Hectorites syntheses in different heating conditions and their evaluation as soot combustion catalysts after impregnation with copper.~~Evaluation of copper/hectorites as soot combustion catalysts~~.

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Abstract

Two microporous hectorites were prepared by conventional and microwave heating, and a delaminated mesoporous hectorite by an ultrasound-assisted synthesis, and these three hectorites were impregnated with copper. The characterization techniques used were XRD, N_2 adsorption, TEM and H_2 reduction after selective surface copper oxidation by N_2O (to determine copper dispersion). The catalytic activity for soot combustion of both the copper-free and the copper-containing hectorites was tested under a gas mixture of 500 ppm NOx/5%O_2/N_2 (and 5% O_2/N_2 in particular cases), evaluating their stability through three consecutive soot combustion experiments.
The delaminated hectorite achieved the highest surface area (353 m^2/g) and also the highest dispersion of copper, and this copper-containing catalyst was the most active for soot combustion among those prepared and tested in this study. It has been also concluded that the Cu/hectorite-catalyzed soot combustion mechanism is based on the activation of the O_2 molecule and not on the NO_2-assisted soot combustion.

Keywords: copper catalysts, delaminated hectorites, diesel soot, soot combustion mechanism.

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1. Introduction.

Soot particles produced by diesel engines have negative effects on health, and their emission must be controlled and is currently regulated. In order to avoid soot emissions, soot particles are collected on filters placed in the diesel exhausts, which must be periodically regenerated by soot combustion. Diesel gas exhausts ~~are composed~~ consist of a high proportion of O_2, CO_2 and H_2O, and in lower concentration NOx, CO and unburned hydrocarbons, and soot must be combusted in such particular environment.

In a diesel exhaust there are three oxidizing gases that can potentially react with soot: O_2, NO and NO_2. Typically, only NO and O_2 are emitted by the engine, and some soot combustion catalysts (like Pt in the commercially available CRT system, for instance (van Setten ~~B.A.A.L~~ et al., 2001; Fino ~~D.~~et al., 2008) accelerate the oxidation of NO to NO_2, which is much more oxidizing than NO and O_2.

A number of catalysts have been reported to accelerate the combustion of soot, such as noble metals (Sánchez ~~B.S~~ et al., 2009; Shimokawa ~~H.~~et al., 2012), alkali metals (Aneggi et al., 2008; Peralta ~~M.A.~~ et al., 2011~~; Aneggi E. et al., 2008~~), transition metals and metal oxides among others (Neeft J.P.A ~~et al.~~, 1996; López-Suárez ~~F.E.~~et al.,2008, 2009; Guillén-Hurtado ~~N.~~et al., 2012). Among these potential catalysts, copper oxide appears as an interesting solution due to its moderate activity but low prize.

It is known that the catalyst support (ceria, alumina, silica, etc.) affects in some cases the activity of the main active component of a soot combustion catalyst. However, as far as we know, the soot combustion activity of hectorites either as catalyst or as catalytic support has not been reported yet.

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Hectorite is a trioctahedral 2:1 ~~mineral clay~~clay mineral, belonging to the smectites group, with formula $(Si_{8.0})[Mg_{6.0-x}Li_x](OH^{\cdot}F)_4O_{20}M^{n+}_{x/n}\cdot mH_2O$, where some substitution of ~~Mg(II) by Li(I) in the Octahedral (O_h) sheet~~Mg^{2+} by Li^{+} in the octahedral (O) sheet causes the negative charge of layers. This charge is compensated by interlayer exchangeable cations. ~~When these cations are exchanged by transition metal cations (Ni^{2+}, Pd^{2+}, Cu^{2+}),~~ ~~M~~metallic nanoparticles of metals with catalytic activity, like, Ni^0, Pd^0 or Cu^0 among others, can be obtained~~, after reduction,~~ in the interlayer space by ionic exchange and further reduction. Hectorites can be used for nanocomposites preparation, in ionic adsorption and in heterogeneous catalysis among other applications (Varma, 2002; Casagrande et al., 2005; Liu ~~X.~~.et al., 2005; ~~.~~Xue ~~S~~ et al., 2008~~;~~ ~~Casagrande M. et al., 2005; Varma R.S. 2002~~). Applications of smectites as catalysts are very extensive, especially in acid and oxidation reactions (Varma 2002; Casagrande ~~M.~~ et al., 2005; ~~Varma R.S. 2002~~). Additionally, they have been also widely used as supports of metal catalysts leading to significant results, for example, in the hydrogenation of styrene oxide to 2-phenylethanol with hectorites and saponites-supported nickel catalysts (Vicente ~~I.~~ et al., 2011~~-~~a, 2011b) or in the hydrogenolysis of glycerol to 1,2-propanediol with delaminated hectorites-supported copper catalysts ~~based on copper supported on delaminated hectorites~~ (Sánchez ~~T.~~ et al., 2012).

