



Research paper

Preparation and characterisation of calcined Mg/Al hydrotalcites impregnated with alkaline nitrate and their activities in the combustion of particulate matter[☆]

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ABSTRACT

The effect of incorporating alkaline nitrates in hydrotalcites for use in the combustion of particulate matter from diesel emissions has been studied. The catalysts were characterised by X-ray diffraction (XRD), N₂ adsorption, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), elemental analysis (EA), atomic absorption spectrophotometry (AAS) temperature programmed reduction (TPR) and Fourier transform infrared spectroscopy (FTIR). Activity measurements were carried out using a thermobalance in air and using a fixed-bed reactor with a NO/O₂ flow. The observed activities decreased in the following order: HTMgAlcCs > HTMgAlcK > HTMgAlcLi > HTMgAlc.

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1. Introduction

Hydrotalcites (HTs), also called layered double hydroxides, are currently garnering attention for their potential uses as adsorbents, catalyst supports, catalysts, and polymer additives, as well as for their applications in the ceramic industry.

The structure of HTs is similar to that of brucite, Mg(OH)₂, where in Mg²⁺ is octahedrally coordinated to six hydroxyl groups. If some Mg²⁺ ions are substituted by Al³⁺, a residual positive charge appears, which is then compensated for with water molecules and anions that are localised in the interlayer region.

HTs are classified as anionic clays with a general formula of [M(II)_{1-x}M(III)_x(OH)₂](A^{m-})_{x/m}·nH₂O, where M(II) is a divalent cation, M(III) is a trivalent cation, A is an anion with charge m⁻, and x is the M(III)/(M(III) + M(II)) molar ratio (Cavani et al., 1991; Vaccari, 1998).

It is possible to prepare a large number of HTs because there are several possible combinations of bivalent and trivalent ions, and there are several anions that can be used.

The emissions of diesel motors are a complex mixture of gaseous compounds and solid particles. The gaseous compounds are carbon dioxide, oxygen, nitrogen, water, carbon monoxide, nitrogen oxides and a variety of hydrocarbons with low molecular weights. The particles consist of a core of elemental carbon with adsorbed polyaromatic hydrocarbons.

Particulate matter (PM) or soot is an undesired sub-product in several combustion systems. In particular, the emissions of diesel motors are very harmful to human health because PM remains inside the lung tissue. PM is an environmental contaminant, and it can be eliminated by catalytic combustion or removed using special filters that can be regenerated.

Recently, calcined-HTs have been applied in the catalytic abatement of NO_x and SO₂ (Perez-Ramirez et al., 1999; Sanchez-Cantu et al., 2010) in oxidative reactions (Sachdev et al., 2010) and in the simultaneous removal of NO_x and soot (Wang et al., 2007). The combustion of soot requires high reaction temperatures at which the storage of NO_x is poor (Li et al., 2009). Thus, the simultaneous removal of soot and NO_x from the gas emissions of a combustion engine muffler at low operation temperatures is difficult to achieve. The study of new catalysts for this task is still a great challenge.

Catalysts containing compounds of alkaline metals (i.e., potassium, lithium and cesium) are particularly active in soot combustion and NO_x storage. Potassium is the most studied element of the group due to its high mobility and strong basicity (Castoldi et al., 2009; Peralta et al., 2011; Ruiz et al., 2012; Sun et al., 2011; Ura et al., 2011; Weng et al., 2011; Yuan et al., 1994).

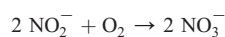
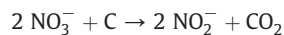
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Thus, in this work, we studied catalysts that are a mixture of the oxides formed during the calcination of hydrotalcite (calcined-HT) and impregnation with alkaline nitrates. Alkaline nitrates have been used for the impregnation of calcined-HT due to their low melting point, which favours contact between the soot and the catalyst (An and McGinn, 2006). Moreover, nitrate anions participate as redox couples in the catalytic process that forms nitrites, a reduced species (Bialobok et al., 2007; Carrascull et al., 2003; Galdeano et al., 2004; Hleis et al., 2008; Lick et al., 2008; Ruiz et al., 2010, 2011).

These nitrites are then oxidised to nitrates by molecular oxygen.



When catalytic reactions of the solid–solid–gas type occur, as in the combustion of soot with O₂ in the presence of a solid catalyst, the contact between the catalyst and the soot is a key factor for the reaction that occurs in a soot–catalyst–O₂ interface. The contact between the catalyst and the PM is very important. The soot combustion performance under tight contact conditions reflects the intrinsic activity of the catalysts. A loose contact condition is similar to the practical conditions that exist between the PM and the catalyst in an exhaust pipe. In the literature, both contact conditions (tight and loose) have been studied. Thermogravimetric analysis is widely used as an analytical tool to follow the progression of a chemical reaction. The advantages of this technique are that it requires small amounts of sample and its rapid analysis time. Moreover, it is a very useful technique for the evaluation of catalysts used in soot oxidation (Aneghi et al., 2006; Bueno-López et al., 2005; Liu et al., 2005; Oliveira et al., 2012; Shimokawa et al., 2012; Uner et al., 2005).

