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Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts for selective hydrodechlorination of 1,2-dichloroethane into ethylene

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Abstract

While 1,2-dichloroethane hydrodechlorination over pure palladium mainly produces ethane, increasing silver or copper content in bimetallic catalysts results in an increase in ethylene selectivity. The specific consumption rate of 1,2-dichloroethane decreases when silver or copper loading increases. The turnover frequency, that is, the number of catalytic cycle per active site (palladium atom and its surrounding silver or copper atoms) and per second, seems to be independent of surface composition of alloy particles and 1,2-dichloroethane hydrodechlorination is insensitive to the atom's nature (silver or copper).

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Keywords: Cogelled xerogel catalysts; Pd–Ag alloys; Pd–Cu alloys; Hydrodechlorination; Turnover frequency

1. Introduction

There is an increasing demand for technology that will convert chlorocarbons as by-products of industrial processes into more useful or environmentally benign products. For example, hydrodechlorination of chlorinated organics is a particularly attractive alternative compared with incineration of wastes from the chlorine industry from both economic and environmental points of view [1]. The hydrodechlorination reaction often consists of the carbon–chlorine bond hydrogenolysis, $\equiv C{-}Cl + H_2 \rightarrow \equiv C{-}H + HCl$, in which hydrogen atoms are substituted for chlorine atoms. Noble metal catalysts (Group VIII) are very active for the hydrodechlorination reaction [2–4]. In the case of 1,2-dichloroethane hydrodechlorination, the noble metal participates in a catalytic cycle in which the reactant is dechlorinated by chlorination of the metal surface, which is then itself dechlorinated by reduction with hydrogen. Because of the high reactivity of hydrogen on noble metals, the dechlorinated organics, C_2H_4 in the present case, is immediately converted into the fully hydrogenated product, C_2H_6, which is much less useful from an industrial point of view [3,4]. However, several authors [5–13] demonstrated the ability of bimetallic catalysts, composed of metals from Groups VIII and IB, to convert chlorinated alkanes selectively into less or not chlorinated alkenes.

The purpose of the present study is to measure catalytic activity and selectivities of 1,2-dichloroethane hydrodechlorination over Pd–Ag/SiO_2 and Pd–Cu/SiO_2 catalysts and to study relationships between catalytic activity and surface properties of bimetallic catalysts. In this way, the surface composition of Pd–Ag and Pd–Cu alloys had been measured from CO chemisorption, X-ray diffraction (XRD) and transmission electron microscopy (TEM) [14,15].

2. Experimental

For bimetallic samples, the presence of Pd–Ag or Pd–Cu alloys is denoted "Pd:Ag x:y" or "Pd:Cu x:y", respectively, where x represents the proportion of palladium and y represents the proportion of silver or copper with regard to the total weight of metals in the sample. For monometallic Pd/SiO_2 and Cu/SiO_2 catalysts, it is used the chemical abbey Pd or Cu, respectively.

The three Pd–Ag/SiO_2 catalysts and the five Pd–Cu/SiO_2 catalysts examined in this paper are xerogels prepared by a one-step sol–gel procedure which consists in the cogelation of the silica precursor, tetraethoxysilane (TEOS), with an

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organically substituted alkoxide capable of forming chelates with palladium, silver and copper ions. The resulting alcogels were dried under vacuum, calcined in air at 400 °C, and finally, reduced in hydrogen at 350 °C. Details of the preparation are given in [16,17]. The bulk composition of alloy nanoparticles in Pd–Ag/SiO_2 and Pd–Cu/SiO_2 is measured from XRD patterns. The surface composition of Pd–Ag and Pd–Cu alloy particles in bimetallic cogelled xerogel catalysts is determined through a combination of various characterization results coming from transmission electron microscopy (TEM), X-ray diffraction (XRD), and carbon monoxide chemisorption. Details of technical equipments are given in [14,15].

All samples were tested for 1,2-dichloroethane hydrodechlorination, which was conducted in a stainless steel tubular reactor (internal diameter: 10 mm) at a pressure of 0.3 MPa. The reactor was placed in a convection oven. A constant flow of each reactant was maintained by a Gilson piston pump for CH_2Cl–CH_2Cl and Brooks mass flow controllers for H_2 and He. The effluent was analyzed by gas chromatography (ThermoFinnigan with FID) using a Porapak Q5 packed column.

