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# L-serine-functionalized montmorillonite decorated with Au nanoparticles: A new highly efficient catalyst for the reduction of 4-nitrophenol

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#### 1. Introduction

Generally, nitroarene compounds such as 4-nitrophenol are the most prevalent pollutants detected in water. They are originated from agricultural and industrial sources [1,2]. The conversion of nitroarene to aminoarene compounds is of great industrial importance, since the latter are an important class of compounds used as intermediates in the synthesis of numerous pharmaceuticals, dyes, polymers and natural products [1,3,4] as well as for bulk chemical production.

The reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) by sodium borohydride was found by Pal et al. [5] in 2002 using silver nanoparticles as catalyst and, since then, it has become the model reaction to test the catalytic performance of catalysts in aqueous solution [6].

Nanosized metal particles have been a topic of great interest and continue to attract immense attention due to their fantastic physical, chemical and biological properties which lead to potential catalytic applications [7,8]. Among them, Au nanoparticles (NPs) have received a great interest in a wide variety of applica-

### ABSTRACT

The conversion of nitroarenes to aminoarenes is of great industrial interest since they are prevalent pollutants in water and aminoarenes are important intermediates in the synthesis of pharmaceuticals, natural products and in bulk chemical production. In this work, two new catalysts for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) were prepared by immobilization of gold nanoparticles onto the surface of K10 montmorillonite clay (K10) functionalized with two new L-serine derivative organosilanes. Transmission electron microscopy showed the presence of 4–5 nm gold nanoparticles after catalysis. The reduction reaction of 4-NP to 4-AP at 25 °C, using NaBH<sub>4</sub> as reducing agent, led to nearly 100% conversion in only 1 minute, presenting pseudo-first-order rate constants normalized for Au loading of K = 630 and 430 mmol<sup>-1</sup> s<sup>-1</sup>. The catalysts showed high stability, leading to substrate conversions of 95–100% after 10 consecutive cycles, with negligible Au leaching.

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tions due to their unique physical and chemical properties [9,10], such as in enantioselective catalysis [11], organic synthesis [12,13], low-temperature CO oxidation [14,15], and in the reduction of 4-NP [16]. However, Au NPs tend to aggregate due to their high surface energy [17], which reduces their activity and restricts their applications.

The immobilization of Au NPs onto solid supports is an ingenious way to overcome this disadvantage. Besides the stabilization improvement by preventing Au NPs agglomeration, this procedure facilitates the recycling of the catalyst. In literature, several reports highlight that Au NPs immobilized onto solid supports, such as graphene oxide [18], titanium dioxide [19] or carbon [20], metalorganic frameworks [21], cerium oxide [22], silica nanoparticles [23], carbon nanotubes [24], ordered mesoporous carbon nanospheres [25] and clavs [26], often show enhanced catalytic activity in comparison to free Au NPs. This is due to the strong synergistic interaction that occurs at the interface of the two components [27]. Clays are of particular interest since they are cheap, environmentally-friendly, readily available and have important tunable properties such as high porosity and easy surface modification. Nevertheless, the direct immobilization of the active metal species onto clays usually leads to significant leaching during the catalytic reaction [28,29]. Hence, the functionalization of the inor-







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ganic support *via* covalent attachment of suitable organic ligands to which the transition metals will coordinate – thus forming the catalytic complex – is one of the best solutions [30].

Recently, we turned our attention to the study of the potential use of L-serine derivatives as ligands for metal complex formation [31]. Serine has two major advantages for this purpose: it is cheap and easily available and has three functional groups that may be easily functionalized, thus allowing chemical and structural design.

In this work, we report the preparation and catalytic performance of two novel gold-based heterogeneous catalysts in the reduction of 4-NP to 4-AP in an aqueous medium in the presence of NaBH<sub>4</sub> reducing agent. The catalysts were prepared by functionalization of K10 montmorillonite clay (K10) with two L-serines presenting different modifications, followed by the immobilization of gold NPs onto its surface. The influence of the type of L-serine on the amount of Au NPs grafted to the support surface and on the catalytic performance was assessed. This work promotes the advance of the design of new gold-based heterogeneous catalysts with high catalytic performance and stability in the reduction of 4-NP.

#### 2. Experimental section

#### 2.1. Chemicals, reagents and solvents

Commercial L-serine 1 (Fmoc-Ser-OH) was purchased from Fluorochem. Sodium borohydride (98%), anhydrous sodium sulfate (≥99%), 4-aminophenol (4-AP, ≥98%), potassium carbonate  $(\geq 99\%)$ , citric acid  $(\geq 99.5\%)$ , *N*,*N*-diisopropylethylamine (DIPEA,  $\geq$ 98%), benzylamine ( $\geq$ 98%), K10 montmorillonite clay, o-(benzotriazol-1-yl)-N,N,N',N'-tetramethyluronium tetrafluoroborate (TBTU, 97%), piperidine (99%), dibutyltin dilaurate (95%) and anhydrous toluene were purchased from Sigma-Aldrich. 3-(triethylsilyl)propyl isocyanate (IsoTES, 95%) was purchased from ABCR. 2-propanol (analytical grade) was acquired from Analar Normapur. Tetrachloroauric(III) acid trihydrate (>49.0% Au basis) was purchased from Alfa Aesar and 4-nitrophenol (4-NP, analytical grade) from Fluka. The solvents methanol, acetonitrile, ethyl acetate, N,N-dimethylformamide and dichloromethane were purchased from Fisher Scientific. All chemicals were used as received without further purification. Milli-Q ultrapure water (18 M $\Omega$  cm) was used in all experiments.

#### 2.2. Materials preparation

#### 2.2.1. Preparation of *L*-serine derivative organosilanes

The chemical structures of the L-serine derivative organosilanes **4** and **5**, as well as the synthetic pathways used for their preparation are represented in Scheme 1.

The procedures used are described as follows:

(S)-methyl-2-((((9H-fluoren-9-yl)methoxy)carbonyl)amino)-3-hy droxypropanoate (**2**): 0.1 g of an acidic resin (Dowex 50W-X2) was suspended in a solution of **1** (1.00 g, 3.05 mmol) in dry methanol (20 mL). The mixture was refluxed overnight under stirring and inert atmosphere. The reaction mixture was filtered and the volatiles evaporated at reduced pressure. The solid residue was purified by chromatographic column (eluent: AcOEt). A white solid was obtained with 92% yield.