Although clays can be found in nature, better composition, reproducibility and higher surface area are necessary in order to improve their catalytic ~~applications~~performance. Preparation of synthetic clay minerals and delamination could solve the limitations of natural clays.~~Synthetic preparation of clays and delamination could solve these requirements, respectively~~. Delaminated hectorites can be ~~synthesised~~synthesized ~~using~~ adding quaternary ammonium salts during the hydrothermal treatment, as proposed by Iwasaki ~~T.~~ et al. (1998) and by Sánchez et al.

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(2012), or using polymers, as proposed by Carrado et al. (1999). Typical methods for preparing supported metal catalysts include impregnation, solid blend and modification of hectorite by cation exchange. Depending on the method, different metal dispersions and support-metal interactions can be obtained (Meister et al., 1995; Vicente ~~I.~~ et al., 2011-a, 2011b ; Sánchez ~~T.~~ et al., 2012~~; Meister A. et al., 1995~~).

Taking this background into account, the goal of this study is to prepare different hectorite samples and to evaluate the potential of these hectorites as soot combustion catalysts in a gas mixture with NOx and O_2, either as catalyst or as copper support.

2. Experimental.

2.1. Catalyst preparation.

2.1.1. Hectorite samples.

Two hectorites, which are referred to as HC and HMw, were prepared according to the procedures reported by Granquist ~~W.T.~~ and Pollack ~~S.S.~~ (1959) and Vicente ~~I.~~ et al. (2009). In both methods brucite sheets were proposed to act as crystallization nuclei of hectorite. Preparation was carried out as follows: a slurry (3 ~~wt.~~mass % solids) containing SiO_2 (Aerosil 380 from Degussa), fresh brucite $Mg(OH)_2$ (synthesized by dropping a 10 M ammonia solution onto $MgCl_{2(aq)}$), and LiF (99.9% from Sigma-Aldrich), in a molar ratio SiO_2:$Mg(OH)_2$:LiF of 8:6:2 was vigorously stirred for 1 h.

~~-~~Then, one of the samples, which is referred to as “HMw”, was aged by microwaves (in a Milestone Ethos Touch Control equipment) at 120ºC for 8 h under magnetic stirring. The treatment was performed~~by~~ in a 85 mL ~~autoclaving in~~ Teflon

autoclave ~~reactors of 85 mL in a laboratory microwave equipment (Milestone Ethos Touch Control) at 120 ºC for 8 h under magnetic stirring (HMw). The second~~Another sample, which is referred to as "HC"~~.~~, was aged ~~in~~ within a Teflon autoclave by conventional thermal heating ~~inside a conventional oven (HC)~~ at 120 ~~-~~ºC for 8 days, in order to compare the conventional aging with the microwave hydrothermal treatment.

A delaminated hectorite~~third sample~~. which is referred to as HD, was also prepared~~, in order to obtain a delaminated hectorite, ~~according to the method reported by Iwasaki ~~T.~~ et al. (1998), which was ~~and later~~ further modified by Sánchez ~~T.~~ et al. (2012) by ~~introducing the use of~~ using ultrasounds for ~~the~~ homogenization of the ~~initial~~ precursors suspension. ~~The molar ratio of reagents was Si:Mg:Li= 8:5.2:0.8.~~ 8.73 g of an acidified sodium silicate solution (SiO_2 27%, d. 1.39 g/cm^3, Sigma-Aldrich) was mixed with the appropriate amounts of $MgCl_2$ and LiF to obtain a molar ratio of Si:Mg:Li reagents of 8:5.2:0.8. Then, a LiOH solution was added until pH=12. The resulting suspension was homogenized for 15 min in an ultrasound bath, washed and dried. Then, the solid was suspended in water and mixed with trimethyldodecylammonium chloride (AQ) (98%, Sigma-Aldrich) in a molar ratio Li:AQ= 1:1. The suspension was submitted to a hydrothermal treatment in a conventional Teflon autoclave at 180 ~~-~~ºC for 1 h. Afterwards, the precipitated sample was ~~separated~~ filtered and calcined to 620 ~~-~~ºC for 75 min (HD).

2.1.2. Cu/hectorite samples.

Cu/hectorite samples were prepared by impregnation according to the method described by Sánchez ~~T.~~ et al. (2012). Impregnated hectorites were prepared mixing 1.5 g of support (HMw, HC or HD) with a 15 ~~wt~~ mass % copper nitrate ethanol solution

under ultrasounds for 15 min, in order to obtain around 40 ~~wt~~ mass % copper after solvent evaporation, calcination, and reduction under pure hydrogen. Impregnated hectorites are referred to ~~have been named~~ as Cu/HMw, Cu/HC and Cu/HD.

