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Novel Carbon Based Catalysts for the Reduction of NO with Coke Petroleum Ashes as Active Phase: Synthesis and Characterisation

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Abstract

Carbon-based catalysts in powder, briquette and monolith forms have been prepared. Powder and briquette samples have been obtained from low-rank coal whereas monolith samples were prepared by coating cordierite monoliths with a blend of two polymers, namely, furan resin and polyethylene glycol. Vanadium was impregnated in these carbon-based catalysts by equilibrium adsorption using the ashes of a petroleum coke (PCA) as precursor and they were tested in the SCR of NO at low temperature. PCA contains around 23 % V, 3 % Fe and 3 % Ni among other transition metals and this use is an undeniable good way for its revalorisation. As-prepared catalysts have demonstrated a considerable efficiency which was enhanced by pre-oxidizing treatments and an increase of vanadium loading. The presence of oxygen surface functionalities is of key importance to achieve an adequate distribution and fixation of the active phase while an excess in vanadium loading can even cause pore blockage decreasing the total efficiency. External diffusion and pressure drop coefficients were calculated for the three kinds of catalysts. As expected, powder catalyst shows the highest pressure drop while briquette and monolith samples show lower pressure drop values with no sign of diffusion limitations. For this reason, these structurated catalysts are considered to be more suitable for industrial applications.

INTRODUCTION

Without any doubt selective catalytic reduction (SCR) in the presence of NH_3 is nowadays one of the most outstanding technologies for the removal of NO_x [1]. Commercially available, this technology is based on vanadium catalysts supported on metal oxides such as TiO_2, Al_2O_3 or SiO_2 [2]. Although this technology presents a high efficiency, there are some challenges related to the used catalysts that should be overcome in the coming years. These main drawbacks are the high temperature range (300–500 °C) needed for optimal operation, as well as SO_2 and particle poisoning [3]. To avoid these problems, the SCR unit is usually placed downstream of the desulphuration and particle removal device where both SO_2 and ashes have been removed, the gas being subsequently reheated to the required temperature [4, 5]. However, since the temperature at this point is typically below 200 °C another alternative is to use a catalyst that allows operation at lower temperatures being resistant to SO_2 poisoning at the same time. Catalysts prepared using carbon materials have shown to fulfil these two requirements as it has been demonstrated earlier by some authors such as Zhu *et al.* [20, 21], Marban *et al.* [22] or García-Bordejé *et al.* [23].

Carbonaceous materials are effective supports which present a wide range of advantages over commercial catalysts like the simplicity of the preparation process, a potentially lower production cost, easy availability of coal, possibility of obtaining samples with proper geometry, good mechanical resistance and especially an efficient performance at low temperature in the NO reduction [6]. The potentially lower production cost of carbon-based catalysts is enhanced providing that a residue is used as active phase. With this objective in mind, petroleum coke ashes (PCA) with high vanadium content have been supported on powder catalysts [7] as active phase showing efficiencies similar to other vanadium model compounds. In this work, PCA have been used as active phase of structured carbon based catalysts. Structured catalysts (briquettes and monoliths) present the advantage of causing a lower pressure drop what avoids additional operational costs to the stationary plants where they are applied [8]. These catalysts have been tested and characterized by means of N_2 adsorption and temperature programmed desorption (TPD) showing that carbon supports, vanadium loading as well as temperature operation range have a great influence on their whole performance.

EXPERIMENTAL

Catalyst preparation

Three kinds of carbon based catalysts under different forms and compositions have been prepared. Firstly, powder catalysts with a particle size between 0.2–0.5 mm was obtained from a low-rank coal from SAMCA mines in Teruel (Spain). This coal was pyrolysed in N_2 at 800 °C, activated with 20 % steam in N_2 and finally oxidized with HNO_3 as described in detail elsewhere [9]. Secondly, briquette carbon support was obtained from the above mentioned coal and commercial pitch. Briefly the preparation process consists in coal pyrolysis, blending with the ground commercial tar pitch, briquetting process by pressure performed in a device specially designed to this purpose, curing in an electric furnace with air, pyrolysis of briquettes under N_2, activation either with 20 % of water vapour in N_2 or CO_2 at different temperatures and oxidation with HNO_3 (1 M). The activation, as well as the pyrolysis, were conducted in a fixed-bed reactor as described in more detail elsewhere [10]. Finally, cordierite monolith carbon based supports were prepared. In this case cordierite monoliths were coated with a carbon layer by means of the dipcoating method as described in detail elsewhere [11]. Briefly, it consists in dipping the cordierite monolith (400 cpsi, 1 cm diameter and 5 cm length) into a liquid polymer that is subsequently cross-linked and carbonised. To coat the monoliths two carbon precursors were used: polyethyleneglycol 6000 molecular mass (Sigma–Aldrich) (PEG) and Furan resin (Huttenes–Albertus). After dipcoating, the sample was cured, carbonized in Ar, activated with CO_2 and treated with HNO_3 (2 M and 4 M) at room temperature to create oxygen superficial groups [12].

