



Suzuki–Miyaura cross-coupling of aryl iodides and phenylboronic acid over palladium-free CeO₂ catalysts



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ABSTRACT

The Suzuki–Miyaura cross-coupling reaction between *p*-iodotoluene and phenylboronic acid is carried out over a series of ceria catalysts, at 150 °C, under N₂ atmosphere, employing DMF as the solvent. The ceria catalysts present different BET area (determined from N₂ isotherms at 77 K), different Ce⁴⁺/Ce³⁺ ratio (as measured by XPS), and different concentration and strength of acid sites (as measured by potentiometric titration with *n*-butylamine). The activity of the different samples depends on the concentration and strength of acid sites, although the participation of Ce³⁺ centers should not be neglected. Ceria catalysts are less active and less selective than a Pd/SiO₂ sample. Although the catalytic performance of ceria catalysts is lower than the one corresponding to Pd/SiO₂, the fact that a transition metal-free catalyst is active for SM reaction is highlighted.

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1. Introduction

The Suzuki–Miyaura (SM) cross-coupling of aryl halides with aryl boronic acids is one of the most important synthetic routes for the production of asymmetric biaryls [1–5], which plays an important role in industrial chemistry, appearing in commercial products ranging from performance materials to pharmaceuticals. Traditionally, SM coupling is carried out over homogeneous palladium catalysts. However, in the last years heterogeneous catalysts have been increasingly employed since they show well known advantages, compared to their homogeneous counterparts [6].

A large variety of palladium supported catalysts have been employed for SM coupling reaction [7–10,5,11–23]. Most of them are highly active and selective, showing high yields for the cross-coupling product, under mild experimental conditions. However, some investigations on SM cross-coupling over heterogeneous Pd catalysts have indicated that the true acting catalyst would be soluble palladium species. Probably connected with this fact, palladium leaching was evidenced [15]. This is an important drawback, since most of the fine chemicals and pharmaceutical products must be completely free of residual metal. Besides, for some of these heterogeneous catalysts the activity drops following recycling [16].

In the last decade, metal-free catalysts have emerged as a promising alternative to the current Pd-based ones [24–31], although transition metal-free Suzuki–Miyaura cross-coupling has scarcely been studied. In a very recent work [30] some of us reported that high surface area ceria, HSA-CeO₂, in the absence of palladium, efficiently promotes the SM cross-coupling reaction. Agawane and Nagarkar also employed bare ceria for catalyzing Ullmann coupling reactions [31].

Ceria possesses exceptional redox and acid–base properties [32], both of them enable this oxide to catalyze numerous organic reactions as dehydration [33], ketonization [33,34], hydrogenation [35], and oxidation [36]. However, it is important to note that, to the best of our knowledge, there is no other report than the above-mentioned works regarding coupling reactions over cerium oxide.

In a recent communication some of us concluded that the SM reaction is catalyzed by a commercial high surface area ceria (HSA-CeO₂), following an *in situ* calcination pre-treatment at 150 °C. It was suggested that acidic ceria sites would be responsible for the activation of the substrate molecules [30]. However, a more detailed and precise explanation about the nature of the ceria active sites was not provided in that work.

With this scenario in mind, in the present work, a series of CeO₂ samples are characterized and tested for carrying out the SM cross-coupling, using *p*-iodotoluene and phenylboronic acid as model compounds, in the presence of K₂CO₃ as a base and employing *N,N*-dimethylformamide (DMF) as the solvent. The ceria samples are characterized by X-ray photoelectron spectroscopy (XPS), powder

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X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and potentiometric titration with *n*-butylamine. In the basis of the characterization and the catalytic results, the nature of the ceria active sites for performing the SM reaction in metal free conditions is discussed.

2. Experimental

2.1. Preparation and characterization of the catalysts

One of the samples is a high surface area oxide, HSA-CeO₂, from Rhône Poulenc (Acalys HSA 5) with a surface area of 240 m² g⁻¹ and a pore volume of 0.2 ml g⁻¹, previously tested by us for the interest reaction [30] and also as a support for gold catalysts in Ref. [37]. This sample was calcined at 800 °C for 4 h for obtaining another catalyst, with lower surface area (LSA-CeO₂). A combustion synthesis was followed to obtain C-CeO₂. Approximately 7.5 g of Ce(NO₃)₃·6H₂O (99.99% Sigma Aldrich) were dissolved with a minimum amount of water. Sacarose (Aldrich, 98%) was added to this mixture. The temperature was raised up to 400 °C, while stirring. Following the evaporation of water a combustion reaction was observed. The resulting solid was dried at room temperature for 24 h. Afterwards the solid was calcined at 400 °C during 2 h. In order to avoid contamination with carbonate, the sample was kept in a N₂ box.

