

CO and VOCs oxidation over Pt/SiO₂ catalysts prepared using silicas obtained from stainless steel slags

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Abstract

Stainless steels slags are mainly composed of low specific surface area calcium silicates together with a variable amount of metallic cations dispersed in such silicate matrix. These silicates due to their heavy metals content have to be considered as hazardous wastes that cannot be reclaimed easily. An alternative to reclamation is the production of valuable materials designed to accomplish processes without economic profit as the abatement of VOCs. In this paper we describe a method for obtaining high specific surface area (up to 290 m² g⁻¹) metal-doped SiO₂ and SiO₂/Al₂O₃ supports for catalytic applications using as raw materials stainless steel slags. The acid digestion of these slags followed by a hydrothermal treatment results in transition metal oxides doped silicas and silica-aluminas that are used as support for platinum catalysts. The prepared catalysts are active in the total oxidation of CO and toluene, showing comparable activities to those shown by Pt catalysts supported on commercial SiO₂. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

In stainless steels mills, by-products generated in the production process are obtained as a result of the different operations required for obtaining the final product. These by-products are silica-rich solids, silica content is typically ca. 30% by weight, having variable amounts of transition metal oxides, alkaline and alkaline-earth oxides together with other elements like sulfur, fluorine or carbon resulting from the different operation process, e.g. desulphurization slags contain appreciable amounts of sulfur. The promoting effects of the transition metal content [1,2] and alkaline and alkaline-earth elements [3] of slags, transform slags (hazardous wastes) into potentially valuable materials as catalysts and/or catalyst supports. Moreover, these materials have the advantage of their negative cost. In this sense, the use as catalyst for the total oxidation of CO and VOCs of blast furnace slags modified with transition metal ions has been described [4]. However, the low specific surface area of

these solids (<3 m²/g) and their compositional variability let us propose a low-cost method for obtaining a high surface area material with controlled textural properties and reproducible chemical composition from stainless steel slags.

Several methods have been described for obtaining high surface area silica using sol-gel procedures [5]. When mineral acids react with a silicate, silicic acids are produced that further polymerize and polycondense giving micelles [5]. The final surface area of these solids depends on the size of the micelles and the conditions of ripening and drying. Hydrothermal treatments at temperatures ranging between 100 and 300 °C are usual ripening treatments, the textural and structural modifications underwent by silica depending on the ripening temperature and time.

Here we report data on procedures for obtaining high surface area transition metal-doped silicas from stainless steel slags by means of acidic digestions [6] and further hydrothermal treatments. The use of these silicas as supports for platinum catalysts for the total oxidation of CO and toluene is reported. The results are compared to those obtained when commercial silica is used as support on the basis of the modification of the acid-base properties of the prepared supports.

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Table 1
Chemical composition of the slags (weight %)

Weight %	Reduction slag	Ladle transfer slag
Na ₂ O	–	0.15
MgO	4.78	8.69
Al ₂ O ₃	3.22	10.07
SiO ₂	33.29	29.71
P ₂ O ₅	0.09	0.01
SO ₃	0.08	0.25
K ₂ O	–	0.04
CaO	50.88	43.27
TiO ₂	0.50	2.06
V ₂ O ₅	0.02	0.06
Cr ₂ O ₃	2.84	2.39
MnO	2.94	1.86
Fe ₂ O ₃	1.36	1.43

2. Experimental

2.1. Materials

Two slags generated in different steps of the production of stainless steel (reduction and ladle transfer slags) have been used as raw material to obtain silicas. Slags have been supplied by the stainless steel factory ACERINOX, S.A. placed in Los Barrios (Cádiz, Spain). Table 1 shows their chemical composition obtained by XRF.

Silicas were obtained by digestion of the slags with HNO₃ 9.60 M, using a liquid/solid ratio of 20 (v/w). Slag was slowly added to a beaker containing the acid and placed into an ultrasonic bath (J.P. Selecta, 100 W, 40 Hz). After each addition the mixture was stirred to avoid particles agglomeration. After 45 min of digestion, the mixture (whose temperature reached 60 °C) was placed into an autoclave and submitted to hydrothermal treatment at 130 °C for 24 h. After that, the resulting mixture was filtered, to separate solid and liquid fractions. The solid one was washed with deionized water (ratio L/S 50 v/w), dried overnight at 90 °C and calcined at 500 °C for 2 h. A second set of samples was prepared drying and calcining the solid after filtration, without washing it. The average yield for washed samples was 33% (final weight in relation with initial weight), what represents the maximum possible yield for silica, taking into account the slag composition. If the washing step is skipped the average yield was 49% indicating the existence of other components in addition to silica. Table 2 shows the identification codes for the prepared samples as a function of the nature of the slags and post-digestion treatment.

Pt loaded catalysts were prepared by the incipient wetness technique [5]. The required amount of an aqueous solution of Pt(NH₃)₄(OH)₂ (Alfa-Aesar Johnson Matthey, 9.09% Pt) was slowly added to the support to give a solid with a final Pt content of about 1% weight. After impregnation, samples were dried at 120 °C during 2 h and calcined 4 h at 500 °C, at a heating rate of 2.5 °C/min. Average size of Pt particles was calculated from images obtained by transmission electron microscopy. To designate the catalysts, “Pt” was added to the nomenclature shown in Table 2. The impregnated commercial silica (Kali Chemie AF125) was named CIAL Pt.

