

NO REDUCTION BY GRAPEFRUIT SKIN-BASED CARBON CATALYST

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Abstract

NO reduction has been studied at different temperatures (300-500° C) and NO concentrations (200 to 800 ppm) in a fixed-bed reactor using a grapefruit skin-based activated carbon as catalyst. Partial gasification of grapefruit skin with CO₂ at 700° C and low activation degree produced an activated carbon with a relatively high surface area and a high concentration of potassium. The porous structure of the carbons has been characterized by N₂ adsorption-desorption and CO₂ adsorption at -196 and 0° C. The surface chemistry of the catalyst has been analyzed by XPS and TPD. NO conversion of 90% at about 500° C has been obtained. The only nitrogen product observed during the NO reduction by the activated carbon was N₂. The grapefruit skin-based activated carbon submitted to an acid washed process shows a lower NO reduction activity than the non washed carbon, indicating that inorganic matter of the carbon (mainly K) presents a significant catalytic effect for this reaction. The presence of CO in the inlet gas increase the NO reduction to N₂, favoring the CO oxidation. SO₂ produces an irreversible poisoning of the activated carbon for the reduction of NO. However, the presence of SO₂ showed an important enhancement of the NO reduction by CO. The presence of propylene did not show any relevant effect on the NO reduction for the temperature range studied.

Introduction

Activated carbon is a common and effective catalyst support as well as a powerful reducing agent (Zhu et al. 2000) and it can be obtained by different carbonaceous precursors derived from lignocellulosic residues or industrial byproducts (Tancredi et al. 1996, Rodríguez-Mirasol et al. 1993, Márquez-Montesinos et al. 2002). Some authors have studied the NO_x-carbon reactions and found that potassium-supported carbon exhibits a very high reactivity over the whole temperature range studied (Illán-Gómez et al. 1995a,b, Illán-Gómez et al. 1996, Illán-Gómez et al. 1999).

Citrus fruits represent one of the most important agricultural products. A significant proportion of the citric production is destined to transformation activities, as juices and jams manufacturing, which generate considerable amounts of skin residues. These wastes present high mineral matter content, with a significant contribution of potassium. Activated carbons from grapefruit skin with high potassium content have been obtained (Márquez-Montesinos et al. 2002).

The aim of this work is the study of NO reduction reaction on grapefruit skin activated carbon, analyzing the influence of potassium as catalyst and other reducing gases on the NO-carbon reaction.

Experimental

The starting material for this work was the skin of grapefruit harvested from Guadalhorce Valley (Málaga, Spain). The grapefruit skin was carbonized at 700 °C for 2 hours, with a heating rate of 10 °C/min in an inert flow. The char was partially gasified using CO₂ at 700° C for 2 hours, reaching an activation degree of about 50%. The activated carbon is denoted by SC-G. Part of this carbon was acid washed with HCl (2%) and subsequently rinsed with distilled water at room temperature. This activated carbon is designated by SC-GW.

The porous structure of the activated carbons was characterized by N₂ adsorption-desorption isotherms at -196° C and CO₂ adsorption isotherms at 0° C. The surface chemistry of the samples was analyzed by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS).

The NO reduction experiments were performed at different temperatures and atmospheric pressure in a fixed bed reactor, using 300 mg of sample (80mg of activated carbon, diluted with 220 mg of SiC), for a total flow rate of 200 ml/min. NO and NO₂ concentrations were measured by a chemiluminiscent analyzer (EcoPhysics, CLD 700 AL model), and the CO and CO₂ concentrations by means of a non-dispersive infra-red system (Ultramat 22, Siemens model). The rest of the gases were measured by a mass spectrometer (Balzers MsCube). The inlet gas concentrations used for the NO reduction experiments were: 200-800 ppm_v of NO, 2%_v of CO, 1500 ppm_v C₃H₆, 1000 ppm_v SO₂.

Results and discussions.

Table 1 summarizes the values of the structural parameters, derived from the N₂ adsorption-desorption isotherms and from the CO₂ adsorption isotherms, that characterize the porous structure of the carbons studied. The potassium content of SC-G obtained by XPS analysis is also included in the Table. SC-G presents mainly a microporous structure with a low contribution of mesopores and a relatively high surface area. This activated carbon presents a relatively high concentration of potassium. Potassium was completely removed by the acid washing process, which increased the microporous structure of the carbon.