(S)-(9H-fluoren-9-yl)methyl (1-(benzylamino)-3-hydroxy-1-oxo propan-2-yl)carbamate (**3**): To a solution of **1** (1.00 g, 3.05 mmol) in anhydrous dichloromethane (50 mL) was added TBTU (0.98 g, 3.1 mmol), DIPEA (0.52 mL, 3.1 mmol) and benzylamine (0.34 mL, 3.1 mmol). The solution was stirred under inert atmosphere at room temperature during 2 h (the reaction mixture tends to form a gelatinous crude due to the very low solubility of the product; hence, the amount of solvent should be enough to avoid gelatinization and the consequent poor reaction homogenization). The solvent was evaporated and the residue was dissolved in hot AcOEt (50 mL). Hot water was added (50 mL), the aqueous phase was separated and the organic phase was washed twice with hot water (50 mL) and brine. The aqueous phase was extracted again with hot AcOEt (50 mL) and the organic layers were gathered and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated at reduced pressure and the gelatinous residue was further purified by recrystallization in AcOEt. After complete dryness over reduced pressure, a white solid was obtained with 85% yield.

Organosilylation of clays: The silylation of L-serines **2** and **3** was performed by following our previously described protocol [32,33]. To a solution of serine **2/3** in anhydrous acetone, 1 eq. of 3-(triethylsilyl)propyl isocyanate and a catalytic amount of dibutyltin dilaurate (DBTDL) were added. The solution was heated up to 120 °C under microwave irradiation (MW) in a closed vessel (CEM 908010 from CEM Discover) until no further evolution of the reaction was verified (monitored by thin-layer chromatography). After cooling, a polystyrene-NH<sub>2</sub> resin was added to the solution, followed by stirring overnight. The resin was filtered off and the solution was evaporated under reduced pressure. Electrospray ionization mass spectrometry (ESI-MS) analysis of the reaction mixture confirmed the formation of the desired products **4** and **5**.

The crude compounds **4/5** were immediately dissolved in anhydrous toluene (50 mL) and a previously dried (12 h at 100 °C) amount of K10 was added (0.8 g mixture/0.8 g K10). The mixture was refluxed for 20 h under inert atmosphere. The resulting materials were washed by reflux in dry toluene during 2 h, filtered and finally dried at 100 °C for 24 h. The functionalized materials will be denoted as K10\_**4** and K10\_**5**, where the number identifies the Lserine derivative organosilane grafted onto K10. The K10\_**4** and K10\_**5** materials were submitted to the ninhydrin test, which gave negative results to the presence of free amine groups (Fig. S1 in the Supporting Information). This test also confirmed the efficiency on the elimination of the unreacted IsoTES by the polystyrene-NH<sub>2</sub> resin, since the isocyanate groups also provided a positive result due to their transformation into amine groups during the test procedure.

Deprotection of the amine group: 1 g of K10\_4 was suspended in DMF (10 mL) and 2 mL of piperidine were added. The reaction was left to react at room temperature for 2 h. The material was filtered, washed with dichloromethane and acetonitrile and dried at 80 °C overnight. The material was submitted to a new ninhydrin test, which gave positive result to the presence of free amine groups (dark blue color, see Fig. S1 in the Supporting Information), thus confirming the formation of the material denoted as K10\_A. A similar procedure was used in order to convert material K10\_5 into material K10\_B.

#### 2.2.2. Immobilization of Au NPs onto L-serine-functionalized K10

Typically, the K10\_**A** or K10\_**B** material (500 mg) was dispersed in 300 mL of 2-propanol by sonication. Then, 160 mg of HAuCl<sub>4</sub>.3-H<sub>2</sub>O (0.05 mmol) and 170 mg of citric acid (0.09 mmol), both separately dissolved in 2-propanol (100 mL), were added dropwise and simultaneously to the functionalized clay dispersion under vigorous stirring. The resulting mixture was kept under vigorous stirring and at room temperature during 2 h. The materials were recovered by filtration through a membrane (Whatman, 0.2 µm) and washed once with 2-propanol (200 mL). The materials will be denoted as K10\_**A**@Au and K10\_**B**@Au.

#### 2.3. Physicochemical characterization

Liquid-state nuclear magnetic resonance (NMR) analyses were performed at Centro de Materiais da Universidade do Porto



Scheme 1. Schematic representation of the preparation of L-serine derivative organosilanes and K10 functionalization protocols: (i) MeOH, Dowex 50W-X2, reflux, 18 h (for 2); TBTU, DIPEA, benzylamine, CH<sub>2</sub>Cl<sub>2</sub>, 2 h (for 3); (ii) IsoTES, DBTDL, acetone, 120 °C, MW; (iii) toluene, reflux, 20 h; (iv) piperidine, DMF, 2 h.

(CEMUP, Porto, Portugal), in a Bruker Avance III 400, using tetramethylsilane (TMS) as internal standard. The chemical shifts are quoted in parts per million (ppm).

Flash column chromatography was performed on silica gel (60 Å, 230,240 mesh) and analytical thin-layer chromatography (TLC) on pre-coated silica gel 60 F254 plates.

ESI-MS analyses were performed on a liquid 35 chromatography Finnigan Surveyor equipment, coupled to a mass detector Finnigan LQC DECA XP MX with an API and an ESI interface.

Fourier transform infrared spectroscopy with attenuated total reflectance (FTIR-ATR) spectra of L-serine derivative silanes were obtained with a Perkin-Elmer Spectrum BX.

Solid-state NMR spectra were recorded on a 9.4 T Bruker Avance 400P spectrometer at the University of Aveiro.

X-ray photoelectron spectroscopy (XPS) was performed at CEMUP in a Kratos AXIS Ultra HSA spectrometer using monochromatized Al K $\alpha$  radiation (1486.6 eV). To correct possible deviations caused by electric charge of the samples, the C 1s band at 284.6 eV was taken as an internal standard. The XPS spectra were deconvoluted with the CASAXPS software, using non-linear least squares fitting routine after a Shirley-type background subtraction.

Gold contents obtained by inductively coupled plasma emission spectrometry (ICP-AES) and nitrogen, carbon and silicon elemental analyses (EA) were performed at Laboratório de Análises, IST, Lisboa, Portugal.

The electronic spectra of gold-based catalysts were recorded at room temperature in the 200–800 nm wavelength range using a Cary spectrophotometer.

Scanning electron microscopy (SEM) and energy-dispersive Xray spectroscopy (EDS) studies were performed at CEMUP, using a high-resolution environmental scanning electron microscope (FEI Quanta 400 FEG ESEM) equipped with an energy-dispersive X-ray spectrometer (EDAX Genesis X4M).

Transmission electron microscopy (TEM) images and EDS spectra were collected with a LEO 906E microscope at 120 kV at UTAD, Vila Real, Portugal. The samples were prepared by dispersion in ethanol under sonication, followed by the immersion of formvar/ carbon-coated 400 mesh copper grids in the resulting suspensions and subsequent air-drying. The average particle sizes and size distributions were calculated from the diameters of more than 60 particles randomly selected from the TEM micrographs.