A palladium supported catalysts was also prepared, from the wet impregnation method employing a solution of palladium acetylacetonate, Pd(AcAc)₂ (Aldrich, 99.9%) in toluene. The support was SiO₂ (Davison with 210 m² g⁻¹). The palladium loading of this sample, as measured by atomic absorption spectroscopy, was 0.8 wt%. The mean particle size of Pd in the catalyst is 4.8 nm and it was measured by transmission electron microscopy with a Jeol 100 CX2 (Tokyo, Japan).

The ceria samples were analyzed by X-ray diffraction (XRD) in a diffractometer with CuK α radiation, within a 2θ range of 5–82°, with a scanning speed of 1.2°/min. Textural characterization of the catalysts was carried out by N₂ adsorption at 77 K in a Quantachrome Nova 1200e sorptometer. The specific surface areas (S_{BET}) were calculated employing the BET equation, following a evacuation for 4 h at 120 °C. The catalysts were analyzed by Fourier transform infrared spectroscopy (FTIR) in a Nicolet Nexus apparatus. The samples were previously calcined at 300 °C and then transferred to the analysis chamber under N₂ flow. The spectra were obtained with a resolution of 2 cm⁻¹ using 50 scans. Samples were also characterized by X-ray photoelectron spectroscopy (XPS) in a multitechnique Specs equipment provided with a Mg X-ray source. The samples were previously treated in the pre-chamber of the equipment under chromatographic air at 300 °C. The analysis of Ce³⁺ and Ce⁴⁺ peaks was carried out in the 870–930 eV range of binding energies (BE). The charging correction was performed with the C1s peak. A quantitative analysis was carried out for determining the Ce³⁺/Ce⁴⁺ ratio from the integrated area of the peaks. The acidity of the ceria samples was measured by potentiometric titration with *n*-butylamine. The solid was dispersed in 100 ml of acetonitrile and the mixture was stirred for 1 h. Afterwards it was titrated with a 0.1 M solution of butylamine employing a AT500N automatic potentiometric titrator. The total surface acidity was evaluated from the amount of base added to reach the plateau in the titration curve, while the first point of the titration (E_0 in mV) was employed for analyzing the acid strength [38,39].

2.2. Catalytic test

The SM reaction was conducted in a 50 ml Parr Instrument, in batch mode, at 150 °C. The stirring was set at 800 rpm. The

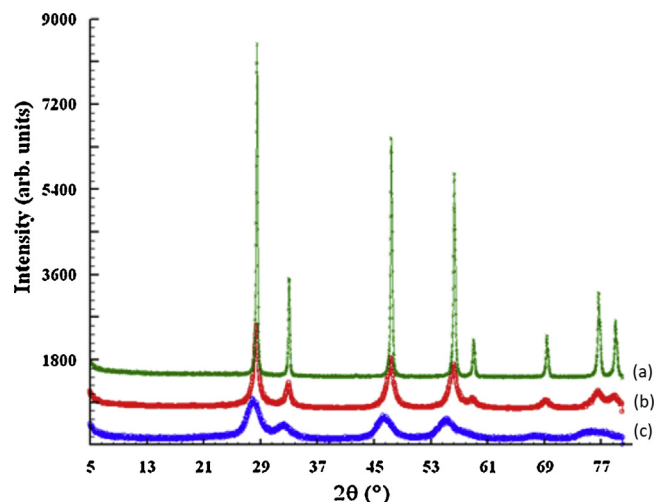


Fig. 1. XRD pattern of ceria catalysts (a) LSA-CeO₂, (b) HSA-CeO₂, (c) C-CeO₂.

reactive mixture was composed by 1 mmol of phenylboronic acid and 0.7 mmol of *p*-iodotoluene in 30 ml of DMF. In a typical experiment, the catalyst (with a mass of approximately 200 mg) and K₂CO₃ (which is employed as the base for SM) are treated in the reactor under air flow (chromatographic quality) at 150 °C for 1 h. Afterwards, the air flow is switched to a nitrogen flow and the reactive mixture is introduced into the reactor. Finally the pressure is raised to 0.1 MPa of nitrogen, the stirrer is switched on and the reaction is considered to be started. During the reaction, aliquots of the reactive media were analyzed by GC-MS in a Perkin Elmer Claurus equipment, provided with a HP5 column and coupled to a mass-spectrometry detector.