Table 1. Structural parameters derived from the N₂ adsorption-desorption isotherms and the CO₂ adsorption isotherms and potassium content obtained by XPS analysis.

Sample	A _{BET(N₂)} (m ² /g)	V _{t(N₂)} (cm ³ /g)	A _{t(N₂)} (m ² /g)	V _{mes(N₂)} (cm ³ /g)	A _{DR(CO₂)} (m ² /g)	V _{DR(CO₂)} (cm ³ /g)	K(%w)
SC-G	511	0.210	81	0.083	525	0.200	10.7
SC-GW	795	0.345	78	0.082	769	0.293	-

Figure 1 represents the NO conversion as a function of temperatures for SC-G and SC-GW at 200 ppm(v) NO in He and for SC-G at 200 ppm(v) NO and 2%(v) CO. Nitric oxide conversion of 90% has been obtained at about 500° C for SC-G. The presence of K on the surface of this carbon seems to be responsible of the high conversion level at this temperature, given that its removal from the sample lower the activity of the activated carbon. The presence of CO in the inlet gas increases the NO conversion. This enhancement of the NO reduction may be due to a direct reaction of CO with NO catalyzed by the carbon surface or to the reaction of CO with chemisorbed oxygen deposited by NO on the surface, creating a free active site for further reaction with NO (Li et al. 1998).

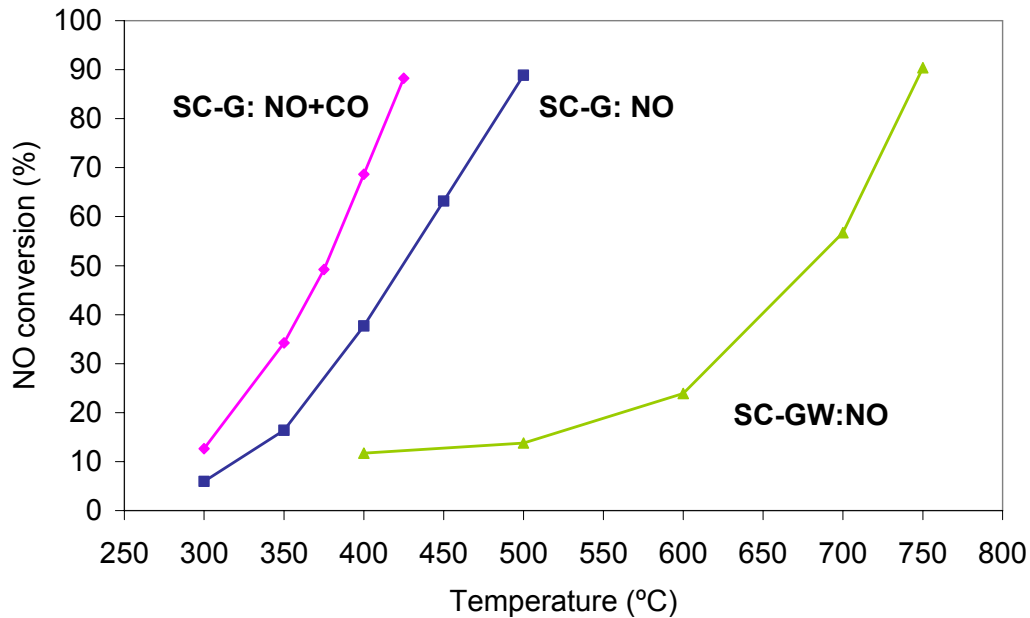


Figure 1. NO conversion as a function of temperatures for SC-G and SC-GW (200 ppm(v) NO in He) and for SC-G (200 ppm(v) NO and 2%(v) CO).

