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Low-cost carbon-based briquettes for the reduction of no emissions from medium–small stationary sources

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Abstract

In this paper, a novel method for preparing low-cost carbon-based briquettes is described. This procedure includes the briquetting of the carbon material, subsequent activation and finally an equilibrium adsorption impregnation of the active phase. A local low-rank coal was used for the preparation of the carbon briquettes, while both a model vanadium compound (V_2O_5) and the ashes of a petroleum coke (PCA) were used as the precursors of the active phase. The catalytic briquettes have been tested for NO reduction. The effect of a HNO_3-oxidation previous to the impregnation has been also evaluated. The reduction tests have been carried out in presence of oxygen and with the addition of ammonia as reducing agent. The briquettes have shown to be active for NO reduction at low temperature (100–300 °C). Surface chemistry as well as the porous structure of the support, affect the catalyst behaviour. In general terms, higher NO reduction efficiencies were measured for the catalysts prepared using the pre-oxidised briquettes.

Keywords: Briquettes; Petroleum coke ashes (PCA); Vanadium

1. Introduction

Exhaust gases from stationary and mobile combustion sources contain nitrogen oxides that cause a variety of environmentally harmful effects such as urban smog acid rain or ozone depletion and contribute to the greenhouse effect. Removal of these contaminants to fulfil the environmental emission standards is necessary and therefore various wet and dry processes have been put forward. Among these processes, the selective catalytic reduction (SCR) of nitrogen oxides, using ammonia or urea as reducing agents, has gained eminent importance in the last decades [1,2].

A great variety of different catalysts have been reported to be active in SCR of NO_x (NO, NO_2), but only a few of them are applied in practice, the most prominent being V_2O_5/TiO_2 promoted by WO_3 and/or MnO_3. These vanadia/titania-based catalysts are suitable for application in a relatively narrow temperature window 300–400 °C. At higher temperatures (>400 °C) nitrous oxide is formed [3] and at lower temperatures they are irreversibly poisoned by SO_2 [4,5]. In addition, these catalysts may involve a considerable economic effort for all medium–small stationary sources, which in the near future will have to fulfil the each time stricter legislation.

Recently, the catalysts that are able to work in a lower temperature window have found significant interest due to their possible application in small stationary sources to make the treatment of effluent gases as easy as possible, as their use would avoid retrofitting or reheating of the flue gas at the SCR reactor inlet. Carbonaceous supports doped with various transition metal oxides have shown large potential for their application as SCR catalysts at low temperatures. In this way, several carbon materials have been impregnated with Cu [6,7], Fe [8,9], Mn [10–12] and V [13] compounds.

In previous works, really interesting results have been found for vanadium oxide and petroleum coke ashes supported on activated carbons, prepared from a low-rank coal [14,15]. In these studies, considerable activity and selectivity were reported at temperatures between 150 and 200 °C, in presence of ammonia and oxygen excess. The characteristics of the carbon support were found to be decisive for the catalytic activity of the materials prepared.

The use of carbon materials presents unique advantages over other catalyst supports, like the simplicity of the preparation process, their potentially low-cost and an easy availability of

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coal. Moreover, the carbon support can be shaped as low-pressure-drop aggregates, like carbon briquettes and pellets, with good mechanical resistance to withstand abrasion phenomena. In the present paper, novel catalytic carbon-based briquettes, using both vanadium oxide and petroleum coke ashes (PCA) are presented as catalysts for the SCR of NO in presence of ammonia. The carbon support is prepared using a local low-rank coal as precursor. The use of a petroleum waste (PCA) for producing catalytic briquettes is supposed to be a totally innovative way of increasing it in value. In addition, both the use of a low-rank coal and PCA could make the production cost of these catalytic briquettes considerably lower.

The influence of the modification of the different parameters of the preparation procedure (temperature, activation agent, oxidation process and finally active phase) in the NO reduction efficiency of the resulting catalysts is evaluated.