3. Results

3.1. Characterization of the ceria catalysts

XRD analysis of the different ceria catalysts indicated the presence of pure fluorite phase (Fig. 1). No peaks other than those corresponding to CeO₂ were observed in the diffraction patterns. The peaks corresponding to C-CeO₂ and HSA-CeO₂ are relatively narrow indicating that these samples present small crystallites. On the other hand, the diffraction peaks of LSA-CeO₂ are intense and narrow ones, showing that both samples are well crystallized solids. The size of the ceria crystallites was determined from the width of the (1 1 1) peak, following the Scherrer approximation. The corresponding values were 123 nm for HSA-CeO₂, 244 nm for C-CeO₂ and 546 nm for LSA-CeO₂.

BET surface area (S_{BET}) of the ceria samples are reported in Table 1. It can be observed that both C-CeO₂ and HAS-CeO₂ posses high values of S_{BET} . On the other hand, the corresponding values for LSA-CeO₂ is relatively low. The results of S_{BET} are in line with

Table 1
Physicochemical properties of CeO₂ catalysts.

Sample	BET area (m ² g ⁻¹)	Ce ⁴⁺ /Ce ³⁺ atomic ratio ^a	Acid. sites (mEq g ⁻¹)	Acidity ^b	E_0 ^c (mV)
HSA-CeO ₂	240	2.1	0.72	S	18.2
C-CeO ₂	110	8.5	1.82	vs	65.2
LSA-CeO ₂	40	7.5	0.01	w	-65.1
Pd/SiO ₂	210	-	0.00	-	-

^a Ce³⁺/Ce⁴⁺ atomic ratio calculated from XP peaks area ratios.

^b Measured by potentiometric titration, w: weak acidity, s: strong acidity, vs: very strong.

^c E_0 : mV corresponding to the first point of the titration.

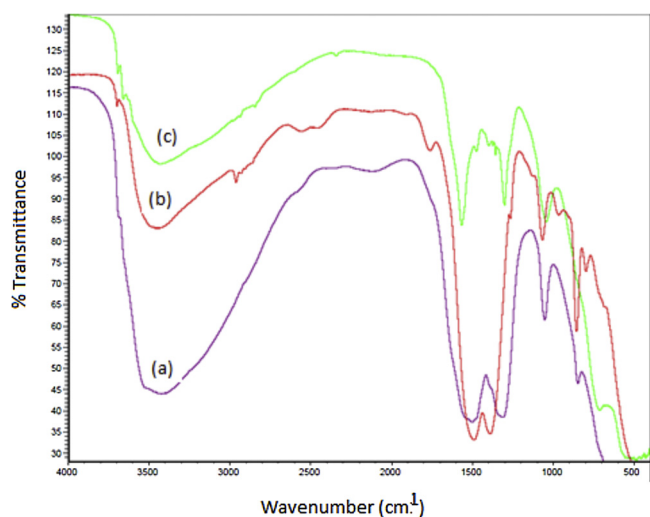


Fig. 2. FT-IR spectra of: (a) HSA-CeO₂, (b) C-CeO₂, (c) LSA-CeO₂.

the values of the crystal size of the samples (as measured from XRD) since the catalysts with lowest crystal size shows the highest specific surface area.

The FT-IR spectra of the samples are shown in Fig. 2. The intensity of the OH stretching band (4000–3200 cm⁻¹) is high for both C-CeO₂ and HSA-CeO₂, due to their large specific surface area.

The chemical nature of the ceria catalyst surface was studied by XPS. The cerium 3d transition peaks, appearing in the 870–930 eV range of binding energy (BE), are shown in Fig. 3 for LSA-CeO₂, C-CeO₂ and HSA-CeO₂. The ν_0 , ν' , and ν'' peaks are attributed to Ce³⁺; while ν , ν'' , ν''' , u , u'' , and u''' are characteristic of Ce⁴⁺ [40]. The BE values and the percentage of the integrated area of these peaks are reported in Table 2. From the integrated area, the relative amounts of Ce³⁺ and Ce⁴⁺ species were estimated for the samples. The highest relative concentration of Ce³⁺ was found for HSA-CeO₂, while C-CeO₂ and LSA-CeO₂ show relatively low concentrations of Ce³⁺. The LSA-CeO₂ sample is obtained from the calcination at high temperature of the HSA-CeO₂ catalyst; this treatment leads to a decrease of S_{BET} and, as could be expected, of the concentration of Ce³⁺. For the case of C-CeO₂ sample, the low concentration of Ce³⁺ is probably related with the combustion method followed for preparing this sample.