In all cases after carbon support preparation, catalysts were loaded with 1, 3, 5 or 6 % (w/w) V by equilibrium adsorption using either V_2O_5 as a model vanadium compound or PCA. A solution/suspension of each of these compounds in distilled water was stirred and the sample was introduced inside for 3 h. After stirring samples were rinsed and dried overnight.

PCA supplied from a coke form the Delayed Coke Unit in the REPSOL refinery in Puertollano, in Spain, were obtained by combustion under air at a temperature up to 650 °C. The PCA contain mainly 23 % (w/w) of V, 3.5 % (w/w) of Fe and 3 % mass of Ni among other components as described in [13].

Catalyst characterisation

Carbon support and catalysts were physically and chemically characterised by means of two different methods and techniques: adsorption of N_2 at 77 K and temperature-programmed desorption (TPD). Specific surface area was calculated from the N_2 adsorption isotherms applying BET equation in an ASAP-2000 apparatus. On the other hand, TPD tests were 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 a TCD.

Activity tests

The NO reduction efficiency of the catalysts was determined by passing a gas mixture containing 1000 ppm of NO, 1500 ppm of NH_3 and 3.5 vol. % of O_2 in Ar through a fixed bed containing 0.4 g of sample in the case of powder and briquette samples or just a single monolith in the last case. The composition of the gas exiting the reactor was continuously measured in a quadrupole mass spectrometer (Balzers 422) connected on-line. The conversion of NO was calculated as follows:

$$\%\,\mathrm{NO\,reduction} = (C^i_{\mathrm{NO}} - C_{\mathrm{NO}})C^i_{\mathrm{NO}}100$$

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

RESULTS AND DISCUSSION

Influence of carbon support on the NO reduction efficiency

Carbon support characteristics have shown to be a key factor in the NO reduction efficiency of the catalysts prepared. At the sight of the results presented in Table 1, porosity development obtained by an increase in temperature and residence times of activation process is thought to be essential for achieving large metal dispersions, which usually results in a high catalytic activity [14]. Therefore and

TABLE 1

Values of S_{BET}, total micropore volume (V_{mic}), CO and CO_2 evolved in TPD runs and catalytic activity of powder, briquette and monolith carbon based supports and % NO reduction with either PCA or V_2O_5 as active phase of prepared catalysts

Sample	S_{BET}, m^2/g	V_{mic}, cm^3/g	V_{med}, cm^3/g	CO + CO_2, cm^3/g	CO + CO_2, cm^3/g oxidized	% NO reduction	
						PCA	V_2O_5
			Powder carbon supports				
SC800	55	0.001	0.022	24.4			
SCA600	213	0.043	0.051	37.0			
SCA750	398	0.114	0.069	47.4			
SCAOX	309	0.052	0.12		93.3		
			Powder carbon-based catalysts				
SC800	7.5	0	0.0012			26	29
SCA600	8.2	0	0.0017			27	33
SCA750	344	0.145	0.021			45	55
SCAOX						88	85
			Briquette carbon supports				
Br/A/600/2/H_2O	145.2	0.046	0.024	49	78		
Br/A/750/2/H_2O	309.1	0.084	0.064	32	54		
Br/A/700/2/CO_2	259.7	0.072	0.048	49	62		
Br/A/800/1/CO_2	255.9	0.067	0.049	41	59		
			Briquette carbon-based catalysts				
Br/A/600/2/H_2O	2.8	0.064	0.032			34	36
Br/A/750/2/H_2O	277.7	0.070	0.045			52	47
Br/A/700/2/CO_2	105.6	0.012	0.013			42	42
Br/A/800/1/CO_2	181.9	0.039	0.038			50	54
			Monolith carbon-based support				
Mn + HNO_3 2N	825	0.21	1.52		125		
Mn + HNO_3 4N	775	0.20	1.48		98		
			Monolith carbon-based catalysts				
Mn 3 % V					43.3	43	
Mn 6 % V					61.2	74	

