all bimetallic Pd–Cu/C samples, this selectivity gradually increased with time on stream. XPS studies of freshly reduced and post-reaction catalysts did not support the hypothesis that during hydrodechlorination the surface of Pd–Cu is being gradually enriched in copper, as could be expected of a higher affinity of copper to chlorine. Post-reaction deposits investigated by the temperature programmed hydrogenation (TPH) showed substantial amounts of chlorine on the copper catalyst, whereas all palladium-containing Pd–Cu/C samples exhibited only carbon-containing deposit, with C_2-hydrocarbons desorbing at a relatively low temperature (300 °C). Suggested interpretation of catalytic data includes both the role of C_2H_x species building up on catalyst's surface during hydrodechlorination as well as the role of Pd–Cu mixed sites in the mechanism of hydrogen-assisted dechlorination of 1,2-dichloroethane.

1. Introduction

Chloroorganic compounds are large and toxic by-products of several large-scale industrial processes and are pollutants in the environment [1,2]. One of them is 1,2-dichloroethane (1,2-DCA), widely used as degreaser and reactant in chemical manufacture, including production of vinyl chloride, tri- and tetra-chloroethene, ethenediamine, vinylidene chloride, etheneglycol, nylon, and various plastics. The chlorinated waste streams from industrial and military operation are treated through incineration, catalytic oxidation, biological treatment or photo-catalytic decomposition. An attractive alternative for them is the catalytic hydrodechlorination. Because of their value, ethene and chloroethene (well-known as vinyl chloride monomer) are the most desired products of 1,2-DCA hydrodechlorination.

Palladium and platinum are very active catalytic metals in HdCl of vicinal alkyldi- and trichlorides, such as 1,2-dichloroethane, 1,2-dichloro- or 1,2,3-trichloropropane reaction [3–14]. In the presence of hydrogen, 1,2-dichloroethane is readily dechlorinated to ethene (desired product), but because of a high hydrogenation power of noble metals it is immediately converted to ethane (much less valuable product). Interestingly, several authors showed the ability of Pt- and Pd-containing bimetallic catalysts (Pd–Ag [3–9], Pd–Cu [8–10], Pt–Cu [10–16]), to convert chlorinated alkanes selectively into less or not chlorinated alkenes. Recent microcalorimetric studies [17] showed that the adsorption strengths of 1,2-dichloroethane and H_2 on Pt/SiO_2 catalyst decrease with the introduction of Cu, suggesting that Cu plays an important role in moderating adsorption and activation ability for reactants and enabling the progress of the dechlorination reaction. Microcalorimetry of ethylene adsorption indicated that nondissociative species of ethylene could be the intermediate on Pt–Cu/SiO_2 catalysts in the hydrodechlorination procedure. As expected, the introduction of Cu to Pt/SiO_2 catalyst lowered the bonding strength of adsorbed ethylene, causing reversible adsorption of ethylene on Pt–Cu/SiO_2 at reaction tem-

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perature. Therefore, the adsorbed ethylene could be easily desorbed as ethylene in the dechlorination reaction.

Another interesting finding was that for bimetallic Pt–Cu [14], Pd–Cu [8,10] and Pd–Ag [3] catalysts the selectivity toward ethene was developed with time on stream. This effect, analyzed in detail by Luebke et al. [14] for Pt–Cu/C catalysts was attached to an increase in the degree of alloying under reaction conditions. Similar interpretation was suggested for Ni–Au/Al_2O_3 catalysts used in HdCl of 2,4-dichlorophenol [18]. In that case a gradually higher selectivity (toward partial dechlorination) was linked to a surface reconstruction resulting in a more homogeneous combination of Ni and Au [18]. The surface enrichment with copper of Pd–Cu catalysts resulted from the pretreatment with HCl was also considered as a factor in shaping the hydrodechlorination behavior of Pt–Cu catalysts [14].

The abovementioned beneficial effect of Pd alloying was found for silica-supported Pd–Cu [8,9] catalysts. Although, in terms of its inertness against HCl (unavoidable hydrodechlorination product) silica seems to be a suitable support for carrying metal phases active in hydrodechlorination, application of active carbon as a convenient support appeared to us also very interesting. Carbon is the support of industrial choice for a number of reasons, including low price, high specific surface area and stability against corrosion by halogen-containing species. The aim of this work was to prepare carbon-supported Pd–Cu catalysts and to test them in 1,2-DCA hydrodechlorination.

2. Experimental

2.1. Catalyst preparation and characterization

The 2 wt.% metal-loaded palladium–copper catalysts were prepared by an incipient wetness co-impregnation of active carbon. Before preparation the support (Sibunit carbon) was washed with a boiling mixture of concentrated HCl and HF. After subsequent rinses with large amounts of redistilled water and drying in an air oven, the support was stored in a glass-stoppered bottle and kept in a desiccator. Its nitrogen BET surface area was 387 m^2/g, BJH pore volume (from desorption branch) 0.75 cm^3/g and average pore diameter ca. 7 nm. Cumulative micropore volume (Horvath–Kawazoe) was 0.11 cm^3/g as estimated at relative pressure 0.012, and median micropore diameter was 0.59 nm.

A series of Sibunit-supported catalysts were prepared from metal chloride salts, $PdCl_2$, $CuCl_2{\cdot}2H_2O$, both of analytical purity from POCh, Gliwice, Poland. During impregnation and preliminary drying with infrared lamps, a good mixing was assured by the rotary motion of a beaker containing the catalyst precursor. Then, the solids were further dried overnight in an air oven at 90 °C and stored in a desiccator.

Temperature programmed reduction (TPR) of catalyst precursors was followed with an MA200 mass spectrometer from Dycor-Ametek, Pittsburgh, USA. The main reason of using mass spectrometry, instead of a typical TCD detector, was our intention to monitor HCl evolution (m/z 36) during TPR run. HCl liberated from metal chlorides during their reduction by hydrogen (m/z 2) would be retained by active carbon. TPR (catalyst samples of ~0.10 g) runs were performed by flowing a 10% H_2/Ar mixture (25 cm^3/min) at a 10 °C/min ramp.