2.2. Characterization techniques.

2.2.1. X-~~R~~ray ~~D~~diffraction (XRD).

XRD measurements were made using a Siemens D5000 diffractometer (Bragg–Brentano parafocusing geometry and vertical θ–θ goniometer) fitted with a curved graphite diffracted-beam monochromator and diffracted-beam Soller slits, a 0.06° receiving slit, and scintillation counter as a detector. The angular 2θ diffraction range was between 2 and 70°. The samples were ~~dusted~~ milled and placed on ~~to~~ a low background signal Si(510) sample holder. The data were collected with an angular step of 0.05° at 3 s per step and by sample rotation. Cukα radiation was obtained from a copper X-ray tube operated at 40 kV and 30 mA. The X-ray diffractograms ~~was~~ were analyzed using the program TOPAS 3.0. Reflection (001) was selected to determine the basal spacing ~~of the samples~~(Sánchez et al., 2012) and~~.~~ r~~R~~eflection (060) was used to calculate the crystallite size of the sample ~~sheets~~layers.

2.2.2. N_2 adsorption-desorption.

N_2 adsorption-desorption isotherms were recorded at -196~~—~~ºC using a Micromeritics ASAP 2000 surface analyzer. Prior to analysis samples were outgassed at 150~~-~~ºC. Specific surface areas were calculated from BET method.

2.2.3. Transmission Electron Microscopy (TEM).

Transmission electron micrographs were obtained with a JEOL 1011 transmission microscope operating at an accelerating voltage of 100 kV and magnification values at 300000.

2.2.4. Temperature-Programmed Reduction (TPR).

Copper dispersion was determined by selective temperature-programmed reduction of surface copper following the method described by Gervasini ~~A.~~ and Bennici ~~S.~~ (2005). These experiments were carried out in a Micromeritics device, model Pulse ChemiSorb 2705. 100 mg of catalyst were heated at 10 ºC/min from 25 to 400 ºC under a 5% H_2/Ar flow (15 ml/min), holding the maximum temperature for 30 min. The H_2 consumption was monitored with a TCD detector. Then, the selective oxidation of the surface copper ~~surface~~ to Cu_2O was performed under 0.53% N_2O/Ar flow (15 ml/min) at 50 ºC for 1 h. Surface Cu_2O ~~surface~~ was further reduced with 5% H_2/Ar (15 ml/min) by raising the temperature at 20 ºC/min from 25 to 900 ºC, following the H_2 consumption with the TCD detector. The potential interference of H_2 consumption by the supports was ruled out in experiments performed with the supports (without copper).

Surface copper was determined considering the stoichiometry of the reaction:

$$H_2 + Cu_2O_{surface} \longrightarrow 2Cu_{surface} + H_2O$$

‘‘Dispersion (%)’’ was calculated as the ratio between the amount of surface copper and total copper in the catalyst:

$$\text{Dispersion (\%)} = \frac{Cu_{surface}}{Cu_{total}} \cdot 100$$

A CuO sample (supplied by Micromeritics) was used as reference to quantify H_2 consumption.

2.3. Catalytic activity tests.

Catalytic tests were performed in a tubular quartz reactor coupled to specific NDIR-UV gas analyzers for CO, CO_2, NO, NO_2 and O_2 monitoring. 20 mg of soot and 80 mg of the selected hectorite sample were mixed in the so-called loose contact conditions (Neeft ~~J.P.A.~~ et al., 1996) and diluted with SiC to avoid pressure drop and favor heat transfer. Uncatalysed combustion experiments were also performed under the same conditions but only with soot. The model soot used was carbon black from Evonik-Degussa~~.~~ (Printex-U), with 92.2% C, 0.6% H, 0.2% N, and 0.4% S. The ash and adsorbed hydrocarbon percentages were <0.1 and 5.2%, respectively, and the BET surface area was 95 m^2/g. The gas mixtures used contained either 500 ppm NOx/5% O_2/N_2 or 5%O_2/N_2, and the gas flow was fixed at 500 ml/min in all cases (GHSV = 30000 h^{-1}). The experimental set-up was designed to minimize the uncatalysed oxidation of NO to NO_2 on the gas stream.

The catalytic tests were carried out in temperature programmed conditions followed by an isothermal step, that is, once the gas mixture is fed to the reactor and all lectures of the gas analyzers were stable, the temperature was increased from room temperature until 600 ºC at 10 ºC/min, and the maximum temperature was maintained for 30 minutes. Three consecutive soot combustion experiments were performed with each sample. Once the first soot combustion test was finished, the reactor was cooled down to room temperature under 5%O_2/N_2 gas flow, the used hectorite was mixed again with soot following the procedure previously described in the experimental

section, and a second catalytic test was performed. In the same way, a third run was performed with each hectorite sample.

3. Results and discussion.

3.1. Characterization of hectorite and Cu/hectorite samples.

Table 1 shows some characterization data of the hectorite samples. XRD patterns of the three samples were typical of clay minerals, as it is shown in the reference ~~clays materials~~ (Sánchez ~~T.~~ et al., 2012). However, reflection (001), related to the layer stacking, was only observed in hectorites HC and HMw (Table 1). The low degree of order stacking in sample HD, related to the absence of reflection (001) in the diffraction pattern (Fig 1), could be associated with delamination.~~,~~ ~~as~~ As confirmed by TEM, ~~since we can observe~~ nano-size~~d~~ layers are observed, which are aggregated to make mesopores (Fig. 2). In order to evaluate the crystallinity of the layers, crystallite sizes were calculated from (060) reflection using the Scherrer equation (Table 1). The hectorite prepared ~~with~~ by microwaves heating (HMw) showed higher crystallite size (10.5 nm) than that synthesized by conventional heating HC (7.9 nm). This is in agreement with the increase of crystallinity expected for materials prepared with microwaves (Bergadà et al., 2007; Vicente ~~I.~~ et al., 2009, 2010~~; Bergadà O. et al., 2007~~). Delaminated hectorite, HD, had the lowest crystallite size (6.0 nm). This can be explained by the shorter time of hydrothermal treatment used to prepare this sample (1 h).

