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PdCu alloy nanoparticles on alumina as selective catalysts for trichloroethylene hydrodechlorination to ethylene

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PdCu bimetallic catalysts supported on alumina were prepared by different common impregnation protocols and by a polyol nanoparticles synthesis route. These materials were studied in order to establish the relationship between structure, particle size, Pd–Cu interaction and catalytic activity/selectivity in the hydrodechlorination of trichloroethylene (TCE) in gas phase. The surface properties and the interaction between Cu and Pd in the bimetallic particles, as well as their catalytic behaviour are strongly influenced by the preparation protocol. Depending on the synthesis, PdCu alloy formation or isolated phases were observed. The presence of isolated Pd particles leads to high ethane selectivity, whereas upon alloy formation or strong interaction between Pd and Cu a higher ethylene yield was obtained. By the nanoparticles polyol synthesis, Pd-Cu alloy formation was obtained, leading to total selectivity to ethylene in the TCE hydrodechlorination reaction. On the Pd monometallic catalysts larger particle size resulted in higher levels of ethylene formation.

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1. Introduction

Chlorinated organic compounds, despite their wide spread industrial applications, have been categorized as high priority environmental pollutants. They represent hazardous ozone depleting compounds with high carcinogenic activity. Catalytic hydrodechlorination (HDC) is a promising technology to transform them into more useful, but less harmful hydrochlorocompounds [1–4], obtaining valuable products that could be applied in other processes. Trichloroethylene (TCE) is one of the harmful pollutants for humans that must be removed from the environment. The gas phase catalytic hydrodechlorination of TCE can lead to a wide variety of products with added value. Mostly, noble metal catalysts have been used for this reaction converting the TCE to the fully hydrogenated product ethane [5–8].

In the last decade, it was discovered that the modification of the noble metal catalysts by the addition of a second metal modifies the catalytic performance in the hydrodechlorination reactions leading to valuable olefins [9]. Since then, a number of transition metal additives have been studied such as Pt–Cu [10–13], Pt–Sn [14] or Pd–Ag [15,16]. Several explanations have been proposed to explain the change in the selectivity towards the olefin using bimetallic systems, related with an electronic modification of the noble metal [12], or structure-sensitivity [1,2,17] versus structure-insensitivity [4,18]. In general, the high ability of the noble metals for the hydrogenolysis of C–Cl bonds results in the fully hydrogenated products. In the case of non-noble metal like Cu, the dechlorination step occurs selectively leading to the olefin, in the case of TCE to ethylene.

Previous works [19,20] showed the requirement of alloy formation of the metals in order to obtain highly active and selective catalysts towards ethylene, avoiding deactivation. Barrabés et al. [19,21,22] showed that the metal-metal interaction strongly affected the catalytic behaviour in the TCE HDC reaction on copper hydrotalcite-derived catalysts. In this work, the influence of the particle size and of the metal amount was not studied. By studying the effect of the particles size and the metals ratio, while maintaining complete alloy formation and minimizing the noble metal amount required, optimization of such catalysts for the TCE hydrodechlorination process should be achieved. The interaction of the metals and the dispersion on the surface is directly related with the preparation method employed. Most of the methods used to prepare bimetallic catalysts on alumina are based on







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co-impregnation, sequential impregnations, co-exchange with the salts of the two metals or redox reaction [23]. An alternative route employed in the last years in catalysis, in order to control the surface chemistry of the catalysts, is the use of metal nanoparticles (NPs) prepared in solution. NPs have unique physical and chemical properties different from bulk materials due to the reduction of particle size. Extremely high surface areas and therefore high fractions of metal atoms occupying positions on or close to the surface as well as the presence of various types of active sites make such nanoparticles ideal candidates as key components of catalytic systems [24].

The present work aims at the optimization of bimetallic catalysts for the TCE hydrodechlorination by comparing several preparation protocols including the synthesis of bimetal nanoparticles in solution. The study of the structure and surface chemistry of the catalysts achieved by various preparation procedures and the influence on the catalytic behaviour will allow the elucidation of the optimal parameters.

In the first step, Pd-Cu bimetallic catalysts supported on alumina have been prepared by different impregnation procedures from dissolved metal salts as precursors. Controlled surface reaction (CSR), sequential impregnation (SI), sequential reduction impregnation (SRI) and co-impregnation (COI) protocols have been employed. From the different preparations, we expected different degrees of metal-metal interaction, such as isolated metals and alloy formation. Then, in order to achieve control over the particle size and composition and to optimize the metals amount and ratio in the catalysts, Pd and Pd-Cu alloy nanoparticles were prepared following a polyol-method using 1-hexadecylamine, as reported previously by Meshesha et al. [25]. This method leads to uniform, nanosized and spherical metal particles, which were subsequently supported on alumina. All catalysts were characterized by several techniques in order to study the structure and surface properties and tested in the gas phase TCE hydrodechlorination reaction.

2. Experimental

2.1. Catalyst synthesis

Two different approaches were utilized to prepare γ -alumina supported bimetallic Pd-Cu catalysts: (1) materials prepared by impregnation from a metal salt precursor solution will be referred to as "impregnation catalysts"; (2) catalysts prepared from (bi)metallic nanoparticles by a polyol method followed by loading the nanoparticles onto the alumina support will be referred to as "nanoparticles catalysts" in this work. Details on the preparation are described in the following.

2.1.1. PdCu/Al₂O₃i catalysts synthesis by impregnation

Four different impregnation-based procedures were applied to prepare bimetallic Pd2Cu1.2/Al₂O₃i (2 wt% Pd, 1.2 wt% Cu, molar ratio 1:1) catalysts, which are illustrated in Scheme 1: SI, SRI, CSR, and COI on γ -alumina (Sasol Germany GmbH, Puralox SBA 200, specific surface area 250 m²/g). Furthermore, monometallic catalysts were prepared as well. In the first step, the monometallic 2 wt% Pd/Al₂O₃ was prepared by impregnation using an aqueous solution of the precursor salt, Pd(NO₃)₂·2H₂O. This step consists of a cationic exchange between the metallic complex and the alumina surface in an aqueous solution at pH 11 obtained by the addition of ammonia. After evaporation of the aqueous phase, the catalyst was dried at 120 °C and calcined in air at 450 °C.