Fig. 4 shows the XPS peaks corresponding to O1s for C-CeO₂ and HSA-CeO₂. The presence of two different oxygen species are concluded since two contributions are detected in each spectrum. The peak at 528.7 eV is attributed to lattice oxygen, while the one at higher BE (530.5 eV) has been assigned to oxygen species coming from the interaction of water with ceria surface [41] and concomitantly the amount of the latter species increases with increasing surface area. Some researchers have argued that this peak is related to the Ce(III) oxide on the surface [42–44], and others have stated that the peak arises from hydroxyl groups on the surface or oxygen chemisorbed on the surface [45]. The amount of these species increases with increasing surface area, thus the corresponding peak is higher for HSA-CeO₂ than for C-CeO₂ as can be observed in Fig. 4.

The amount of acid sites per gram of catalyst, determined from the titration curves of with *n*-butylamine, as well as the strength of those sites, are reported in Table 1 for all the catalysts. The corresponding titration curves are presented in Fig. 5. The potentiometric measurements indicate that both C-CeO₂ and HSA-CeO₂ show acidic properties, possessing a relative high concentration of sites with quite strong acidity. HSA-CeO₂ shows lower acidity strength and also lower concentration of acid sites than C-CeO₂. On the other hand, the low surface area ceria sample, LSA-CeO₂, should

be considered as a weakly acid solid, with negligible amounts of acid sites measured by titration. Although both catalysts, HSA-CeO₂ and C-CeO₂ should be considered as acid ones, the former shows less acidity properties than the latter.

3.2. Catalytic test: the Suzuki–Miyaura cross-coupling reaction

Three ceria catalysts were tested for the SM reaction. In Fig. 6 the dependence of the conversion of *p*-iodotoluene on time is shown for the samples previously submitted to an *in situ* calcination treatment followed by purging with inert gas.

An induction period is observed for the samples, probably related with the delay of the substrate molecules to diffuse from the solution to the ceria surface.

In Table 3 the conversion and the selectivity to the desired product attained following 3 h of reaction time are reported, as well as the specific activity (expressed as moles of *p*-iodotoluene converted per hour and per gram of ceria). The conversion levels and the specific activities are much higher for HSA-CeO₂ and for C-CeO₂ than for LSA. For all the catalysts, the presence of soluble cerium species in the reaction media was disregarded based on ICP measurements of the reaction media at 6 h of reaction time.

Regarding the selectivity, the main product is the cross-coupling one. A low selectivity toward the homo-coupling product was measured for all the ceria catalysts, suggesting that an Ullmann-type homo-coupling reaction of the starting *p*-iodotoluene occurs over certain surface ceria sites. On the other hand, the use of *p*-bromotoluene or *p*-chlorotoluene as starting aryl halides gave no coupling products under the same reaction conditions. This was an expected result based on our preliminary findings [30].

For the sake of comparison, a SiO₂ supported Pd catalyst was also evaluated under the same operational conditions as for the ceria series; the only difference being the mass of catalyst employed (70 mg for the noble metal catalysts against 200 mg for ceria one). The corresponding results are shown in Fig. 6. It is clear that the noble metal catalyst is much more active and more selective than the ceria ones.

Although ceria catalysts are less active and less selective than a traditional palladium supported catalyst, the fact that the CeO₂ surface presents active sites for SM reaction is a highly interesting result. The presence of traces of Pd or other noble metal in the different ceria samples was disregarded based on AAS measurements.

3.3. Influence of the ceria catalysts pretreatments on the catalytic pattern

In order to investigate on the nature of the ceria active sites, HSA-CeO₂ was submitted to the following treatments before catalytic testing: (i) the sample is treated in the reactor under air flow at 150 °C, cool down to room temperature and without purging with an inert gas (it is important to note that the catalytic results reported in Section 3.2 correspond to a calcination pre-treatment and a subsequent purging in N₂ at high temperature) it is put in contact with the reactive mixture and the air flow is switched to N₂. Finally the temperature is raised up to 150 °C (ii) the catalyst is reduced at 300 °C under H₂ flow for 1 h. Afterwards the sample is cooled down to 150 °C, the reactive mixture is introduced into the reactor and the H₂ flow is switched to N₂.