The possible existence of gas–solid mass transfer resistance must be considered, but, according to Yezerets et al. (2003), mass transfer resistances are not limiting for soot combustion in TGA systems due to the relatively low reaction rates at temperatures below 600 °C. To make a comparison with results obtained from different catalytic systems, experiments need to be conducted under the same experimental conditions, including the catalyst/soot/diluent ratio, amount of sample, reaction temperature and air/nitrogen ratio.

The aims of this study are the following: i) to prepare a non-contaminating catalyst from calcined-HT precursors with calcination at 600 °C and impregnation with alkaline metal nitrates; ii) to evaluate the catalytic activity in the combustion of soot under different experimental conditions, such as tight and loose contact conditions and in the presence and absence of NO_x; iii) to explain the different catalytic behaviours of various HTs through their physical and chemical characteristics and through the set of experiments performed here; and iv) to test the stability of the most active catalyst in reuse cycles and hydro-treatment experiments.

2. Experimental

2.1. Catalyst preparation

The Mg and Al hydrotalcite was prepared via coprecipitation (Cavani et al., 1991). An aqueous solution containing 53.37 g Mg(NO₃)₂ · 6 H₂O and 25.16 g Al(NO₃)₃ · 9 H₂O in 150 ml of water (solution A) was prepared while maintaining an Mg/Al molar ratio of 3. A solution containing 36 g NaOH and 14.40 g Na₂CO₃ in 450 ml of water (solution B) was prepared separately. Solutions A and B were simultaneously added dropwise into distilled water under vigorous mechanical stirring while maintaining a constant pH (9.5–10) and temperature (55 °C). The slurry was aged for 30 min under vigorous stirring at 55 °C and was allowed to stand in its mother liquor for 3 h. The precipitate was washed several times until a pH of 7 was attained and was then dried

at 110 °C for 12 h. The calcined-HT was obtained by calcining the hydrotalcite at 600 °C for 4 h. The first solid was labelled as HTMgAl, and the second solid was labelled as HTMgAlc. The catalysts, promoted by lithium, potassium and cesium, were prepared by impregnation (incipient wetness) using the corresponding metallic nitrates while maintaining a nitrate (NO₃⁻) concentration of approximately 4.5 wt.%. The calcined-HT samples promoted by alkaline metals were calcined at 500 °C for 2 h. These solids were labelled as HTMgAlcMe, where Me was Li, K or Cs.

2.2. Ageing experiments with feed containing water vapour

Ageing experiments were carried out on samples of fresh catalyst loaded in a quartz reactor fed with a gaseous current (Q_{total} = 30 cm³ min⁻¹) containing 10% O₂ and 90% N₂ saturated with water vapour (7 vol.%). The ageing treatments were performed at 500 °C for 6 h.

2.3. Catalyst characterisation

The degree of crystallinity of the catalysts was studied by X-ray diffraction (XRD) using a D-Max III diffractometer (Rigaku) with Cu K radiation (λ = 1.5378 Å, 40 kV, 30 mA). The surface areas and pore volumes were determined from nitrogen adsorption isotherms measured at -196 °C in a Gemini V2.00 surface analyser (Micromeritics Instrument Corp.). The semiquantitative analysis of the components present in the catalysts was performed with a LEO 1450 VP Screening Electronic Microscope attached to an EDAX Genesis 2000 energy dispersive spectrometer (EDS) at 20 kV and a working distance (WD) of 15 mm.

Samples were also studied by XPS with a Physical Electronics PHI-750 spectrometer, equipped with an Mg-K_α (1253.6 eV) X-ray source. To measure the binding energies (α 0.1 eV), the signal of adventitious C 1 s that appears at 284.8 eV was used as a reference. All samples were outgassed for 12 h previous prior to analysis under ultra-high vacuum (<1.3 × 10⁻⁶ Pa).

The elemental nitrogen, carbon and oxygen contents were determined via elemental analysis (EA) with a CHNS LECO 932 analyser.

The bulk lithium, potassium and cesium contents were determined by atomic absorption spectrophotometry (AAS) with a PerkinElmer AAnalyst 800 spectrophotometer.

The presence of anions in the catalysts was studied by FTIR with a Perkin-Elmer Spectrum RX1 instrument.