2. Experimental

2.1. Preparation of the carbon support

SAMCA coal from SAMCA mines in Teruel, Spain, was used as carbon support precursor. The properties of this low-rank coal have been shown in detail elsewhere [16]. This coal was pyrolysed at 800 °C in nitrogen. The obtained char was blended with ground commercial tar pitch, SP-110, used as binder agent for the preparation of briquettes. The briquetting process was performed in a device which was specially designed to this purpose. Details of the pitch as well as briquetting procedure are given elsewhere [17,18]. The coal and the binder agent were blended and cold pressed at 125 MPa in a plug and mould press to produce cylindrical briquettes of approximately 10.5 mm diameter, 13.5 mm height and 1.2 g weight. After briquetting the process of curing takes place. This process was carried out in an electric furnace with air. The temperature was risen with a heating rate of 2 °C/min up to 200 °C in 2 h. The pyrolysis was performed at 800 °C and pressure of 0.1 MPa under N_2. The pyrolysis runs were carried out in a bench scale reactor that has been described earlier [16]. The resulting briquettes were activated either using 20% of water vapour in N_2 between 600 and 750 °C, or with CO_2 between 700 and 800 °C. The activation as well as the pyrolysis, were conducted in a fixed-bed reactor. Table 1 shows a short description of the carbon briquettes prepared.

Pre-oxidation of the carbon support was performed in liquid phase at room temperature. HNO_3 (1N) was used as oxidising agents. The prefixed ‘Ox-’ before the sample names indicates this treatment.

2.2. Petroleum coke ashes

A coke from the Delayed Coke Unit in the REPSOL refinery in Puertollano, Spain, was used for the production of the PCA, by combustion under air at a temperature up to 650 °C. Open flat ceramic vessels were used to contain the coke. The temperature was raised at a rate of 10 °C/min. The PCA contain, as it was described before, 23% (w/w) of V, 3.5% (w/w) of Fe and 3% (w/w) of Ni, determined by atomic absorption spectroscopy. Other components such as Mg, Zn, Cu, Cr, Mn, Pb, Sb and Ca are also present in this material. A more complex description of PCA can be found in [19].

2.3. Catalyst production

The impregnation was carried out by equilibrium adsorption of vanadium. Thus, the briquettes were loaded with suspensions containing 3% (w/w) of V in distilled water, using either V_2O_5 as a model vanadium compound or PCA. Briquettes were immersed in these suspensions, stirred for 3 h and carefully washed up in distilled water afterwards. Finally, the catalysts were dried overnight in an oven at 108 °C. Table 1 includes also a short description of the catalysts prepared.

2.4. Physical and chemical characterisation

Carbon briquettes were physically and chemically characterised by means of two different methods: Adsorption of N_2 at 77 K and temperature programmed desorption (TPD). Specific surface area was calculated from the N_2 adsorption isotherms applying the Brunauer–Emmett–Teller (BET) equation and yields important information about structural features. The tests were performed in a Micromeritics ASAP-2000. On

Table 1
Description of the carbon briquettes and catalysts prepared

Name	Description
Br/P/800/0.5/N_2	Briquette pyrolysed at 800 °C for 0.5 h with N_2
Br/A/600/2/H_2O	Briquette activated at 600 °C with 20% water vapour for 2 h
Br/A/700/2/H_2O	Briquette activated at 700 °C with 20% water vapour for 2 h
Br/A/700/2/CO_2	Briquette activated at 700 °C with CO_2 for 2 h
Br/A/800/1/CO_2	Briquette activated at 800 °C with CO_2 for 1 h
Br/A/600/2/H_2O + PCA	Briquette activated at 600 °C with 20% water vapour for 2 h + 3% V as PCA
Br/A/700/2/H_2O + PCA	Briquette activated at 700 °C with 20% water vapour for 2 h + 3% V as PCA
Br/A/700/2/CO_2 + PCA	Briquette activated at 700 °C with CO_2 for 2 h + 3% V as PCA
Br/A/800/1/CO_2 + PCA	Briquette activated at 800 °C with CO_2 for 1 h + 3% V as PCA
Br/A/600/2/H_2O + V_2O_5	Briquette activated at 600 °C with 20% water vapour for 2 h + 3% V as V_2O_5
Br/A/700/2/H_2O + V_2O_5	Briquette activated at 700 °C with 20% water vapour for 2 h + 3% V as V_2O_5
Br/A/700/2/CO_2 + V_2O_5	Briquette activated at 700 °C with CO_2 for 2 h + 3% V as V_2O_5
Br/A/800/1/CO_2 + V_2O_5	Briquette activated at 800 °C with CO_2 for 1 h + 3% V as V_2O_5