For the treatment (i), a low conversion level (lower than 10%) was attained after 6 h of reaction time. Besides, the selectivity toward the cross-coupling product was much lower than that corresponding to the sample upon the original pre-treatment. The homo-coupling product was mainly formed (with a selectivity of approximately 80%) over the cross-coupling one. It is likely that the Ullman coupling reaction of *p*-iodotoluene is taking place over

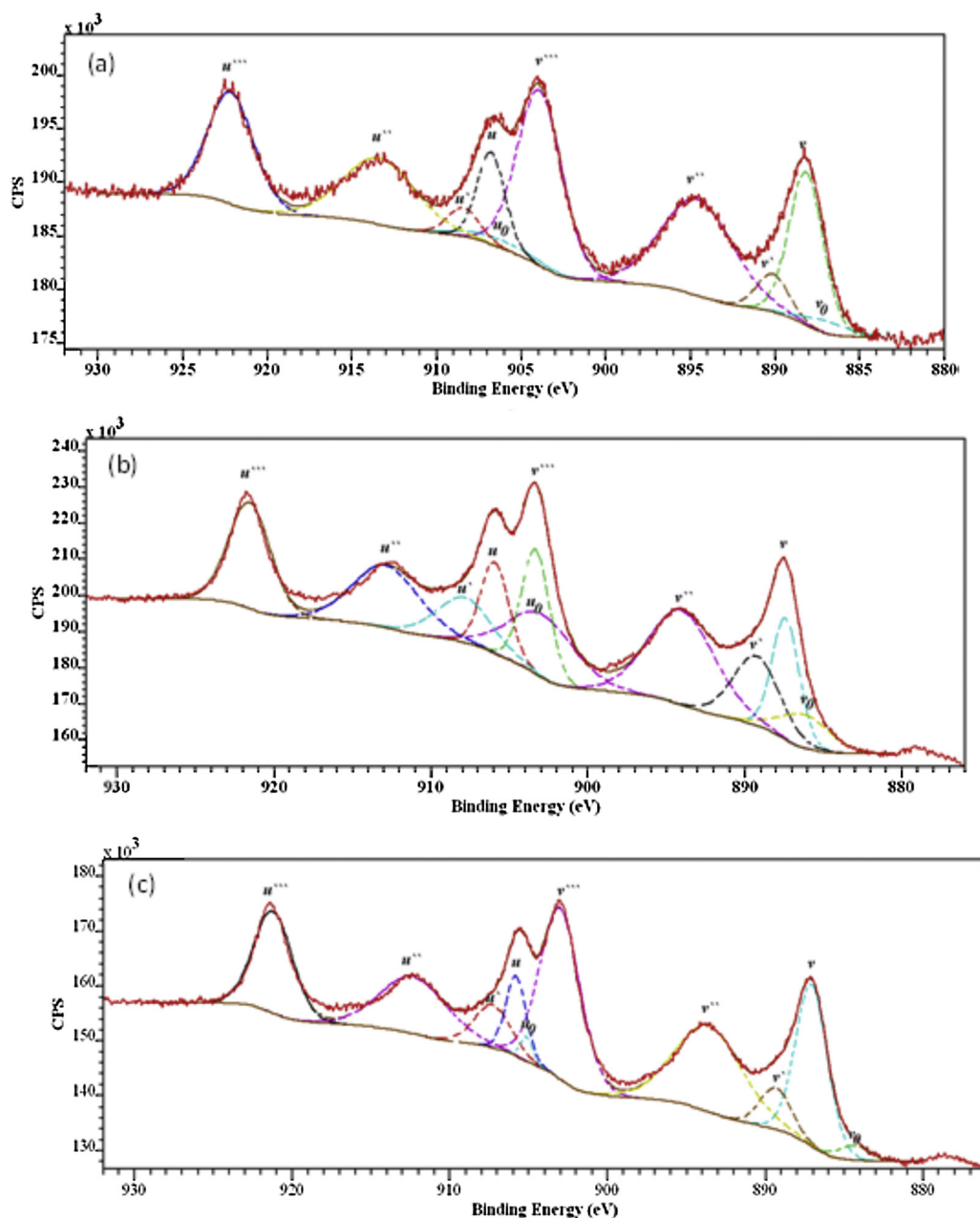


Fig. 3. Ce 3d XPS spectra of ceria catalysts. Solid lines for experimental spectra and dotted lines for peaks fit. (a) C-CeO₂ (b) HSA-CeO₂, (c) LSA-CeO₂.