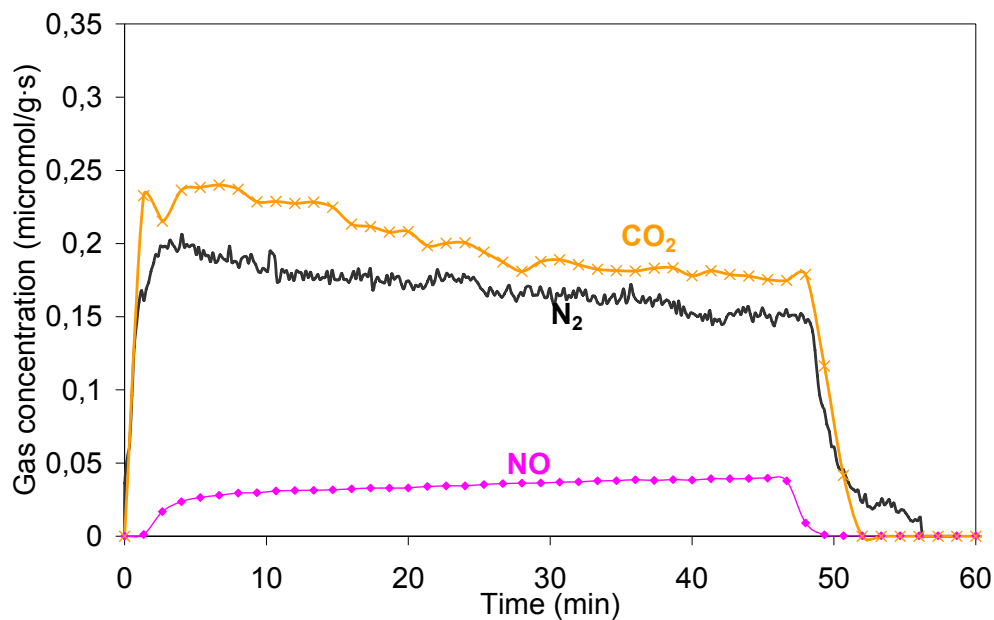


Figure 2. Outlet gas concentration as a function of reaction time for NO reduction by SC-G at 500° C (200 ppm_v NO).

Figure 2 shows the outlet gas concentration as a function of reaction time for the NO reaction on SC-G at 200ppm_v NO and 500° C. NO is reduced by the carbon to N₂ and CO₂ as the only products and the balance of oxygen and nitrogen are almost totally closed at this temperature.

Figure 3 shows the influence of CO on the NO reaction with SC-G carbon at 400 °C. The presence of CO in the gas flow increases the NO activity and the products remains the same as in the absence of CO, N₂ and CO₂. The nitrogen and oxygen balance is in concordance with the equimolar reaction between NO and CO. When CO is removed from the inlet gas flow the initial NO conversion is reached.

The influence of SO₂ on the NO-carbon reaction was studied at different temperatures and different concentrations of SO₂. Figure 4 represents the outlet gas concentrations for the reduction of NO by SC-G in the presence of SO₂ at 375° C. The presence of SO₂ produces a notably decrease of the NO conversion and the carbon remains irreversible poisoned. XPS analysis reveals a significant amount of sulfur on the carbon surface, mainly as sulfates and, in a minor extent, as sulfides. A higher SO₂ concentration in the inlet gas showed a faster decrease in the NO activity at the same experimental conditions.