After that, the monometallic Pd catalyst was directly impregnated with the copper salt (SI), or reduced under hydrogen flow at 300 °C for 1 h before impregnation with the copper salt solution (SRI), or introduced to an aqueous solution containing a copper nitrate salt under hydrogen flow (CSR). The COI catalysts were prepared by direct impregnation with a solution containing the two metals $(Pd(NO_3)_2 \cdot 2H_2O)$ and $Cu(NO_3)_2 \cdot 3H_2O)$. Then the samples were dried, calcined at 300 °C for 2 h, and finally reduced at 400 °C under hydrogen flow for 1 h.

2.1.2. Synthesis of PdCu/Al₂O₃np nanoparticles catalysts

A modified procedure of the previously described protocol [25] was adopted in order to prepare 1-hexadecylamine (HDA) capped Pd and Pd-Cu nanoparticles. Analytically pure Pd acetyl acetonate (Pd(AcAc)₂) and Cu(NO₃)₂·2H₂O were used as the starting material without further purification. In a typical synthesis procedure, 100 ml of ethylene glycol solution of the respective metal salt(s) was mixed with an appropriate amount of HDA in a round-bottom flask equipped with a magnetic stirrer, refluxing device and thermometer. The mixture was mixed thoroughly in an ice bath to prevent rapid reduction of the noble metals in ethylene glycol and HDA solutions at room temperature. The solution was then heated rapidly to 140 °C and kept there for 12 h. The nanoparticles were synthesized maintaining HDA/metal molar ratio of three. Nanoparticles with different Pd/Cu molar ratios were synthesized.

A solution of Pd and Pd-Cu nanoparticles in toluene was used to impregnate the particles onto the γ -alumina support. After evaporation of the solvent in a rotavapor the catalyst was dried overnight at 100 °C, calcined in air at 350 °C for 2 h and reduced by flowing hydrogen at 300 °C for 2 h prior to reaction. The calcination and reduction of the catalysts were performed at the lowest temperature required to remove the organic species from the catalyst surface and fully reduce particles. The materials synthesized from the nanoparticle precursors are labelled as Pd1/Al₂O₃np, Pd1Cu1/Al₂O₃np (Cu/Pd molar ratio 1.64), Pd1Cu5/Al₂O₃np (Cu/Pd molar ratio 8.33), and Pd1.6Cu1/Al₂O₃np (Cu/Pd molar ratio 1). For example Pd1Cu1/Al₂O₃np contains 1 wt% Pd and 1 wt% Cu metal impregnated on alumina.

For direct comparison, an additional bimetallic catalyst was prepared from the same precursor salts as the nanoparticles and calcined and reduced under identical conditions. This material contains 1 wt% of both, Pd and Cu, and was prepared by simultaneous impregnation of Cu(NO₃)₂ and Pd(AcAc)₂ salts followed by calcination at 350 °C. This reference catalyst is referred to as Pd1Cu1/Al₂O₃ref.

2.2. Characterization techniques

The chemical composition of the samples was determined by ICP-OES with a PerkinElmer Plasma 400 instrument.

The structure and crystallinity of the supported catalysts after calcination was investigated by X-ray diffraction carried out on a Siemens D5000 diffractometer (Bragg–Bentano for focusing geometry and vertical θ – θ goniometer) fitted with a grazing incident (ω : 0.52°) attachment for thin film analysis and scintillation counter as a detector.

Selected catalysts were characterized with TEM and HRTEM techniques. TEM was operated at 100 kV (JEOL JEM-2000 EX II). High-Resolution Transmission Electron Microscopy (HRTEM) was carried out at 200 kV with a JEOL 2010F instrument equipped with a LaB₆ source. The point-to-point resolution of the microscope was 0.20 nm. Samples were deposited on holey-carbon-coated grids from alcohol suspensions. More than 100 individual particles were used in each sample for particle size determination.

The temperature programmed reduction (TPR) studies were performed in a ThermoFinnigan (TPORD 110) apparatus equipped with a thermal conductivity detector (TCD). Before the TPR analysis, the samples (around 100 mg) were dried under flowing argon at 120 °C for 24 h. The analysis was carried out using 3% H₂/Ar flowing



Scheme 1. Synthesis protocols for Pd2Cu1.2/Al₂O₃i impregnation catalysts.

at 20 ml/min by heating from room temperature to 900 $^\circ\text{C}$ with a ramp of 10 $^\circ\text{C}$ min^{-1}.

The Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS 28 spectrometer equipped with an MCT detector at a resolution of $4 \,\mathrm{cm^{-1}}$. The measurement cell is connected to a vacuum system working in the 10^{-6} mbar range and allowing in situ pre-treatments of samples. The catalysts were pressed into self-supporting wafers and were reduced in 500 mbar of pure H₂ at 300 °C. After keeping the catalyst in hydrogen atmosphere at that temperature for 30 min, the cell was evacuated for another 30 min at the reduction temperature. CO adsorption measurements were carried out at 20 °C in 5 mbar of pure CO static atmosphere, followed by evacuation of the gas phase CO at 20 °C.

2.3. Catalytic activity and selectivity measurements

The catalysts were tested for gas-phase hydrodechlorination reaction of TCE using a continuous fixed-bed quartz glass reactor setup described previously [19]. The gas feed at a total flow of 60 ml/min was obtained by flowing an inert gas (He) and hydrogen through a saturator kept at 25 °C by a thermostat, containing TCE in liquid phase. The TCE partial pressure was 92 mbar and the TCE flow was 5.5 ml/min. The molar ratio of H₂/TCE was maintained at 3.5, near the stoichiometric amount required to obtain ethylene. The gas flows were adjusted by mass flow controllers (Brooks Instrument) and introduced into the reactor, which is placed in a furnace coupled with a temperature controlling system. The outlet of the reactor is connected by a six-way valve to a gas chromatograph (HP 5890 series II, HP Poraplot column, FID). For all measurements 100 mg of catalyst were charged in the reactor. Catalytic conversion and selectivity were calculated by analyzing the calibrated peak areas of TCE and the respective products.

