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ScienceDirect
Catalysis Today 137 (2008) 209–214
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Carbon based catalytic briquettes for the reduction of NO: Catalyst scale-up

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Available online 21 February 2008

Abstract

Exhaust gasses from small and medium stationary sources contain NO_x that will be regulated by new European legislation in the coming years. Among all the processes the SCR-NH_3 seems to be the more promising one. However, the application of commercial catalysts to these new facilities presents some drawbacks such as the high and narrow operation temperature, its low withdraw to SO_2 or its high cost production.

In order to improve this technology, in previous works, carbon-supported catalytic briquettes have shown a good kinetic performance under the above commented conditions. In this study, other aspects such as thermal stability, long-term performance, spatial velocity influence and mechanical resistance were evaluated. Finally, a simple economic assessment was carried out providing a three times lower cost production than commercial catalysts. From all the data collected, there are some evidences that these catalyst briquettes will have a good performance in small and medium facilities, being an interesting alternative to commercial ones.

Keywords: Briquette; Carbon based catalysts; SCR-NH_3

1. Introduction

Exhaust gases from stationary and mobile combustion sources contain NO_x that cause a variety of environmentally harmful effects. Taking into account these problems, governments from developed countries propose an each stricter legislation in the coming years that will also affect to the medium and small stationary sources like IGCC plants, static diesel engines or adiptic acid production plants.

Among all the technologies the selective catalytic reduction (SCR) of NO_x by NH_3 has gained eminent importance because of its high efficiency. However, it is widely known that, nowadays this technique, with the available commercial catalysts, implies an important economic effort for all medium–small stationary sources. Moreover, the current TiO_2 supported catalysts present very serious drawbacks to be successfully installed in this kind of facilities. In the high temperature window (300–500 °C) where they operate, SO_2 and particle poisoning are great disadvantages [1]. In addition, the effluent gas should be re-heated after the particle removal equipment and the desulfuration device, because at this point the temperature is about 250 °C, being this fact an extra operation cost. Understandably, therefore, there is an increasing interest in developing low temperature catalysts (<250 °C) capable of working without the need for re-heating the gas. Eventually, it would be desirable that these novel catalysts have a good mechanical performance, thermal stability, long performance as well as a low production cost.

Carbon has been studied as catalyst support for the low temperature SCR of NO_x by a number of authors [2–4] due to its high surface area, chemical stability and good performance. Moulding this support into a structured shape with low pressure drop presents some advantages over powder conventional catalysts. According to these objectives, a procedure for preparing catalysts supported on low-rank coal briquettes with coke petroleum ashes (PCA) as an active phase has been developed [5]. PCA contains a high amount of vanadium, iron and nickel among other transition metals showing a good performance in the low temperature SCR [6–8]. In previous works, really interesting results have been found for low-rank coal briquettes doped with PCA [5]. In these studies, considerable activity and selectivity were reported at temperatures between 150 and 250 °C, in presence of ammonia and oxygen excess and in addition, they presented kinetic

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2007.11.004

parameters similar to other catalysis reported in literature and proposed for the same application [6]. In the present paper, catalytic briquettes prepared as described in Ref. [5] are tested in a bed fixed reactor, economically evaluated and taken into account their thermal stability, long performance, spatial velocity influence and mechanical properties. Therefore, the main aim of this work is to analyze the suitability of this new product for medium–small stationary sources considering different topics apart from the kinetic ones to know if the product could have been easily introduced into the market.

2. Experimental

2.1. Preparation of the catalytic briquettes

The main materials used to produce catalysts have been described in more detail elsewhere [9]. In a few words, a low-rank coal, from SAMCA mines in Teruel, Spain, and a commercial pitch of SP-110 were ground and sieved, subjected to pressure briquetting process, pyrolyzed and subsequent activated as it is described in elsewhere [10]. Two major types of catalytic briquettes were produced: (1) briquettes with an oxidized carbon support and (2) briquettes with a non-oxidized carbon support. The oxidation procedure was carried out before the impregnating one with 1N acid nitric solution. Oxidized samples were named adding-+HNO_3 to the activation name. A coke from the Delayed Coke unit in the REPSOL refinery in Puertollano, Spain, was used for the production of the PCA, as it was explained in elsewhere [11]. The PCA contain 23% (w/w) of V, 3.5% (w/w) of Fe and 3% (w/w) of Ni among other transition metals [12]. The briquettes were impregnated by equilibrium adsorption of 3% (w/w) vanadium.

2.2. Thermal stability

Support and some catalytic briquettes were characterized by thermogravimetric analysis in a CAHN TG 2151 equipment. A piece (around 200 mg weight) was heated under a heating rate of 10 °C/min in an Ar flow of 2000 cm^3/min from room to desired test temperature. When test temperature was reached, gas reaction mixed consisting of 1000 ppmv NO, 1500 ppmv NH_3 and 3.5% (v/v) O_2 in Ar was introduced and maintained for approximately 2 h. Weight loss was calculated as a percentage from the stable weight once reaction temperature was reached.

2.3. Mechanical characterization

Mechanical strength was tested by means of impact resistance index (IRI) and water resistance index (WRI), as described in Ref. [13]. The IRI values were as a function of the number of drops and the number of pieces into which each briquette breaks when it is repeatedly dropped from a stationary starting point at 2 m height onto a concrete floor until it fractured. The WRI values were obtained immersing a weighted briquette in cold tap-water and checking for any tendency to disintegrate.

2.4. Catalytic measurements

All the samples were tested for NO reduction with a mass spectrometer (Quadrupole Balzers 422) connected online as detection system. The mass spectrometer was calibrated using known standard cylinders. Long-term performance, spacial velocity influence as well as catalytic activity tests were carried out in a quartz reactor of 7 mm of diameter with a catalysis weight of 0.4 g. Standard conditions fed to the reactor were 1000 ppmv of NO, 1500 ppmv of NH_3 and 3.5% (v/v) of O_2 in Ar. The NO reduction efficiency was calculated as follows:

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

where C^{i}_{NO} is the measured initial concentrations of NO and C_{NO} corresponds to its concentration once steady state is reached.

2.5. Economic assessment

The economic analysis was carried out by reckoning the costs of investment, energy and other operation costs necessary to set in a factory which produces 1 t per day of catalytic briquettes. The briquette production factory is assumed to be consisted of carbon millers, coke millers, tar millers, blenders, briquetting machines, curing ovens as well as drying ovens, fixed bed for activation and pyrolysis of briquettes, tanks for the impregnation of the support and finally a packing machine as shown in Fig. 1. In the same way, it will be necessary to provide the factory with auxiliary equipment such as compressors, heat exchangers, a boiler, IGCC and piping. Information was obtained from industrial suppliers as well as from other chemical industries which are operating at present. Apart for the investment and operation costs a rough feasibility analysis was carried out taking into account the most common parameters for this kind of production plants.

3. Results and discussion

Since the aim of this work was to evaluate catalytic briquettes for their operation in small and medium stationary NO_x sources some aspects apart from kinetic ones, evaluated in previous works [5,6,14], are discussed below.

3.1. Thermal stability

One of the main drawbacks of carbon supports, previously reported in the literature [15,16], is the lower withstand to temperature in comparison to metal oxide based catalysts. In order to evaluate thermal stability of catalytic briquettes and support some thermogravimetric tests were carried out. First of all, the thermal stability of carbon support was considered as reported in Ref. [14]. For this purpose, a briquette activated at 700 °C (2 h with a 20% steam in N_2) was heated up at three different temperatures as shown in Fig. 2. Even at the highest temperature (400 °C) carbon support does not shown any