the other hand, chemical characterisation was carried out by means of TPD. TPD has become one of the most common techniques to characterise the functional groups on carbonaceous surfaces [20]. TPD was performed heating 600 mg of sample at a constant rate (10 °C/min) from 150 to 1050 °C in a flow of 30 ml/min of He. Samples were collected in gas sample bags and CO and CO_2 were measured in a chromatograph equipped with TCD (HP-5890).

2.5. Activity tests

All the catalysts were tested for NO reduction with a mass spectrometer (Quadrupole Balzers 422) connected online as detection system. The mass spectrometer was calibrated using standard mixtures of 2000 ppm NO/Ar, 1000 ppm N_2/Ar, 3000 ppm NH_3, 7% O_2, 1000 ppm N_2O.

A piece of 0.4 g of the catalytic briquette was ground to a particle size between 0.2 and 0.5 mm and placed into a cylindrical quartz reactor of 7 mm internal diameter. The sample was previously heated in Ar until the reaction temperature was reached. Then, the experiment was initiated by substituting Ar by 22.2 ml/min of a reaction mixture containing 1000 ppmv of NO, 1500 ppmv of NH_3, 3.5% (v/v) of O_2 in Ar. The NO reduction tests were all performed at temperatures between 75 and 350 °C and 1.4 s of residence time.

The NO conversion and selectivity towards N_2 were calculated as follows:

$$\text{NO conversion}\,(\%) = \frac{C^{\mathrm{i}}_{\mathrm{NO}} - C_{\mathrm{NO}}}{C^{\mathrm{i}}_{\mathrm{NO}}} \times 100 \tag{1}$$

$$\text{Selectivity}\,(\%) = \frac{C_{\mathrm{N_2}} - C^{\mathrm{i}}_{\mathrm{N_2}}}{(C_{\mathrm{N_2}} - C^{\mathrm{i}}_{\mathrm{N_2}}) + (C_{\mathrm{N_2O}} - C^{\mathrm{i}}_{\mathrm{N_2O}})} \times 100 \tag{2}$$

where $C^{\mathrm{i}}_{\mathrm{NO}}$, $C^{\mathrm{i}}_{\mathrm{N_2O}}$ and $C^{\mathrm{i}}_{\mathrm{N_2}}$ represent the initial concentrations of NO, N_2O and N_2, respectively, and C_{NO}, $C_{\mathrm{N_2O}}$ and $C_{\mathrm{N_2}}$ correspond to their concentrations at the end of each experiment, once steady state is reached.

3. Results and discussion

Three aspects have been considered for comparison between samples: the influence of vanadium sources, the activation procedure and the oxidation procedure.

3.1. Influence of activation process

The influence of the activation process is discussed below. In a previous paper [19], it was predicted that for an optimum behaviour, V components should be loaded on the activated char better than on the char and subsequent activation. This statement was checked and confirmed later on in further work carried out by this group [14,21], and as a result, the samples in this study were firstly activated and subsequently impregnated.

According to these previous studies [14,21], steam and CO_2 activation of the carbon briquettes was carried out in order to improve their capability to accommodate the future vanadium load.

With respect to the activity of the different catalysts prepared, Fig. 1a shows the NO conversion measured at 150 °C of four briquettes, Br/A/600/2/H_2O, Br/A/700/2/H_2O, Br/A/700/2/CO_2 and Br/A/800/1/CO_2 impregnated with V_2O_5. The values NO conversion reached with these catalysts alters between 38 and 57%. Selectivity towards N_2 was above 90% in all cases.

It is observed that the activation process has a main influence in the catalyst activity. Generally speaking, an increase in temperature and residence time results in an improvement in the NO reduction efficiency. When the activation process is carried out at the same conditions except for the activating agent, it can be observed that the NO reduction capability of CO_2 activated briquettes is slightly higher that the steam activated ones.