Prior to each experiment, Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts were reduced in situ at atmospheric pressure in flowing H_2 (0.023 mmol s^{-1}), while being heated to 350 °C at a rate of 350 °C/h and were maintained at this temperature for 3 h, except sample Cu, which was reduced at 400 °C and maintained at this temperature for 4 h. After reduction, Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalyst were cooled in flowing H_2 to the desired initial reaction temperature of 200 °C.

For each catalytic experiment, 0.11 g of catalyst pellets, sieved between 250 μm and 500 μm, were tested. The total flow of the reactant mixture was 0.45 mmol s^{-1} and consisted of CH_2Cl–CH_2Cl (0.011 mmol s^{-1}), H_2 (0.023 mmol s^{-1}), and He (0.42 mmol s^{-1}). The temperature was successively kept at 200 °C, 250 °C, 300 °C, 350 °C and 300 °C. The effluent was analyzed every 15 min.

3. Results

Metal loadings and values obtained for the bulk and surface compositions are presented in Table 1. A very marked impoverishment in palladium, and hence, a very marked enrichment either in silver for Pd–Ag alloy particles' surface or in copper for Pd–Cu alloy particles' surface compared to their bulk is observed. It is clear that it is difficult to prove with an unambiguous evidence, the existence of Pd–Ag or Pd–Cu alloys in Pd–Ag/SiO_2 and Pd–Cu/SiO_2 catalysts from XRD patterns: indeed, the metallic particles are very small (less than 3 nm) and the XRD reflections are very diffuse and small. So, the broad peaks could be composed of several overlapping reflections. Nevertheless, the presence of alloys has been already observed in Pd–Ag/SiO_2 cogelled xerogel catalysts synthesized by Heinrichs et al. [8,12,14] and in Pd–Cu/SiO_2 catalysts synthesized by Renouprez et al. [18]. Furthermore, the surface composition of Pd–Ag and Pd–Cu alloy particles in these Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts has been determined by combining three experimental techniques: CO chemisorption, XRD and TEM [14,15]. These values are in complete agreement with surface composition curves calculated in other studies by means of Auger electron and infrared spectroscopies [19], low energy ion scattering [18,20], and X-ray photoelectron spectroscopy [21].

Table 1

Surface compositions of alloy particles in Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts

Samples	Metal loading (wt.%)		x_{Pd} (at.%)	x_M (at.%)	x_{Pd_s} (at.%)	x_{M_s} (at.%)	d_{TEM} (nm)
	Pd	M[a]					
Pd:Ag 2:1	1.50	0.75	71	29	51	49	2.3 ± 0.3
Pd:Ag 1:1	1.50	1.50	57	43	22	78	2.2 ± 0.4
Pd:Ag 1:2	1.50	3.00	53	47	12	88	2.0 ± 0.2
Pd	1.50	–[b]	100	0	100	0	1.8 ± 0.3
Pd:Cu 2:1	1.50	0.75	51	49	28	72	2.6 ± 0.3
Pd:Cu 1:1	1.50	1.50	45	55	22	78	3.3 ± 0.4
Pd:Cu 1:2	1.50	3.00	32	68	12	88	3.6 ± 0.4
Cu	–[b]	1.50	0	100	0	100	3.5 ± 0.3

x_{Pd}, x_M, atomic ratios or bulk compositions of alloy particles determined from XRD, where M represents silver or copper; x_{Pd_s}, x_{M_s}, fraction of Pd atoms and fraction of Ag or Cu atoms present at the surface of Pd–Ag or Pd–Cu alloy particles; d_{TEM}, mean diameters of alloy particles measured by TEM.

[a] M represents silver or copper.

[b] Nonexistent.