Regarding the BET surface area values (Table 1), mesoporous delaminated hectorite (HD) showed the highest surface area, as expected, in agreement with its

delamination observed by TEM (Fig. 1). With respect to porosity, it is important to remark that all synthesized hectorites exhibited adsorption isotherms with contribution of mesoporosity (type IV), but with different hysteresis loop (Sánchez T. et al., 2012). For HC and HMw, hysteresis was type B (following Boer classification (of Boer J.H. 1958) (Table 1). Hysteresis type B is associated to lamellar particles that are packed together with formation of open slit-shaped capillaries with parallel walls, whereas hysteresis type D is more characteristic of lamellar particles that are packed without parallel orientation (Sánchez T. et al., 2012). The hysteresis loop of HD was identified as a mix of B and D types, with higher contribution of D (Fig. 3). This agrees with the disorder observed in the lamellar distribution for this sample.

Table 2 shows the amount of copper and the dispersion obtained for the Cu/hectorite samples. Dispersion values can be directly related to the surface area of the supports. Thus, delaminated hectorite, which had higher surface area, showed the highest dispersion of copper. Although the dispersion values are low, it is important to remark the significant amount of copper on the surface of the catalysts. This will be later correlated with the catalytic results.

3.2. Soot combustion tests: catalysts screening.

Fig. 4 shows the soot conversion profiles obtained during the third soot combustion test performed with each copper-free and copper-containing hectorite in the 500 ppm NOx/5% O_2/N_2 gas flow. The copper-free microporous hectorites (HC and HMw) present null activity as soot combustion catalysts while the mesoporous hectorite (HD) was able to slightly accelerate the combustion reaction. As expected, the copper-containing hectorites were more active than the supports, and among them, the catalyst

Cu/HD, prepared with the mesoporous hectorite, was the most active one. The highest amount of surface copper on this catalyst justifies this fact. As a general behavior, the Cu/hectorite catalysts tested were less active than some other soot combustion copper catalysts, such as Cu/alumina (López-Suárez ~~F.E.~~ et al., 2008) or Cu/$SrTiO_3$ perovskites (López-Suárez ~~F.E.~~ et al., 2009).

The stability of the hectorite supports and Cu/hectorite catalysts was evaluated in three consecutive soot combustion experiments performed with the 500 ppm NOx/5% O_2/N_2 gas flow. Fig. 5 compiles the time required to achieve 90% soot conversion in each experiment. In all cases, minor differences were noticed among the three consecutive cycles, that is, the soot combustion capacity is not significantly affected under the experimental conditions of these tests (López-Suárez ~~F.E.~~ et al., 2008, 2009).

One important feature of soot combustion catalysts to be taken into account is the carbon products selectivity, since CO is hazardous and toxic while CO_2 is the desired product. CO selectivity results are compiled in Fig. 6 for all the supports and catalysts tested in three consecutive combustion cycles under 500 ppm NOx/5% O_2/N_2. The uncatalysed combustion of soot yielded 60% CO, and some of the hectorite samples tested lowered this value. The Cu/hectorite catalysts presented CO selectivity values between 10 and 33%, and among the supports, only HD was able to lower the CO selectivity to around 45%. These results suggest that these Cu/hectorite samples catalyze the oxidation of CO, which is evolved as primary soot combustion product, to CO_2. This is in agreement with the results obtained with some other soot combustion copper catalysts (López-Suárez ~~F.E.~~ et al., 2008, 2009).

3.3. Soot combustion mechanism.

In order to analyze the Cu/hectorite-catalyzed soot combustion mechanism, a soot combustion experiment was performed with the most active catalyst among those tested (Cu/HD) ~~with~~ under a 5%O_2/N_2 gas flow. The soot conversion curve obtained in this experiment is plotted in Fig. 7 together with the counterpart curve obtained ~~with~~ under 500 ppm NOx/5% O_2/N_2. Both curves are almost equal, evidencing that NOx is not playing a key role in the soot combustion mechanism, that is, the NO_2-assisted soot combustion mechanism can be ruled out.

Additional information about the soot combustion mechanism was obtained from the NO_2 formation and NOx removal profiles corresponding to the soot combustion and blank experiments (without soot) performed with the Cu/HD catalyst with 500 ppm NOx/5%O_2/N_2 (Fig. 8). A little amount of NOx was chemisorbed on the catalyst during the blank experiment, and the shape of the NO_2 profile obtained in this blank experiment was similar to those typically reported for some other catalysts (López-Suárez ~~F.E.~~ et al., 2008, 2009). The NO_2 level increased with temperature until the thermodynamic equilibrium of the NO_2 formation reaction was achieved. On the contrary, NOx chemisorption and NO_2 formation were not detected during the soot combustion experiment.