Hydrogen chemisorption experiments were carried out in a glass pulse-flow system equipped with thermal conductivity detector, Gow-Mac kept at 0 °C, in the manner described elsewhere [19,20]. Before chemisorption the prepared catalysts were reduced in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature from 20 to 400 °C (at 8 °C/min) and kept at 400 °C for 3 h. All the gases (H_2, Ar and 10% H_2/Ar mixture, all 99.999%) were further purified by passing through drying and MnO/SiO_2 traps. The results of chemisorption studies together with catalyst designation are shown in Table 1.

Table 1
Characteristics of Pd–Cu/C catalysts.

Catalysts[a]	Metal dispersion (H/Me)[b]	H/Pd from TPHD[c]
Pd100	0.177	0.23
Pd75Cu25	0.031	0
Pd50Cu50	0.014	0
Pd25Cu75	0.006	0
Pd10Cu90	0.003	0
Cu100	0	0

[a] In the notation Pd*X*Au*Y*, *X*, and *Y* denote atomic percentages of Pd and Cu in metal phase, i.e. $X + Y = 100$ at.%.

[b] From irreversible hydrogen uptake at 70 °C. M = Pd + Cu.

[c] Hydrogen released during a temperature programmed hydride decomposition (TPHD) run.

After chemisorption, the samples were cooled down to room temperature and subjected to subsequent temperature programmed study in 10% H_2/Ar flow, ramping the temperature from 20 to 150 °C, at 8 °C/min. Since the samples had already been reduced, the aim of such experiments was to monitor hydrogen evolution in the decomposition of β-hydride, in the temperature programmed hydride decomposition (TPHD). For details, see [19,20].

XRD experiments with Pd–Cu/C catalysts (reduced and post-reaction samples) were performed on a standard Rigaku Denki diffractometer using Ni filtered Cu-Kα radiation. All samples, prior to and after reaction, were scanned by a step-by-step technique, at 2θ intervals of 0.04°.

Temperature programmed hydrogenation (TPH) of post-reaction deposits from Pd–Cu/C catalysts was also followed with an MA200 mass spectrometer from Dycor-Ametek, Pittsburgh, USA. Several masses were monitored during the experiment, but major changes were seen only for m/z 15 and 16 (methane evolution), m/z 36 and 38 (HCl liberation), m/z 28 and 30, suggestive of C_2-hydrocarbons release. Evolution of m/z 62 (desorption of 1,2-DCA) was not practically detected in all TPH experiments.

XPS spectra of reduced and used Pd50Cu50/C and Pd75Cu25/C catalysts were recorded on a Physical Electronics PHI 5000 VersaProbe scanning ESCA Microprobe using monochromatic Al-Kα radiation ($h\nu = 1486.6$ eV) induced from an X-ray source (25 W and 15 kV) operating at 100 μm spotsize. Both survey and detail XPS spectra were recorded using the analyzer pass energy of 117.4 eV and 23.5 eV and the energy step size of 0.4 eV and 0.1 eV, respectively. Fresh samples for XPS studies were pressed in a hydraulic die to form thin, smooth wafers, and placed in the preparation chamber. After reduction at 400 °C for 3 h, the samples were transferred to the analytical chamber of the spectrometer without contact with air. The samples of post-reaction Pd–Cu/C catalysts were only degassed in a preparation chamber before analysis. Prior to analysis, a residual pressure of less than 1×10^{-8} mbar was reached. Due to very small intensities of the Pd 3d and Cu 2p XPS peaks a counting around these peaks was performed with a large number of scans (200). A PHI Multipak software was used to evaluate the XPS data (Shirley type background subtraction).

2.2. Catalytic tests

The reaction of hydrodechlorination of 1,2-dichloroethane (1,2-DCA, HPLC grade, 99.8% pure from Sigma–Aldrich, Germany) was carried out at atmospheric pressure, in a glass flow reactor equipped with fritted disk to place a catalyst charge. Prior to reaction, the catalyst sample was reduced in flowing 10% H_2/Ar (25 cm^3/min), ramping the temperature from room temperature to