Mean values of 1,2-dichloroethane conversion and C_2H_6, C_2H_4 and C_2H_5Cl selectivities are given at each temperature in Table 2 for all samples. It is observed that all samples were active for 1,2-dichloroethane hydrodechlorination between 200 °C and 350 °C. Sample Pd, containing 1.5 wt.% Pd, mainly produces ethane, C_2H_6, with a selectivity between 74% at 200 °C and 100% at 350 °C. Two secondary products are observed: ethyl chloride, C_2H_5Cl, and ethylene, C_2H_4. Sample Cu, containing 1.5 wt.% Cu, presents very low conversions at each temperature and mainly produces C_2H_4 with a selectivity between 94% at 200 °C and 100% at 350 °C. Small amounts of C_2H_6 are observed between 200 °C and 300 °C. For samples, Pd:Ag 2:1, Pd:Ag 1:1, Pd:Ag 1:2, Pd:Cu 2:1, Pd:Cu 1:1 and Pd:Cu 1:2, increasing silver or copper content in bimetallic catalysts results in an increase in ethylene selectivity, and for samples Pd:Ag 1:2 and Pd:Cu 1:2, this selectivity reaches 100% in the conditions of the catalytic test. Conversion of 1,2-dichloroethane decreases at each temperature when the silver or copper loading is increased. A slight deactivation is observed with all samples. Nevertheless, this deactivation becomes slower when the Ag or Cu loading is increased and is scarcely distinguishable with samples Pd:Ag 1:2, Pd:Cu 1:1 and Pd:Cu 1:2. Furthermore, all bimetallic catalysts clearly show that ethylene selectivity increases, not only

Table 2
Kinetic data for 1,2-dichloroethane hydrodechlorination over Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts

Samples	T (°C)	Conversion (mol%)	Selectivities (mol%)			r (mmol $kg_{cat}^{-1} s^{-1}$)	TOF_M (s^{-1})	TOF_{Pd} (s^{-1})
			C_2H_4	C_2H_6	C_2H_5Cl			
Pd:Ag 2:1	200	2.5	4	93	3	2.9	0.06	0.05
	250	7.1	19	80	1	8.2	0.17	0.14
	300	23	45	55	–[a]	28	0.59	0.46
	350	46	76	24	–[a]	–[b]	–[b]	–[b]
	300	17	64	36	–[a]	19	0.40	0.31
Pd:Ag 1:1	200	1.6	7	91	2	1.9	0.02	0.05
	250	6.0	65	35	–[a]	6.7	0.07	0.19
	300	19	88	12	–[a]	22	0.22	0.62
	350	41	93	7	–[a]	–[b]	–[b]	–[b]
	300	17	90	10	–[a]	19	0.19	0.53
Pd:Ag 1:2	200	0.8	80	17	3	0.65	0.005	0.04
	250	2.9	96	3	1	2.3	0.02	0.13
	300	10	98	2	–[a]	9.4	0.08	0.52
	350	25	100	–[a]	–[a]	–[b]	–[b]	–[b]
	300	9.7	100	–[a]	–[a]	9.3	0.08	0.52
Pd	200	8.0	8	74	18	8.9	–[b]	0.13
	250	17	5	85	10	19	–[b]	0.27
	300	30	2	92	6	33	–[b]	0.46
	350	58	–[a]	100	–[a]	–[b]	–[b]	–[b]
	300	21	–[a]	96	4	24	–[b]	0.34
Pd:Cu 2:1	200	1.1	12	84	4	1.2	0.02	0.04
	250	5.1	24	73	3	5.7	0.08	0.18
	300	15	52	46	2	17	0.23	0.55
	350	30	77	22	1	–[b]	–[b]	–[b]
	300	12	57	41	2	14	0.19	0.45
Pd:Cu 1:1	200	0.7	22	73	1	0.8	0.01	0.04
	250	3.5	52	47	1	3.8	0.05	0.17
	300	11	79	21	–[a]	12	0.15	0.53
	350	26	87	13	–[a]	–[b]	–[b]	–[b]
	300	10	79	21	–[a]	10	0.13	0.44
Pd:Cu 1:2	200	0.5	89	10	1	0.5	0.005	0.04
	250	2.6	94	6	–[a]	2.9	0.03	0.22
	300	10	99	1	–[a]	11	0.11	0.84
	350	24	100	–[a]	–[a]	–[b]	–[b]	–[b]
	300	10	100	–[a]	–[a]	11	0.11	0.84
Cu	200	0.04	94	6	–[a]	0.04	–[b]	–[b]
	250	0.2	97	3	–[a]	0.22	–[b]	–[b]
	300	0.6	99	1	–[a]	0.76	–[b]	–[b]
	350	1.3	100	–[a]	–[a]	1.6	–[b]	–[b]
	300	0.5	100	–[a]	–[a]	0.42	–[b]	–[b]

r, Consumption rate of 1,2-dichloroethane reported to catalyst mass; TOF_M, turnover frequency, that is, the number of 1,2-dichloroethane molecules consumed per active surface silver or copper atom and per second; TOF_{Pd}, turnover frequency, that is, the number of 1,2-dichloroethane molecules consumed per active surface palladium atom and per second.

[a] Not observed.