Temperature programmed reduction (TPR) experiments were carried out using conventional equipment. The reduction experiments were performed using 10% hydrogen in nitrogen at a flow rate of 20 cm³ min⁻¹ and a heating rate of 10 °C/min up to 700 °C. The mass of the loaded sample was 20 mg.

2.4. Activity measurement

Because the contact between the soot and the catalyst is a key factor in this process, experiments were performed under both loose and tight contact conditions. For the loose contact experiments, the soot and the catalyst were mixed together with a spatula; for the tight contact tests, the two components were ground together in an agate mortar. In both cases, the mixing step was performed prior to introducing the sample into the thermogravimetric reactor.

Soot combustion was performed in a thermobalance (TG-60 Shimadzu) thermogravimetric reactor, with a heating rate of 10 °C/min, an air flow rate of 40 cm³ min⁻¹ and a nitrogen flow of 20 cm³ min⁻¹. The soot (Printex-U, Degussa) and the catalyst were ground together at a 1/10 ratio in an agate mortar (tight contact) with alumina as the diluent; this mixture was then introduced into the reactor. The weight loss and temperature were recorded as a function of time. The derivative curves (DTGA) were obtained from the weight loss information as a

function of time, and from these curves, the temperature at the maximum combustion rate (T_{\max}) was obtained. Catalyst reuse and water ageing were also studied in the thermogravimetric reactor experiments.

The influence of the addition of NO_x on the catalytic behaviour was analysed in a fixed bed quartz microreactor (id = 0.8 cm). The reaction mixture was supplied by three individually controlled lines: NO/He , O_2/He and He for balance. The composition of the mixture was 8 vol.% of O_2 and 1500 ppm of NO ($Q_{\text{total}} = 50 \text{ cm}^3 \text{ min}^{-1}$) for the experiment performed in the presence of NO . In the absence of NO , only 8 vol.% of O_2 ($Q_{\text{total}} = 50 \text{ cm}^3 \text{ min}^{-1}$) was fed into the reactor. Particulate matter was mixed into the catalyst with a spatula prior to being introduced into the fixed bed micro-reactor (loose contact). The mass of the particulate matter/catalyst mixture (1/10, wt/wt) that was loaded into the reactor was 33 mg. The temperature range studied was between 200 °C and 600 °C, and the heating rate was 1.5 °C/min. The reaction products were analysed with a Shimadzu model GC-8A gas chromatograph with a TCD detector. The reaction products were separated in a CTRI concentric column (Altech). This system permitted the identification and quantification of O_2 , N_2 , CO_2 and CO . The amount of combustion soot produced was calculated from the chromatographic information of CO_2 and CO (Ruiz et al., 2011).

2.5. Reuse of the catalysts

To study catalyst reuse, the used catalyst was mixed with fresh Printex-U and the burning cycle was performed again. This procedure was repeated three times.

3. Results and discussion

Fig. 1 shows the diffractograms of the hydrotalcite (HTMgAl), the hydrotalcite calcined at 600 °C (HTMgAlc), and the calcined-HT promoted with lithium, potassium and cesium nitrates (HTMgAlcLi, HTMgAlcK, and HTMgAlcCs, respectively). When this hydrotalcite is calcined at 600 °C, periclase, a form of magnesium oxide, is observed. The diffractogram of the calcined-HT promoted with cesium nitrate shows reflection lines characteristic of crystalline cesium nitrate. For LiNO_3 and KNO_3 impregnation, the formation of crystalline lithium and potassium nitrate was not observed by XRD, most likely due to the small size of the crystallites and to the high dispersion of these species (Zhang et al., 2007). The crystalline phase of MgO (dephased periclase) was observed in catalysts promoted with Li and K.

The surface area was determined using BET. These values, as well as the pore volumes and average pore sizes of the hydrotalcites, are

Table 1
Textural properties of the hydrotalcites.

Sample	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	Average pore size (Å)
HTMgAl	160	–	–
HTMgAlc	269	0.277	46.1
HTMgAlcLi	240	0.331	50.8
HTMgAlcK	257	0.328	46.8
HTMgAlcCs	199	0.249	47.5

listed in Table 1. The surface areas of the calcined-HT promoted with lithium nitrate and potassium nitrate remained nearly constant, whereas that of the calcined-HT promoted with cesium nitrate decreased slightly. This decrease in surface area can be correlated with XRD studies in which there was a structure with a higher degree of crystallinity in the HTMgAlcCs sample.