Powder X-ray diffraction (XRD) measurements were performed at Universidade de Trás-os-Montes e Alto Douro (UTAD, Vila Real, Portugal), at room temperature over the range  $2\theta = 3-70^{\circ}$  with a PW 3040/60 X'Pert Pro Röntgen diffractometer using Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) and the Bragg–Brentano  $\theta/2\theta$  configuration.

The FTIR spectra of the materials were obtained with a Jasco FT/ IR Plus spectrophotometer using KBr pellets in the 400–4000 cm<sup>-1</sup> region with a resolution of 4 cm<sup>-1</sup> and 32 scans. The samples were diluted in KBr (99%, spectroscopic grade, Sigma-Aldrich) and studied as pellets containing 0.2 wt% of sample.

#### 2.4. Catalytic reactions

The catalytic reduction of 4-NP to 4-AP was carried out at room temperature on a quartz optical cell by monitoring the electronic spectra at 10 second intervals on an Agilent 8453 UV-Vis spectrometer with diode array detector. The degradation of 4-NP was monitored by the absorbance decrease of the electronic band at  $\lambda$  = 400 nm due to nitrophenolate ion in basic media and by the development of a new electronic band at  $\lambda$  = 300 nm corresponding to the formation of 4-AP. The reaction conditions were adapted from a previous work on Au-based catalysts for 4-NP reduction [34], by increasing the substrate concentration and decreasing the NaBH<sub>4</sub> concentration towards Au loading. A stock solution of 4-NP (0.05 mM, 1 L) was prepared. For the kinetic studies, 3 mL of 4-NP solution were transferred to the UV-Vis cell and 0.15 mmol of NaBH<sub>4</sub> were added. Upon addition of the reducing agent, the electronic band at  $\lambda$  = 318 nm shifted to  $\lambda$  = 400 nm corresponding to nitrophenolate ion, remaining unaltered until addition of the catalyst (3 mg of catalyst, C = 1 mg mL<sup>-1</sup>). To test the reusability of the heterogeneous catalysts, a 10 times scale-up experiment was carried out in a 50 mL round bottom flask. In this case, the electronic spectra of the reaction mixtures were acquired every minute by withdrawing 3 mL aliquots from the reaction medium; the reactions were stirred at controlled temperature (25 °C). After each catalytic cycle, the catalysts were filtered and then reused in a new cycle. This procedure was repeated 9 times and at the end of the 10 reuse cycles, the materials were dried and characterized as described in the results and discussion section (Section 3.3.2). Control experiments were performed with the L-serine-functionalized clays (K10\_A and K10\_B) using the same catalytic reaction conditions. Adsorption of 4-NP substrate into the catalysts was also evaluated using similar catalytic reaction conditions, but in the absence of NaBH<sub>4</sub>. The catalytic performance of gold immobilized directly onto K10 was also assessed on the 4-NP reduction.

#### 3. Results and discussion

#### 3.1. Characterization of L-serine-functionalized K10 supports

Two L-serine-functionalized K10 montmorillonite clay materials – K10\_A and K10\_B – were prepared as shown in Scheme 1 and used as solid supports for the immobilization of Au NPs. <sup>1</sup>H and <sup>13</sup>C NMR and ESI-MS were used to monitor the formation of the intermediate serine derivatives; elemental analyses, FTIR and solid-state NMR (<sup>29</sup>Si and <sup>13</sup>C) were performed in order to characterize the prepared solid supports K10\_A and K10\_B.

The <sup>1</sup>H NMR data of the L-serines **2** and **3** is provided in Figs. S2 and S3 in the Supporting Information. <sup>13</sup>C NMR spectroscopy was also performed for **2** (all these spectra are provided in the Supporting Information). For compound **2** it is possible to clearly identify the methyl ester group by the presence of signals corresponding to OCH<sub>3</sub> and C=O groups in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, respectively. The structure of compound **3** is also easily confirmed by the presence of new signals corresponding to the NH amide bonds and benzyl moieties.

The silylation of L-serines **2** and **3** was performed by following our previously described protocol [32], and the formation of the desired compounds **4/5** was confirmed by TLC and by ESI-MS spectrometry. The silylated L-serines **4** and **5** were not isolated because the silylation reactions were not complete and the purification of these compounds through chromatographic column results in significant losses due to hydrolysis of the triethoxysilane group.

The grafting of the silylated serines **4** and **5** onto K10 was also performed following our previously described methodology, in which the mechanism was also studied [32]. The K10\_**4** and K10\_**5** materials were subsequently treated with piperidine in order to deprotect the amine group, thus obtaining the desired materials K10\_**A** and K10\_**B**, respectively. As previously mentioned, the success of this step was confirmed by the ninhydrin test, which gave negative results for K10\_**4** and K10\_**5** and positive results for K10\_**A** and K10\_**B**. These tests clearly confirmed the grafting of the L-serine organosilanes onto K10 and presence of free amine groups on the resulting materials surface (see Fig. S1 in the Supporting Information).

The functionalization of K10 with L-serine derivatives was assessed by FTIR, solid-state NMR ( $^{29}$ Si and  $^{13}$ C) and elemental analyses. The FTIR spectra of the resulting materials K10**\_A** and K10**\_B** are presented in Fig. 1.

For all samples, characteristic vibrational bands of montmorillonite clay are present in the corresponding FTIR spectra: a band around 3620 cm<sup>-1</sup> corresponding to stretching vibrations of O–H groups coordinated to octahedral cations (mainly Al, but also Mg and Fe) [34], bands at 3394 and 1640 cm<sup>-1</sup> assigned to O–H stretching and bending vibrations of interlayer water (physically adsorbed water), respectively [34,35], a strong and broad band at 1045 cm<sup>-1</sup> with a shoulder at ~1093 cm<sup>-1</sup> corresponding to Si–O–Si asymmetric stretching vibrations and a shoulder at 917 cm<sup>-1</sup> due to Al–OH–Al bending vibrations [34–36]. The band near 800 cm<sup>-1</sup> could be assigned to several vibrations namely to the presence of quartz mixture in the sample [35], to Si–O–Si vibrations [37] or to Al–O–Si vibrations [38]. The band at 525 cm<sup>-1</sup> corresponds to Si–O–Al (octahedral Al) vibration and the band at 468 cm<sup>-1</sup> is assigned to Si–O–Si bending vibrations [36,39].