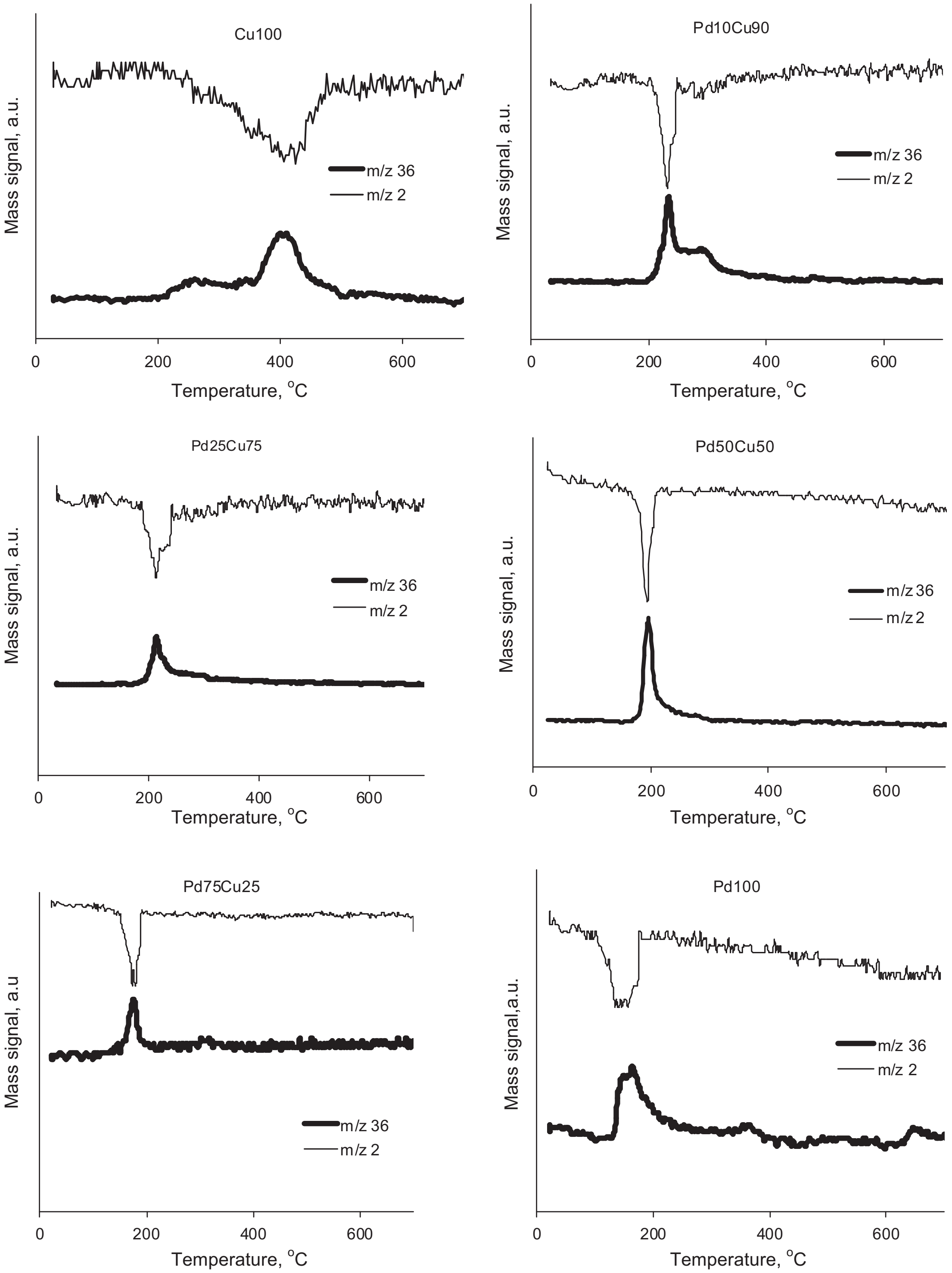

Fig. 1. Temperature programmed reduction profiles of Sibunit-supported Pd–Cu catalysts.

400 °C (at 8 °C/min) and kept at 400 °C for 3 h. After reduction, the catalysts were cooled to 230 °C, then contacted with the reaction mixture (H_2 + Ar + 1,2-DCA) at 41.2 cm^3/min. 1,2-DCA was provided from a saturator kept at 0 °C, to give the partial pressure of 1,2-DCA of 2.9 kPa. The partial pressure ratio $p_{H_2}/p_{1,2\text{-DCA}}$ was 1:1. The flows of all gases, except 1,2-DCA, were fixed by using Bronkhorst Hi-Tec mass flow controllers. After screening at 230 °C for overnight and reaching a steady-state, the temperature of reaction was gradually decreased to 220 and 210 °C, and new experimental points collected. Finally, the reactor was heated to 230 °C, and, in nearly all cases, the previous results collected at 230 °C were restored. The reaction was followed by gas chromatography, using a HP 5890 series II gas chromatograph with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco. The results of GC analysis were elaborated using HP Chemstation. The total FID signal from the first two analyses was somewhat reduced compared to that observed in subsequent GC analyses. A satisfactory carbon balance (within ~95%) was found for further GC analyses. The mass of catalysts used for reaction was 0.2 g for Cu-rich catalysts and 0.1 g for Pd-rich samples (i.e. for Pd100 and Pd75Cu25), in order to not exceed conversion

levels beyond 15%, at steady state, at 230 °C, i.e. at the highest temperature used in this study. Only in the case of Pd100/C the conversion was slightly higher than 15%. A typical run lasted ~15 h. Blank experiments with Sibunit carbon showed very low activity at 230 °C. Reproducibility of results (checked for two independent samples of Pd100/C, Pd25Cu75/C and Pd50Cu50/C catalysts) was fair, ±10% (total activity) or good, ±2% (product selectivities toward ethene, ethane and ethyl chloride).

3. Results and discussion

3.1. Catalyst characterization

As it is discussed below, TPR spectra for active carbon supported Pd–Cu ex-chlorides precursors, show that the incipient wetness impregnation leads to deposition of both metal salts which interact with each other (Fig. 1), unlike in the case of previously investigated Pd–Ni ex-chlorides precursors where TPR spectra did not reflect any special interaction between them [19]. This finding, strengthened by XRD and TPHD results (*vide infra*), clearly speaks for a better mutual contact of metal chloride precursors in Pd–Cu/C than in Pd–Ni/C catalysts. A frequently invoked interpretation considering hydrogen spillover from an easily to a harder reducible metal component [21] does not seem to work here because the presence of dissociated hydrogen on palladium should similarly facilitate reduction of copper(II) and nickel(II) species.

Reduction of $PdCl_2$/C occurs at a relatively low temperature (TPR peak at <200 °C) while reduction of $NiCl_2$/C [19] and $CuCl_2$/C proceeds at much higher temperatures (TPR peak at ~400 °C, Fig. 1). For mixed Pd–Ni chloride precursors, the Pd chloride was still reduced at <200 °C, while reduction of the remaining, Ni-based material occurred at ~350 °C [19]. A ~50 °C decrease of reduction temperature was attributable to the availability of dissociated hydrogen formed on a prereduced palladium [19]. In contrast, for mixed Pd–Cu chloride/C precursors, the principal TPR maxima occur at ~200 °C, i.e. very close to the TPR maximum found for reduction of $PdCl_2$/C. It clearly suggests that palladium chloride and copper chloride strongly interact with each other in the precursor state. In addition, the amounts of hydrogen consumed during TPR runs reflect well a complete reduction of Pd(II) and Cu(II) species (±5%). HCl evolution (from reduction of metal chlorides, Fig. 1) occured at similar temperatures as hydrogen consumption, indicating no special HCl retention by Sibunit carbon. TPH studies of post-reaction deposits, carried out up to ~800 °C showed only negligible amounts of Cl released from the surface of Pd-rich catalysts subjected to HdCl (*vide infra*). The XPS spectrum of reduced Pd–Cu/C catalysts showed that the presence of chlorine at the surface was extremely small (~0.1%), comparable with the overall chlorine content in the starting Sibunit carbon material (~0.2% [22]).