Table 2
Nomenclature of the prepared materials

Slag	Treatment		Nomenclature
	Washed	Non-washed	
Reduction	X		RL
		X	RSL
Transfer ladle	X		CL
		X	CSL

2.2. Characterization techniques

Chemical composition of the obtained solids was obtained by X-ray fluorescence (XRF), employing a PANalytical AXIOS sequential spectrophotometer with a rhodium tube as source of radiation. XRF measurements were performed onto pressed pellets (sample including 6 wt.% of wax).

X-ray diffraction (XRD) analysis was carried out on a Siemens diffractometer D500. Diffraction patterns were recorder with Cu K α radiation (40 mA, 40 kV) over a 2 θ -range of 10–70° and a position-sensitive detector using a step size of 0.05° and a step time of 1 s.

The textural properties were studied by N₂ adsorption measurements at liquid nitrogen temperature. The experiences were performed in a Micromeritics ASAP 2010 equipment. Before analysis, the samples were degassed for 2 h at 150 °C in vacuum.

Transmission electron microscopy (TEM) observations were carried out in a Philips CM200 microscope operating at 200 kV. The samples were dispersed in ethanol by sonication and dropped on a copper grid coated with a carbon film.

DRIFTS spectra were obtained in a Thermo Nicolet Nexus infrared spectrometer with a KBr optic and a MCT/B detector working at liquid nitrogen temperature. An environmental DRIFTS chamber (Spectra-Tech 0030-101) equipped with ZnSe windows, allowing in situ treatments up to 500 °C and 1 atm was coupled to the spectrometer. The sample was placed inside the chamber without packing or dilution. The spectra are obtained by co-adding 100 scans at 4 cm⁻¹ resolution. The spectra are referenced to that obtained for an aluminum mirror and presented in absorbance mode without any further manipulation.

Granulometry of the samples was measured on a Malver Mastersizer laser diffractometer. Before the analysis the sample were dispersed in water using an ultrasonic bath and adding sodium metaphosphate as dispersant.

2.3. Catalytic activity

In order to avoid the pressure drop that the small particle size of the solids could imply, it was necessary a previous preparation before their use as catalyst supports consisting in pressing the samples in a die to obtain pellets which are broken in a mortar and sieved to separate the adequate fraction (300–500 μ m).

The catalytic tests of CO oxidation were carried out in a conventional continuous flow U-shape glass reactor working at atmospheric pressure. Eighty milligrams of the catalyst were

Table 3
Chemical composition of the prepared materials

	Weight%								
	RL	RSL	CL	CSL	RL Pt	RSL Pt	CL Pt	CSL Pt	CIAL Pt
Pt	–	–	–	–	1.62	1.51	1.31	1.71	1.07
MgO	0.11	2.20	1.35	3.91	–	1.92	1.31	4.14	–
Al ₂ O ₃	0.03	0.82	1.99	4.23	–	0.62	1.87	3.98	0.31
SiO ₂	97.54	71.84	83.61	48.29	95.80	68.36	82.28	48.03	98.47
CaO	0.44	19.15	1.72	30.93	0.38	20.57	2.02	30.44	0.03
TiO ₂	0.24	0.50	1.18	1.45	0.24	0.51	1.29	1.52	0.06
Cr ₂ O ₃	1.34	3.42	8.54	7.75	1.72	4.16	8.46	7.29	–
MnO	0.23	1.64	1.19	2.76	0.24	1.96	1.12	2.29	–
Fe ₂ O ₃	0.07	0.43	0.42	0.68	–	0.37	0.34	0.62	0.06

placed between two plugs of glass wool. A thermocouple in contact with the catalyst assures the right measure of temperature. The reactor was surrounded by an electrical furnace equipped with a temperature programmer. The feed mixtures were prepared using mass flow controllers (Bronkhorst). The reaction was followed by mass spectrometry, using a Balzers Thermostar benchtop mass spectrometer controlled by the software Balzers Quadstar 422 with capabilities for quantitative analysis.

The light-off curves of CO oxidation (500 °C, 5 °C/min) were obtained with a mixture 3.4% CO and 21% O₂ balanced by He at a total flow rate of 42 ml/min. Empty reactor (without catalyst) shows no activity under such conditions. The catalysts were pre-activated “in situ” during 1 h at 500 °C with a mixture of 21% O₂ in He at a flow of 30 ml/min and then stabilized at room temperature before the light-off curve started.

Toluene oxidation reaction was carried out in a conventional continuous flow U-shape glass reactor working at atmospheric pressure. Mass flow controllers (Brooks 5850TR) were used to prepare the feed mixture. He (Air Liquide, 99.999%) was bubbled through two thermostated and pressurized saturators containing toluene (Panreac, P.A.). This stream was further mixed with purified compressed air in order to set the feed stream composition at 1000 ppm of toluene and passed through the catalyst placed on a carborundum bed, between two plugs of glass wool. The temperature was measured by a thermocouple placed just at the beginning of the catalyst bed. The reactor was surrounded by an electrical furnace equipped with a temperature programmer. The ignition curves were constructed by following both the VOC disappearance and the CO₂ appearance at a controlled heating rate of 2 °C/min (from 100 to 400 °C). Analyses were done by mass spectrometry (Balzers Omnistar). The CO₂ concentration was continuously monitored by means of an IR sensor (Sensotrans I.R.). The catalysts were treated under 100 cm³ air/min at 400 °C for 1 h before reaction, and then cooled in air to the starting reaction temperature.