3. Results and discussion

3.1. Characterization results

3.1.1. PdCu/Al₂O₃ impregnation catalysts

HRTEM analysis was performed in order to study the particle size distribution (Fig. 1) and alloy formation of the metallic particles obtained from different preparation protocols. HRTEM results of monometallic Pd catalyst (not shown) contain well-dispersed Pd particles over the alumina support with particles size of around 2 nm. Lattice fringe images recorded of individual Pd particles exhibited spacing of metallic Pd at 2.3 Å corresponding to Pd(111). A general view of the COI sample is depicted in Fig. 1(A). The metal particle size distribution is broader compared to that of pure Pd, and the main diameter is around 3.5 nm. Fourier transforms analysis (FFT) of high resolution images of individual particles show spots at 2.2 Å, which is lower than the Pd(111) spacing at 2.3, suggesting the possibility of alloying between Pd and Cu in the sample. Both Pd and Cu have fcc crystal structure, and the lattice parameter of Pd is larger than that of Cu. For that reason, alloying Cu with Pd results in a reduction of the (111) lattice parameter.

The sample CSR presents a rather broad size distribution histogram (Fig. 2). The mean particle size is centred at about 5.8 nm. The lattice-fringe image/FFT of a representative particle (Fig. 2(Ba)) presents spots at 2.3 Å characteristic of pure Pd metal (111), and their relative position indicates that the Pd crystallite is oriented along the [110] crystallographic direction. Besides pure Pd particles, the sample also contains Pd-Cu alloy particles. Fig. 1(B-b) shows a high resolution image with a spot at 2.2 Å being identified and the relative position of the spots in the FT pattern reveals again the [110] crystallographic orientation. On the other hand, the SRI sample (Fig. 1(C)) exhibits well-dispersed metal particles on the support with particles size of 4.0 nm. Spots in the FT pattern (Fig. 1(C-a)) at 2.2 and 1.3 Å are significantly lower than for Pd(111) and Pd(220) values, respectively, indicating the alloy formation between Pd and Cu. The angle at 90° between both spots indicates that the crystallite is oriented along the [112] crystallographic direction. Fig. 1(C-b) also shows indicative images of alloy formation. The FT image of the particle marked by an arrow shows spots at 2.2 and 1.8 Å, again at lower values than for Pd(111) and Pd(200), indicative of Pd-Cu alloying.

Fig. 1(C-c) shows spots in the FT pattern at 2.6 Å that can only be ascribed to $(1\ 1\ 0)$ planes of Cu₃Pd (tetragonal structure). Consequently, for this sample the existence of alloying between Pd and Cu is clear. The same is observed for the SI sample (Fig. 1(D)) that contains metal particles of about 5.0 in diameter with spots at 2.2 Å. It is interesting to note that no core–shell structures have been observed in any of the samples, that is, no copper shells develop on the Pd particles. In contrast, alloying of Pd with Cu creates true alloy particles with sharp lattice edges. However, HRTEM cannot



Fig. 1. HRTEM micrographs of Pd2Cu1.2/Al₂O₃i catalysts prepared by impregnation (A: COI, B: CSR, C: SRI and D: SI).

reveal the presence of surface layers enriched in Cu of a few atom layers thickness.

For obtaining more insights into the metal-metal interaction, TPR analysis was performed (Fig. 3). The CuO/Al₂O₃ reduction is characterized by a peak 280 °C [26], related with the reduction of the CuO phase as well as the reduction of Cu⁺ to Cu⁰. The reduction of monometallic Pd catalysts occurs at lower temperatures, around 100 °C. The addition of copper (bimetallic catalysts) modifies the reduction profile. Previous studies demonstrated that the formation of a Pd-Cu alloy arises from the interaction between copper and palladium oxides. Fig. 3 shows that in all the samples a new reduction peak appears between 125 and 200 °C, that can be attributed to the reduction of Cu and Pd from the mixed oxide, Pd_xCu_yO [26]. For the COI preparation method the interaction between palladium and copper also occurs with a reduction peak at 145°C, but the presence of isolated palladium particles leading to peaks between 50 and 100 °C is additionally observed in the TPR profile. When the CSR protocol was used, low intensity and broad peaks are observed, which is related with the fact that the metals are already reduced during the preparation [27], thus no reduction of isolated Pd particles is observed, leading to the lower hydrogen consumption. SI and SRI samples show reduction peaks at 130 °C and 160 °C related with PdCu alloy, as observed by HRTEM.

In order to study the surface composition and accessibility of the metals at the surface, CO adsorption on Cu-Pd catalysts was examined by FT-IR spectroscopy (Fig. 4). CO adsorbed at room



Fig. 2. Particle size histograms.



Fig. 3. TPR profiles of Pd2Cu1.2/Al $_2O_3i$ catalysts prepared by impregnation: (a) CSR, (b) COI, (c) SRI, and (d) SI.

temperature leads to the appearance of several bands between 1920 and 2150 cm⁻¹ related with CO on palladium and copper particles. The region from 1750 to 1900 cm^{-1} is assigned to CO adsorption on three-fold hollow Pd(111) sites [28]. The region from 1900 to 2000 cm⁻¹ is attributed to two-fold bridge CO adsorption. The bands between 2000 and 2100 cm^{-1} are assigned to linearly bonded CO on Pd and Cu⁰. Several bands at higher frequencies >2100 cm⁻¹ which appear additionally in the spectra of the bimetallic catalysts are attributed to CO on oxidized Cu species (Cu⁺, Cu²⁺).

The spectrum (a) is characteristic for CO on metallic Pd. In all bimetallic catalysts, clear changes in the available adsorption sites are visible. The COI catalyst (spectrum (b)) shows a broad CO band between 1700 and $2000 \, \text{cm}^{-1}$, similar to the spectrum of



Fig. 4. FTIR-CO spectra (5 mbar CO, $20 \,^{\circ}$ C) of bimetallic catalysts prepared by impregnation: (a) Pd2/Al₂O₃i, (b) COI, (c) CSR, (d) SRI and (e) SI. Samples were reduced at 300 $^{\circ}$ C prior to CO adsorption.

ab	le	1	

Physical characteristics of Pd-Cu nanoparticle catalysts.