[b] Not calculated because 1,2-dichloroethane conversions are too high and the differential reactor equation is not more applicable.

with temperature, but also with time. In Fig. 1, conversion as well as C_2H_6, C_2H_4 and C_2H_5Cl selectivities are shown as a function of time and temperature over sample Pd:Cu 1:2.

Although it has been demonstrated in a previous study [12] that C_2H_4 and HCl influence kinetic results and although these both products are not present at the reactor inlet, the consumption rate of 1,2-dichloroethane, r, is calculated in first approximation from chromatographic measurements of C_2H_6, C_2H_5Cl and C_2H_4 concentrations in the reactor effluent and from the differential reactor equation when 1,2-dichloroethane conversions are <20%. This equation is written as follows:

$$r = \frac{F_A + F_{Cl} + F_E}{W} \qquad (F_{A0}, F_{Cl0} \text{ and } F_{E0} = 0) \tag{1}$$

where r is the consumption rate (mmol kg_{cat}^{-1} s^{-1}), F_A the molar flowrate of ethane at the reactor outlet (mmol s^{-1}), F_{A0} the molar flowrate of ethane at the reactor inlet

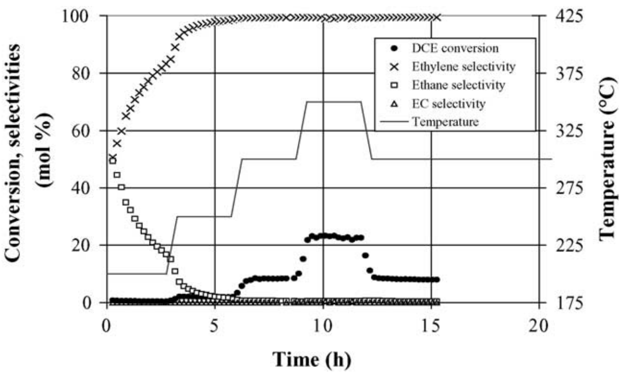

Fig. 1. 1,2-Dichloroethane hydrodechlorination over sample Pd:Cu 1:2.

(mmol s^{-1}), F_{Cl} the molar flowrate of ethyl chloride at the reactor outlet (mmol s^{-1}), F_{Cl0} the molar flowrate of ethyl chloride at the reactor inlet (mmol s^{-1}), F_E the molar flowrate of ethylene at the reactor outlet (mmol s^{-1}), F_{E0} the molar flowrate of ethylene at the reactor inlet (mmol s^{-1}) and W the catalyst mass inside the reactor (kg_{cat}). For all Pd–Ag/SiO_2 and Pd–Cu/SiO_2 catalysts, r has been calculated from Eq. (1) at the temperatures of 200 °C, 250 °C and 300 °C and these results are presented in Table 2. It has been shown in a previous study that the very particular structure of bimetallic cogelled xerogel catalysts allows avoiding diffusional limitations [22]. So, there are no pore diffusion limitations and the observed rate r is equal to the intrinsic rate of the chemical reaction.

4. Discussion

The mechanism of 1,2-dichloroethane hydrodechlorination has been studied in detail by Heinrichs et al. over a 1.9% Pd–3.7% Ag/SiO_2 cogelled xerogel catalyst with a surface composition, $x_{Pd_s} = 10$ at.% [12,14]. This mechanism is based on the sequence of elementary steps, which suggests a process of chlorination of the silver surface by 1,2-dichloroethane followed by a hydrodechlorination of that surface by hydrogen adsorbed on palladium. Used alone, silver deactivates rapidly due to its covering by chlorine atoms. Thanks to its activation power of hydrogen by dissociative chemisorption, palladium present in the alloy supplies hydrogen atoms for the regeneration of the chlorinated silver surface into metallic silver. The presence of hydrogen adsorbed on Pd also causes undesired ethylene hydrogenation leading to a loss of olefin selectivity.