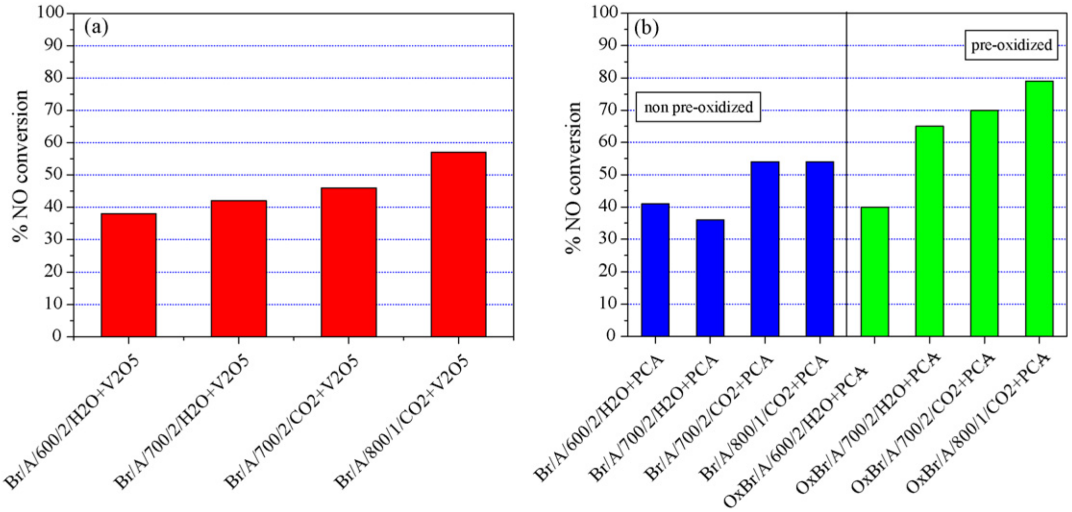

Fig. 1. NO reduction of different catalysts. (a) Catalysts activated under different conditions loaded with V_2O_5 as active phase and (b) catalysts prepared using the non-pre-oxidised and pre-oxidised carbon briquettes, using PCA as active phase.

Table 2
Results of physical and chemical characterisation of the carbon briquettes

Sample	SSA (m^2/g)	CO (cm^3/g cat)	CO_2 (cm^3/g cat)	CO + CO_2 (cm^3/g cat)	CO/CO_2
Pyrolysed briquette	101.5	16	2	18	8
Br/A/600/2/H_2O	145.64	24	25	48	1.04
Br/A/700/2/H_2O	259.25	26	12	38	0.46
Br/A/700/2/CO_2	154.78	31	14	45	0.45
Br/A/800/1/CO_2	255.95	28	13	41	0.46

To clarify the influence of the severity of the support activation process on the activity of the resulting catalysts, the values of SSA as well as the amounts of CO and CO_2 evolved during temperature programmed desorption runs are presented in Table 2. At the sight of these results, it can be observed that in general as a consequence of the activation process higher SSA values have been measured for the activated briquettes in comparison to the non-activated ones, suggesting that physical activation, either with steam or with CO_2, produces an increase in porosity, being likely caused by the opening of blocked pores in the char porosity and the development of new interconnecting pores [22]. As expected, the values of surface area increase when increasing the temperature of the activation process. With respect to the effect of the activation agent, it can be observed that higher values of surface areas have been measured for the carbon briquette activated with CO_2 than for the one activated with H_2O, at the same temperature and residence time. This indicates that the gasification proceeds slowly when using CO_2 as activating agent. Nevertheless, what can be observed is that the surface area of the carbon briquettes is not directly related with the activity of the resulting catalysts. It seems that although a minimum porosity development is needed in order to avoid pore blockage when the active phase is added, once this threshold value of surface area is reached, a further increase of this parameter is not followed by an improvement of the catalytic activity.

During the TPD experiments, the surface acidic groups evolve as CO_2 products, while the less acidic groups evolve as CO. It has been reported, NO conversion is favoured by less basic or more acidic activated carbons [23,24]. These groups are thought to favour the adsorption of the reactants, i.e. NH_3, during reaction. The more basic groups, evolving as CO in TPD runs, such as –OH functionalities, have been proposed as the more favourable sites for the fixation of the vanadium compounds [25]. The slightly increased presence of these functionalities on the surface of the briquettes activated with CO_2 may have been responsible of a stronger fixation of the V_2O_5, resulting in a better dispersion of the active phase and in a favoured interaction with the carbon support, what has led to a higher activity in the reduction of NO.