Catalyst	Metal loadin	g	Particle size ^a (nm)	
	Pd (wt%)	Cu (wt%)		
Pd1/Al ₂ O ₃ np	0.8	-	10	
Pd1Cu1/Al ₂ O ₃ np	0.9	1.1	15	
Pd1Cu5/Al ₂ O ₃ np	0.9	4.7	-	
Pd1.6Cu1/Al ₂ O ₃ np	1.6	1.0	15	
Pd1Cu1/Al ₂ O ₃ ref	0.7	0.8	-	

^a Determined by TEM.

CO adsorbed on Pd2/Al₂O₃i. This range is related with CO species multiply-bonded on neighbouring Pd⁰ sites, indicating no significant dilution of the Pd surface by Cu in the COI sample. In addition, the signal of CO on Cu^{2+} is rather high as compared to the relative intensities observed on the other bimetallic catalysts, which hints to more particles with oxidized Cu species at the surface. Therefore, it can be concluded that isolated Pd and Cu particles are present on the COI sample in addition to alloyed particles, which is in agreement with the TPR results.

The catalysts prepared by CSR, SRI and SI exhibit main CO bands at 2142, 2115, 2065 and 1978 cm⁻¹. CO adsorption on metallic copper leads to a single CO vibration located between 2080 and 2120 cm⁻¹ depending on the crystal plane and the nature of the support [27]. In this way the band around $2115 \,\mathrm{cm}^{-1}$ is attributed to Cu^0 -CO species, while the band at 2065 cm⁻¹ is likely related with carbonyls on zero-valent Pd. Previous studies assigned this band to CO linearly bonded on Pd-Cu alloy [28]. The band of bridgebonded CO at 1978 cm⁻¹ suggests that Pd metal ensembles may also exist at the surface. The vibrational band visible at 2142 cmcan be assigned to CO adsorbed on oxidized Cu⁺. This would indicate the presence of oxidized Cu species in addition to reduced Cu, even though the TPR measurements revealed that most of the Cu is reduced at this temperature (300 °C). An alternative assignment is adsorption to Cu species alloyed with Pd. Borovkov et al. [10] investigated CO adsorption on Pt-Cu catalysts by FTIR spectroscopy and attributed a band at 2135 cm⁻¹ not to CO associated with oxidized Cu species, but with metallic Cu modified by Pt. The blue-shift by about 40 cm⁻¹ of the frequency of CO on Cu was attributed to the modification of the electronic properties upon alloying with Pt [10]. The assignment of CO on Cu species is commonly based on the stability of the CO adsorption complexes against evacuation. The band at 2142 cm⁻¹ was stable against evacuation, which can be an indication for CO adsorbed on Cu⁺. However, a higher stability of the CO on Cu that is alloyed with Pd was obtained by DFT calculations for the Pd-Cu bimetallic system by Lopez and Nørskov [29]. Such a stabilization effect can therefore also be relevant for the present Pd-Cu alloy samples. In light of the potential alternative assignment of the band at 2142 cm⁻¹ the Cu species should be fully reduced under these conditions, which is indeed in good agreement with the TPR measurements.

Overall, the FTIR studies of the bimetallic catalyst showed that the Pd-Cu bimetallic catalysts prepared by redox reaction (SRI, SI and CSR) exhibited a preferential deposition of Cu on the surface of Pd breaking up larger ensembles that can adsorb CO on hollow sites. In the work of Melendrez et al. [30], in contrast, Cu was likely deposited at the low coordination sites (edges and corners).

3.1.2. PdCu/Al₂O₃ nanoparticles catalysts

The PdCu nanoparticles impregnated on γ -alumina have been characterized by different techniques. The molar compositions of the metals were investigated using ICP spectroscopy and the results are summarized in Table 1.

As expected a little deviation from the originally employed metal amount was observed. The decrease in weight percentage



Fig. 5. XRD patterns of (a) γ -Al₂O₃, (b) Pd1/Al₂O₃np, (c)Pd1Cu1/Al₂O₃np, (d)Pd1Cu5/Al₂O₃np (e) Pd1Cu1/Al₂O₃ref, and (f) Pd1.6Cu1/Al₂O₃np nanoparticle catalysts after calcination. Reflections of PdO (\blacksquare) and Pd (\bigcirc) are indicated.

of the active components arises during the preparation and separation of the nanoparticles from the polyol solution. In general, the extraction method isolated more than 90% of the nanoparticles from the polyol solution, showing the efficiency of the preparation methodology.

The presence of crystalline Pd or/and Cu containing phases within calcined Pd-Cu/Al₂O₃np samples was investigated by XRD. The diffractograms are shown in Fig. 5. The pure alumina support shows the typical pattern of transition alumina, assigned to γ -Al₂O₃ (JCPDS-01-079-1558). This pattern is evident in all samples. Broad and diffuse diffraction lines of the support sample indicate poor crystallinity of γ -alumina. In agreement with the previously reported results, it is confirmed that low to moderate total metal loading on high surface area Al₂O₃ support calcined gives highly dispersed Cu and Pd species which are difficult to detect by X-ray diffraction [26]. The Pd and Cu loading influences the intensity of the alumina peaks between 25° and 60°, due to possible diffusion of Cu and Pd atoms into the γ -alumina lattice [11].

In order to clarify the existence and state of Pd and Cu species, the XRD profiles were magnified between 30° and 50° as shown in Fig. 5. In the calcined Pd1/Al₂O₃np catalyst, PdO reflections (JCPDS-00-043-1024) at around 34.4°, 42° and 55° were observed. This species is also present in all bimetallic catalysts. Additional reflections of metallic Pd (JCPDS-01-087-0641) were observed in Pd1.6Cu1/Al₂O₃np at 40.5° and 47.3°. The characteristic reflections of CuO were not clearly visible in all the bimetallic catalysts probably due to an overlap with the diffraction peak of alumina at around 40°. However, there is a clear distortion of the alumina diffraction line around 37.8° probably due to the influence of CuO species.

Two representatives of the bimetallic catalysts, Pd1.6Cu1/Al₂O₃np and Pd1Cu1/Al₂O₃np reduced at 300 °C were characterized using TEM and HRTEM integrated with Fourier transform analysis (Fig. 6). The TEM images for the Pd1/Al₂O₃np catalyst after reduction (not shown) show palladium particles uniformly dispersed on the support with an average particle size of 10 nm. The Pd nanoparticles prepared in solution before impregnation onto the alumina were characterized by a smaller particle size with an average diameter of 4 nm. The increase in particle size for Pd1/Al₂O₃np is probably due to the heat treatments applied in the calcination and reduction.