The same mechanism can be suggested for Pd–Cu/SiO_2 cogelled xerogel catalysts, that is, chlorination of the copper surface by 1,2-dichloroethane followed by its dechlorination. Indeed, samples Pd:Cu 2:1, Pd:Cu 1:1 and Pd:Cu 1:2 present a very marked impoverishment in palladium for Pd–Cu alloy particles' surface (Table 1). Furthermore, the pure copper sample Cu presents a very low activity at each temperature for 1,2-dichloroethane hydrodechlorination (Table 2). Surface chlorine atoms could not be removed easily due to a lack of surface hydrogen. Palladium could, therefore, be needed to provide an abundant source of dissociated hydrogen, to reduce surface CuCl species and form HCl. According to the study of Fung and Sinfelt [23] concerning the hydrogenolysis of methyl chloride CH_3Cl on metals, metals from Group IB, such as Ag and Cu, are able to form a metal–chlorine bond, as demonstrated by the existence of stable chlorides. Furthermore, Vadlamannati et al. [9] suggested the same mechanism for 1,2-dichloroethane hydrodechlorination over Pt–Cu/C catalysts. Moreover, for 1,2-dichloroethane hydrodechlorination over Pt–Cu/SiO_2 catalysts, the addition of CO into the $CH_2Cl–CH_2Cl + H_2$ reaction mixture at 200 °C to block Pt sites only results in an improvement in the ethylene selectivity of the bimetallic catalysts at the expense of ethane. These observations were consistent with the idea that with Pt–Cu catalysts, ethylene forms on Cu sites that were not blocked by carbon monoxide [13].

For pure palladium sample Pd, it is reasonable to suggest that $CH_2Cl–CH_2Cl$ is adsorbed on Pd sites, C–Cl bond scission occurs, and then hydrogenation of the surface alkyl fragment readily takes place to form ethane only as observed previously in [16,24].

In order to examine the nature of the active site on which the reaction occurs, the turnover frequency (TOF), that is, the number of 1,2-dichloroethane molecules consumed per active surface metal and per second will be calculated. Nevertheless, as the nature of the active site is unknown, TOF will be calculated either as a function of active surface silver or copper, or as a function of active surface palladium in Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts.

4.1. Turnover frequency related to active surface silver or copper, TOF_M

Next to small alloy particles with a size of about 2–3 nm and situated inside silica particles, samples Pd:Ag 1:1, Pd:Ag 1:2, Pd:Cu 1:1 and Pd:Cu 1:2 also present some large pure silver or copper particles of about 10 nm observed by TEM and XRD and located outside silica network [17]. These large pure silver or copper particles are completely inactive for 1,2-dichloroethane hydrodechlorination (Table 2). It is, therefore, necessary to know the silver or copper mass present only inside small Pd–Ag or Pd–Cu alloy particles. The total number of metal atoms in one Pd–Ag or Pd–Cu alloy particle, *Metal atom/alloy particle*, is given by:

$$\textit{Metal atom/alloy particle} = \frac{\pi d_{\mathrm{TEM}}^3}{6}\frac{1}{x_{\mathrm{Pd}}v_{\mathrm{Pd}} + x_{\mathrm{M}}v_{\mathrm{M}}} \qquad (2)$$

where d_{TEM} is the mean diameter of alloy particles measured by TEM (nm) (Table 1); x_{Pd} and x_M, where M represents silver or copper, are, respectively, the atomic fractions of Pd and Ag or Cu in alloy particles determined from XRD (Table 1); v_{Pd} and v_M the mean volumes occupied by one metal atom in bulk metal (nm^3). For palladium, silver and

Table 3
Data for turnover frequency calculation for 1,2-dichloroethane hydrodechlorination over Pd–Ag/SiO$_2$ and Pd–Cu/SiO$_2$ cogelled xerogel catalysts

Samples	*Metal atom/alloy particle*	*Pd/alloy particle*	*M/alloy particle*	N_{alloy}	m_{M} (g)	$m_{\mathrm{M}}/m_{\mathrm{a}}$ (wt.%)
Pd:Ag 2:1	459	326	133	2.74×10^{18}	0.07	0.62
Pd:Ag 1:1	414	236	178	3.81×10^{18}	0.12	1.14
Pd:Ag 1:2	314	166	148	5.51×10^{18}	0.15	1.35
Pd:Cu 2:1	692	353	339	2.55×10^{18}	0.09	0.86
Pd:Cu 1:1	1434	645	789	1.40×10^{18}	0.12	1.10
Pd:Cu 1:2	1916	613	1303	1.49×10^{18}	0.21	1.90

Metal atom/alloy particle, total number of metal atoms in one Pd–Ag or Pd–Cu alloy particle; *Pd/alloy particle*, *M/alloy particle*, number of palladium atoms and number of silver or copper atoms in one alloy particle; N_{alloy}, total number of alloy particles in catalyst; m_{M}, total active silver or copper mass into all alloy particles; $m_{\mathrm{M}}/m_{\mathrm{a}}$, active silver or copper loading, where m_{a} is the actual catalyst mass measured after vacuum drying, calcination and reduction steps [17].