the oxidized ceria surface and that purging with an inert gas is necessary for increasing the cross-coupling reaction. Probably the inert gas flow eliminates adsorbed oxygen species which would be responsible for the Ullman-type homo-coupling of the starting aryl

halide. Regarding the pre-treatment (ii), no reaction was observed over the reduced ceria surface. Following this treatment a change in the color of the sample was detected, from pale yellow (as prepared sample or calcined one) to gray (reduced sample), indicating

Table 2

XPS BE of individual peaks of Ce 3d, area ratio and atomic percentage of Ce³⁺ for ceria catalysts.

Sample	Ce ⁴⁺ BE (eV)						Ce ³⁺ BE (eV)			
	<i>v</i>	<i>v</i> '	<i>v</i> ''	<i>u</i>	<i>u</i> '	<i>u</i> ''	<i>v</i> ₀	<i>v</i> '	<i>u</i> ₀	<i>u</i> '
C-CeO ₂	882.9	889.3	898.6	901.5	908.1	916.9	881.7	884.8	900.6	903.2
HSA-CeO ₂	881.8	888.4	897.7	900.3	907.3	915.9	880.5	883.6	897.3	902.3
LSA-CeO ₂	882.1	888.6	898.0	900.8	907.3	916.2	879.4	884.4	900.2	902.3
	Ce ⁴⁺ peak area						Ce ³⁺ peak area			
C-CeO ₂	36,731	49,425	55,076	17,820	34,875	36,381	3824	8426	4007	5938
HSA-CeO ₂	74,865	142,099	77,845	58,358	93,850	99,342	36,632	73,809	94679	56371
LSA-CeO ₂	76038	84987	100022	24206	56460	58303	6693	19171	4457	22941