As mentioned, the results of XRD and temperature programmed hydride decomposition (TPHD) furnished further indications as to alloy homogeneity and metal particle size of the Pd–Cu nanoparticles in Sibunit carbon supported catalysts. Fig. 2 shows that the XRD profiles from Sibunit-supported metal catalysts are considerably influenced by the background from active carbon. In particular, a possible presence of Cu-rich palladium alloys (1 1 1 reflection) is seriously masked by a single (10) peak at ~43.5° (from merged (1 0 0) and (1 0 1) reflections of carbon). Subtraction of the background from Sibunit (Fig. 3) led to XRD spectra (only in the neighborhood of (1 1 1) and (2 0 0) reflections of Pd and Cu) of the Pd75Cu25/C catalyst. The positions of peak maxima well correspond to the lattice parameter of Pd75Cu25 alloy, when one assumes no deviations from the Vegard's law. Single (1 1 1) and (2 0 0) reflections from fcc metal phase suggest that a considerable Pd–Cu alloying has been achieved. Although somewhat broadened XRD lines would result from the presence of a mixture of alloy particles slightly differing in composition, it should be recalled that analogous XRD spectra for Pd–Ni/Sibunit catalysts prepared by the same method, revealed a large portion of unalloyed palladium (upper side of Fig. 3 in Ref. [19]).

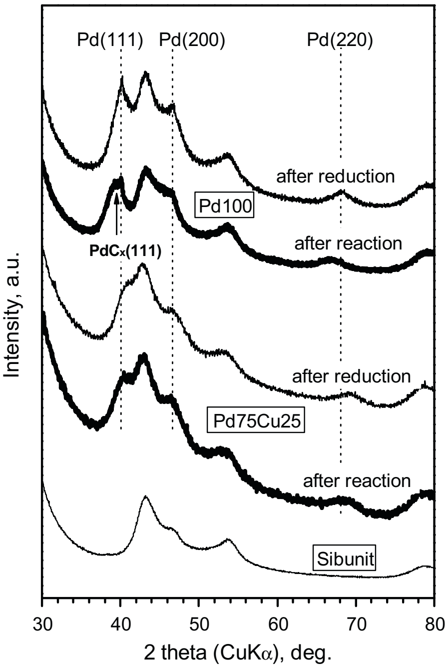

Fig. 2. XRD profiles of carbon-supported Pd100 and Pd75Cu25 catalysts after reduction (thin lines) and subjected to 1,2-dichloroethane hydrodechlorination (thick lines). Bottom line represents the diffractogram from Sibunit carbon support.

Temperature programmed (palladium) hydride decomposition (TPHD) makes use of ability of palladium and palladium-rich alloys of forming the hydride phase (β-PdH). Well-homogenized palladium alloys with larger amounts of added metals (typically, at >20 at.%) lose the ability to form hydrides. Fig. 4 shows obtained TPHD profiles which reveal the presence of the β-hydride phase only for Pd100 sample but not for the Pd–Cu catalysts (finding exemplified for Pd75Cu25/C). The TPHD profile for monometallic palladium catalysts showed two minima: one, bigger, at 56 °C and

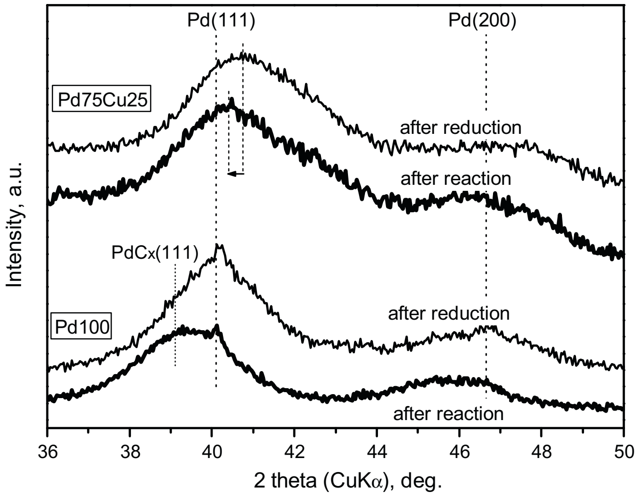

Fig. 3. XRD profiles of Pd75Cu25/C catalyst after subtraction of the background from Sibunit carbon. Only small sections of the previous diffractograms (from Fig. 2) encompassing the vicinity of (1 1 1) and (2 0 0) reflections are exposed. A small shift of the (1 1 1) reflection caused by reaction is marked by arrow.

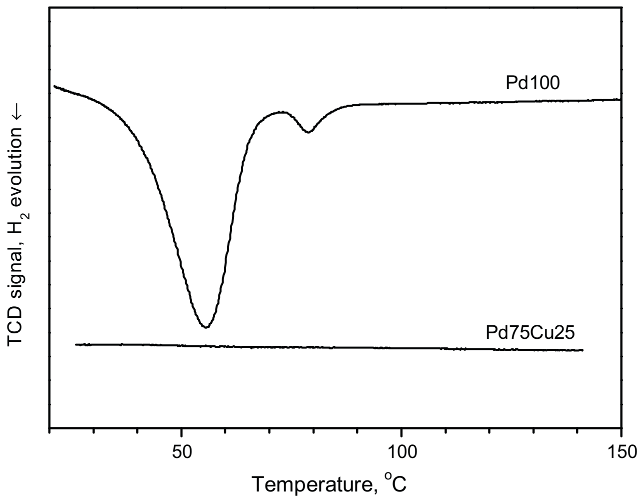

Fig. 4. TPHD profiles of Sibunit-supported Pd100 and Pd75Cu25 catalysts.

one smaller at 78 °C. In the light of a previous analysis of TPHD spectra of supported Pd catalysts [20,23] this profile implies the presence of two palladium phases: a more dispersed (minimum at 56 °C) and the other (less plentiful) characteristic of larger Pd particles (minimum at 78 °C). In this respect, our previous results showed that the nickel-rich Pd25Ni75/Sibunit catalyst prepared by the same method as used in present work still exibited formation of the hydride phase (Fig. 1 in Ref. [19]), suggesting the presence of Pd-rich phase able to form the hydride phase. As mentioned, all investigated Pd–Cu/C catalysts did not show any hydride presence during TPHD runs (see also Table 1). It was known that the Pd–Cu alloys with >20 at.% Cu should not form β-hydride phases at the hydrogen pressures used in our experiments, i.e. at ~10 kPa [24,25]. Therefore, our TPHD experiments with Pd75Cu25/C catalysts confirm much better Pd–Cu alloying than in the case of previously investigated Pd–Ni/C catalysts [19]. Last column in Table 1 (H/Pd ratio from TPHD) shows no hydride formation in all bimetallic Pd–Cu/C catalysts. For the monometallic Pd100/C, H/Pd ratio 0.23, agrees well with the value earlier reported for a similarly metal-dispersed Pd/C catalyst (Fig. 4 in [26]).