copper, the values of v_{Pd} and v_{M} are 0.01470 nm^3, 0.01706 nm^3 and 0.01183 nm^3, respectively [25]. The values of *Metal atom/alloy particle* are presented in Table 3. From Eq. (2), it is now possible to determine the number of silver or copper atoms and the number of palladium atoms in one alloy particle:

$$Pd/alloy\,particle = x_{\mathrm{Pd}} Metal\,atom/alloy\,particles \tag{3}$$

and

$$M/alloy\,particle = x_{\mathrm{M}} Metal\,atom/alloy\,particle \tag{4}$$

The values of *M/alloy particle* and *Pd/alloy particle* are presented in Table 3.

By assuming that all palladium atoms present in the catalyst are contained in alloy particles, the total number of alloy particles in catalyst, N_{alloy}, can be calculated from:

$$N_{\mathrm{alloy}} = \left(\frac{n_{\mathrm{Pd}} 10^{-3}}{Pd/alloy\,particle}\right) N_{\mathrm{Avogadro}} \tag{5}$$

where n_{Pd} is the amount of palladium in the gel (mmol) [17]; N_{Avogadro} the Avogadro's number, equal to 6.02 10^{23} atoms mol^{-1}. The values of N_{alloy} are presented in Table 3. It is now possible to determine the total active silver or copper mass (g) into all alloy particles from Eq. (6):

$$m_{\mathrm{M}} = \frac{N_{\mathrm{alloy}}(M/alloy\,particle)(\mathrm{MM_M})}{N_{\mathrm{Avogadro}}} \tag{6}$$

where MM$_{\mathrm{M}}$ is the silver or copper atomic weight, 107.868 g mol^{-1} and 63.546 g mol^{-1}, respectively. The values of m_{M} and $m_{\mathrm{M}}/m_{\mathrm{a}}$, where m_{a} is the actual catalyst mass measured after vacuum drying, calcination and reduction steps [17], are presented in Table 3.

The turnover frequency related to M (Ag or Cu), TOF$_{\mathrm{M}}$, that is, the number of 1,2-dichloroethane molecules consumed per surface active silver or copper atom and per second is calculated for Pd–Ag/SiO$_2$ and Pd–Cu/SiO$_2$ cogelled xerogel catalysts as follows:

$$\mathrm{TOF_M} = \frac{r}{(m_{\mathrm{M}}/m_{\mathrm{a}})} 10^{-6} (\mathrm{MM_M}) \frac{1}{D_{\mathrm{M}}} \tag{7}$$

where r is the specific consumption rate of 1,2-dichloroethane (mmol s^{-1} kg$_{\mathrm{cat}}^{-1}$) (Table 2); $m_{\mathrm{M}}/m_{\mathrm{a}}$ the active silver or copper loading (Table 3); MM$_{\mathrm{M}}$ the silver or copper atomic weight, 107.868 g mol^{-1} and 63.546 g mol^{-1}, respectively; D_{M} the silver or copper dispersion in small Pd–Ag or Pd–Cu alloy particles located inside silica particles. D_{M} is calculated as follows:

$$D_{\mathrm{M}} = \frac{[D_{\mathrm{Pd-M}}(Metal\,atom/alloy\,particle) - D_{\mathrm{CO}}(Pd/alloy\,particle)]}{(M/alloyparticle)}$$

where $D_{\mathrm{Pd-M}}$ is the overall metal dispersion of alloy particles estimated from TEM [17]; *Metal atom/alloy particle* is the total number of metal atoms in one Pd–Ag or Pd–Cu alloy particle (Table 3); D_{CO} is the palladium dispersion measured by CO chemisorption [17]; *Pd/alloy particle*, *M/alloy particle* are the number of palladium atoms and the number of silver or copper atoms, respectively, in one alloy particle (Table 3). The different values of TOF$_{\mathrm{M}}$ calculated at the temperatures of 200 °C, 250 °C and 300 °C for Pd–Ag/SiO$_2$ and Pd–Cu/SiO$_2$ cogelled xerogel catalysts are presented in Table 2.