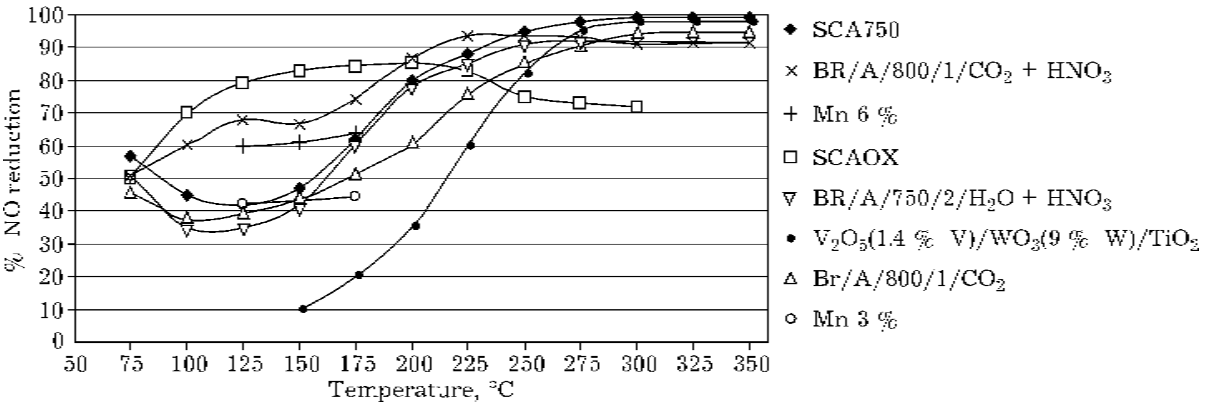

Fig. 1. NO conversion of samples under different temperatures.

especially in powder and briquette samples the activation process results in an increase in porosity due to the opening of constrictions in the char porosity and the development of new interconnecting pores [15]. Samples without a pre-oxidizing treatment showed a possible pore blockage when the surface area of the unloaded support was below 100 m^2/g. This value of surface area is supposed to be the threshold for a good performance in this kind of experiments. Powder and briquette samples have mainly a microporous structure whereas monoliths are mainly mesoporous.

On the other hand, surface chemistry seems to play an important role on the NO reduction. Oxidized briquette and powder catalyst samples have an average increase of 25 % in comparison to non-oxidised samples. This enhancement is expected to be a consequence of HNO$_3$ treatment when new oxygen groups are created. The amounts of CO and CO$_2$ evolved in TPD experiments are presented in Table 1. In the case of monolith catalysts two samples were treated with HNO$_3$ 2 M and 4 M, respectively. Comparing both samples, it is observed that increasing the severity of HNO$_3$ treatment entails some decrease of micro- and mesopore surface area while the variation of pore volume is of little significance. This fact can be explained by the collapse of pore walls and the ensuing widening of the pores, as a consequence of the acidic treatment [16]. It can be also observed that the more severe oxidized sample adsorbs a lower amount of vanadium and therefore reaches a lower catalytic activity. Oxygen surface groups are responsible for the fixation of the metal compound on the support surface [24]. At the same time, these functionalities provide the catalyst surface with Brönsted acid sites where adsorption of basic species, such as NH$_3$, can take place.

Influence of temperature and vanadium loading on the NO reduction efficiency

Operation temperature range of carbon based catalysts is considerably lower than that of commercial catalysts [17]. Taking into account the most common temperature range where catalysts should work in a small stationary source of NO, prepared carbon catalysts were tested in the range of 100 to 300 °C. The eight curves shown in Fig. 1 present a similar appearance. Initially, the percentage of NO conversion decreases with the increase in the temperature up to around 150 °C. From this point on, the activity increases suddenly with the temperature reaching higher values at 300 °C. In the lower temperature part of the curves, the higher NO conversion could be attributed to the adsorption of NO on the catalyst surface and not properly to a reduction reaction. However, N$_2$ production is 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$_2$ is surely taking place at the same time. The higher NO removal efficiency at the lowest temperatures can be due to enhanced NH$_3$ adsorption, as a first step in the reduction reaction. Finally, it can be clearly observed that