The bulk and surface compositions of the alkaline metals were analysed by AAS and XPS analysis, respectively. Table 2 lists these compositions. The surface contents of Cs and K were determined by XPS and were compared to those found using AAS. These results indicate that only part of these cations (approximately 70%) are localised on the surface of the catalysts. For the HTMgAlcLi sample, the presence of Li was not detected by XPS, although its bulk Li concentration was detectable by AAS. Table 3 shows the concentrations of the alkaline nitrates, in wt.%, estimated using the cation concentrations as determined by AAS, as well as the elemental nitrogen concentration from EA. The concentration of LiNO_3 calculated using values from EA analysis is lower than that determined using values from AAS, thus indicating that other Li-containing species were formed during the calcination process with a small amount of lithium nitrate remaining unreacted. Lithium nitrate can decompose into lithium oxide or peroxide. Because the ionic radius of Li^+ is similar to that of Mg^{2+} , Li oxide could be partially solubilised in magnesium oxide, occupying Li^+ substitutional and interstitial sites (Catlow et al., 1990). For KNO_3 and CsNO_3 , the estimated concentrations of the nitrates from elemental analysis also indicated a lower concentration, thus suggesting that nitrate was partially decomposed into oxide.

The FTIR spectra of the solids are shown in Fig. 2. The band at 1630 cm^{-1} corresponds to water bending. The spectra of the HTMgAlcK and HTMgAlcCs samples (curves (c) and (d), respectively) show an absorption band at 1385 cm^{-1} that is assigned to the anti-symmetric stretching N–O vibration of free nitrate. These results indicate the presence of free nitrate species remaining in the catalysts and are in agreement with the EA and AAS results. However, for the HTMgAlcLi sample (curve (b)), two absorption bands at 1400 and 1500 cm^{-1} , corresponding to mono and bidentate nitrates, respectively, are observed, while a band corresponding to the presence of free nitrate is not observed; this sample exhibited characteristics similar to those of HTMgAlc (curve a). From these results, it can be observed that the carbonates are totally decomposed at a calcination temperature of 600 °C for HTMgAlc; this result is in agreement with a report by Perez-Ramirez et al. (1999).

The reducibility of the species present in the catalysts was evaluated using hydrogen temperature programmed reduction. The reduction profiles of the calcined hydrotalcite and the hydrotalcites promoted with lithium, potassium and cesium are shown in Fig. 3.

Table 2
Chemical composition analysis of the solids (in wt.%).

	HTMgAlcLi	HTMgAlcK	HTMgAlcCs
% Li, K y Cs ^a	0.49	2.90	9.44
% K ^b	–	1.97	–
% Cs ^b	–	–	6.30

^a AAS.

^b XPS.

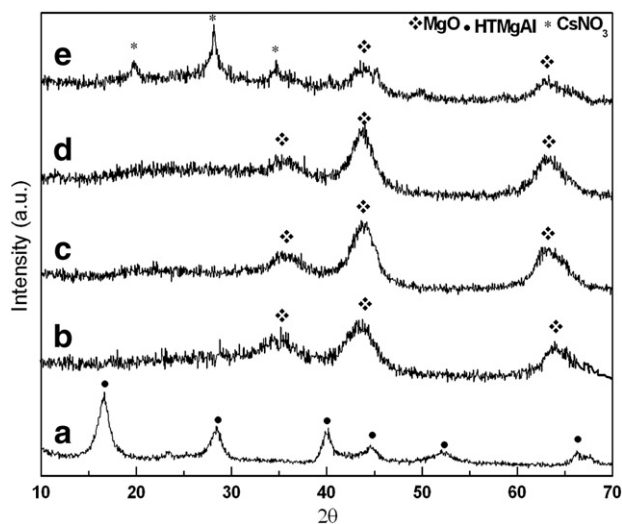


Fig. 1. Powder X-ray diffraction patterns of (a) HTMgAl; (b) HTMgAlc; (c) HTMgAlcLi; (d) HTMgAlcK; and (e) HTMgAlcCs.

Table 3
Chemical compositions of the catalysts (in wt%).

	HTMgAlLi	HTMgAlK	HTMgAlCs
% LiNO ₃	4.87 ^a 0.30 ^b	–	–
% KNO ₃	–	7.49 ^a 4.62 ^b	–
% CsNO ₃	–	–	13.85 ^a 8.61 ^b

^a Estimated from % alkaline cation (AAS).

^b Estimated from % N as determined by elemental analysis.

At approximately 325 °C, hydrogen consumption can be observed in all of the samples. This result may be caused by the reduction of coordinated nitrates that remain following calcination. These nitrates resulted from the metal salts used to prepare hydrotalcite, as seen in the FTIR spectra (Fig. 2). At 490 °C (curve b), hydrogen consumption occurs due to lithium nitrate reduction, and at 520 °C (curve c and d), it occurs due to the reduction of potassium nitrate and cesium nitrate. The increase in hydrogen consumption (HTMgAlLi < HTMgAlK < HTMgAlCs) is in agreement with the results from AAS chemical analysis (Table 3).