Summing up this section, the same preparation method used for Sibunit carbon-supported Pd–Cu and Pd–Ni catalysts gave very different results, much better in the case of the former system. Since both alloy systems show a complete miscibility at 400 °C (catalyst reduction temperature) [27], possible reasons of this variations must involve problems in coimpregnation with solution of mixed chlorides of Pd and Ni. It is possible that in the case of Pd–Ni a more effective "chromatographic" separation of ions takes place in the pore structure of Sibunit carbon [28]. If it was so, then after drying, both metal precursors would be away from each other and a following reduction (at 400 °C) would not be sufficient to bring them together for a proper alloying.

3.2. Catalytic conversion of 1,2-dichloroethane

The representative results of the catalytic conversion of 1,2-dichloroethane for all the Pd–Cu catalysts are presented in Table 2. The major products for the reaction carried out in temperature range 210–230 °C were ethene (for Cu100 and Cu-rich alloys), chloroethene (for Cu100), and ethane and chloroethane (for Pd100 and Pd-rich bimetallic catalysts). Cu100/C had the lowest activity in these temperatures (but still a few times higher than the activity of Sibunit) and showed the highest activation energy (last column in Table 2). Addition of small amounts of palladium to copper drastically changes the overall catalytic activity. The values of turnover frequencies TOF values of Pd–Cu are similar within the series of the catalysts, except Pd100.

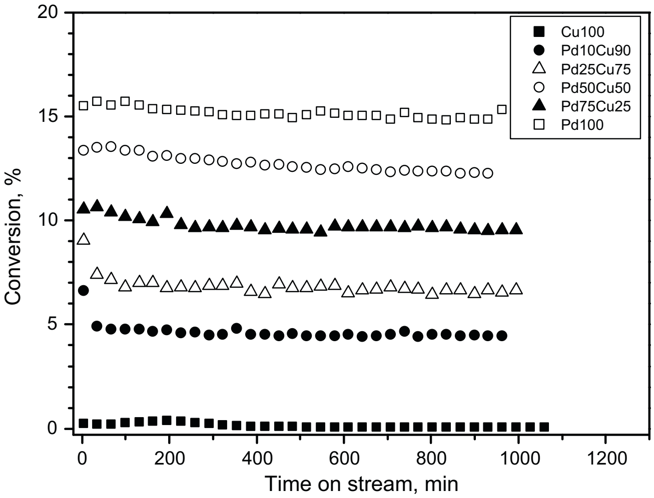

Fig. 5. Conversion changes in 1,2-dichloroethane hydrodechlorination on 2 wt.% Pd–Cu/Sibunit catalysts at 230 °C. The mass of catalysts used for reaction was 0.2 g for Cu-rich catalysts and 0.1 g for Pd100 and Pd75Cu25.

Fig. 5 shows changes of conversion as a function of time on stream in hydrodechlorination of 1,2-DCA. During the time (~15 h of screening) the overall conversion was fairly stable for all tested catalysts. A slight initial deactivation is observed with Pd-rich catalysts (by ~1%), whereas somewhat larger changes (~2%) are for copper-rich bimetallic samples. Cu100/C shows very low activity at 230 °C.

The changes in selectivity to C_2H_4 (desired reaction product) as a function of time on stream are presented in Fig. 6. It is seen that, apart from the behavior of Cu100 (marked decrease of ethene selectivity) and Pd100 (negligible ethene selectivity), this selectivity more or less increases with time on stream. For Cu100, after ~3 h of reaction time, vinyl chloride formation appears to become significant at the expense of ethene production (see Table 2 for steady-state data).

The monometallic Pd100 catalyst was very active for hydrodechlorination of 1,2-DCA. Its high ability to activate hydrogen by dissociative chemisorption leads to the formation of fully saturated products: ethane and chloroethane. This observa-

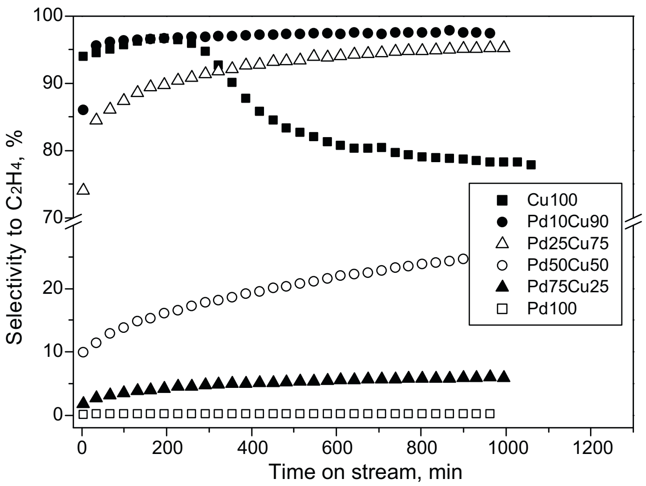

Fig. 6. Time on stream behavior in 1,2-dichloroethane hydrodechlorination on 2 wt.% Pd–Cu/Sibunit catalysts at 230 °C. Changes in the selectivity toward ethene.

Table 2
Representative kinetic data of 1,2-dichloroethane hydrodechlorination over 2 wt.% Pd–Cu/C catalysts: overall conversions, reaction rates, turnover frequencies (TOFs), product selectivities and activation energies.