These results evidence that the Cu/hectorite catalyst was able to accelerate the oxidation of NO to NO_2 and that NO_2 reacts with soot, since NO_2 was not detected in the soot combustion experiment, but the amount of NO_2 produced was not high enough to affect soot combustion. This suggests that the main role of the Cu/hectorite catalyst is the activation of the O_2 molecule rather than to oxidize NO to NO_2. This could explain why the mesoporous hectorite presents higher activity than the microporous ones, since more contact points with soot particles are expected to exist where the activated oxygen species are transferred to soot.

4. Conclusions.

In this study, three different hectorites have been prepared and impregnated with copper. The characterization and the catalytic activity for soot combustion of ~~both~~ the copper-free and copper-containing hectorites have led to the following conclusions:

• Mesoporous delaminated hectorite (HD) presents the lowest crystallite size and the highest surface area, being the only copper free hectorite that slightly accelerates the soot combustion reaction.

• Among the Cu/hectorite catalysts, copper supported on a delaminated hectorite (Cu/HD) is the most active one, showing the highest amount of copper on the surface.

• Regardless the hectorite support, the Cu/hectorite catalysts decrease the selectivity towards CO formation as soot combustion product and the soot combustion capacity is quite stable after three consecutive soot combustion experiments.

•The Cu/hectorite-catalysed soot combustion mechanism is not based on the NO_2-assisted soot combustion, the activation of the O_2 molecule being the main role of these catalysts.

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Komplexe [Cu(bppep)(H_2O)](ClO_4)$_2$ und [Ni(bppep)(Cl)]Cl (bppep = 2,6-Bis[1-phenyl-1-(pyridin-2-yl)ethyl]pyridin) in Hectorit; Anorg. Allg. Chem. 621, 117-121.

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List of Tables

Table 1. Characterization data from XRD~~,~~ and N_2 physisorption techniques.

Sample	Basal spacing (Å)	Crystallite size (0 6 0) (nm)	BET surface area (m^2/g)	Hysteresis type
HMw	14.2	10.5	199	B
HC	13.4	7.9	207	B
HD	---	6.0	353	D,B

Table 2. Results of copper dispersion on the different supports.

Sample	Cu content (~~wt~~ mass %)	Cu dispersion (%)	g surface Cu /g catalyst $x10^{-2}$
Cu/HMw	39.2	4	1.57
Cu/HC	38.7	6	2.32
Cu/HD	40.1	8	3.20

Figure captions

Fig. 1. X-ray diffraction pattern of HD hectorite.

Fig. 2. TEM micrograph of HD hectorite.

Fig. 3. N_2 adsorption-desorption isotherm of HD hectorite.

Fig.4. Soot conversion profiles corresponding to the third run performed with each hectorite sample in the 500 ppm NOx/5% O_2/N_2 gas flow.

Fig.5. Comparison of catalysts during three consecutive soot combustion runs performed in the 500 ppm NOx/5% O_2/N_2 gas flow.

Fig.6. CO selectivity in soot combustion experiments performed in the 500 ppm NOx/5% O_2/N_2 gas flow.

Fig.7. Soot combustion experiments performed with Cu/HD catalyst (fresh sample) with 5% O_2/N_2 and 500 ppm NOx/5% O_2/N_2.

Fig.8. NO_2 formation and NOx removal in soot combustion and blank experiments performed with Cu/HD catalyst (fresh sample) with 500 ppm NOx/5% O_2/N_2.