Pd1.6Cu1/Al₂O₃np sample is comprised of particles with different particle sizes. As a general trend, large particles of about 100 nm in diameter are present, while most of the particles are smaller, varying between 10 and 20 nm. Fig. 6a and b shows bright-field TEM images at low magnification, where both types of particles are easily recognized. High-resolution TEM (HRTEM) cannot be performed over the large particles because they are too thick for lattice-fringe analysis. Fig. 6c and d therefore correspond to HRTEM images of the small particles. The particle depicted in Fig. 6c shows a lattice spacing at 2.62 Å, as deduced from Fourier Transform (FT) analysis (inset). This corresponds to (110) planes of Cu₃Pd



Fig. 6. HRTEM images: Pd1.6Cu1/Al₂O₃np (a-d) and Pd1Cu1/Al₂O₃np (e-h).

alloy. The structure of pure Pd and Cu is cubic (F_{m-3m}) . The same symmetry is found for the CuPd alloy, but the Cu₃Pd alloy is tetragonal (P_{4mm}) and, for that reason, can be easily recognized. Fig. 6d shows a HRTEM image of another particle. In this case, the particle shows two domains, indicated in the figure with labels "a" and "b" with the FT analysis of both domains attached. Domain "a" shows spots at 2.62 and 2.76 Å. Again, crystallographic planes at 2.62 Å can only be ascribed to (110) planes of Cu₃Pd alloy. The spots at 2.76 Å in domains "a" and "b" correspond to (110) planes of pure Pd.

The coexistence of Pd and Cu_3Pd phases is commonly encountered in the sample. A low-magnification view of Pd1Cu1/Al₂O₃np catalyst is shown in Fig. 6e. In this case, the particle size distribution spans from 10 to 25 nm in diameter, with the mean particle size centred at about 14–15 nm. A careful lattice fringe analysis of these particles carried out with HRTEM is shown in Fig. 6f–h. In Fig. 6f, the FT analysis shows the occurrence of spots at 1.94 and 2.24 Å, which correspond to (200) and (111) planes of pure Pd metal, respectively. Another representative particle is shown in Fig. 7g, along



 $\label{eq:Fig.7.} Fig. 7. \ TPR \ profile \ of (a) \ Pd1/Al_2O_3np, (b) \ Pd1Cu1/Al_2O_3ref, (c) \ Pd1Cu1/Al_2O_3np, (d) \ Pd1.6Cu1/Al_2O_3np, (e) \ Pd1Cu5/Al_2O_3np.$

with its FT analysis. In this case, several spots at 2.24 and 2.62 Å are recognized in the FT image, which are ascribed to $(1\,1\,1)$ crystallographic planes of Pd and $(1\,1\,0)$ planes of Cu₃Pd, respectively. The coexistence of these two phases in the particle induces structural stress, which is observed as poor-defined lattice fringes in the HRTEM image. Finally, Fig. 6h shows an individual Cu₃Pd alloy particle exhibiting lattice fringes at 2.62 Å, corresponding to $(1\,1\,0)$ crystallographic planes.

The degree of Pd–Cu interactions was further investigated by H_2 -temperature programmed reduction analysis as shown in Fig. 7. The consumption of hydrogen and reducibility of supported metal catalysts depends on the metal-support interaction, metal–metal interaction and particle size distribution.

The TPR profile for Pd1/Al₂O₃np catalyst showed a main reduction peak at around 107 °C. Different TPR profiles were found for the bimetallic catalysts due to a different degree of interaction, and the respective features are assigned tentatively. As shown in the Fig. 7, the Pd1Cu1/Al₂O₃ref catalyst from salt precursors showed a main reduction peak at around of 151 °C that can be assigned to the reduction of CuO, promoted by nearby Pd. A small reduction peak at around 274 °C is assigned to the reduction of isolated copper species. The main reduction peak for this catalyst shifted to high temperature when compared to the Pd1/Al₂O₃np catalyst. The decrease in the reduction temperature of CuO in bimetallic catalysts, induced by the presence of palladium, indicates that a close proximity between copper and palladium species was achieved.

The consumption of hydrogen of the Pd1Cu5/Al₂O₃np catalyst is much higher than that of Pd1/Al₂O₃np. From the ICP analysis shown in Table 1, it is found that Pd1 and Pd1Cu5 contain similar Pd loading but differ in Cu nominal loading. Converting the weight % into Cu/Pd mole ratio, it was found that copper is around 8-fold higher than Pd. This implies the catalyst is highly enriched in Cu and/or Pd-Cu alloys. Consequently, when Cu is promoted by introducing small amount of a noble metal like Pd, its hydrogen uptake capacity is expected to improve by a higher magnitude as shown in the figure. The sample Pd1.6Cu1/Al₂O₃np and likely also Pd1/Al₂O₃np contain already reduced Pd as observed in XRD (presence of reflections of Pd and PdO).

The TPR profile of Pd1Cu1/Al₂O₃np is characterized by broad peaks around 107 °C and 125 °C, respectively. The peak around 107 °C is probably due to the reduction of isolated PdO species. The main reduction peak located at maximum of 125 °C is likely related to the reduction of Pd-Cu oxide species that are in close vicinity. The lower reduction temperature for the bimetallic PdCu phase



Fig. 8. Catalytic activity of impregnation catalysts in the TCE hydrodechlorination reaction at 300 °C after 180 min (\Box : TCE conversion (%); \bigcirc : ethane selectivity (%) and \bullet : ethylene selectivity (%)). Reaction conditions: total flow 60 ml/min, TCE partial pressure 92 mbar, H₂/TCE molar ratio 3.5, amount of catalyst 100 mg.