3.2. Influence of oxidation process

To obtain carbon briquettes with higher concentrations of acidic surface groups, chemical oxidation using agents like HNO_3 can be performed. As a result, a more hydrophilic surface will be obtained, with a relatively large number of oxygen-containing surface groups that are supposed to improve the wetting of the support surface and that would also contribute to evenly disperse active phase [26]. Comparing the NO reduction reached by oxidised carbon briquettes with the non-oxidised ones, both loaded with PCA, a considerable increase in the activity *can be* observed (see Fig. 1b) in most cases for the catalysts prepared using the pre-oxidised briquettes.

Table 3 shows the results of the physical and chemical characterisation of the oxidised carbon briquettes. A small decrease in the SSA values is measured for the oxidised briquettes in comparison with the non-oxidised ones. This small decrease has been previously reported by other authors [27] and was attributed to the widening of the micropores, as a result of the oxidising treatment. In spite of this, and as a main consequence of HNO_3-oxidation, important differences are observed in the surface chemistry of the carbon briquettes, as shown by the results of the TPD runs. In this way, an important increase in the amount of the CO_2 evolved during the TPD experiments can be generally observed.

Some of the oxygen surface groups generated as a consequence of the oxidation process, may be responsible for a chemically controlled vanadium anchoring on the surface of the carbon briquette, their strong acidic character (i.e. of carboxylic groups) might be responsible for a stronger adsorption of ammonia, what may help to create a reservoir of this reactant while the reaction takes place, thus resulting in an increased catalyst activity. The only exception to this rule is the PCA-loaded OxBr/A/600/2/H_2O briquette, which shows similar activity than the one measured for the catalyst prepared using the non-oxidised carbon briquette. The explanation is not straightforward, but it can be due to the lower SSA of this carbon briquette. The scarcely developed pore structure leads to a non-appropriated dispersion of

Table 3
Results of physical and chemical characterisation of the pre-oxidised carbon briquettes

	SSA (m^2/g)	CO (cm^3/g cat)	CO_2 (cm^3/g cat)	CO + CO_2 (cm^3/g cat)	CO/CO_2
OxBr/A/600/2/H_2O	1.58	34	44	78	1.29
OxBr/A/700/2/H_2O	15.97	34	43	78	1.26
OxBr/A/700/2/CO_2	–	33	35	69	1.06
OxBr/A/800/1/CO_2	113.68	28	31	59	1.11

vanadium, or transition metals in the case of PCA, what results in pore blockage, thus causing a fall in the NO reduction, despite of the increased presence of surface groups after the oxidizing treatment.

However, although it is true that the decrease in specific area after oxidation may not easily be neglected, what we have observed is that the influence of this parameter in the catalytic activity is not as important as the influence of the oxygen surface groups formed by the oxidation process. In previous works [14,15], we have found that once a minimum development of surface area is reached (more than 100 m^2/g, with an important contribution of wide micropores and mesopores), the pore blockage after deposition of the active phase is avoided. Moreover, a further increase of this parameter is not followed by an improvement of the catalytic activity. Thus, the relationship between surface area and catalytic activity is not straightforward.

3.3. Influence of the reaction temperature: PCA versus V_2O_5 as precursors of the active phase

To ensure the performance of these catalysts in a wider temperature window, experiments were carried out at temperatures between 75 and 350 °C. Fig. 2 shows the NO conversion at these temperatures, for two catalysts prepared using PCA or V_2O_5. The variation of reduction efficiency with temperature when using the PCA as the active phase is similar to that observed for the samples doped with V_2O_5. This fact further demonstrates that the metal compounds present in the PCA can be successfully employed for the preparation of SCR catalysts, with similar activities than the ones prepared using model vanadium compounds. The little differences in activity observed can be due to the more complex composition of PCA and to the weaker interactions with the activated carbonaceous support, probably as a result of the less solubility of the PCA, and to the presence of greater amounts of non-dissolved material when using PCA as the precursor of the active phase [19].