Upon silvlation, the FTIR spectra of the two materials clearly show characteristic bands of the grafted organosilanes. In the case of K10\_A (Fig. 1a), the bands at 2915 and 2935  $\text{cm}^{-1}$  are due to C–H stretching vibration modes, the band at 1687 cm<sup>-1</sup> corresponds to the carbonyl group of the ester moiety (C=O stretching). The bands at 1630 and 1570 cm<sup>-1</sup> are assigned to the carbonyl group stretching vibration (superimposed with H–O–H bending vibrations from adsorbed water) and to the N—H bending of carbamate, respectively. The band at 1440 cm<sup>-1</sup> is assigned to CH<sub>2</sub> bending deformations [32]. In the case of K10\_B (Fig. 1b), the peak at 3040 cm<sup>-1</sup> is due to stretching vibration modes of aromatic C–H bonds, the peaks at 2925 and 2870  $\rm cm^{-1}$  correspond to C–H stretching vibrations, the band at 1690  $\rm cm^{-1}$  is related to vibration modes of superimposed carbonyl groups of carbamate and amide moieties, the band at 1555 cm<sup>-1</sup> is assigned to N-H bending of carbamate moieties and the band at 1455 cm<sup>-1</sup> is assigned to CH<sub>2</sub> bending vibrations [32].

Solid-state <sup>13</sup>C CPMAS NMR gave vital information about the surface silicon environments and attached L-serine silanes, specifically of their grafting mechanisms. The solid-state <sup>13</sup>C CPMAS NMR spectra of K10**A** and K10**B** are presented in Fig. S4 in the Supporting Information. In both spectra, carbonyl signals are identified near  $\delta$  = 160 and 173 ppm and the signals corresponding to CH, CH<sub>2</sub> and CH<sub>3</sub> are in the range of  $\delta$  = 5–60 ppm, as expected [32].

The spectrum of K10\_**B** also shows peaks at  $\delta$  = 127 and 144 ppm corresponding to the phenyl ring. The intensity of the peaks corresponding to SiOCH<sub>2</sub>CH<sub>3</sub> and SiOCH<sub>2</sub>CH<sub>3</sub> carbon signals (expected near  $\delta$  = 20 and 60 ppm, respectively) is in accordance with a successful bidentate grafting and a possible partial hydrolysis of the remaining ethoxy group to afford a silanol [R–Si(OH) (O–K10)<sub>2</sub>] or a lateral condensation of silanes [R–Si(O–Si(O–K10) <sub>2</sub>–R)(O–K10)<sub>2</sub>] (R = L-serine organosilane) [32].

The <sup>29</sup>Si MAS NMR spectra of K10**\_A** and K10**\_B** are presented in Fig. S5 in the Supporting Information, in which the peaks are identified according to the commonly used  $Q^n$  and  $T^n$  notation and the chemical shifts are summarized in Table 1.

The spectra present an intense peak corresponding to Q<sup>4</sup> resonances ( $\delta = -111$  ppm) which is attributed to fully condensed silica units that do not react with the organosilane molecules and two smaller peaks at  $\delta = -93$  and -102 ppm corresponding to  $Q^2$  and Q<sup>3</sup> resonances, respectively, and are associated to the germinal silanol groups and one terminal silanol group [32,40-42]. The spectra also exhibit additional peaks at  $\delta = -57$  ppm and  $\delta = -58$ ppm for K10\_**A** and K10\_**B**, respectively, and a peak at  $\delta = -67$ ppm in both materials associated to T<sup>2</sup> and T<sup>3</sup> silicon environments, revealing the anchorage of organosilated L-serines by bidentate and tridentate grafting on the K10 surface [32,43,44]. In both K10\_A and K10\_B the  $T^2$  and  $T^3$  sites are observed with similar intensity. However, the possibility of lateral condensation of grafted organosilanes – which results in T<sup>3</sup> signals – also needs to be considered. These observations are in agreement with previously reported results for related materials [32,42].

The relative concentrations of the Q<sup>n</sup> and T<sup>n</sup> sites ascertained by deconvolution of the <sup>29</sup>Si MAS NMR spectra are presented in Table 1. They allow estimating the amount of grafted organosilane in K10 as 10.7 and 9.0% for K10\_**A** and K10\_**B**, respectively (based on  $(T^3 + T^2)/(T^2 + T^3 + Q^2 + Q^3 + Q^4)$ ).



Fig. 1. FTIR spectra of K10 materials before functionalization with L-serine organosilanes, after functionalization, after gold NPs immobilization and after use in catalytic tests: (a) K10\_A-based materials; (b) K10\_B-based materials.

#### Table 1

Chemical shifts determined by solid-state <sup>29</sup>Si MAS NMR analysis of K10\_A and K10\_B materials

Material	Chemical shift (ppm)						T area ratio (%)	
	$T^1$	T <sup>2</sup>	T <sup>3</sup>	Q <sup>2</sup>	Q <sup>3</sup>	Q <sup>4</sup>	$T/(T + Q)^a$	
K10_ <b>A</b> K10_ <b>B</b>	-	-57 -58	67 67	-92 -93	-102 -102	-111 -112	10.7 9.0	

<sup>a</sup>  $T = T^2 + T^3$ ;  $Q = Q^2 + Q^3 + Q^4$ .

#### Table 2

Si, C and N bulk contents determined by EA, amount of grafted organosilane (G) and grafting efficiency (E) for K10\_A and K10\_B materials

Material	Si (mmol g <sup>-1</sup> )	$C \pmod{g^{-1}}$	N (mmol $g^{-1}$ )	$G^{a}$ (mmol g <sup>-1</sup> )	$G^{\mathrm{b}}$ (mmol g <sup>-1</sup> )	E <sup>c</sup> (%)
K10_ <b>A</b>	10.0	10.2	1.7	1.0	1.1	49
K10_ <b>B</b>	10.0	12.3	2.1	0.8	0.9	39

<sup>a</sup> Calculated based on the carbon content obtained by EA.

<sup>b</sup> Calculated considering the total Si content determined by atomic absorption spectroscopy and the area ratio of T/(T + Q) sites determined by <sup>29</sup>Si NMR (Table 1).

<sup>c</sup> Calculated using the mean value of *G* and the 2 mmol of organosilane used in the grafting process.

The nitrogen, carbon and silicon bulk contents determined by EA are presented in Table 2, as well as the calculated amount of grafted organosilane (G/mmol g<sup>-1</sup>) considering a bidentate covalent grafting, and the grafting efficiency (E) of the L-serine organosilanes onto the clays.

Table 2 shows a good agreement between the *G* values calculated by the two employed methods: (a) determination based on the carbon elemental analysis and (b) evaluation considering the total Si content in the material (determined by atomic absorption spectroscopy) and the area ratio of the T/(T + Q) sites determined by <sup>29</sup>Si MAS NMR (presented in Table 1). Considering the average of the determined *G* values, one may conclude that the grafting efficiency (*E*) was slightly higher in the preparation of K10\_**A** than in K10\_**B**.