3. Results and discussion

3.1. Catalyst characterization

Chemical composition of the prepared solids expressed as % weight of oxides is showed in Table 3. Silica contents are higher

in the samples prepared from reduction slags than in those obtained from ladle transfer slag, because of the higher silica content in the first one. On the other hand, washed samples present also higher silica content than non-washed ones. The washing procedure eliminates a certain amount of metals, mainly calcium, as stated in Table 3. Transition metal contents are markedly higher in samples prepared from ladle transfer slag in spite of the similar initial contents in both slags; it could be caused by the greater Al₂O₃ and MgO content in this slag which could drives to a higher retention of metals. The Al₂O₃ content of the prepared materials is between 0 and 4%, being higher in the solids prepared from ladle transfer slag. From here, it is clear that this method allows prepare materials from nearly pure silica to SiO₂/Al₂O₃ ones. This observation is important because the most used industrial catalyst supports are based on SiO₂ and mixtures SiO₂/Al₂O₃, having different acid–base properties which depend on the silica-to-alumina ratio. Since our method allows to obtain solids with different silica-to-alumina ratios, we can tailor the preparation only by using different slags or mixtures of slags as raw materials, in order to obtain a solid with the required acid–base properties.

XRD patterns of all prepared samples present typical diagrams of an amorphous silica. Besides this, peaks ascribed to crystalline silica and/or metal oxides are observed for washed samples (Fig. 1A), and peaks due to metal oxides and calcite (calcium carbonate) or CaO are detected in non-washed ones (Fig. 1B).

Fig. 2 shows DRIFTS spectra of prepared silicas at room temperature in the 3900–3060 cm⁻¹ (Fig. 2A) and 2200–500 cm⁻¹ (Fig. 2B) ranges. In the hydroxyl stretching region (Fig. 2A), the spectra are dominated by a band at 3746 cm⁻¹ which is assigned to OH groups in free silica [7,8], and a broad band between 3000 and 3700 cm⁻¹ associated with hydrogen bonded hydroxyls and adsorbed molecular water. It has to be highlighted that the band at 3746 cm⁻¹ is almost negligible in non-washed samples (RSL and CSL), indicating that the species which are eliminated during the washing process were adsorbed on these surface hydroxyl groups.

The main adsorption band observed in the framework region appears at 1354 cm⁻¹ (Fig. 2B). This band has been ascribed to longitudinal (LO) and transversal (TO) modes in Si–O–Si asymmetric vibration for pure silica [7,9]. The position of this band changes in different samples, in such a way that it is

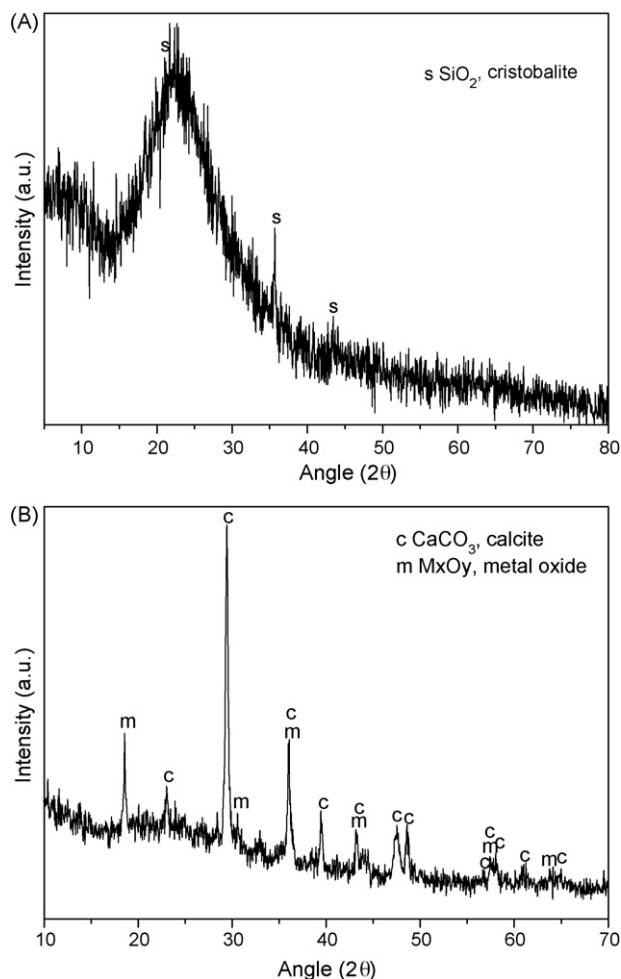


Fig. 1. XRD diagrams of a washed sample (A) and a non-washed sample (B).

possible to find a relation between the band position and the metal content of the silica. Higher is the metal content, lower is the vibration frequency observed (Fig. 3). This relation has been earlier reported for alkali-doped Pt/SiO₂ catalysts [7]. Besides this, the band at 1630 cm⁻¹ characteristic of deformation modes (δ_{HOH}) of adsorbed water molecules is clearly observed in all samples. On the other hand, the IR spectrum of non-washed samples shows new bands at 1436 and 1508 cm⁻¹ due to carbonate species, probably calcium carbonate, as could be deduced from the XRD and XRF data.