The two curves present similar appearance. Initially, the percentage of NO conversion decreases with the increase in the temperature up to 100 °C. Then, the activity increases suddenly with the temperature reaching higher values at 300 °C. The first part of the curves could be attributed to the increased adsorption of the gases, probably of NH_3, in the catalysts or in the activated carbon surface. However, some N_2 production was observed during reaction at low temperatures, thus indicating that although adsorption of NO on the catalyst surface might be occurring to some extent, a catalytic reduction of NO to N_2 may be taking place at the same time.

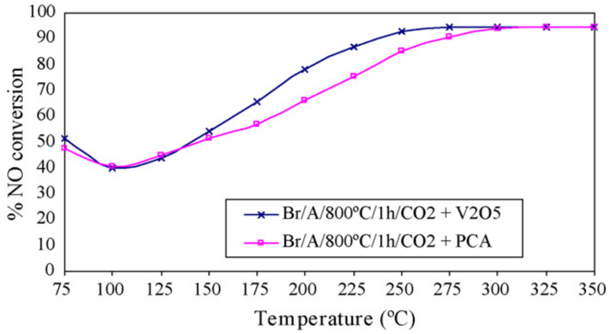

Fig. 2. NO conversion at temperatures between 75 and 350 °C, for the catalysts Br/A/800/1/CO_2 + V_2O_5 and Br/A/800/1/CO_2 + PCA.

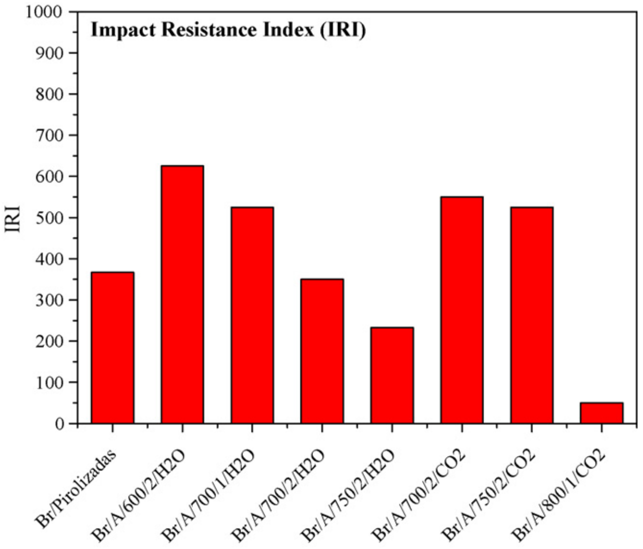

Fig. 3. Impact Resistance Index (IRI) determined for the carbon briquettes prepared.

3.4. Mechanical strength

Mechanical strength was tested by means of Impact Resistance Index (IRI). This index has been calculated according to the specifications of Richards [28]. Fig. 3 shows the impact index determined for some of the briquettes that are presented in this paper. It can be observed the values of all samples were above the minimum values recommended by Richards (IRI = 50).

4. Conclusions

The catalytic briquettes presented in this paper have shown to be considerably active for the NO reduction (NO reductions between 40 and 80%) with the addition of ammonia at a wide range of temperatures (75–350 °C). The most efficient catalysts are those prepared with the stricter activating conditions and an additional oxidation process before impregnation of the active phase.

It has been observed that although a proper development of the porous structure is fundamental in order to avoid pore blockage, the presence of oxygen surface functionalities is of key importance to achieve an adequate distribution and fixation of the active phase. The presence of these groups may contribute also to the adsorption of the reactants during the NO reduction reaction.

Although slightly lower NO conversions were measured for the samples prepared with PCA, it can be concluded that they are useful for the preparation of active catalysts for the reduction of NO under the conditions tested.

Mechanical strength, determined by means of Impact Resistance Index, shows values above the minimum recommended in literature for fuel briquettes.

The expected low-cost, the considerable activities measured even at low temperatures and the particular shape of these catalysts, make them suitable for being applied in small and medium facilities, thus avoiding some of the main problems of the use of the nowadays commercial TiO_2-based catalysts.

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