## 3.2. Morphological and structural characterization of Au-based materials

K10\_A and K10\_B were used as supports for the immobilization of Au NPs. In order to confirm the successful immobilization of Au NPs on the L-serine-functionalized supports surface, the materials were characterized by XPS, ICP-AES, SEM, TEM, XRD and FTIR.

The surface atomic percentages, the core-level binding energies (BEs) and the surface contents (in mmol  $g^{-1}$ ) of the different elements determined by XPS (Tables 3, 4 and S1 in the Supporting Information) provide insights concerning the materials chemical composition/structure and bonding.

Both K10\_**A**@Au and K10\_**B**@Au catalysts are mainly composed of O and Si and the high-resolution XPS spectra exhibit the typical bands in the O 1s and Si 2p regions, centered at about 532.2 eV and 102.6 eV (for the Si  $2p_{3/2}$  component), respectively [45]. The presence of small amounts of Mg, Al, K and Fe (Table 3) is in accordance with montmorillonite chemical composition [46]. Furthermore, the XPS results of both catalysts reveal the presence of carbon in a much higher surface content relatively to that in the parent K10 clay (22.5 mmol g<sup>-1</sup> for K10\_A@Au and 20.5 mmol g<sup>-1</sup> for K10\_B@Au *versus* 1.7 mmol g<sup>-1</sup> for K10, Table 4), indicating the successful grafting of the L-serines onto K10 (and confirming the slightly higher amount of L-serine in K10\_A).

It is also verified an increment of N surface content relative to that in the parent K10, which also proves the successful grafting of the L-serines. Since the L-serine grafted onto K10\_**B** has an amide group in addition to the amine, the percentage of N is superior in K10\_**B** over K10\_**A**, which also attests the integrity of the serines upon gold immobilization.

Upon the immobilization of Au in the two L-serine functionalized K10, the target element gold is detected in both samples (Tables 3 and 4) confirming its successful incorporation in similar amounts.

For both catalysts, the high-resolution C 1s spectra exhibit bands at 284.6 and 286.0–286.5 eV assigned to C—H/C—C and C—O/C—N bonds, respectively [47], as well as bands at about 287.3–287.9 eV and 288.9–289.3 eV ascribed to O=C—O and C=O bonds, respectively present in the L-serines structure.

The high-resolution N 1s spectra exhibit, in both cases, a band centered at 399.7–399.8 eV, which is assigned to free amine groups C-NH<sub>2</sub> with a shoulder at 401.7–401.8 eV probably due to a slight protonation of the amines (C-NH<sub>3</sub>) of the grafted L-serines [48].

Table 3
Surface atomic percentages for gold-supported catalysts obtained by XPS analysis

Material	Atomic %										
	C 1s	N 1s	O 1s	Mg 1s	Al 2p	K 2p	Si 2p	Fe 2p <sub>3/2</sub>	Cl 2p	Au 4f	Na 1s
K10	3.4	0.5	65.4	1.3	5.0	0.3	23.6	0.5	-	-	-
K10_ <b>A</b> @Au	38.3	5.0	38.6	0.5	2.0	0.3	14.2	0.3	0.6	0.2	-
K10_ <b>A</b> @Au_Cat	32.1	4.1	42.7	0.7	2.8	0.2	15.4	0.5	0.3	0.2	1.0
K10_ <b>B</b> @Au	35.1	6.3	40.2	0.4	2.2	0.1	14.8	0.3	0.4	0.2	-
K10_ <b>B</b> @Au_Cat	29.7	4.6	43.9	0.7	3.2	0.1	15.8	0.4	0.2	0.2	1.2

<sup>a</sup> Determined by the areas of the respective bands in the high-resolution XPS spectra.

#### Table 4

Chemical composition of the parent K10 and Au-based catalysts

Material	N (mmol $g^{-1}$ )	$C \pmod{g^{-1}}$	Si (mmol g <sup>-1</sup> )	Au (mmol $g^{-1}$ )	
	XPS <sup>a</sup>	XPS <sup>a</sup>	XPS <sup>a</sup>	XPS <sup>a</sup>	ICP
K10	0.2	1.7	12.0	-	-
K10_ <b>A</b> @Au	2.9	22.5	8.3	0.1	0.081
K10_ <b>A</b> @Au_Cat	2.3	18.3	8.8	0.1	0.086
K10_ <b>B</b> @Au	3.7	20.5	8.6	0.1	0.076
K10_ <b>B</b> @Au_Cat	2.6	16.7	8.9	0.1	0.081

<sup>a</sup> Surface contents determined from XPS data in Table 3: mmol element/weight of material = atomic% element/>[atomic% (i) x Ar(i)].

The high-resolution Au 4f spectra of both Au-based catalysts (Fig. 2) can be deconvoluted in two components with BEs of 84.3–84.5 and 87.9–88.2 eV, which are respectively attributed to Au  $4f_{7/2}$  and Au  $4f_{5/2}$  peaks with a spin-energy separation of 3.7 eV and are typical of Au(III) [49]. Curiously, these results indicate

that the citric acid was not strong enough to reduce Au(III) to Au<sup>0</sup> [49,50], probably because the N,O coordinating atoms of the grafted L-serine derivatives acted as strong coordinating sites for Au(III), decreasing the effectiveness of the reduction reaction by citric acid.



Fig. 2. Deconvoluted high-resolution Au 4f XPS spectra of: (a) K10\_A@Au; (b) K10\_A@Au after catalysis; (c) K10\_B@Au; (d) K10\_B@Au after catalysis.

In the Au 4f spectra deconvolution, a peak at 87.8–87.9 eV corresponding to Mg 2s was also included (band in blue, in Fig. 2), due to the clay Mg(II) ions [51].

To ascertain the gold immobilization efficiency, the gold bulk contents were determined by ICP-AES (Table 4). The gold NPs anchoring efficiencies calculated as the amount of anchored Au NPs/amount of gold used in the immobilization procedure  $\times$  100, were 81 and 76% for K10\_A@Au and K10\_B@Au, respectively. Even though XPS analysis reveals a similar Au surface atomic percentage for both samples (0.1 mmol g<sup>-1</sup>), ICP-AES results point to a higher amount of Au in K10\_A, which is consistent with the slightly higher amount of L-serine derivative in K10\_A than in K10\_B (higher grafting efficiency). These results indicate that K10\_A and K10\_B have similar affinity to gold, which are coordinated by the L-serine ester or amide. In any case, both L-serines revealed to be efficient linking agents to anchor Au to the clay support.

UV–Vis spectroscopy was performed to confirm the formation of Au NPs (Fig. S6 in the Supporting Information). None of the samples presented the characteristic plasmonic band of gold NPs [52] in the region of  $\lambda$  = 500–580 nm, which is a typical feature of gold NPs with diameter above 2 nm [53]. This can be due to several factors: no significant formation of Au NPs, the size of gold aggregates being below 2 nm [54], the gold clusters with metallic-like behavior not being the major component or the optical signal being screened due to the high absorbance of the substrate.