Catalyst	Reaction temperature (°C)	Conversion (%)	Reaction rate[a] (μmol s^{-1} g_M^{-1}) (TOF (s^{-1}))[b]	Product selectivity (%)					Activation energy (kJ/mol)
				C_2H_4	C_2H_6	C_2H_3Cl	C_2H_5Cl	Other products[c]	
Pd100	210	7.8	28.1 (0.017)	0.1	64.9	–	34.9	0.1	65.2 ± 0.4
	220	11.0	39.5 (0.024)	0.1	67.4	–	32.4	0.1	
	230	15.3	55.0 (0.033)	0.1	69.9	–	29.7	0.2	
Pd75Cu25	210	5.1	19.9 (0.061)	3.3	87.8	–	8.9	–	62.6 ± 1.0
	220	7.0	26.9 (0.083)	4.4	87.3	–	8.3	–	
	230	9.3	35.8 (0.11)	5.9	86.4	–	7.7	–	
Pd50Cu50	210	6.4	13.0 (0.083)	17.8	78.7	–	3.5	–	64.4 ± 4.4
	220	9.1	18.5 (0.107)	20.9	75.8	–	3.3	–	
	230	11.8	24.1 (0.14)	23.0	73.8	–	3.2	–	
Pd25Cu75	210	3.3	6.35 (0.074)	94.4	5.1	0.2	0.3	–	68.8 ± 1.4
	220	4.9	9.34 (0.109)	94.5	5.0	0.1	0.4	–	
	230	6.7	12.8 (0.15)	95.2	4.2	0.2	0.4	–	
Pd10Cu90	210	3.2	6.38 (0.122)	97.5	1.6	0.3	0.2	0.4	65.9 ± 2.6
	220	3.3	6.63 (0.127)	97.7	1.5	0.2	0.2	0.4	
	230	4.2	8.38 (0.16)	97.5	1.6	0.2	0.2	0.5	
Cu100	210	0.02	0.0383	81.3	–	18.7	–	–	99.4 ± 2.8
	220	0.03	0.0574	79.5	–	20.5	–	–	
	230	0.05	0.0957	77.9	–	22.1	–	–	

[a] Reaction rate expressed in micromoles of reacted 1,2-DCA per second and gram of metal (Pd + Cu).

[b] TOF based on metal dispersion (H/M) from Table 1. No hydrogen uptake for Cu100 (Table 1) renders TOF calculation impossible.

[c] Mainly C_1, C_3 and C_4 hydrocarbons.

tion is in agreement with literature data and our earlier experience [5–10,29–32].

Beneficial modification of Pd- and Pt-containing hydrodechlorination catalysts by Cu has already been appreciated by several researchers [8–15]. Combination of a high hydrogenation power of Pd with a high dechlorination activity of less noble metals (Cu, Ni) gives interesting results. The role of palladium in Pd–M alloys (where M = Cu, Ni, Co, Ag) is based on its hydrogenation ability but the role of the second metal has not yet been elucidated unequivocally. For example, Vadlamannati et al. [12] suggested that Cu added to Pt catalyst dilutes the Pt ensembles and suppresses the hydrogenolytic ability of platinum, leading to cleavage of the C–Cl bond and enhancing desorption of the $^{\bullet}CH_2–CH_2^{\bullet}$ species as ethene. On the other hand, in their study on Pd–Ag/SiO_2 catalysts, Heinrichs et al. [5] proposed, that in contrast to hydrogen, 1,2-DCA is dissociatively adsorbed on the Ag surface as the $^{\bullet}CH_2–CH_2^{\bullet}$ species, and, finally, desorbed as ethene. Lambert et al. [10] proposed a mechanism of the hydrodechlorination of 1,2-dichloroethane, which can be adapted for interpretation of the results for Pd–Cu catalysts. Based on it, during hydrodechlorination of 1,2-DCA on monometallic palladium catalyst mainly ethane is produced, because of strong hydrogenative properties of this noble metal. Increasing copper content in Pd–Cu alloys results in an increase of their catalytic activity to ethene, since the hydrogenation ability is reduced. 1,2-Dichloroethane hydrodechlorination on monometallic copper catalyst gives ethene as a major product, but chlorine deposition on its surface rapidly deactivates the catalyst. It was concluded that copper itself is not able to activate hydrogen in such a way in order to supply a sufficient flux of hydrogen atoms which could fully regenerate the chlorided surface.

The increase of ethene selectivity with time on stream of Pd–Cu bimetallic catalysts needs a more detailed analysis. It seems that during hydrodechlorination, when massive amounts of HCl are formed, copper, due to a higher than palladium affinity to chlorine, migrates to the alloy surface. Such proposition is in line with recent results of Bloxham et al. [33], who suggested that segregation of the copper to the surface was under the influence of chlorine and chloride species produced during reaction hydrodechlorination of trans-1,2-dichloroethene. At first glance, this conclusion seems to be strenghtened by XRD profile of used Pd75Cu25 catalysts (Fig. 3). A small, but recognizable shift of (1 1 1) and (2 0 0) lines toward lower diffraction angles suggests some copper deficit in Pd–Cu crystallites. Although this deficit would result from the situation where a relatively thin shell of a copper-richer phase envelops a Pd-richer core (detected by XRD), another interpretation of this shift seems more likely. It is known that when palladium dissolves carbon, its lattice constant increases from ~0.389 to ~0.399 nm [34–36] resulting in a downward shift in the XRD spectrum. Some presence of PdC_x phase was detected in the XRD profile of used Pd100/C catalyst (Figs. 2 and 3). Therefore, we cannot exclude that a similar, although probably a more subtle, shift for Pd75Cu25/C catalyst is associated with carbon dissolution.

XPS studies of reduced and post-reaction Pd–Cu/C samples are supposed to verify a hypothesis that Cu surface segregation occurs during HdCl. Fig. 7a shows an example of typical survey XPS spectrum, where essentially only carbon 1s core level spectrum is seen. A large number of scans (200) around a Pd 3d and Cu 2p XPS peaks (Fig. 7b) led to estimation of surface composition of reduced and post-reaction Pd50Cu50/C and Pd75Cu25/C catalyst samples (Table 3). The results collected in Table 3 do not confirm the effect of surface segregation of copper induced by HdCl (Table 3).

Arsenault and Gonzalez [9] also found an increase of ethene selectivity during HdCl of 1,2-DCA. They linked this effect with catalyst's coking. Additional kinetic experiments carried out by us showed that changes in ethene selectivity are reversible (results not presented in figures). After ~15 h on stream, the Pd25Cu75/C (or Pd50Cu50/C) catalyst was pretreated in H_2/Ar flow at 300 °C for 1 h, and the hydrodechlorination reaction was allowed to continue, showing exactly the same time-on-stream behavior as presented in Fig. 6. This result seems also speak against surface segregation of Cu during HdCl.