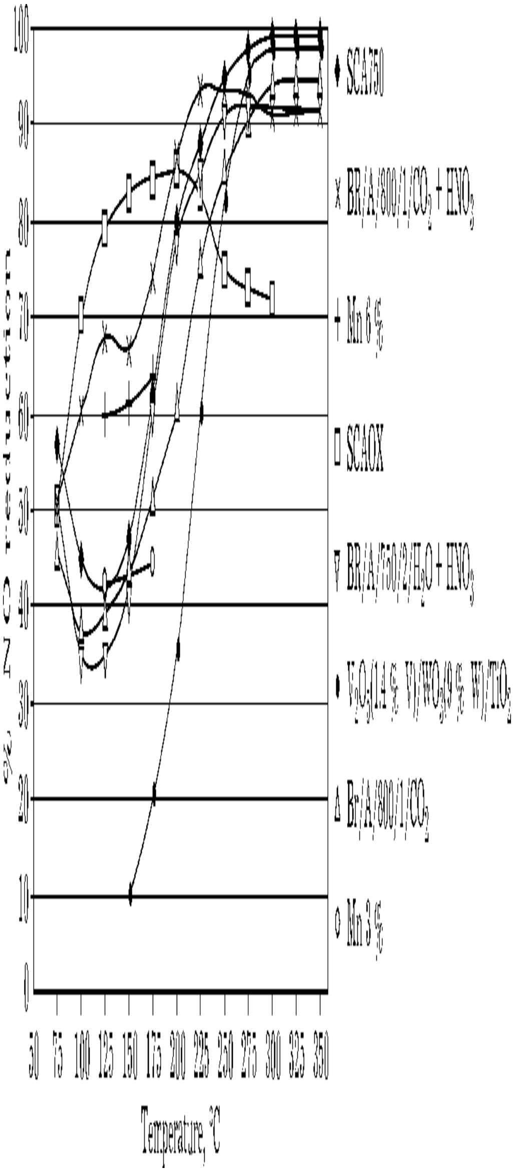

Figure 2. SEM pictures of catalysts (SCA750/PCA) prepared with different amounts of vanadium from PCA, %: 1 (*a*), 3 (*b*), 5 (*c*).

the V_2O_5–WO_3/TiO_2 [18] catalyst is less effective than the activated carbon-based catalysts, in the removal of NO in the temperature range between 150 and 250 °C.

An increase of vanadium loading leads in all cases to an enhancement of the activity. As shown in Table 1, an increase in the model vanadium compound loading (V_2O_5) leads to an important increase in the catalytic activity whereas an increase in the PCA vanadium loading only triggers a slightly increase in the catalytic activity. This fact could be attributed to a possible pore blockage when PCA are used as active phase. According to SEM pictures shown in Fig. 2, the higher the PCA loading the higher the agglomeration of the active phase on the surface and consequently the worse the dispersion of vanadium causing a decrease in the NO reduction efficiency.

Influence of structuration on efficiency

In order to study the influence of structuration on the catalytic activity, several calculations have been carried out. Generally speaking, the more structured the catalyst is, the lower activity it reaches and the lower pressure drop it presents, this fact could be explained through the diffusion limitations (external or internal) that usually present structurated catalysts and which avoids reaching the maximum NO conversion. However, in industrial applications it is, to some extent, recommended to have a lower pressure drop in a flue gas cleaning system while the NO reduction is slightly lower.

For these reasons and just for the sake of comparison, an estimation of the diffusion limitations was reckoned for all catalysts by means of Fuller, Schtteler and Giddings method as well as the pressure drop as described in [19]. The apparent constant was calculated considering a first order reaction with respect to NO. As shown in Table 2, there are no diffusion limitations in the case of powder catalysts while monolith and briquette samples present closer values between diffusion and

TABLE 2

External diffusion coefficient and pressure drop values

Sample	% NO reduction average	D_p, mm	K_{app}, s^{-1}	K'', s^{-1}	Δh, Pa
Powder	60	0.35	0.837	463.0	8512.16
Briquette	40	10 × 12	0.123	42.1	$7.05\ 10^{-5}$
Monolith	60	10 × 50	0.016	34.1	0.084

apparent constants. Although the smaller difference in the cases of briquettes and monolith samples, these values suggest a non-diffusion limitation. According to the pressure drop, powder catalyst presents the highest pressure drop, followed by briquette samples and finally monolith samples. Taking into account these data, monoliths seem to be the best catalyst form to be used in industrial applications.

CONCLUSIONS

In this work, carbon-based catalyst in powder, briquette and monolith samples was shown to be considerably active for the NO reduction with the addition of ammonia at a wide range of temperatures (75–350 °C). The most efficient catalysts are those prepared by means of an oxidizing pre-treatment with HNO_3 before impregnation of the active phase. It has been observed that even though 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 contributes also to the adsorption of any of the reactants involved in the reduction of NO, such as NH_3.

Petroleum coke ashes (PCA) have demonstrated to reach NO reduction efficiency similar to other vanadium model compounds when used as active phase. An increase of vanadium loading leads in all cases to an enhancement of activity. However, an increase in vanadium loading coming from PCA causes a lower increase in the catalytic activity than an increase in the vanadium loading coming from V_2O_5. This fact could be attributed to a possible pore blockage when PCA are used as active phase.

The operation temperature range of carbon based catalyst has shown to be lower than that of commercial catalyst. Prepared catalysts were tested under different temperatures (100–300 °C) showing a good performance on the whole range and reaching the highest values (around 90 %) at 300 °C. This fact should be taken into account for industrial applications since it avoids the necessity of reheating flue gasses before entering the SCR unit.

Finally, a rough comparison between the three kinds of prepared catalysts was carried out. For the sake of comparison, external diffusion coefficients and pressure drop values where calculated. As expected, powder catalyst shows the highest pressure drop values whereas there is no sign of external diffusion control. Briquette and monolith samples show higher external diffusion coefficients without being of importance and much lower pressure drop values. Taking into account these values, it can be sentenced than carbon-based monolith catalysts doped with PCA as active phase are the most suitable catalysts for their application under industrial conditions.

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