To provide insights on the morphology and presence of Au NPs, the catalysts were also characterized by SEM-EDS (Fig. 3).

The SEM images of K10\_A@Au and K10\_B@Au (Figs. 3a1 and b1) show the presence of some bright structures that correspond to large gold clusters. The EDS spectra presents the peaks corresponding to gold, confirming its nature. In order to unravel the presence of small Au NPs on the surface of the materials, TEM characterization was performed, which is presented in Fig. 4.

The TEM images in Figs. 4a1 and b1 do not show the presence of Au NPs, which is in agreement with UV–Vis and XPS data, and suggests that the formation of Au NPs probably did not occur during the immobilization/reduction process, taking place the coordination of Au(III) from the gold precursor onto the L-serine derivatives; nevertheless, some partial Au(III) reduction cannot be excluded.

XRD experiments were performed to evaluate the basal spacing of the clay, confirm the presence of Au NPs and estimate their



Fig. 3. SEM micrographs with EDS as inset of: (a1) K10\_A@Au; (a2) K10\_A@Au\_Cat; (b1) K10\_B@Au; (b2) K10\_B@Au\_Cat.



Fig. 4. TEM images and particle size histograms with a Gaussian curve fitting (inset) of gold nanoparticles immobilized onto L-serine-functionalized K10 clay: (a1) K10\_A@Au; (a2) K10\_A@Au\_Cat; (b1) K10\_B@Au and (b2) K10\_B@Au\_Cat.

particle size. XRD patterns of K10, K10\_**A** and K10\_**B** and the catalysts K10\_**A**@Au and K10\_**B**@Au are presented in Fig. 5.

In the low-angle diffractograms  $(3.5^{\circ} \le 2\theta \le 10^{\circ})$  of all samples it is possible to identify a diffraction peak at  $2\theta$  = 8.8° corresponding to the (0 0 1) reflection of the montmorillonite clay. After functionalization with organosilylated L-serines and immobilization of the Au NPs, the position of the (0 0 1) reflection remains unchanged, indicating that the structure of the K10 clay is preserved.

The wide-angle diffractograms (Fig. 5b) present several  $2\theta$  peaks located at approximately 20, 35 and 62° which are assigned to the clay structure [55]. Several peaks due to impurities present in the clay can be observed, such as quartz, cristobalite and feld-spar [56]. The two peaks at  $2\theta = 38.2^{\circ}$  and  $2\theta = 44.4^{\circ}$  (highlighted with a rectangle in Fig. 5b) correspond respectively to the (1 1 1) and (2 0 0) Bragg reflections of metallic Au with a face centered cubic structure (JCPDS card 04-0784) [57,58]; these may correspond to the large gold clusters that were observed in SEM images.

The FTIR spectra of the materials after immobilization of gold (K10\_**A**@Au and K10\_**B**@Au) are presented in Fig. 1. After gold

immobilization, the intensity of the band at  $\sim$ 3400 cm<sup>-1</sup> corresponding to –OH stretching decreases. The vibration bands in the range of 1700–1500 cm<sup>-1</sup>, corresponding to N–H vibrations, showed a shift towards higher wavenumbers, which may be an indication of the successfully immobilization of Au to the coordination sites of the grafted L-serine derivatives.

#### 3.3. Catalytic reduction of 4-NP

#### 3.3.1. Catalytic reaction and kinetic analysis

The catalytic activity of the gold-supported catalysts K10\_A@Au and K10\_B@Au was assessed in the reduction of 4-NP at room temperature (25 °C) in the presence of NaBH<sub>4</sub>. The reactions were monitored by UV–Vis spectroscopy, as described in the experimental section, and the time-dependent UV–Vis spectra of the 4-NP reduction catalyzed by both gold-supported catalysts are presented in Fig. 6.

As shown in Fig. 6, after the addition of the catalyst, the intensity of the absorption band at  $\lambda \sim 400$  nm corresponding to 4-nitrophenolate ion decreases and a new absorption band at  $\lambda \sim$ 



**Fig. 5.** XRD diffractograms of gold-supported K10 catalysts before and after catalysis: (a) low angles and (b) wide angles.

300 nm shows up, confirming the formation of 4-aminophenol [59]. No electronic band was observed at  $\lambda$  = 388 or 302 nm, indicating that no 4-benzoquinone monoxime or 4-nitrosophenol was generated [60].

Both gold-supported catalysts were highly active in the 4-NP reduction, with the reaction catalyzed by K10\_A@Au reaching the total substrate conversion (100%) within 40 seconds, while with K10\_B@Au as catalyst the total substrate conversion was reached after 60 seconds of reaction time. NaBH<sub>4</sub> was not able to reduce 4-NP without adding catalyst even after more than 1 week (not shown). The L-serine-functionalized supports K10\_A and K10\_B were also tested as catalysts in the 4-NP reduction (Fig. S7 in the Supporting Information), only leading to a slight decrease of the 4-NP band intensity (after 4 h of reaction the band decreased 8.2% and 10.7% for K10\_A and K10\_B, respectively); however, no electronic band corresponding to 4-AP was observed, revealing the lack of catalytic activity of both functionalized supports.

Gold-supported catalyst prepared using non-functionalized K10 clay was also tested in the 4-NP reduction in order to access the necessity of using linking agents such as L-serines for Au immobilization to produce stable and robust catalysts. Upon addition of the catalyst, there was a shift of the 4-nitrophenolate ion electronic band at  $\lambda \sim 400$  nm to  $\lambda \sim 317$  nm that corresponds to the 4-NP electronic band; this may be due to the acidic character of the original K10 (Fig. S8 in the Supporting Information). During the catalytic reaction only a slight change in the intensity of the 4-NP absorption band was observed, but there was no formation of 4-AP band, indicating that the gold-supported K10 clay was not catalytically active.

Adsorption tests of the 4-NP substrate onto both heterogeneous catalysts without the addition of NaBH<sub>4</sub> were also performed (not shown). These tests only revealed a shift of the wavelength of the electronic band corresponding to 4-nitrophenolate ion at the maximum absorption ( $\lambda \sim 400$  nm) to the wavelength of 4-NP ( $\lambda \sim 317$  nm), without any decrease of its intensity, which indicates that no adsorption phenomena were observed.

The kinetic profiles of the 4-NP reduction using both goldsupported catalysts are presented in Fig. 6c, by the representation of  $\ln(A_t/A_0)$  as a function of the reaction time, where  $A_t$  and  $A_0$  are the absorbance values of 4-NP at times *t* and 0 min, respectively.