In order to eliminate surface adsorbed water and to a better observation of the hydroxyl structure, the samples were heated in situ into the DRIFTS cell at 500 °C under 50 ml/min N₂ flow. In the obtained spectra, presented in Fig. 4, the band at 1630 cm⁻¹ (δ_{HOH}) has disappeared and, consequently, the broad band at 3000–3700 cm⁻¹ ($\nu_{\text{O-H}}$) has diminished in intensity. Although the hydroxyl structure is similar in all the samples, there are changes in the intensity of their characteristic bands. In fact, a linear relationship between the area of these bands by square meter of sample, and its metal content is observed (Fig. 5). This observed increment of the number of free OH groups with the metal content of the silica is in opposition to other published results [7]. However, it is possible to relate the increasing of free OH with the break of siloxane

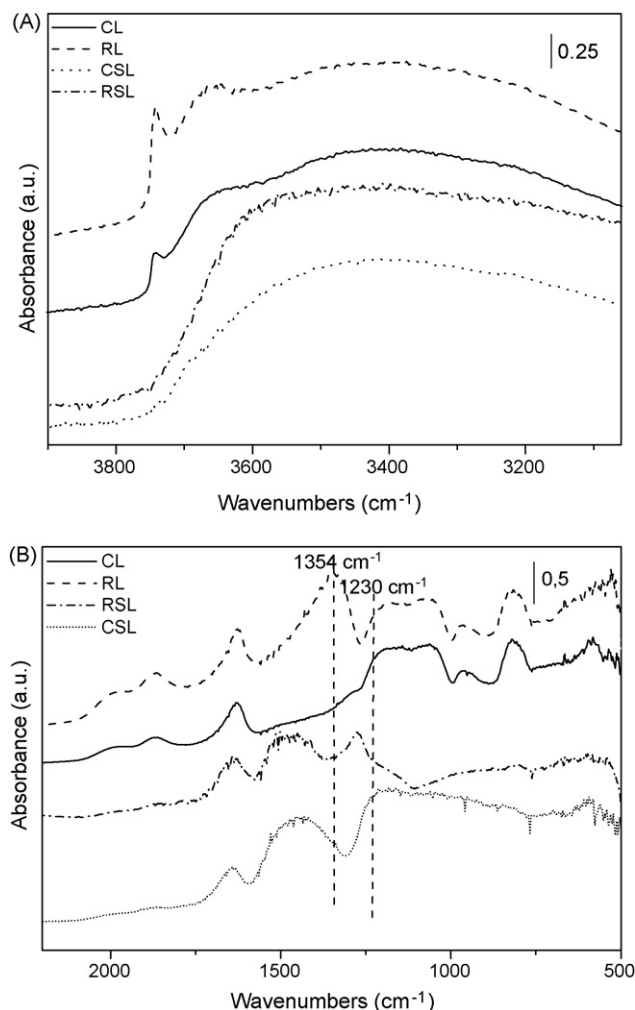


Fig. 2. DRIFTS spectra of RT samples.

groups of the solid because of the polarizing power of metallic cations, resulting in Si–O–Ca bonds which are further hydrolyzed with atmospheric CO₂, producing Si–OH groups and CaCO₃. In this sense, this latter compound is detected by IR spectroscopy and XRD in non-washed samples. Besides this,

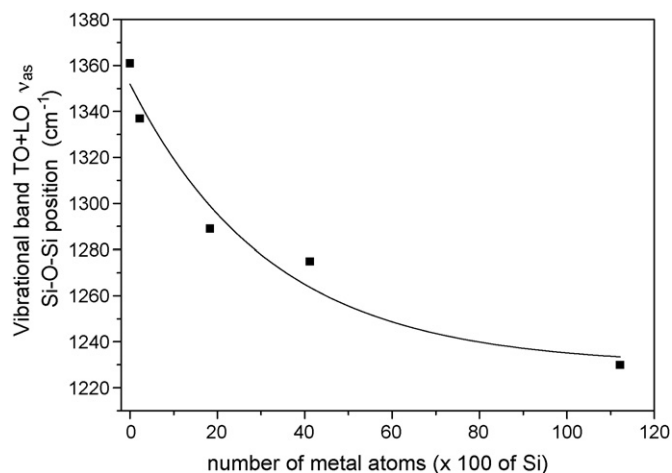


Fig. 3. TO + LO ν_{as} Si–O–Si band shift as a function of silica metal content.