Fig. 4 shows the catalytic results from the use of a thermogravimetric reactor under tight contact conditions in a plot of conversion soot vs. temperature. Curve (e) corresponds to the combustion of soot without catalyst. In all samples studied, the conversion of soot increased with increasing temperature. HTMgAlCs (curve a) was the most active, achieving 50% soot conversion at 410 °C, whereas HTMgAlK (curve b) and HTMgAlLi (curve c) required temperatures of 430 °C and 490 °C, respectively, to achieve the same level of conversion. At 450 °C, soot conversion using HTMgAlCs was 94%, the conversion using HTMgAlK was 81%, and the conversion using HTMgAlLi was only 7.5%. HTMgAlc (curve d), the catalyst without any alkaline nitrates, possessed a much lower activity.

Table 4 shows the maximum combustion rate temperature (T_{max}) obtained for the combustion of the particulate matter in the presence of air, using tight and loose contact conditions, in a thermogravimetric reactor. This table also includes the ΔT that corresponds to the differences between the T_{max} of the particulate matter with and without a catalyst. The HTMgAlc sample exhibited low catalytic activity and yielded a ΔT of only 30 °C. When using the promoted hydrotalcites, the observed ΔT was between 120 °C and 200 °C for the reactions under tight contact conditions and was in the range of 60 °C to 180 °C for the reactions under loose contact conditions. HTMgAlCs had the greatest decrease in T_{max} . The differences observed between the experiments using both conditions (tight and loose contact) confirm the

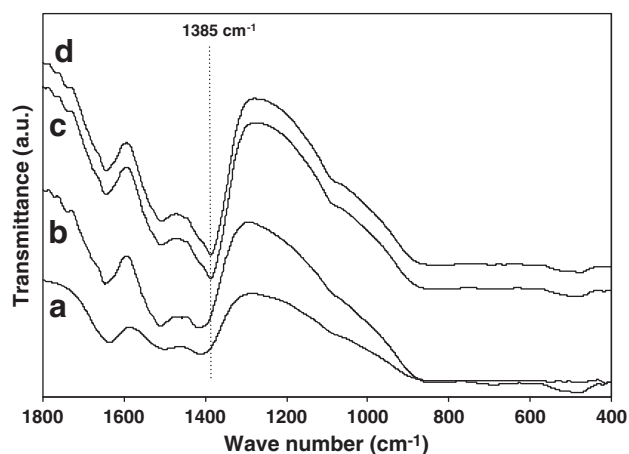


Fig. 2. FTIR spectra for (a) HTMgAlc; (b) HTMgAlLi; (c) HTMgAlK; and (d) HTMgAlCs.

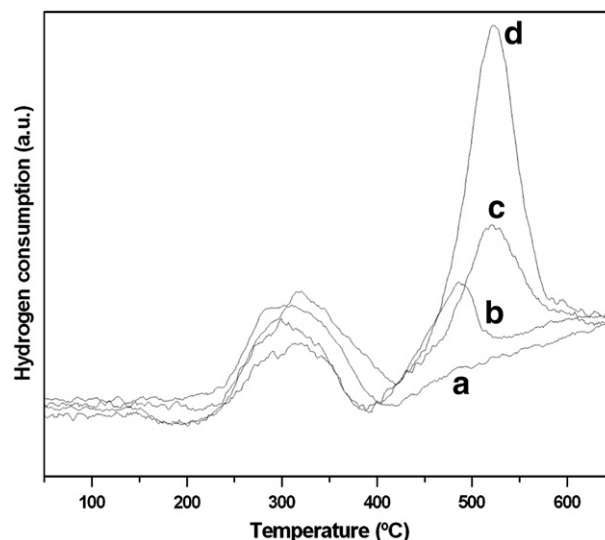


Fig. 3. Reduction curves for (a) HTMgAlc; (b) HTMgAlLi; (c) HTMgAlK; and (d) HTMgAlCs.

necessity of using the same mixture conditions when comparing results from thermogravimetric reactor. However, the T_{max} values for HTMgAlCs used in both tight and loose contact conditions are similar. This similarity could be associated with the high concentration of cesium nitrate on the surface, which may have melted and consequently increased contact.

Fig. 5 shows the catalytic results using the fixed bed reactor with a NO/O₂ flow balanced with helium. Fig. 6 shows the activity of the catalysts with only oxygen balanced with helium, fed into the reactor. The evolution of the reaction was analysed by measuring the amounts of CO₂ and CO that were produced.