In the used experiment conditions, the reduction of 4-NP may be considered of pseudo-first-order owing to the large excess of NaBH<sub>4</sub> used. Therefore, the rate constant values, *k*, calculated from the slopes of the linear ranges of the  $\ln(A_t/A_0) = -kt$  plots [61], as well as the half-life time values ( $t_{1/2}$ ) are summarized in Table 5.

The induction period  $t_0$  is not observed using both catalysts, contrary to that found in the literature [47,62,63], indicating that the initial adsorption of 4-NP ions at the active sites is instantaneous and the conversion of nitro into amine groups starts immediately.

A good linear relation between  $\ln(A_t/A_0)$  versus t is verified, confirming that the experimental data match a pseudo-first-order kinetics. The k value for K10\_A@Au is 0.153 s<sup>-1</sup> while for K10\_B@Au is 0.098 s<sup>-1</sup>.

A more accurate comparison between the catalytic activities of the catalysts can be performed by normalizing the *k* values to the amount of gold on each catalyst. In this context, a second constant *K* was determined, normalizing the *k* values to the gold contents determined by ICP-AES. The *K* value (presented in Table 5) is slighter higher in the case of K10\_A@Au (630 mmol<sup>-1</sup> s<sup>-1</sup>) relatively to K10\_B@Au (430 mmol<sup>-1</sup> s<sup>-1</sup>). This can be due to the lower grafting efficiency of serine **5** onto K10 which may be related to the lower solubility of this serine, interfering with the grafting process.

The obtained results show higher rate constants than those previously reported in recent works of 4-NP reduction using gold NPs as homogeneous catalyst or immobilized onto several types of solid supports, namely silica-coated magnetic nanoparticles, carbon nanotubes, etc. (Table 6). In fact, a 729% enhancement of *k* is achieved when compared with the best catalyst reported in the literature (HNTs/Fe<sub>3</sub>O<sub>4</sub>@Au, Table 6) [64].

The analysis of the normalized values of the rate constant K, indicates that the highest value corresponds to Au NPs [47] since the total amount of catalyst corresponds to gold, but this catalyst is very difficult to remove from the reaction medium consequently limiting its catalytic applications and reutilization. In the case of the gold-supported catalysts and comparing the results of the normalized rate constant, the K10\_A@Au catalyst presents a catalytic activity 23.2 higher than the best catalyst in literature [65] summarized in Table 6.

#### 3.3.2. Recycle studies and catalyst characterization

To study the recyclability of the gold-supported catalysts, K10\_**A** and K10\_**B** were reused in ten sequential reaction cycles using the experimental conditions: 50 mg of catalyst, 50 mL of 0.05 mM 4-NP and 0.15 mmol of NaBH<sub>4</sub>. After each use, the catalysts were separated from the reaction medium by filtration without washing. Both catalysts exhibited high catalytic activity without any loss of efficiency, Fig. 7.

The K10\_A@Au catalyst presented substrate conversion values between 98 and 100% in the 10 catalytic cycles with only a slight increase of the reaction time to 2 min, while the catalyst K10\_B@Au had a slightly inferior catalytic activity with conversions between 95 and 100% during 10 catalytic runs and an increase of the reaction time to 3 min.



Fig. 6. Time-dependent UV-Vis spectra of the 4-NP reduction catalyzed by the gold-supported K10 catalysts (a) K10\_A@Au and (b) K10\_B@Au and (c) pseudo-first-order plots of 4-NP reduction catalyzed by K10\_A@Au and K10\_B@Au, in the presence of NaBH<sub>4</sub>.

#### Table 5

Rate constants of pseudo-first-order, half-time reaction and Au content normalized rate constants of 4-NP reduction with K10\_A@Au and K10\_B@Au as catalysts

	Pseudo-first-order ki	Pseudo-first-order kinetic model					
	k (s <sup>-1</sup> )	R <sup>2</sup>	<i>t</i> <sub>1/2</sub> (s)	$K ({\rm mmol}^{-1} {\rm s}^{-1})$			
K10_ <b>A</b> @Au K10_ <b>B</b> @Au	0.153 0.098	0.9505 0.9708	4.53 7.06	630 430			

Table 6

Comparison of the catalytic rate constants (k) and normalized rate constants (K) for heterogeneous Au-based catalysts in the reduction of 4-NP<sup>a</sup>

Catalyst	$C_{4\mathrm{NP}}(\mathrm{mM})$	n <sub>Au</sub> (mmol)	$k (s^{-1})$	$K ({\rm mmol}^{-1} {\rm s}^{-1})$	Reference
Au NPs	0.05	-	0.0094	6266	[47]
Mn@SiO <sub>2</sub> @Au	0.05	0.00048	0.0066	13.75	[65]
Resin@Au	0.10	-	0.00016	-	[66]
Au(5)/TiO <sub>2</sub>	0.20	_	0.0028	-	[19]
dendrimer@Au	0.04	0.95	0.002	0.0021	[67]
CNT@Au	0.05	1.75	0.0077	0.0044	[47]
Fe <sub>3</sub> O <sub>4</sub> @Au	4.33	0.88	0.0105	0.0119	[68]
HNTs/Fe <sub>3</sub> O <sub>4</sub> @Au	5.00	_	0.021	_	[64]
Montmorillonite@Au	0.10	_	0.0046	_	[69]
HNTs@Au	0.10	0.056	0.0095	0.17	[70]
Au/MCN	0.19	0.00102	0.0057	5.7	[25]
K10_ <b>A</b> @Au	0.05	0.000243	0.153	630	This work
K10_ <b>B</b> @Au	0.05	0.000228	0.098	430	This work

<sup>a</sup>  $C_{4NP}$ : concentration of 4-NP,  $n_{Au}$ : amount of Au in the catalyst.

The reaction yields obtained in the 10 consecutive cycles were in the ranges of 62-100% and 63-100% with K10\_A@Au and K10\_B@Au as catalysts, respectively. The values of yield below

100% obtained in some cycles can be probably due to the partial 4-AP adsorption onto the solid supports used for the immobilization of the gold NPs.



Fig. 7. Recycling tests performed with gold-supported catalysts in the reduction of 4-NP using NaBH<sub>4</sub> as reducing agent.

After the ten consecutive cycles, the gold-supported catalysts were further characterized by several techniques in order to understand the relationship between the observed enhanced catalytic activity, stability and catalyst structure.

The FTIR spectra of K10\_A@Au and K10\_B@Au after the recycling tests (Fig. 1) do not exhibit significant changes when compared with the FTIR spectra of the original gold-supported catalysts, which confirms that their structure was preserved upon recycling and reuse.