Figure 1

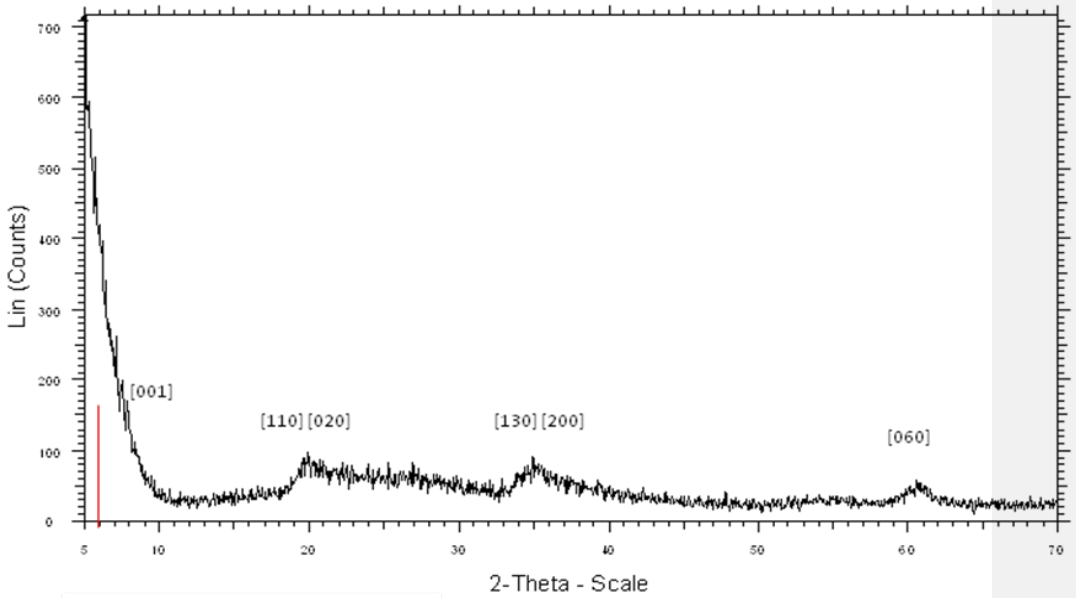


Figure 2

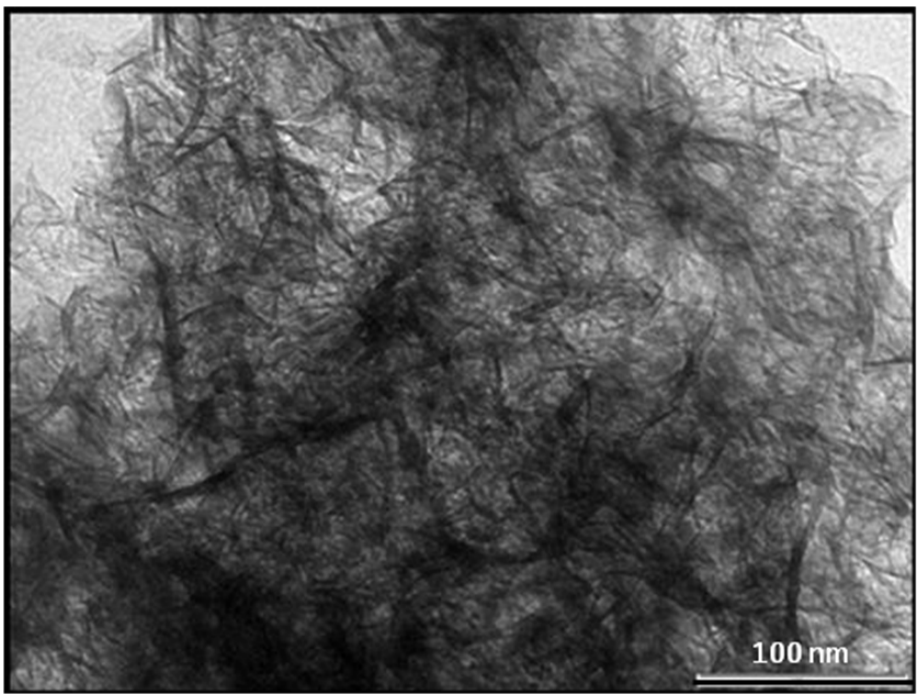
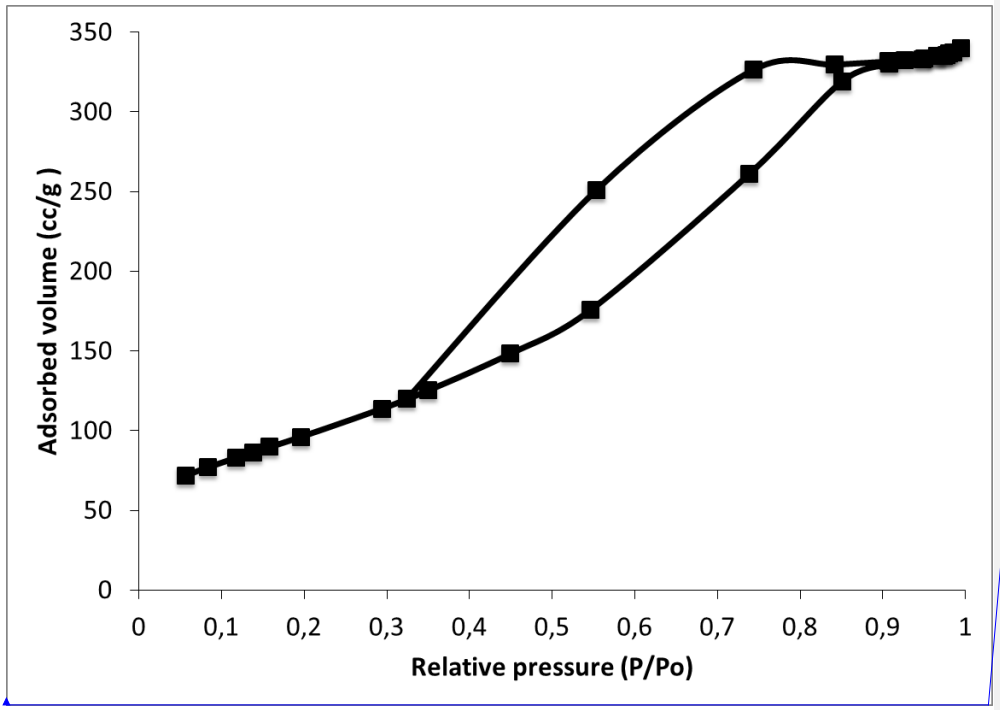