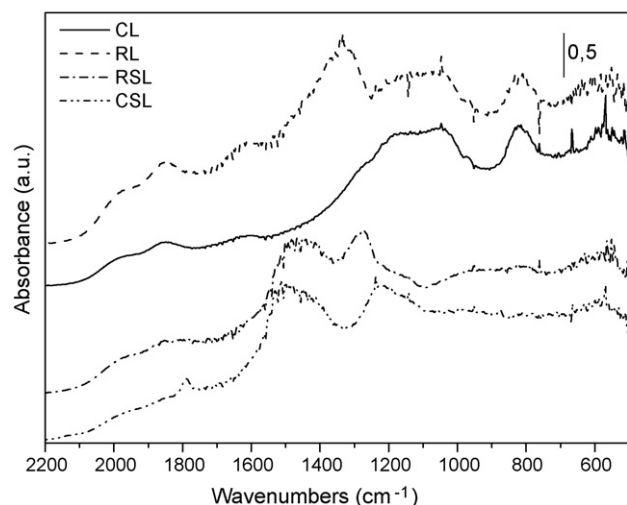
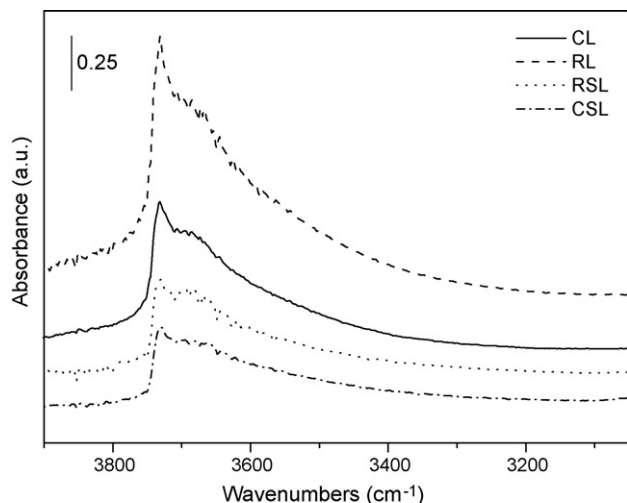


Fig. 4. DRIFTS spectra of non-impregnated samples at 500 °C.

the contribution of any other hydroxyl groups associated, for example, to calcium hydrated species cannot be fully discarded.

Table 4 shows the textural properties of the prepared materials. Fig. 6 shows, as an example, the nitrogen adsorption–desorption isotherms and the pore size distribution curve for the

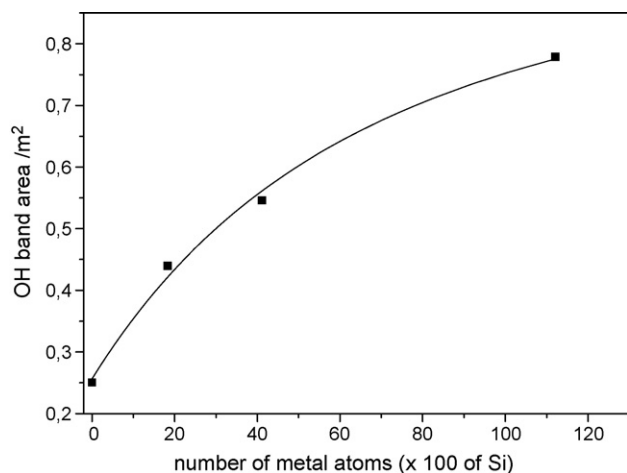


Fig. 5. OH band area (by m² of silica) versus metal content.

Table 4
Textural properties of the prepared solids

Material	S_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)	d_p (Å)	Particle size average (μm)
RL	290	0.95	130	3.4
RL 300–500 μm	267	0.39	58	–
RL Pt	253	0.4	63	–
RSL	108	0.57	213	–
RSL 300–500 μm	84	0.27	129	–
RSL Pt	53	0.21	158	–
CL	231	0.9	157	2.3
CL 300–500 μm	193	0.33	69	–
CL Pt	159	0.32	81	–
CSL	84	0.46	217	1.3
CSL 300–500 μm	55	0.22	164	–
CSL Pt	52	0.21	161	–
CIAL	287	0.80	111	–
CIAL Pt	221	0.74	134	–

original sample RL, the fraction between 300 and 500 μm (RL 300–500 μm) and the Pt impregnated sample (RL Pt). All the prepared solids, with and without Pt, present N₂ type IV adsorption–desorption isotherms, with H1 hysteresis cycle,

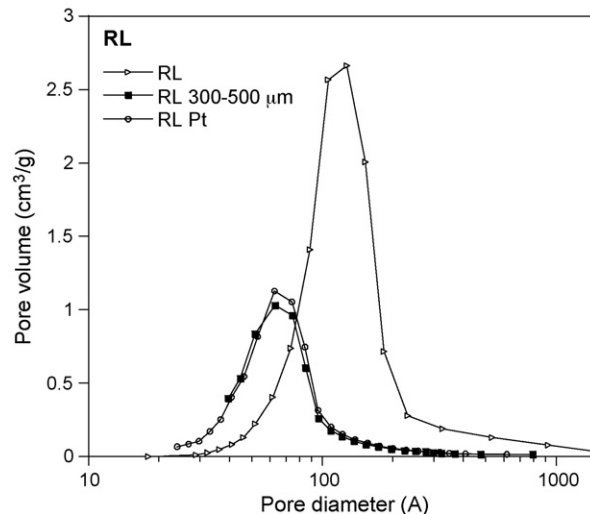
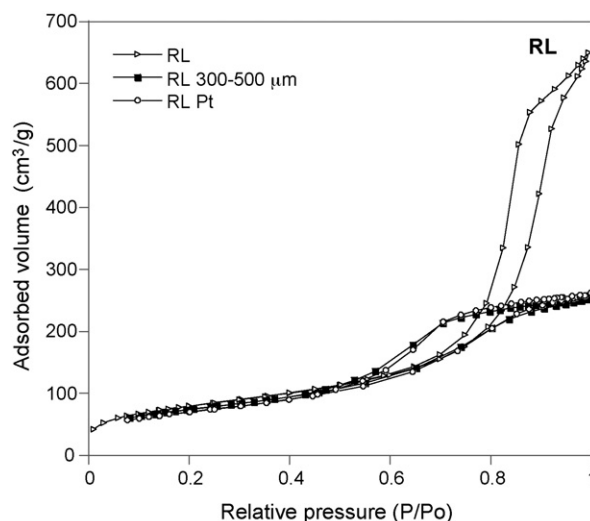