The combustion curve of the particulate matter without a catalyst (Fig. 5, curve (e)) has a maximum temperature at 585 °C and total combustion selectivity of 57%. In the presence of a catalyst, all maxima shifted to much lower temperatures. The HTMgAlc catalyst possessed low activity and a T_{max} at 490 °C, with a selectivity to CO₂ of 83%. The catalysts promoted with alkaline nitrates exhibited good activities, with T_{max} values of 360 °C, 393 °C and 431 °C for HTMgAlCs, HTMgAlK and HTMgAlLi, respectively, and a CO₂ selectivity of 87%.

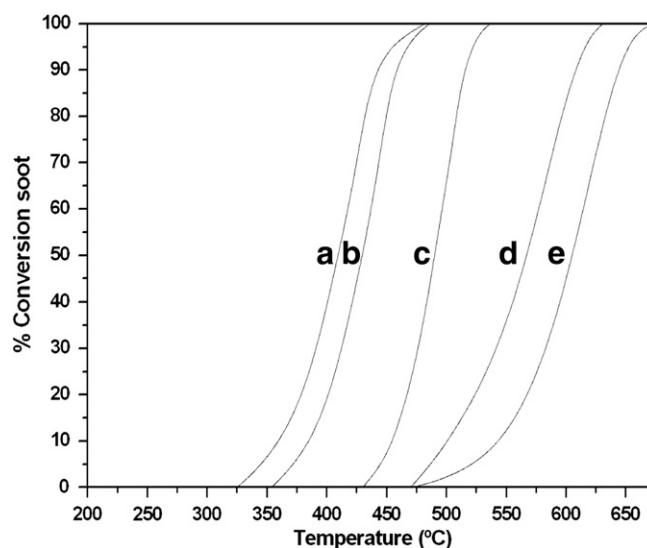


Fig. 4. Conversion of soot under tight contact conditions: (a) HTMgAlCs; (b) HTMgAlK; (c) HTMgAlLi; (d) HTMgAlc; and (e) no catalyst.

Table 4
Maximum combustion rate temperature determined with the thermobalance.

Catalyst	Tight contact		Loose contact	
	T_{\max} (°C)	ΔT (°C)	T_{\max} (°C)	ΔT (°C)
MP	616	0	616	0
HTMgAlc	586	30	608	8
HTMgAlcLi	492	124	555	61
HTMgAlcK	434	182	488	128
HTMgAlcCs	414	202	440	176

The T_{\max} values were 450 °C, 455 °C and 555 °C for HTMgAlcCs, HTMgAlcK and HTMgAlcLi, respectively (Fig. 6), when fed into the reactor using only oxygen.

In the presence of either NO/O₂/He or O₂/He, the most active catalyst is HTMgAlcCs. This behaviour has also been observed with other supports such as zirconia and silica (Galdeano et al., 2004; Ruiz et al., 2010, 2011). When the feed contained NO, the temperature decreased as a consequence of the presence of NO. This behaviour may be associated with the capacity of the catalysts to adsorb NO and to generate superficial NO₂, which is more oxidising than either oxygen or nitrate ions. The effect of NO addition is evident in the catalytic activity of HTMgAlcLi; the concentration of the remaining nitrate ion was low (Table 3) because it became an oxidised species during calcination.

Fig. 7 shows the FTIR spectra of the promoted hydrotalcites after reaction with a NO/O₂ flow. In all cases, an absorption band at 1385 cm⁻¹ is observed and is attributed to the presence of free nitrate. For the HTMgAlcLi catalyst, the band can be seen after the reaction, whereas in the fresh catalyst, it not was observed (Fig. 2). Moreover, an absorption band at 1268 cm⁻¹, assigned to the antisymmetric N–O stretching of free nitrite species, can be observed in these FTIR spectra. Similar results were previously reported with KNO₃/ZrO₂ catalysts (Lick et al., 2008) and also with supported CsNO₃ (Ruiz et al., 2011). These results indicate that the presence of NO favours the formation of nitrate ions in situ that are then reduced to nitrite. These nitrite ions are then finally oxidised to nitrate in the presence of air.

Aluminium oxide is not the active phase in soot combustion. It has been observed that calcined-HT containing magnesium and aluminium behave similarly in the combustion reaction to that containing the divalent cation oxide (Zhang et al., 2010). There are several factors that affect the solid–solid–gas reaction system of catalytic soot combustion. To improve the catalytic activity of calcined-HTs, these have been impregnated with alkaline metal nitrates due to their high mobility. The high mobility increases the efficiency of contact