could depict that the surface is enriched with Pd species. The broad peak located >150 °C can be assigned to the reduction of isolated CuO species. The TPR profile for Pd1Cu5/Al₂O₃np in general shows a uniform broad peak with a maximum around 197 °C. No peak related to the reduction of isolated PdO species at lower temperatures was detected for this catalyst. The reduction peak at 197 °C is related to reduction of CuO species. These species are likely affected by the presence of Pd as they are reduced at lower temperatures. The TPR profile for Pd1.6Cu1/Al₂O₃np catalyst did not reveal a uniform reduction peak but reveals the existence of different species. The profile consists of distinct peaks located around 96 °C, 123 °C and 208 °C, respectively. The first peak at 96 °C is associated to the reduction of isolated PdO species, similar as Pd1/Al₂O₃np. The main reduction peak located at around 123 °C is assigned tentatively to Pd-Cu oxide species that are in close vicinity, whereas the high temperature reduction peak at 208 °C is related to reduction of isolated CuO species as observed also for the Pd1Cu5/Al₂O₃np catalyst. The existence of different reduction peaks shows the heterogeneity of the surface species in the bimetallic nanoparticle catalysts. The presence of different TPR reduction peaks indicate that the bimetallic catalyst prepared using the polyol synthesis protocol did not result in uniform alloy formation. Instead, isolated Cu and Pd and Pd-Cu alloys exist, whereas the Pd1Cu1/Al₂O₃ref catalyst shows a rather uniform reduction peak associated with PdCu species.

3.2. Catalytic activity

3.2.1. PdCu/Al₂O₃ impregnation catalysts

All materials were tested in the gas phase catalytic hydrodechlorination of TCE at 300 °C using a molar ratio TCE/H₂ of 3.5. The results are shown in Fig. 8. Whereas the Pd monometallic catalyst (Pd2/Al₂O₃i) leads to high conversion of TCE to mainly ethane (not shown), the use of bimetallic catalysts resulted in strongly increased selectivity towards ethylene, in agreement with [9,10].

A different catalytic behaviour is obtained depending on the synthesis protocol employed for bimetallic Pd1.2Cu1/Al₂O₃ i catalysts. The catalysts showed conversion levels between 50% and 75% under these conditions. CSR and SI protocols led to the higher conversion (70% and 75%, respectively), whereas COI and SRI protocols exhibited somewhat lower conversion (64% and 49%, respectively). In terms of selectivity, all the catalysts showed selectivity values to ethylene higher than 75%. However, the selectivity to ethylene was improved even more for the SRI and SI materials (between 90 and 95%). This can be explained taking into account the close interaction between Pd and Cu, leading to mostly bimetallic active sites



Fig. 9. TCE conversion at 300 °C over monometallic Pd and PdCu nanoparticles catalysts with time on stream. The reaction was carried out at a total flow of 60 ml/min with a TCE partial pressure of 92 mbar and a H_2 /TCE molar ratio of 3.5. 100 mg of catalyst were employed.

as observed by TPR and HRTEM. The bimetallic sites are responsible for the selective HDC of TCE to ethylene. Characterization results reported in Section 3.1.1 have shown that SRI and SI synthesis protocols lead to narrow particles size distribution around 5 nm and Pd-Cu alloy formation. In contrast, the COI and CSR syntheses resulted in a less homogeneous particle size distribution. CSR and COI catalysts exhibited isolated monometallic phases beside bimetallic particles. Thus, in the catalytic reaction a higher selectivity to ethane was observed attributed to pure Pd particles. High selectivity to ethylene is related to the presence of bimetallic particles.

As described in Section 3.1.1 alloy formation was confirmed by HRTEM and TPR. The Pd-Cu alloy formation created the active sites responsible for ethylene formation. The SI catalyst showed higher activity than SRI. In the TPR, major reduction processes were observed at 160 °C for the SRI sample, and around 135 °C for the SI material. This temperature difference in reduction might be related with a different alloy composition depending on the synthesis protocol.

3.2.2. PdCu/Al₂O₃ nanoparticles catalysts

In order to investigate whether the catalytic performance in the gas phase HDC of TCE depends on the Pd/Cu molar ratio, degree of interaction and particles size, PdCu nanoparticles deposited on Al₂O₃ were tested for this reaction. Fig. 9 shows the catalytic activities of the catalysts vs. time on stream.

The monometallic Pd1/Al₂O₃np catalyst showed an initial conversion of 55%, and after 180 min on stream the activity decreased to 20%. The catalytic performance of Pd-Cu bimetallic catalysts, with different Pd/Cu weight loading, showed similar trends as the monometallic Pd catalyst (Fig. 9), with also some deactivation going on with time on stream. The highest initial catalytic activity was observed for Pd1.6Cu1/Al₂O₃np catalysts showing an initial conversion of 70% mainly due to the higher Pd metal loading. In contrast, Pd1Cu1/Al₂O₃np, Pd1Cu1/Al₂O₃ref, and Pd1Cu5/Al₂O₃np exhibited moderate catalytic activities of around 52%, 48% and 46%, respectively. After 3 h of reaction the conversion decreased over all the catalysts, but to different extents. The decrease in conversion was similar on the nanoparticle catalysts with various metal ratios, amounting to around 35% for Pd1Cu1/Al₂O₃np, while

the conversion decreased by 66% on Pd1Cu1/Al₂O₃ref. The Pd1Cu1/Al₂O₃ref catalyst prepared by impregnation from metal salts for comparison showed the highest rate of deactivation in comparison to the nanoparticles catalysts. In addition, the degree of deactivation on the bimetallic nanoparticles catalysts Pd1.6Cu1/Al₂O₃np and Pd1Cu1/Al₂O₃np was less as compared to the monometallic Pd1/Al₂O₃np catalyst.