Temperature programmed hydrogenation of post-reaction deposits show a massive release of C_2-hydrocarbons (mainly ethene) at ~300 °C and no chlorine retention, except for Cu100/C (Fig. 8b and c). Therefore, some accumulation of C_2H_x surface species seems important for shaping ethene selectivity. Methane evolution, resulting from hydrogenation of C_1 species, during TPH seems less indicative here because its main release occurs at a

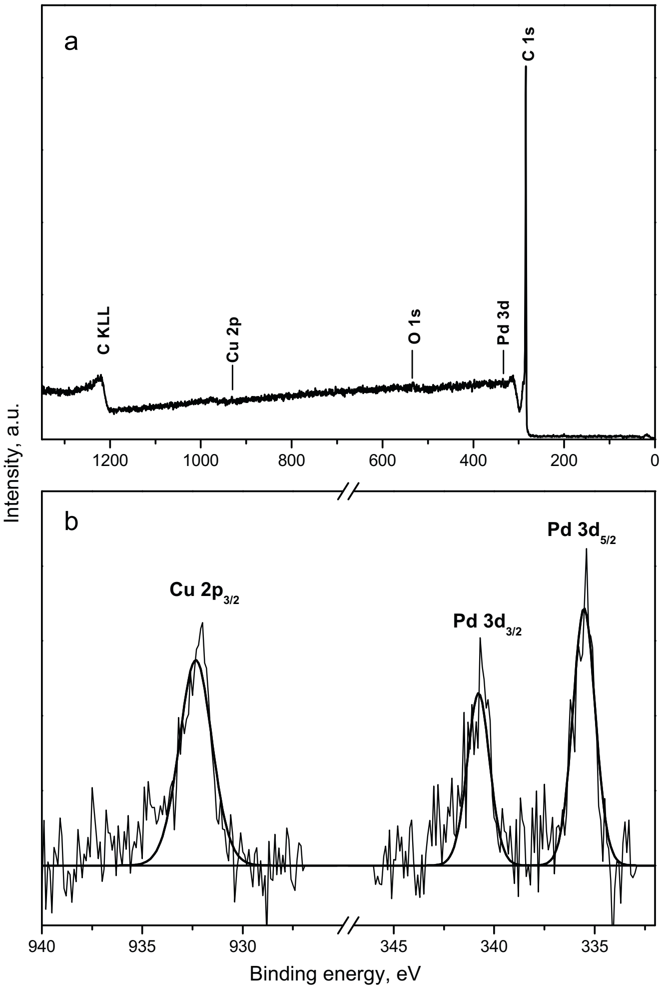

Fig. 7. XPS spectrum of the Pd50Cu50/C catalyst after hydrodechlorination: (a) survey spectrum, (b) Cu 2d and Pd 3p regions after ∼200 scans.

rather higher temperatures, resulting from support methanation (Fig. 8a).

Fig. 9 compiles the activity for ethene formation for all tested catalysts. The best ethene productivity is observed for the Pd75Cu25/C catalysts. This synergy would be discussed in terms of electronic (ligand) effect in catalysis by metal alloys [37]. For Pd–Cu alloy, nonnegligible electronic perturbations of Pd and Cu observed

Table 3

XPS parameters obtained for reduced and used carbon supported Pd–Cu bimetallic catalysts: the binding energy (BE) of the main XPS peaks (Pd $3d_{5/2}$ and Cu $2p_{3/2}$), the full width at half maximum (fwhm), in parentheses, and the surface composition resulted from XPS spectra.

Catalyst[a]	BE (fwhm) (eV)		Surface composition of Pd–Cu phase (at.%)
	Pd $3d_{5/2}$	Cu $2p_{3/2}$	
Pd75Cu25 after H_2 reduction	335.4 (1.3)	932.0 (1.9)	Pd67Cu33
Pd75Cu25 after HdCl	335.5 (1.3)	932.3 (2.1)	Pd66Cu34
Pd50Cu50 after H_2 reduction	335.4 (1.2)	932.1 (1.7)	Pd52Cu48
Pd50Cu50 after HdCl	335.5 (1.3)	932.3 (1.9)	Pd53Cu47

[a] Catalyst designation (as in Table 1) reflects the nominal Pd–Cu composition (at.%) resulted from catalyst preparation.