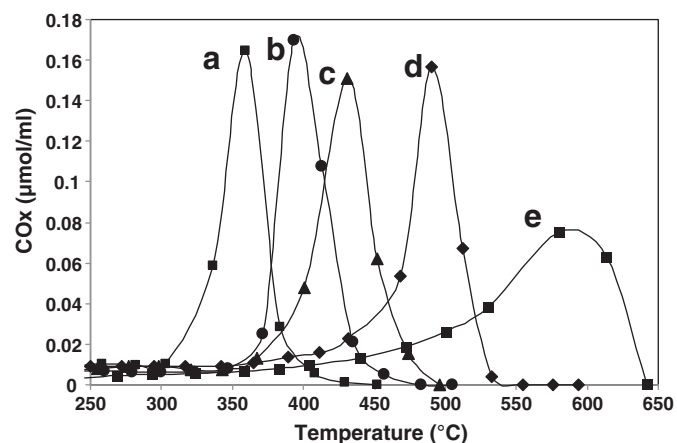


Fig. 5. Combustion of soot in the presence of NO/O₂ for (a) HTMgAlcCs; (b) HTMgAlcK; (c) HTMgAlcLi; (d) HTMgAlc; and (e) soot without catalyst.

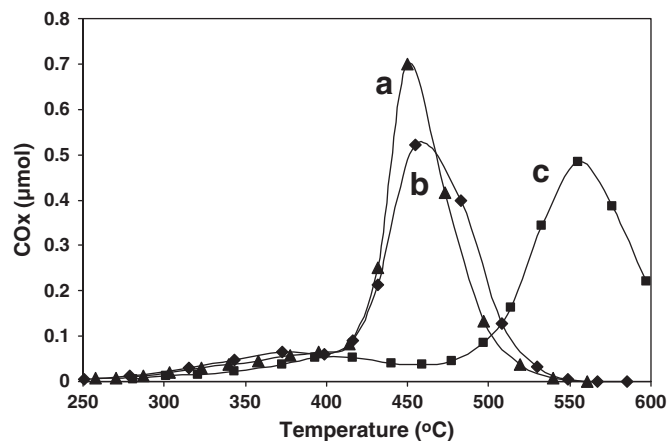


Fig. 6. Combustion of soot in the presence of O₂ for (a) HTMgAlcCs; (b) HTMgAlcK; and (c) HTMgAlcLi.

between the soot and the catalyst. In our study, the three nitrate salts used have melting points within the operating range of diesel exhaust (170–400 °C). Thus, the melting point is not sufficient to differentiate the impact on activity.

Another important factor that could improve the combustion activity of this type of solid is the oxygen species in the bulk. In the literature, potassium, introduced as KNO₃ or K₂CO₃, increased the catalytic activity in soot combustion because it weakened the Mg–Al–O bonds and allowed the surface lattice oxygen to migrate to the surface and become available for reaction (Zhang et al., 2007, 2010).

Finally, redox properties due to the presence of the nitrogen species could have a significant impact on the catalytic behaviour of these compounds. Nitrate ion reduction has been proposed as a reaction mechanism for soot combustion (Hleis et al., 2008; Lick et al., 2008; Ruiz et al., 2010, 2011). The presence of NO in the diesel emission of the exhaust pipe favours the combustion reaction due to the regeneration of nitrate ions, as was demonstrated by FTIR (Figs. 2 and 7). Because cesium nitrate is the only nitrate observable in the XRD results, it can be assumed that this species is more readily available for participation in the oxidation reaction as part of the redox cycle.

The lower activity exhibited by calcined-HT impregnated with lithium nitrate, compared to that of the other metals, could be

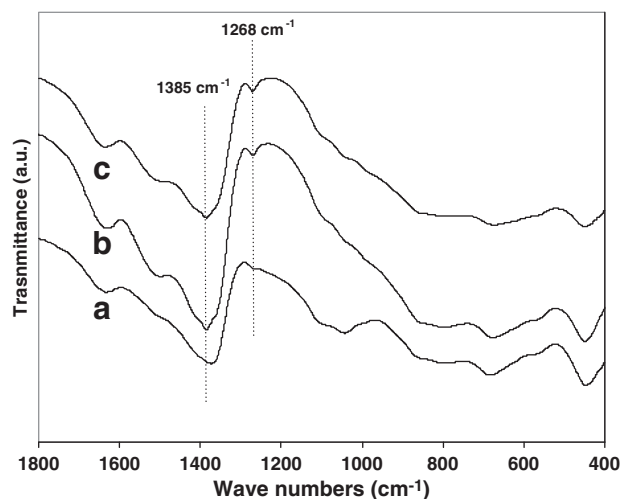


Fig. 7. FTIR spectra of catalysts used in the soot combustion reaction with NO/O₂/He: (a) HTMgAlcLi, (b) HTMgAlcK, and (c) HTMgAlcCs.