Fig. 6. Nitrogen adsorption–desorption isotherms and pore size distribution in sample RL.

except the sample with the highest surface area (RL), whose curve fits a type H2 hysteresis, indicating a more heterogeneous size and shape pore distribution. The average pore diameter is bigger in the non-washed samples than in the corresponding washed ones, which could be related with the high calcium content of the non-washed samples. Calcium, probably as calcium carbonate, could be placed into the smallest pores of the material blocking or expanding them. In both cases, a higher average pore diameter is measured. On the other hand, the sample compaction process carried out in the preparation procedure prior to the catalytic test, produces the drop of the surface area and pore volume of the material. Finally, Pt deposition process does not affect in the same way the textural properties of the different samples. Thus, some samples (RL Pt, CSL Pt) maintain their surface areas, while other ones suffer a significant fall (RSL Pt, CL Pt) in this value. However, the pore volume is not affected in any case.

The measured average particle sizes are always greater for the washed samples (Table 4), pointing out that the fraction eliminated during washing has a lower particle size than that of the insoluble fraction. Concerning the platinum particles deposited, their average size has been estimated from TEM micrographs to be 9 nm, although some bigger particles up to 20 nm are also detected (Fig. 7).

3.2. Catalytic activity

Catalytic tests over pure supports were carried out in order to know the influence of the metal content of the supports in the activity of the prepared Pt/SiO₂ catalysts. Fig. 8 presents the obtained CO conversion versus temperature. Table 5 shows the conversion obtained at 500 °C and the metal contents of each support calculated from its chemical composition. In spite of the low conversion values, there is a relationship between the observed conversion and the metal content. Higher is the metal content, higher is the final conversion, despite their lower

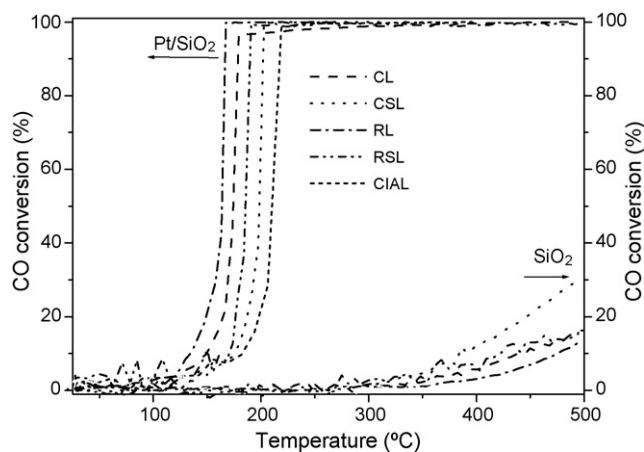


Fig. 8. CO conversion results over non-impregnated supports and catalysts.

Table 5

CO conversion at 500 °C and metal contents of the non-impregnated materials

Material	Conversion at 500 °C (%)	Metal atoms ($\times 100$ of Si)
RL	14	2
RSL	16	18
CL	16	41
CSL	30	112

surface area. This fact induces to think that metals present in the silica supports have a positive effect over the activity of the prepared Pt/SiO₂ catalysts.

The CO conversion for the Pt-impregnated silicas is also presented in Fig. 8. The introduction of Pt induces a higher activity in all the samples. Table 6 presents the T_{50} values calculated from the light off curves and the number of metallic atoms others than Pt in the catalysts, being T_{50} the temperature at which 50% of conversion is achieved. As the platinum concentration in all the samples is not exactly the same, Table 3,

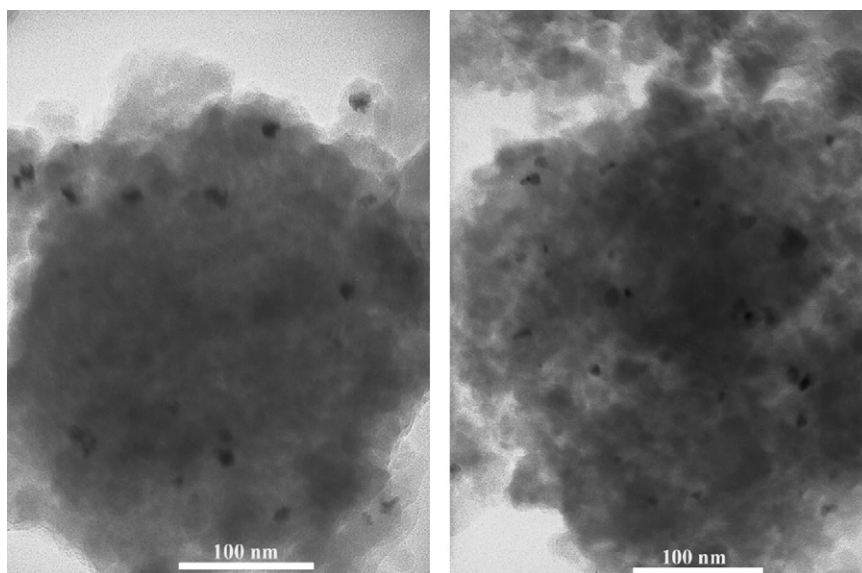


Fig. 7. TEM images of sample RL impregnated with Pt.