Deactivation is an interesting issue in HDCl. It is well known that during the hydrodechlorination reaction of chlorinated compounds using supported metal catalysts, the chloride species formed during the reaction can interact with the metallic sites of the catalyst leading to deactivation. This was a main topic of a recent work of us on Pd-Cu catalysts [19]. In the previous work Cl poisoning of the Cu was identified as the origin of deactivation of bimetallic Pd-Cu catalysts. The deactivation was less severe the better the interaction between Pd and Cu was, and did not play a role on well-alloyed samples exhibiting constant catalytic performance. Flushing in H₂ at elevated temperatures (i.e. 300 °C) fully restored the conversion and selectivity of deactivated samples. Cl poisoning on samples with incomplete alloying was suggested to be due to less efficient removal of Cl from poisoned Cu species. In the present work the conversion decreased only at the very beginning from the first measurement after 5 min TOS to the conversion determined after 30 min on stream, after this initial period a stable conversion was observed. However, due to the rather large particle size of the np samples (with mean particle sizes between 10 and 20 nm) TEM measurements did not reveal significant changes in particle size of used catalysts therefore giving no clear indication whether sintering could occur. Based on our previous work [19] and in agreement with other studies dedicated to deactivation (e.g. [31]) the most likely cause of the initial activity loss followed by a period of constant activity is Cl poisoning. Only the sample Pd1Cu1/Al₂O₃ref shows a continuous decrease in conversion, which is probably due to a less efficient interaction between Cu and Pd. The most pronounced loss of activity is observed on the Pd1Cu5 catalyst. This can be explained by a large fraction of isolated copper surface without nearby noble metal particles, which are able to efficiently regenerate Cu from chloride species on the surface deposited during the dechlorination reaction. When an optimum composition of the metals is reached (such as Pd1Cu1) leading to extensive alloy formation and avoiding isolated metal particles a high stability with time of stream is obtained.

Considering the degree of conversion, an increase of the Pd amount resulted in a higher activity (Pd1.6Cu1/Al₂O₃np catalysts). All the catalysts containing 1 wt% Pd showed almost similar initial conversion. However, the Pd amount does not affect the stability of the catalysts. Pd1.6Cu1/Al₂O₃np and Pd1Cu1/Al₂O₃np catalysts showed the best performance in terms of stability.

The main products formed on the nanoparticle catalysts were ethylene, ethane, chloroethylene and also some traces of dichloroethylenes (<0.5%). The selectivity evolution with reaction time is shown in Fig. 10.

Unexpectedly, monometallic Pd1/Al₂O₃np exhibits a high selectivity towards ethylene as shown in Fig. 10a. While the bimetallic samples exhibited a very stable selectivity (Fig. 10b–e), the ethylene selectivity on the monometallic Pd1/Al₂O₃np catalyst increased with time on stream (Fig. 10a). 63% ethylene and 28% selectivity to ethane was obtained at 5 min time of reaction. Ethylene selectivity increases during time on stream to 87%, and ethane formation declined to 10% of ethane formation after 180 min.

This result indicates that the use of nanoparticles synthesis changes completely the catalytic behaviour of the monometallic catalyst Pd1/Al₂O₃np with respect to the selectivity, as compared to the Pd2/Al₂O₃i catalyst (Section 3.2.1). An increasing production of ethylene was found in comparison with that previously reported for Pd impregnation catalysts, where full hydrogenation



Fig. 10. Selectivity vs. time on stream (min) at 300 °C for Pd1/Al₂O₃np (a), Pd1Cu1/Al₂O₃ref (b), Pd1Cu1/Al₂O₃np (c), Pd1Cu5/Al₂O₃np (d), Pd1.6Cu1/Al₂O₃np (e) catalysts. The reaction was carried out at a total flow of 60 ml/min with a TCE partial pressure of 92 mbar and a H₂/TCE molar ratio of 3.5. 100 mg of catalyst were employed.

was observed [6,8]. Possible reasons are differences in particle size and morphology, as well as different reaction conditions such as temperature and H₂:TCE ratio. Nevertheless, the bimetallic catalysts always showed higher ethylene selectivity than monometallic Pd catalysts. The ratio between the metals (Pd/Cu) and the total metal loading seem to affect the catalytic behaviour. As is shown in Fig. 10, the Pd-Cu bimetallic catalysts with similar Pd contents but different copper:palladium molar ratios exhibit different selectivity. Pd1Cu1/Al₂O₃np (Fig. 10c) and Pd1Cu5/Al₂O₃np catalysts (Fig. 10d) showed total ethylene formation at initial reaction time (5 min), whereas Pd1Cu1/Al₂O₃ref (Fig. 10b) and Pd1.6Cu1/Al₂O₃np (Fig. 10e) produce ethylene at selectivities around 80% and 90%, respectively, with additional formation of ethane.

As the time of reaction increases the selectivity to ethylene over Pd1/Al₂O₃np, Pd1Cu1/Al₂O₃ref and Pd1.6Cu1/Al₂O₃np catalysts

also increases accompanied by the initial loss of catalytic activity. The increase in ethylene selectivity is most pronounced on the monometallic Pd sample. A likely reason for the change in selectivity can be coke formation which reduces the hydrogen supply on the Pd. This was recently demonstrated by Srebowata et al. [31] who detected a PdC_x phase by XRD on a used Pd catalyst after HDCl of 1,2-dichloroethane. The improved selectivity could also be related with a dilution of the noble metal by the presence of Cl species on the surface decreasing the concentration of hydrogen available at the surface. A similar effect but less pronounced can be valid for the Pd-rich Pd1.6Cu1/Al₂O₃np catalyst.

3.2.3. Comparison of the catalytic behaviour obtained using different synthesis protocols

The use of bimetallic nanoparticles preparation in solution in comparison with the conventional impregnation synthesis routes

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Table	2

Comparison of th	e catalytic performanc	e results ^a over impregnated and	1 nanoparticles catalysts.
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Catalyst	Mean particle size (nm)	(Bi)metal state	TCE conversion (%)	Selectivity (%)		
				Ethylene	Ethane	Chloroethylene
Pd2/Al ₂ O ₃ i	2.0	Pd	84	32	68	0
Pd2Cu1.2/Al ₂ O ₃ i SI	5.0	Cu₃Pd alloy	75	90	10	0
Pd2Cu1.2/Al ₂ O ₃ i SRI	5.0	PdCu alloy	49	95	5	0
Pd2Cu1.2/Al ₂ O ₃ i CSR	5.8	Pd, PdCu alloy	70	80	20	0
Pd2Cu1.2/Al ₂ O ₃ i COI	3.5	Pd, Cu, PdCu alloy	64	75	25	0
Pd1/Al ₂ O ₃ np	10	Pd	55	63	28	9
Pd1Cu1/Al ₂ O ₃ np	15	Cu₃Pd alloy	52	100	0	0
Pd1Cu5/Al ₂ O ₃ np	_	_	46	100	0	0
Pd1.6Cu1/Al ₂ O ₃ np	15	Pd, Cu, Cu₃Pd alloy	69	90	10	0
$Pd1Cu1/Al_2O_3ref$	-	-	48	81	15	3

^a Reaction conditions: 300 °C reaction temperature, total flow 60 ml/min, TCE partial pressure 92 mbar, H₂/TCE molar ratio 3.5, amount of catalyst 100 mg.

to prepare Pd/Al_2O_3 and $PdCu/Al_2O_3$ catalysts leads to different catalytic behaviour in the TCE hydrodechlorination reaction. Table 2 shows a summary of the catalytic results obtained over both types of catalysts.