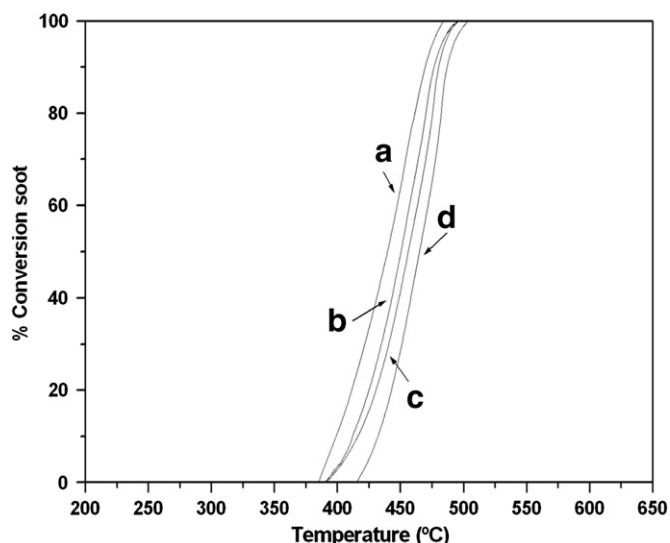


Fig. 8. Soot conversion with tight contact of HTMgAlcCs: (a) fresh, (b) first reuse, (c) second reuse, and (d) third reuse.

attributed to the nearly complete decomposition of the salt, forming lithium oxide that subsequently formed a solid solution in magnesium oxide (Catlow et al., 1990). However, some of these sites are on the surface and can be regenerated in the presence of nitrogen oxides (Fig. 7).

Because HTMgAlcCs was the most active, it was used for stability experiments. To demonstrate that the same sample could be used repeatedly for soot oxidation, the catalyst was used in four successive catalytic cycles, and the results are shown in Fig. 8. As shown, the reuse cycles slightly affect the catalyst activity. The curves that represent the catalytic reaction with this catalyst shifted to temperatures that were higher by approximately 25 °C with successive reuse.

Fig. 9 shows the catalytic results obtained from the use of the hydro-treated sample. The results are plotted as soot conversion versus reaction temperature. The change in the conversion due to the hydro-treatment (curve (b)) is negligible up to 30% conversion. At higher conversions, a slight improvement could be observed with respect to the fresh catalyst (curve (a)).

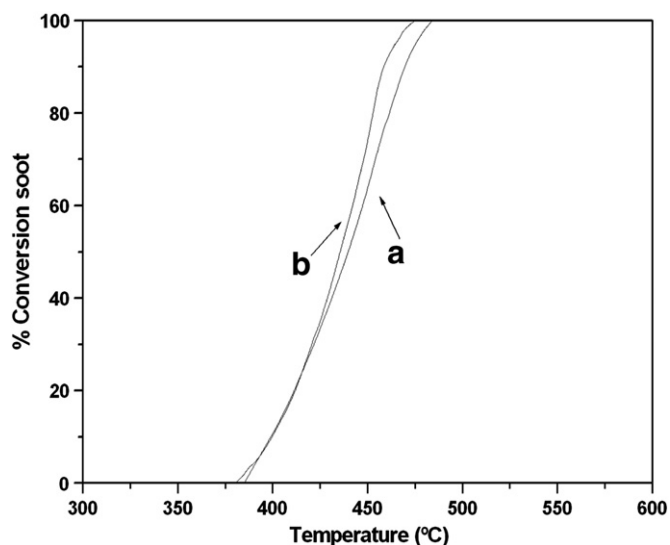


Fig. 9. Soot conversion with tight contact of HTMgAlcCs: (a) fresh and (b) hydro-treated.

4. Conclusions

It has been observed that calcined-HT containing magnesium and aluminium exhibit behaviour in the combustion reaction similar to that observed for the divalent cation oxide. To improve the catalytic activity of the calcined-HT samples, these have been impregnated with alkaline metal nitrates due to their high mobility. The high mobility increases the efficiency of contact between the soot and the catalyst.

The redox properties due to the presence of the nitrogen species could have a significant impact on the catalytic behaviour of these compounds. Nitrate ion reduction has been proposed as a reaction mechanism for soot combustion by our group in previous publications. The presence of NO in the feed favours the combustion reaction due to the regeneration of nitrate ions, which was demonstrated by FTIR. Furthermore, cesium nitrate is more available than the nitrates of Li and K for participation in the oxidation reaction as part of the redox cycle because cesium nitrate crystallises. The lower activity exhibited by the calcined-HT impregnated with lithium nitrate could be attributed to the salt being almost completely decomposed and to the partial solubilisation of the Li oxide in magnesium oxide; however, in the presence of NO, the nitrates are generated again.

Stability studies conducted with HTMgAlcCs demonstrated that the catalyst could be used for three consecutive cycles. The activity has been slightly modified. The change in the conversion due to hydro-treatment is negligible up to 30% conversion, and at higher conversions, a slight improvement was observed with respect to the fresh catalyst.

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