Table 6
 T_{50} values obtained in CO oxidation and metal contents of the prepared catalysts

Material	T_{50} (°C)	Metal atoms ($\times 100$ of Si)
RL Pt	164	2.76
CL Pt	174	19.18
RSL Pt	186	46.42
CSL Pt	199	111.29
CIAl Pt	210	0

the T_{50} values have been plotted versus the number of Pt atoms per catalyst m^2 surface area, Fig. 9.

Comparing catalysts with similar Pt contents, the ones prepared using materials obtained from digested and washed slags have a higher activity than those prepared from commercial silica. This could indicate a positive effect on the CO oxidation activity of the transition metal atoms present in the catalyst and coming from the initial slag composition, as said above for the prepared materials without platinum. Catalysts obtained from digested and non-washed slags show lower activities than those obtained from the washed ones in spite of their higher platinum and transition metal contents. This fact could be explained by the lowest surface area and pore volume of these supports because of the presence of metals, mainly calcium, into the material pores, affecting the deposition of Pt, and leading to a worse dispersion. Moreover, a negative effect of calcium, inducing modifications in the acid–base properties of the material, could not be fully discarded. It has to be highlighted that the activities of catalysts prepared from transfer ladle slag (CL Pt and CSL Pt) are lower than those obtained from reduction slag (RL Pt and RSL Pt). This must be related to the different composition of the obtained materials, in particular because of the different percentages of Al_2O_3 and MgO that influence not only the support acid–base properties but also the dispersion of the active phase.

The catalytic activity towards toluene oxidation of the synthesized materials has also been measured. All the supports present very low activities (Fig. 10 and Table 7). The influence

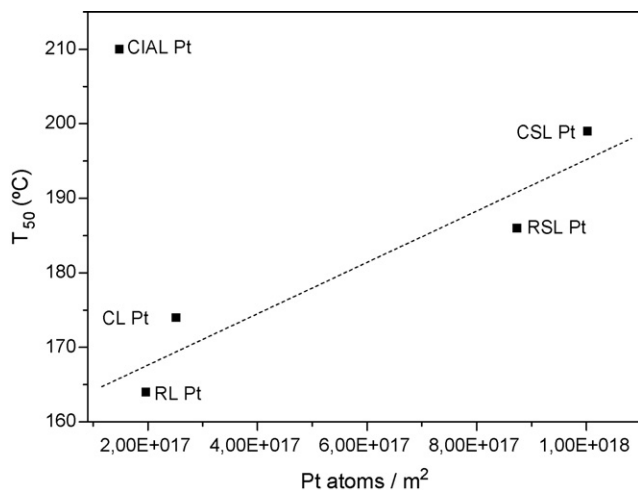


Fig. 9. T_{50} values calculated for CO oxidation reaction versus Pt content of the considered catalysts.

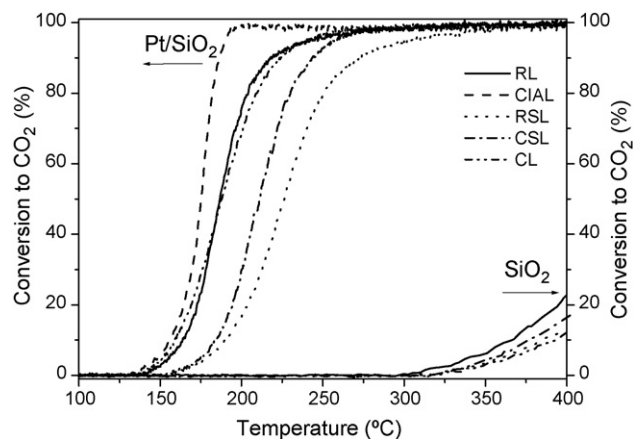


Fig. 10. Toluene to CO_2 conversion over non-impregnated supports and catalysts.

Table 7
 Toluene conversion over non-impregnated supports at 400 °C

Material	Conversion (%)
RL	22
CL	14
RSL	14
CSL	19

of the transition metal content of the materials in their toluene oxidation performances is shown in Fig. 11. Toluene conversion increases with the transition metal content on the support. On the other hand, from this figure, it is evidenced the higher importance of the specific surface area of the sample in the oxidation of toluene than in the CO one. For instance, sample RL shows the biggest toluene conversion in spite of their lowest metal content. The high specific surface area of this sample could be claimed as responsible of such a high activity.