Figure 3



Con formato: Inglés (Estados Unidos)

Figure 4

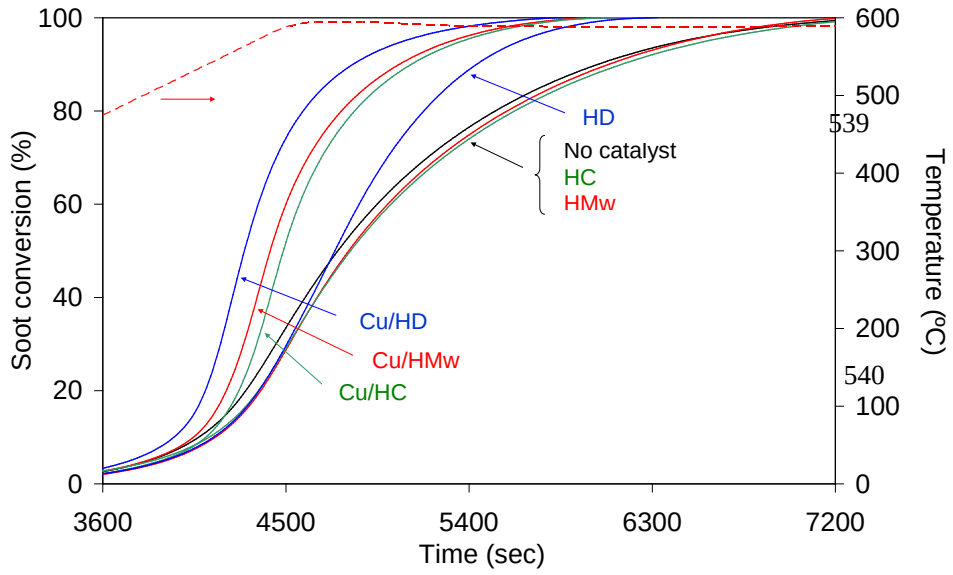

Soot conversion (%)
Temperature (°C)
Time (sec)
100
80
60
40
20
0
600
500
400
300
200
100
0
3600
4500
5400
6300
7200
HD
No catalyst
HC
HMw
Cu/HD
Cu/HMw
Cu/HC

Figure 5

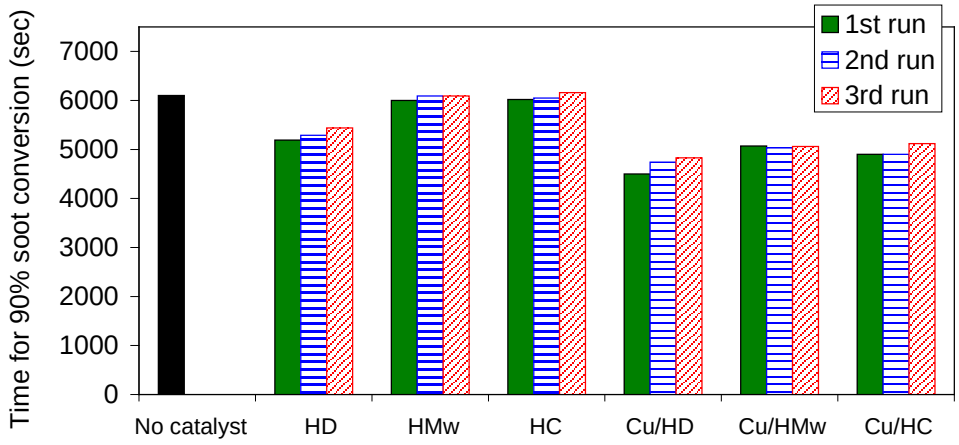

Time for 90% soot conversion (sec)
7000
6000
5000
4000
3000
2000
1000
0
No catalyst
HD
HMw
HC
Cu/HD
Cu/HMw
Cu/HC
1st run
2nd run
3rd run