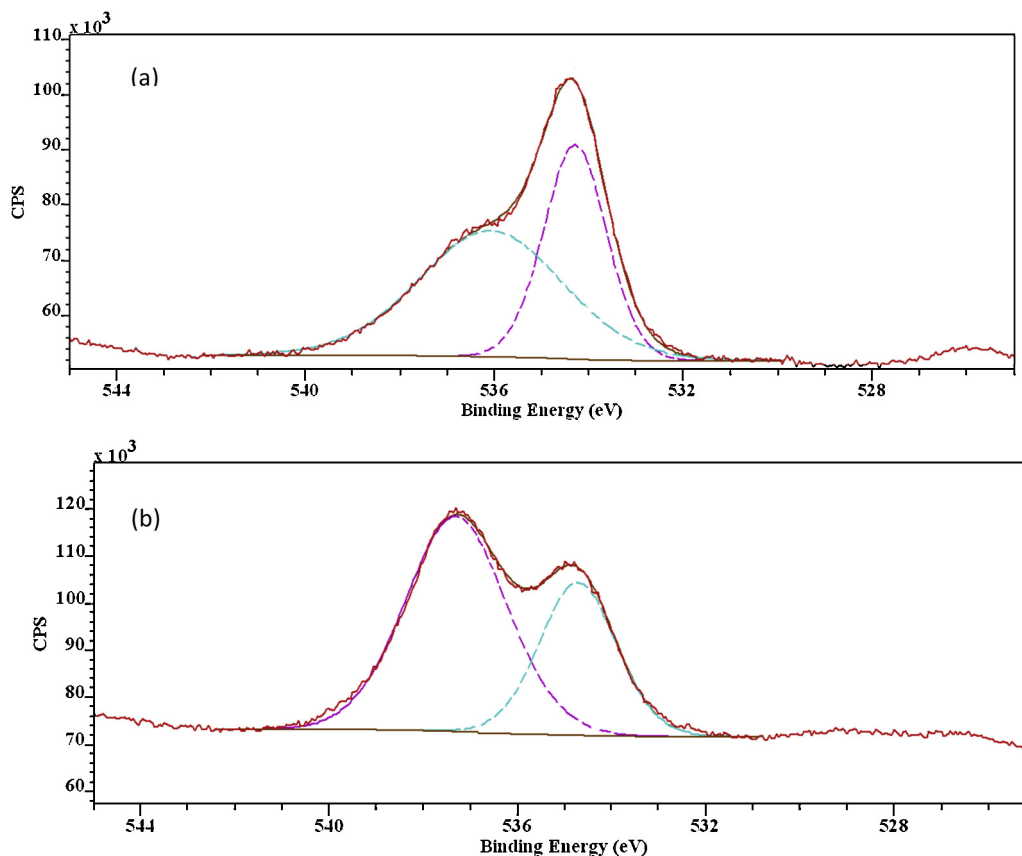


Fig. 4. O1s spectra for (a) HSA-CeO₂ and (b) C-CeO₂.

that a notable increase of Ce³⁺ concentration occurs following the reduction treatment. The inactivity of the reduced ceria sample strongly suggests that Ce³⁺ centers are not engaged in the SM reaction.

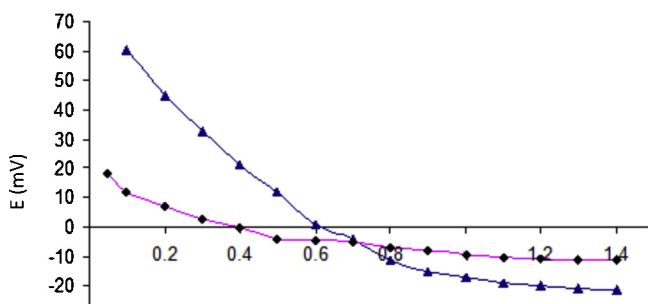


Fig. 5. Potentiometric titration curves with *n*-butylamine of: (◆) HAS-CeO₂ and (▲) C-CeO₂.

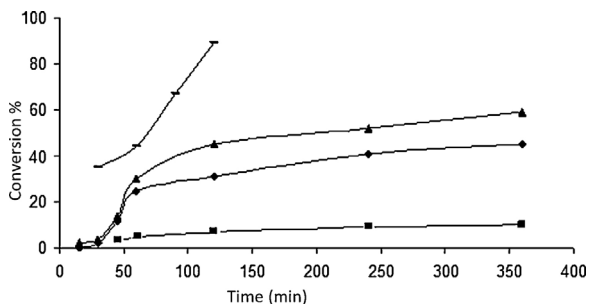


Fig. 6. Dependence of conversion of *p*-iodotoluene on time on stream of: (◆) HAS-CeO₂, (▲) C-CeO₂, (●) LSA-CeO₂ HSA-CeO₂, (–) Pd/SiO₂.

3.4. Reuse of the ceria catalysts and heterogeneity of the reaction

The spent HSA-CeO₂ catalyst was tested for a new reaction. Following 3 h of reaction the HSA-CeO₂ sample was withdrawn from the reactor, rinsed thoroughly with fresh solvent, and submitted to the original pre-treatment. The catalytic pattern of the reused sample was similar to the one corresponding to the fresh sample. The conversion of the spent ceria was slightly lower than the one corresponding to the original sample, related with the fact that certain amount of catalyst is lost during this procedure. This procedure was repeated and once again the conversion measured over the used sample was similar to the original one. *S*_{BET} as well as the amount of acid sites of the spent HSA-CeO₂ were measured, leading to values similar to that of the fresh sample. These results show that the surface properties of ceria are recovered following the corresponding pre-treatment.

The fact that HSA-CeO₂ can be reused and that the same surface properties are found for the spent catalyst would indicate the heterogeneous nature of SM reaction over this catalyst. However, it could be argued that soluble cerium species leached from the support would be highly active and that very low concentration of

Table 3
Catalytic properties of CeO₂ catalysts.

Catalyst	X% ^a	S% ^b	Act. (mmole g ⁻¹ h ⁻¹) ^c
HSA-CeO ₂	41	89	0.48
C-CeO ₂	52	92	1.82
LSA-CeO ₂	8	90	0.15
Pd/SiO ₂	100	100	4.76

^a Percentage of conversion at 3 h of reaction time.

^b Percentage of selectivity to the cross coupling product.

^c mmole of *p*-iodotoluene converted per hour and per gram of catalyst.

such species would give rise to the observed conversion. No concentration of cerium species was measured by ICP-AES analysis in the liquid reaction media (withdrawn from the reactive mixture at the reaction temperature) following 3 h of reaction time. For this reason we conclude that the actual active sites are located at the surface of HSA-CeO₂.