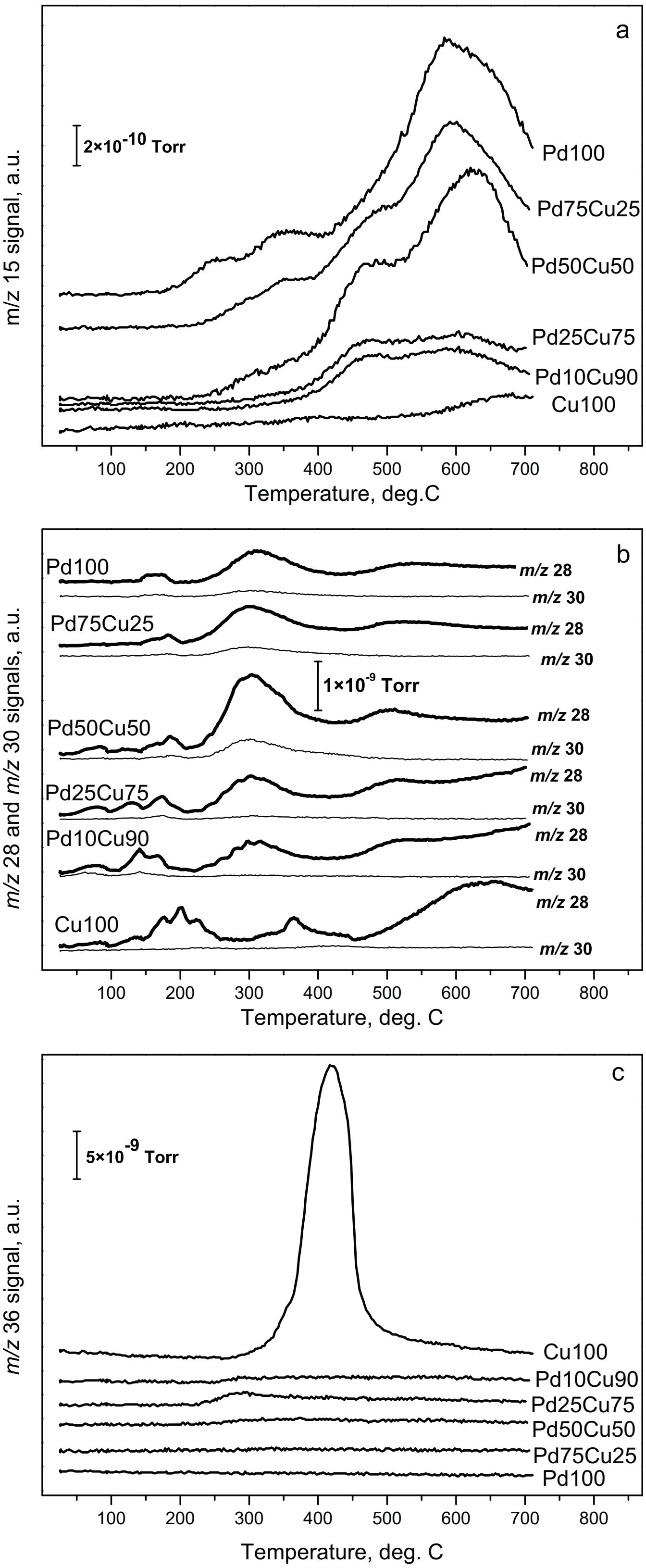

Fig. 8. Temperature programmed hydrogenation profiles of post-reaction deposits. (a) Methane evolution (m/z 15 was selected for presentation because CH_4 liberation observed by monitoring m/z 16 is somewhat misinterpreted due to water evolution, especially at around 100 °C). (b) m/z 28 and 30 evolution for showing the release of C_2H_x species. (c) HCl (m/z 36) evolution.

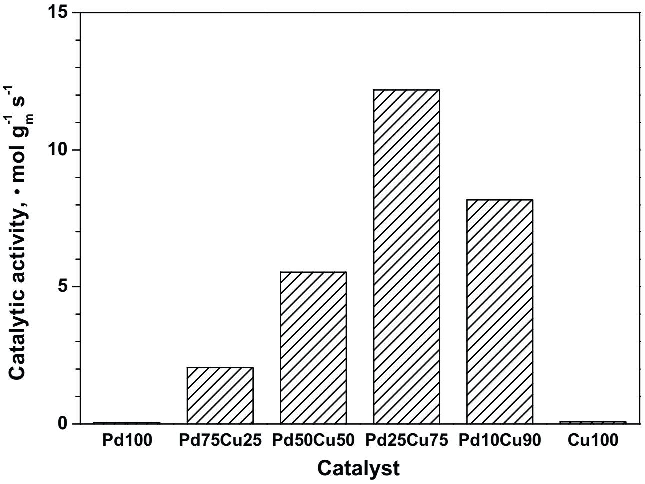

Fig. 9. Catalytic activity of Pd–Cu/C catalysts in hydrodechlorination of 1,2-dichloroethane to ethene at 230 °C.

by XPS appeared in the valence as well as in the core levels region [38–40]. Mårtensson et al. [38] proposed an explanation concerning a charge transfer in Pd–Cu alloy, i.e. Pd is electron-enriched in at the expense of Cu. More recent DFT study of small Pd–Cu clusters [41] also showed that the formation of Pd–Cu intermetallic bond strongly changes the electronic structure of individual atoms with total negative charging of palladium atoms. Electronic modification of both components on Pd–Cu alloying was confirmed by XANES on Pd–Cu alloying [42]. In other work [43] the Pd–Cu interactions were interpreted in terms of bond formation between the almost full valence "sd" band of Pd and the resonant "dsp" band of Cu near the Fermi level. The adsorption energies of CO, NO, H_2 decreased on Pd and increased significantly on Cu in alloy with respect to adsorption on pure metals. It appears that π-backdonation, associated with the formation of a hybridized molecular orbital, decreases for Pd and increases for Cu. Both facts, i.e. weakening of Pd–ethene and strenghtening of originally very weak Cu–ethene bonds would be beneficial for ethene selectivity in HdCl of 1,2-dichloroethane. Similarly, the Pd–H bond, resulting from "sd" levels of Pd and "s" level of H overlap, also appears weaker on Pd–Cu than on pure Pd. A weakening H-to-catalyst bonding [43] would lead to some decrease of a hydrogenating power of Pd–Cu and contribute to a higher ethene selectivity. A closer comparison of apparent activation energies listed in last column of Table 2 seems to support the operation of electronic/ligand effect in HdCl of 1,2-DCA on Pd–Cu alloys. Very high apparent activation energy (99.4 kJ/mol) found for Cu100 (Table 2) matches well the E_a value for ethene formation from 1,2-DCA on Cu/SiO_2 (22.8 kcal/mol = 95.3 kJ/mol) reported by Xie et al. [44]. The same work also shows that for Pt and Pt50Cu50 catalysts, i.e. for samples showing a high selectivity toward ethane, the E_a in ethane formation is only 16 kcal/mol (~66 kJ/mol), matching the respective E_a values obtained in our work for Pd100/C and Pd-richer Pd–Cu/C catalysts (up to Pd50Cu50), which were found very selective toward ethane. So, only Pd25Cu75 and Pd10Cu90 appear to "deviate" from this correlation, because they show very high selectivity for ethene and the E_a level still about 65 kJ/mol, characteristic for samples selective for ethane formation. We hypothesize that this "deviation" would result from the operation of ligand effect in the case of Pd–Cu but not for Pt–Cu alloys. Recent IR study of adsorbed (labelled) CO on Pt–Cu/SiO_2 catalysts suggested that the ligand effect does not influence strongly the catalyst performance [15]. Instead, the ensemble size/geometric effect seems decisive in determining high ethene selectivity in HdCl of 1,2-DCA on Pt–Cu catalysts.

4. Conclusions

1. Incipient wetness coimpregnation of Sibunit carbon with an aqueous solution of $PdCl_2$ and $CuCl_2$ leads to preparation of well-mixed Pd–Cu catalysts.
2. Sibunit carbon supported Pd–Cu catalysts showed good and stable activity in the hydrodechlorination of 1,2-dichloroethane at relatively low reaction temperatures (210–230 °C).
3. Selectivity to ethene is very high for copper-rich Pd–Cu catalysts and negligible for pure palladium which produces mainly ethane and chloroethane.
4. Post-reaction deposits investigated by the temperature programmed hydrogenation showed substantial amounts of chlorine on monometallic copper catalyst, whereas palladium-containing samples showed basically a carbon-containing material, mainly strongly bound C_2H_x species.
5. Carbonaceous species building up on the surface of Pd–Cu seem to be advantageous in developing ethene selectivity.
6. Synergy in the catalytic behavior of Pd–Cu alloys is attributed to modification of electronic structures of Pd and Cu upon alloying (electronic/ligand effect).

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