Figure 6

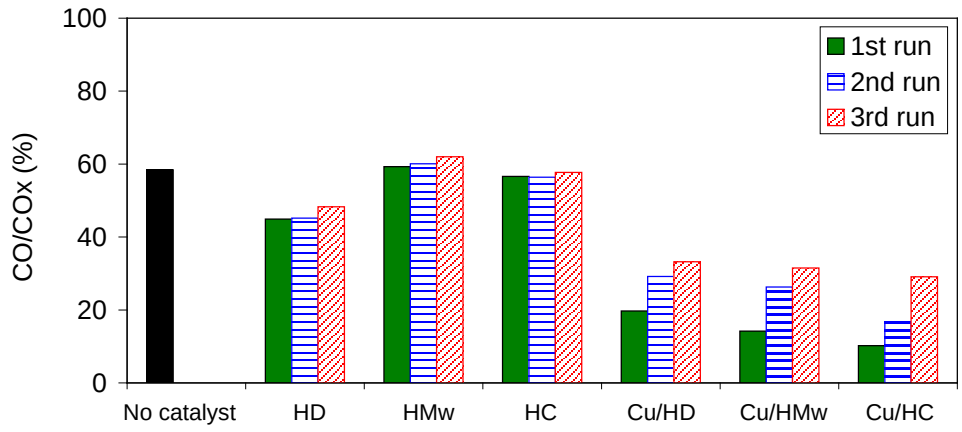

100
80
60
40
20
0
CO/COx (%)
1st run
2nd run
3rd run
No catalyst
HD
HMw
HC
Cu/HD
Cu/HMw
Cu/HC

Figure 7

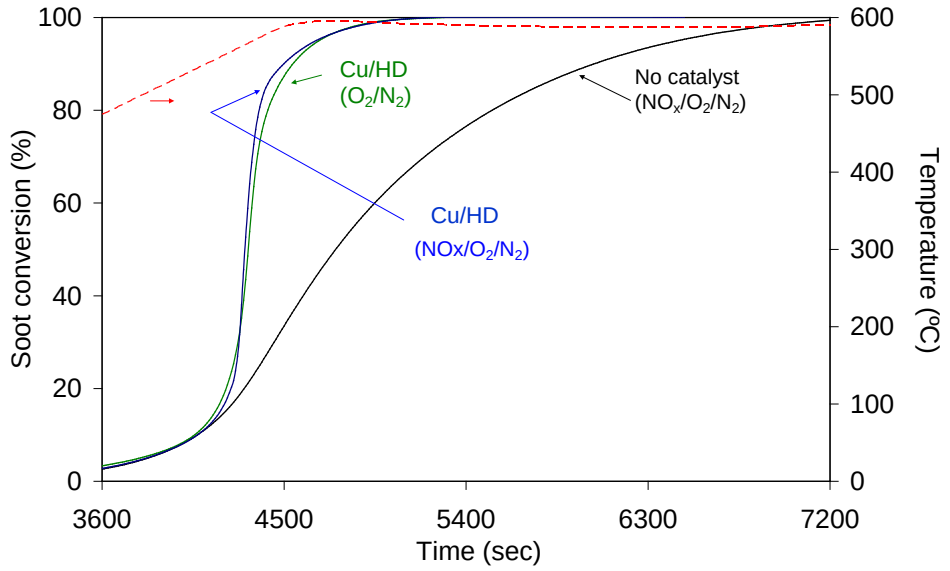
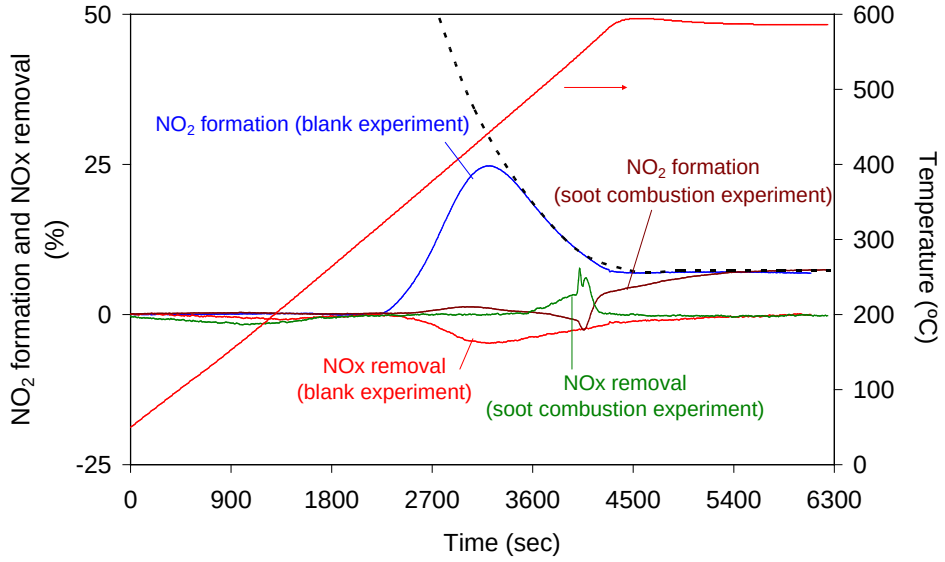

Soot conversion (%)
Temperature (°C)
Time (sec)
Cu/HD
(O2/N2)
No catalyst
(NOx/O2/N2)
Cu/HD
(NOx/O2/N2)
100
80
60
40
20
0
600
500
400
300
200
100
0
3600
4500
5400
6300
7200

Figure 8


50
25
0
-25
600
500
400
300
200
100
0
0
900
1800
2700
3600
4500
5400
6300
Time (sec)
NO2 formation and NOx removal (%)
Temperature (°C)
NO2 formation (blank experiment)
NO2 formation (soot combustion experiment)
NOx removal (blank experiment)
NOx removal (soot combustion experiment)