4. Discussion

In the present work, the SM reaction was carried out over a commercial ceria sample, but also over other synthesized cerium oxide catalysts. Some of these catalysts were active for the SM reaction and although they were less active and less selective than Pd/SiO₂, the fact that a transition metal-free system is able to catalyze the SM cross-coupling reaction is a very interesting and novel result.

Ceria has been employed as a support of palladium or gold in the formulation of active catalysts for different coupling reactions in liquid phase [16,46–48]. In those studies it was concluded that ceria shows an effect on the stabilization of specific oxidation state of gold or palladium and that it plays no direct role in the activation of the reactants. For the active ceria catalysts tested in this work, HSA-CeO₂ and C-CeO₂, the presence of trace amounts of transition metals in the samples was disregarded, since AAS determination of such impurities, at ppm levels was negative. Even more, the fact that reduced ceria sample showed no activity for the title reaction is another proof showing that transition metal species are not involved, even if present at sub-ppm levels.

The high temperature calcination treatment of HSA-CeO₂ leads to a sample with a notably lower specific surface area and concomitantly a lower concentration of active sites (whatever its nature). For this reason, the low surface area ceria, LSA-CeO₂ showed a lower activity (expressed as moles of *p*-iodotoluene converted per hour and per gram of ceria) than that of its parent catalyst.

Regarding the nature of the active sites on ceria surface, it is worthy of note that unraveling their nature is quite difficult considering the complex nature of SM reaction. It could be considered that both acid–base and redox centers are engaged in the activation of the reactants. It is known that ceria is able to catalyze a large number of reactions although it is generally not possible to describe the exact nature of the active centers and to relate the activity to a unique and well described site [32].

In the present work it was observed that the activity of ceria notably depends on the nature of the pre-treatment (calcination, purging with inert gas, reduction at high temperature). This fact indicates that the concentration of the active sites varies from one treatment to another. A relatively low Ce⁴⁺/Ce³⁺ ratio was detected by XPS analysis on HSA-CeO₂, while such a ratio was higher for C-CeO₂. Both samples show high conversion levels, but the specific activity of C-CeO₂ sample (expressed as mole converted per hour and per gram of ceria) is higher than the corresponding to HSA-CeO₂. Thus the activity would not be related with the concentration of Ce³⁺. Furthermore, if the activity is calculated on a specific surface base (moles converted per m² of ceria) the higher performance of C-CeO₂ than HSA-CeO₂ is even more notorious, since it is 0.013 mmole m⁻² h⁻¹ for the former and 0.003 mmole m⁻² h⁻¹ for the latter catalyst.

Previously reduced ceria (at high temperature, under H₂), with a high Ce³⁺ concentration, is almost inactive. In this way, one could postulate that redox sites are not engaged, at least in a direct way, in the SM reaction.

It is well known that oxygen vacancies are present on ceria surface, and that over these sites molecules could be activated [49,50]. The concentration of these vacancies increases along with the concentration of Ce³⁺. Once again, the fact that ceria is almost inactive for SM following a reduction pretreatment would indicate

that oxygen vacancies are not engaged as active site. Furthermore, the highest concentration of Ce³⁺ is detected for HSA-CeO₂ sample, which is not the most active one.

Based on the above comments, redox sites should not be considered as active sites, at least in a direct way, and attention should be paid to acid or basic sites on ceria surface.

The acid–base properties of ceria are versatile and depend on the nature and the temperature of the pre-treatments [32,51]. The presence of Lewis–base on ceria was concluded mainly from CO₂ chemisorption studies and this basic property is insensitive to the state of ceria; *i.e.*, reduced or unreduced [52–54]. On the other hand, CO and pyridine are chemisorbed on ceria showing the acidic character of this oxide. Moreover, in contrast to the Lewis basicity, the Lewis acidity would decrease upon reduction of ceria [32,50]. With this scenario in mind, and taking into account that the activity for SM reaction is developed only for calcined samples, it is plausible that acid Lewis sites are involved in the reaction. In line with this, C-CeO₂ showing the highest concentration of these sites (as measured by potentiometric titration) develops the highest activity.

Summing up, the results of the characterization of the samples, and the analysis of the influence of the nature of the pre-treatment on the catalytic patterns would indicate that acid sites play a role in the SM reaction. However, the participation of other sites (basic and redox one) should not be neglected, considering mainly the complex nature of the SM reaction.

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