Fig. 10 also shows the toluene light-off curves obtained for the prepared platinum catalysts and Table 8 presents the T_{50} values calculated from the curves. As for CO oxidation, the

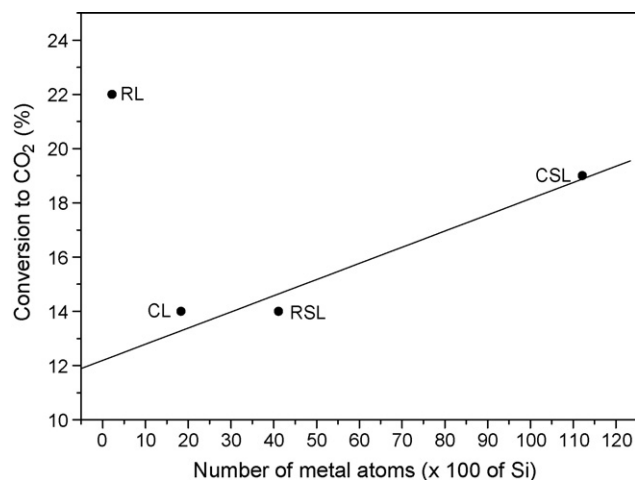


Fig. 11. Toluene to CO_2 conversion over non-impregnated supports as a function of metal content.

Table 8
 T_{50} values obtained in toluene oxidation reaction over the prepared catalysts

Material	T_{50} (°C)
CIAL Pt	175
RL Pt	183
CL Pt	188
CSL Pt	217
RSL Pt	225

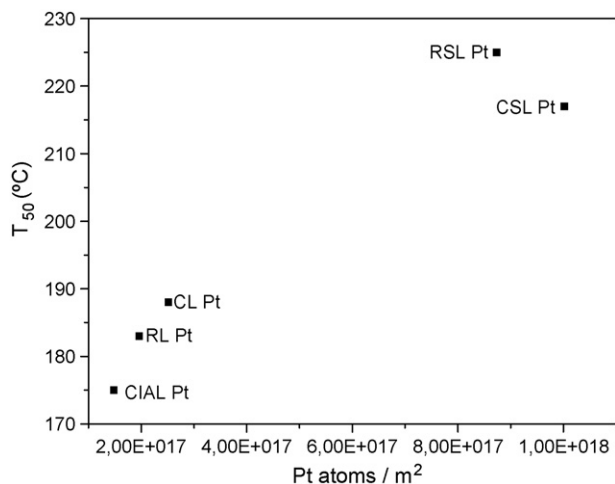


Fig. 12. T_{50} values calculated for toluene oxidation reaction versus Pt content of the considered catalysts.

introduction of platinum results in a high enhancement of the toluene conversion.

When the T_{50} is plotted versus the number of Pt atoms per catalysts surface area (Fig. 12), the values for commercial silica and washed prepared materials are closer than in the case of the CO oxidation reaction. From here, it seems that the transition metal content of the prepared solids has a lower influence in the measured activity for toluene oxidation than in the CO one. However, the observed influence of the specific surface area BET is higher in the former reaction. This fact could be related with the different reaction pathways and sizes of the reactant molecules (CO and toluene).

On the other hand, the catalytic systems prepared from non-washed samples present the worst activity results in spite of their greater number of Pt atoms by square meter. The explanation of this observation should again be related with the worse platinum dispersion, which can be due to the lower surface area of the supports, and/or their different acid–base properties because of their higher calcium contents.

The catalyst prepared from commercial silica presents the highest toluene oxidation activity of all the platinum systems studied. However, this sample has the worst catalytic CO oxidation performances. This different behavior could be related to the higher importance of Pt dispersion in the toluene oxidation reaction than in CO oxidation one. In CO oxidation, the positive effect of the transition metal content in the materials prepared from the stainless steel slags seems to balance the negative effect of the worse dispersion of platinum, achieving those samples better activities than the catalyst prepared from commercial silica. Nevertheless, the role of

transition metal content seems to be less important in toluene oxidation, acquiring the dispersion a greater relevance.

4. Conclusions

The solids obtained by acidic digestion and further hydrothermal treatment of stainless steel slags have been shown as useful materials as catalyst supports. These solids are composed mainly by SiO_2 or $\text{SiO}_2/\text{Al}_2\text{O}_3$, with alumina contents up to 4% and variable amounts of metals (Cr, Fe, Mn, Ti, Ca, Mg) depending on the nature and composition of the raw slag used. Transition metals content affects the catalytic performances of the solid towards CO oxidation reaction, improving their activity when the metal content increases. The catalysts prepared from non-washed digested slag present lower activities than those prepared from washed ones, which could be related with their lower specific surface BET area and/or the presence of calcium atoms into the pores of the material that could cause worse Pt dispersions. On the other hand, the catalysts prepared from ladle transfer slag present lower activities than those prepared from reduction slags, being the difference in activity higher in the systems prepared from the non-washed supports, which could be related to the higher amount of Al_2O_3 and MgO in these materials.

Concerning to toluene oxidation reaction, it seems that the transition metal content does not play a role as relevant as in the case of CO oxidation, being more important the influence of the specific surface area and the dispersion of the active metal. Thereby, catalysts obtained from non-washed supports present the lowest activities because of their lower surface area and higher Pt contents, which implies worse Pt dispersions. Pt/ SiO_2 catalysts prepared using commercial silica shows the highest activity in this reaction. It could be explained by its greater pore volume that induces a better Pt dispersion and, consequently, a better activity.

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