The gold bulk content before and after catalysis remained similar (Table 4) evidencing the absence of Au leaching during the catalytic reactions. Similarly, from XPS analysis of the catalysts after their recycling/reuse in the reactions, it is possible to verify that there are no significant differences in all atomic percentages, indicating that there was no leaching nor support modification. The Au surface content determined by XPS after the catalytic tests also reveals that the Au percentage remains unchanged (0.1 mmol  $g^{-1}$ ) for both catalysts (Table 4). The results from these techniques clearly indicate that gold leaching upon recycling and reuse is negligible, confirming the robustness of the catalysts.

The XPS high-resolution Au 4f spectra of both Au-based catalysts after catalysis exhibit asymmetric peaks, Figs. 2b and d, suggesting the presence of gold species with different oxidation states [71]. The most intense bands at lower binding energies of 83.5–83.6 eV and 87.1–87.3 eV correspond to Au  $4f_{7/2}$  and Au  $4f_{5/2}$  peaks, respectively (Table S1 in the Supporting Information), and are assigned to Au<sup>0</sup>, confirming the presence of Au NPs [72,73]. Moreover, the weaker bands at higher binding energies, 85.0–85.1 eV and 88.7–88.8 eV, assigned to  $4f_{7/2}$  and Au  $4f_{5/2}$  peaks, respectively (Table S1 in the Supporting Information), may be due to Au(III) species: unreduced Au(III) coordinated to L-serine derivatives or partially oxidized Au NPs.

Furthermore, after catalysis, the color of both Au-based catalysts changes from pale yellow to reddish (inset of Fig. S6 in the Supporting Information), which was confirmed by the UV–Vis spectra through the appearance of a new electronic band at  $\lambda \sim$ 530 nm, which is attributed to the characteristic surface plasmon resonance of Au NPs [52], confirming the formation of small gold NPs during the catalytic reactions.

Finally, the SEM images of both catalysts after the catalytic reactions (Fig. 3) reveal that the catalysts contain Au NPs on the supports surface, indicating that the Au(III) immobilized onto the clay support through the grafted L-serines was *in situ* reduced to Au NPs during the catalytic reactions due to NaBH<sub>4</sub> that was used as catalytic reaction reducing agent. In fact, NaBH<sub>4</sub> is a stronger reducing agent when compared with citric acid which, combined with its excess in the catalytic reaction, allowed overcoming the

strong coordination chelate effect exhibited by L-serine N,Ocoordinating atoms towards Au(III). This allowed the reduction of the coordinated Au(III) cations, with the L-serines acting simultaneously as an effective capping agent for the as-formed Au NPs, as confirmed by the stability and robustness of the catalysts in the recycling studies.

The TEM images of the catalysts confirm the presence of Au NPs immobilized on the surface of the K10\_A@Au and K10\_B@Au samples, with average particle sizes of 5±2 nm and 4±2 nm, respectively (Figs. 4a2 and b2).

Finally, the X-ray diffractograms of both catalysts after catalysis continue to exhibit the peaks at  $2\theta = 38.2^{\circ}$  and  $44.4^{\circ}$  (highlighted with a rectangle in Fig. 5b), but now exhibiting broader and less intense peaks, indicating the presence of Au NPs. In the low-angle X-ray diffractograms of both catalysts, no  $d_{001}$  basal spacing changes are observed when compared with those of the asprepared catalysts, indicating no change in the clay support structure upon the catalytic cycles.

Additional stability tests were performed for both catalysts using them one and two months after the recycling tests. These experiments correspond, respectively, to an eleventh and twelfth catalytic cycle for each catalyst. After one month, the total conversion of 4-NP to 4-AP occurred within 4 and 7 min using catalyst K10\_A@Au and K10\_B@Au, respectively (97 and 95% conversion). After two months, the reaction was complete within 6 and 7 min (95 and 90% conversion), respectively. It is important to remember that the reaction times verified at the 10<sup>th</sup> cycle were of 2 and 3 min, respectively. The increase of reaction time can be probably due to the difficulty of dispersing the catalysts in the reaction medium when they are dried after used.

Furthermore, in order to evaluate the catalysts stability under storage, another aging test was performed using a new amount of the original catalysts 4 months after their synthesis. The reaction time of the total reduction of 4-NP to 4-AP was of 30 and 90 s using the catalysts K10\_A@Au and K10\_B@Au, respectively. This reaction time is in accordance with those obtained in the first studies (40 and 60 s). The rate constant for K10\_A@Au was 0.195 s<sup>-1</sup> while for K10\_B@Au was 0.0471 s<sup>-1</sup> versus 0.153 and 0.0982 s<sup>-1</sup>, respectively, obtained on the previous studies. These results reveal the good stability of these catalysts upon storage with a slightly higher catalytic activity of K10\_A@Au catalyst when compared to K10\_B@Au.

#### 4. Conclusions

K10 clay functionalized with two different L-serine organosilanes, K10\_**A** and K10\_**B**, were successfully prepared and used for the coordination of Au(III) and subsequent immobilization of Au NPs. In fact, the used techniques showed that the N,Ocoordinating atoms from the grafted L-serine derivatives were very efficient in the coordination of Au(III) in high extent (0.08 mmol  $g^{-1}$ ), but simultaneously prevented the Au(III) reduction by citric acid during the catalyst preparation. However, during the catalytic reaction, the coordinated Au(III) cations were reduced to metallic Au NPs with average size of 5 nm by the NaBH<sub>4</sub> reducing agent.

Both K10\_**A**@Au and K10\_**B**@Au showed very good catalytic activity in the reduction of 4-NP to 4-AP, with total substrate conversion and *K* values (corresponding to the *k* values normalized for Au content) of 630 and 430 mmol<sup>-1</sup> s<sup>-1</sup>, respectively. The slightly lower catalytic activity of K10\_**B**@Au is related to the slightly inferior grafting efficiency of serine **5** onto K10 and, consequently, of Au NPs. Regardless of that, both catalysts presented a catalytic activity significantly higher than that reported in the literature for other Au-based heterogeneous catalysts, and preserved their performance during 10 cycles, with negligible Au leaching. The high robustness and stability of the catalysts could be assigned to the strong coordination of the Au NPs to the grafted L-serine derivatives, which acted as efficient capping agents towards the as-formed gold NPs. The aging tests also showed a very good catalytic stability of the prepared catalysts under storage.

This study is an outstanding example of the versatility of Lserines as polydentate coordinating ligands for transition metal cations and as potential capping agents for metal NPs, since their structure and coordinating atoms can be easily adapted to include specific properties. Their silylation allowed the preparation of Lserine organosilane derivatives that can be used for the functionalization of several other supports, besides K10 clay used in this work, opening new horizons on the design of new heterogeneous recyclable metal complex-based catalysts, as well as metalsupported catalysts for oxidation and reduction reactions.

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#### **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.02.027.

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