The common impregnation catalysts always show higher TCE conversion than the nanoparticles catalyst, although the differences in the metal content and particle sizes must be taken into account.

The monometallic $Pd2/Al_2O_3i$ catalyst from salt precursor showed very high selectivity to ethane (68%). Such catalytic behaviour of noble metals was reported previously owing to the noble metals ability to hydrogenate the C=C double bond. However, the monometallic Pd1/Al_2O_3np catalyst prepared from the nanoparticle precursor, showed a higher selectivity to ethylene (62%) and a lower conversion (55%). The main differences between the impregnation and the nanoparticle catalyst are a higher metal loading in the former catalyst (2 wt% instead of 0.8 wt%) and a different mean particle size of 2 nm and 10 nm, respectively. Another possible explanation could be differences in morphology.

The introduction of copper increases the selectivity to ethylene in all the catalysts. The best catalytic performance within the nanoparticles catalysts with high and stable activity and selectivity to ethylene was obtained on Pd1Cu1/Al₂O₃np and Pd1.6Cu1/Al₂O₃np. Within the series of catalysts prepared by impregnation from salt precursor solutions, the sequential impregnation and sequential reduction impregnation routes led to materials with 90% and 95% ethylene selectivity at initial conversion levels of 75% and 49%, respectively.

PdCu alloyed nanoparticles, mainly of the composition Cu₃Pd, were obtained both by the nanoparticle precursor synthesis and by the impregnation route. Depending on the synthesis protocol, isolated Pd and/or Cu particles were present in some samples in addition to the PdCu alloy, which affected activity and selectivity. Upon PdCu alloy formation Cu modifies the electronic properties of Pd [32,33] and has thereby been proposed to weaken ethylene adsorption. A lower bonding strength of ethylene on Pt-Cu/SiO₂ catalysts was observed in microcalorimetric measurements in [34]. Consequently, ethylene would desorb more easily from Pd in PdCu than hydrogenate further to ethane.

In this sense, isolated and small Pd particles are very active for the hydrogenation of TCE leading to ethane as the main product. Emphasizing on the monometallic Pd catalysts prepared by the two different protocols, the effect of the interaction of the Pd nanoparticles with the support Al_2O_3 plays an important role in the selectivity to ethane. The monometallic Pd catalyst obtained from metal nanoparticles is characterized by larger particle size (10 nm) and hence possesses lower interaction with the support as compared to the monometallic Pd catalyst obtained from salt impregnation with small particles of around 2 nm. As a result, the former catalyst yields higher selectivity to ethylene. This could be

explained taking into consideration that small metal particles (particles with high interaction with the support) exhibit a high amount of atoms with low coordination that are very active for HDC reaction, but with a poor selectivity to olefins. The low-coordinated sites present on small nanoparticles bind ethylene more strongly than terrace sites and simultaneously such low-coordinated sites exhibit lower hydrogenation barriers than terrace sites. In order to increase the selectivity to ethylene it is necessary to decrease or deactivate these low-coordinated atoms. It seems that the introduction of copper forming Pd-Cu alloy plays an important role bringing about this effect. As described previously, 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 [12]. A dilution of Pd ensembles by Cu can also be deduced from the FTIR spectra of adsorbed CO, as described in Section 3.1.1. Even though the literature concerning the structure-sensitivity of C-Cl bond dissociation on Group VIII metals is contradictory [10], here we can see clearly the effect of the particle size on the selectivity of Pd monometallic catalysts towards ethylene formation, despite the metal loading difference.

4. Conclusion

Different preparation procedures for Pd-Cu bimetallic catalysts supported on γ -alumina were compared in this work, including conventional impregnation and preparation of bimetallic nanoparticles from a polyol solution. The catalyst synthesis protocol affects the catalytic properties in the hydrodechlorination of TCE. On all materials, better ethylene selectivity was achieved than over monometallic Pd catalysts. Differences in catalyst performance were connected with differences in metal–metal interaction and particle size as main factors governing the selectivity.

The highest selectivity to olefins with values up to 100% was reached on catalysts where Pd-Cu alloy formation was detected by HRTEM and TPR. Catalysts exhibiting isolated monometallic phases in addition to bimetallic particles, such as the Pd1Cu1.2/Al₂O₃ i catalysts prepared by CSR and COI route, yielded more ethane, which was attributed to the reactivity of the Pd particles for total hydrogenation. SRI and SI catalysts composed of uniform bimetallic particles with a narrow particle size distribution around 5 nm reached ethylene selectivities higher than 90%.

Aiming to have control over the particle size and interaction between the metals, bimetallic Pd-Cu nanoparticles with different Pd:Cu ratios were prepared by a polyol method using 1hexadecylamine as stabilizing agent. The catalytic activity mainly depended on the amount of the noble metal, with the highest activity on Pd1.6Cu1/Al₂O₃np, and the selectivity on the amount of copper. In general, increasing copper content resulted in an increase in ethylene selectivity at comparable TCE conversion. Another issue that was clearly observed is the influence of the Pd particle size on the performance of monometallic Pd catalysts. Larger Pd particles resulted in higher selectivity to ethylene, as observed by comparing Pd2/Al₂O₃i with 2 nm mean particle size with Pd1/Al₂O₃np exhibiting ~10 nm sized particles. This may be related to the stronger interaction of small particles with the support and the presence of a higher concentration of low coordinated sites with a high activity for ethane formation. On small nanoparticles more low-coordinated sites are present which bind ethylene more strongly and exhibit lower hydrogenation barriers than terrace sites. Alloying with Cu can modify the electronic properties of Pd thus weakening ethylene adsorption. In addition hydrogen supply is reduced by diluting the Pd surface. Overall, on large Pd particles and on PdCu alloy particles, ethylene formation is strongly enhanced.

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