4.2. Turnover frequency related to active surface palladium, TOF$_{Pd}$

By assuming that all palladium atoms present in the catalyst are contained in alloy metal particles, the turnover frequency related to Pd, TOF$_{\mathrm{Pd}}$, that is, the number of 1,2-dichloroethane molecules consumed per surface active palladium atom and per second is calculated for Pd–Ag/SiO$_2$ and Pd–Cu/SiO$_2$ cogelled xerogel catalysts as follows:

$$\mathrm{TOF_{Pd}} = \frac{r}{(m_{\mathrm{Pd}}/m_{\mathrm{a}})} 10^{-6} (\mathrm{MM_{Pd}}) \frac{1}{D_{\mathrm{CO}}} \tag{9}$$

where r is the specific consumption rate of 1,2-dichloroethane (mmol s^{-1} kg$_{\mathrm{cat}}^{-1}$) (Table 2); $m_{\mathrm{Pd}}/m_{\mathrm{a}}$ the palladium loading (Table 1); MM$_{\mathrm{Pd}}$ the palladium atomic weight, 106.42 g mol^{-1}; D_{CO} the palladium dispersion in small Pd–Ag or Pd–Cu alloy particles located inside silica particles calculated from CO chemisorption measurements [17]. The different values of TOF$_{\mathrm{Pd}}$ calculated at the temperatures of 200 °C, 250 °C and 300 °C for Pd–Ag/SiO$_2$ and Pd–Cu/SiO$_2$ cogelled xerogel catalysts are presented in Table 2.

In Fig. 2a, TOF$_{\mathrm{M}}$ is presented as a function of the fraction of silver or copper atoms present at the surface of Pd–Ag or Pd–Cu alloy particles, $x_{\mathrm{M_s}}$ (Table 1), at the temperatures of 250 °C and 300 °C (first level) for samples Pd:Ag 2:1, Pd:Ag 1:1, Pd:Ag 1:2, Pd:Cu 2:1, Pd:Cu 1:1 and Pd:Cu 1:2. It is observed that TOF$_{\mathrm{M}}$ for 1,2-dichloroethane hydrodechlor-

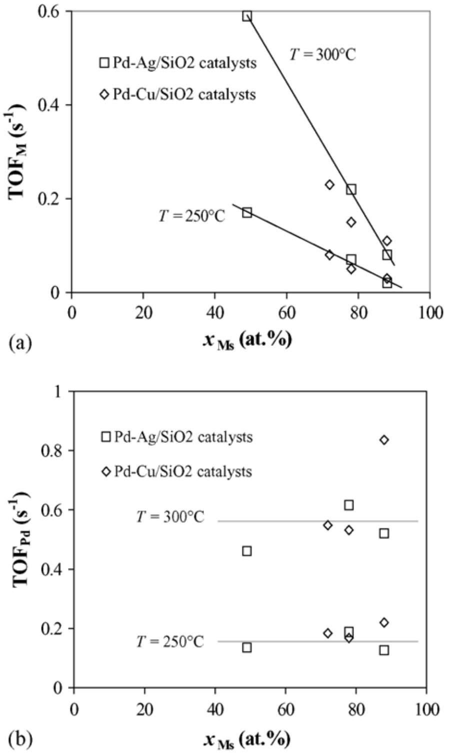

Fig. 2. TOF_M (a) and TOF_{Pd} (b) as a function of the fraction of silver or copper atoms present at the surface of Pd–Ag or Pd–Cu alloy particles, x_{M_s}.

ination over Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts increases with temperature. At the same temperature (250 °C or 300 °C), TOF_M increases when the fraction of silver or copper atoms present at the surface of Pd–Ag or Pd–Cu alloy particles, x_{M_s}, decreases and this trend seems to be the same for Pd–Ag/SiO_2 and Pd–Cu/SiO_2 catalysts. Thus, at each temperature, a single line is adjusted with all Pd–Ag and Pd–Cu samples.

In Fig. 2b, TOF_{Pd} is presented as a function of the fraction of silver or copper atoms present at the surface of Pd–Ag or Pd–Cu alloy particles, x_{M_s} (Table 1), at the temperatures of 250 °C and 300 °C (first level) for samples Pd:Ag 2:1, Pd:Ag 1:1, Pd:Ag 1:2, Pd:Cu 2:1, Pd:Cu 1:1 and Pd:Cu 1:2. It is observed that TOF_{Pd} for 1,2-dichloroethane hydrodechlorination over Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts increases with temperature. At the same temperature (250 °C or 300 °C), for all Pd–Ag/SiO_2 and Pd–Cu/SiO_2 catalysts, within the experimental error, it seems that TOF_{Pd} does not significantly vary with the fraction of silver or copper atoms present at the surface of Pd–Ag or Pd–Cu alloy particles, x_{M_s}. Thus, at each temperature, a single horizontal line represents the mean value calculated from TOF_{Pd} values for all Pd–Ag and Pd–Cu samples.

According to the study of 1,2-dichloroethane hydrodechlorination mechanism over a 1.9% Pd–3.7% Ag/SiO_2 cogelled xerogel catalyst ($x_{Ag_s} = 90$ at.%)[12], the slow step of the sequence of elementary steps is the first C–Cl bond breaking of 1,2-dichloroethane, which occurs on silver. By assuming that 1,2-dichloroethane hydrodechlorination mechanism is the same over Pd–Ag/SiO_2 and Pd–Cu/SiO_2 cogelled xerogel catalysts of this present work, it is difficult to understand why TOF_M decreases when x_{M_s} increases, unless it is supposed that, when x_{M_s} increases, more and more silver or copper atoms present at the surface of Pd–Ag and Pd–Cu alloy particles do not participate in the hydrodechlorination reaction. In this case, in Eq. (7), the specific consumption rate of 1,2-dichloroethane, r, is divided by the total number of silver or copper atoms present in alloy particles among which more and more are inactive when x_{M_s} increases. Thus, it could be assumed that inactive silver or copper atoms are those which are not next to surface palladium atoms, and which are rapidly deactivated due to their covering by chlorine atoms without a possible regeneration of the chlorinated silver or copper surface into metallic silver or copper by reaction with hydrogen adsorbed on palladium. In this way, TOF_M could not be a correct estimation of actual turnover frequency because inactive silver or copper atoms could occur for its calculation.

In Fig. 2b, at the same temperature (250 °C or 300 °C), it seems that TOF_{Pd} does not significantly vary with the fraction of silver or copper atoms present at the surface of Pd–Ag or Pd–Cu alloy particles, x_{M_s}. According to 1,2-dichloroethane hydrodechlorination mechanism described in [12] (chlorination of the silver surface by 1,2-dichloroethane followed by a hydrodechlorination of that surface by hydrogen adsorbed on palladium), and by the fact that more and more silver or copper atoms present at the surface of Pd–Ag and Pd–Cu alloy particles do not participate in the hydrodechlorination reaction as explained above, it can be assumed that the active site, on which the catalytic cycle is realized, is constituted of one palladium atom and its surrounding silver or copper atoms. The number of these active sites is equal to the number of palladium atoms present at the surface of Pd–Ag or Pd–Cu alloy particles. Thus, TOF_{Pd} represents the number of catalytic cycle per active site (palladium atom and its surrounding silver or copper atoms) and per second. According to Fig. 2b, TOF_{Pd} could be independent of surface composition, x_{M_s}, for samples studied in the present work (49 at.% $< x_{M_s} <$ 88 at.%).

It is entirely remarkable to observe that the atom nature (silver or copper) does not significantly influence TOF_{Pd}, but TOF_M also. Indeed, at the temperatures of 250 °C and 300 °C, Pd–Ag samples are located on the same line as Pd–Cu samples (Fig. 2a and b). In other words, 1,2-dichloroethane hydrodechlorination is insensitive to the atom's nature (silver or copper).

5. Conclusions

The surface composition of Pd–Ag and Pd–Cu alloys, measured from the combination of results from CO chemisorption, XRD and TEM, indicate a very pronounced surface enrichment with silver or copper.

While 1,2-dichloroethane hydrodechlorination over pure palladium mainly produces ethane, increasing silver or copper content in bimetallic catalysts results in an increase in ethylene selectivity. Used alone, these metals deactivate rapidly due to their covering by chlorine atoms. Thanks to its activation power of hydrogen by dissociative chemisorption, palladium present in the Pd–Ag or Pd–Cu alloy supplies hydrogen atoms for the regeneration of the chlorinated silver or copper surfaces into metallic silver and copper. The specific consumption rate of 1,2-dichloroethane decreases when silver or copper loading increases. The turnover frequency, that is, the number of catalytic cycle per active site (palladium atom and its surrounding silver or copper atoms) and per second, seems to be independent of surface composition of alloy particles and 1,2-dichloroethane hydrodechlorination is insensitive to the atom's nature (silver or copper).

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