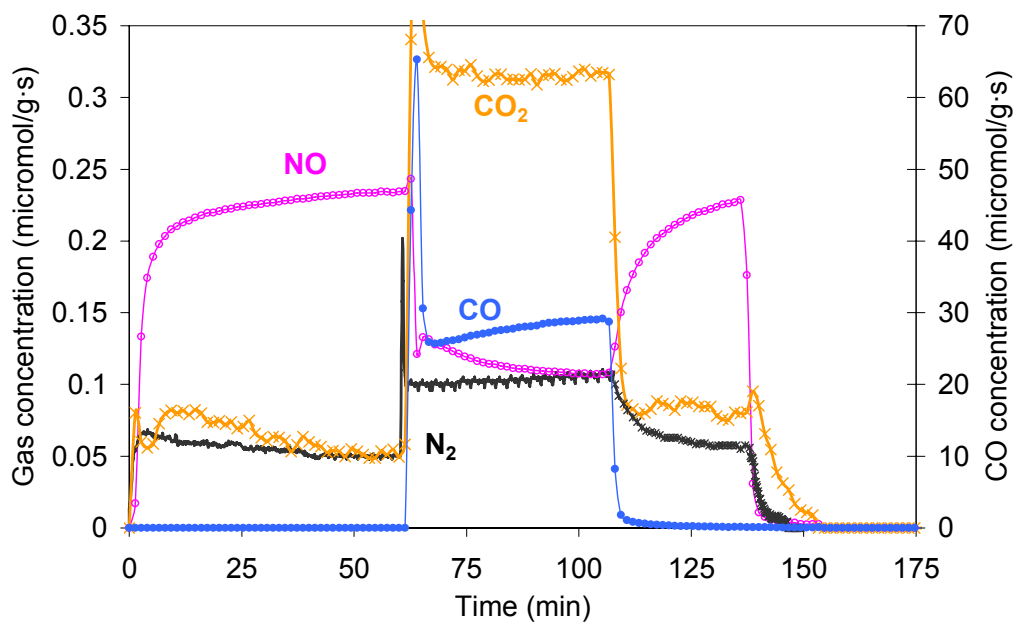


Figure 3. Outlet gas concentration as a function of the reaction time for NO reduction on SC-G at 400° C (200ppm_v NO and 200 ppm_v NO + 1% CO).

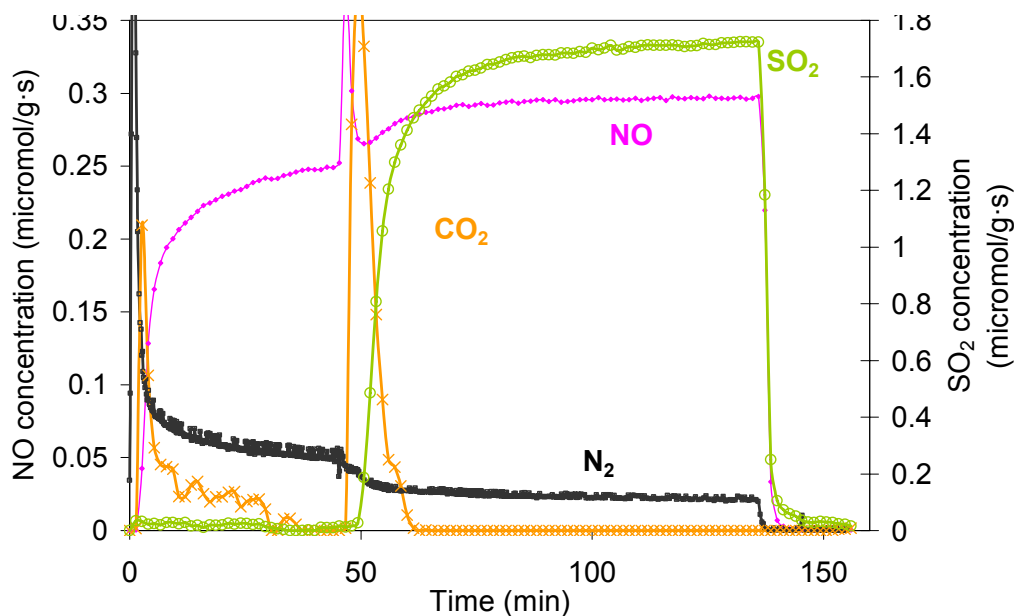


Figure 4. Outlet gas concentration as a function of the reaction time for the NO reduction on SC-G in the presence of SO₂ at 375° C (200ppm_v NO and 200ppm_v NO+1000ppm_v SO₂).

The influence of SO₂ was also studied for NO reduction by CO on SC-G at the same experimental conditions. Figure 5 represents the outlet gas evolution as a function of reaction time for the NO reduction by CO on SC-G in the presence of SO₂ at 375° C, where the gases are introduced successively in the order NO/NO-CO/NO-CO-SO₂. The horizontal continuous lines show the inlet NO and SO₂ concentrations. The presence of SO₂ substantially increases the NO reduction by CO on SC-G carbon. NO is reduced to

N₂ and other products are formed such as COS and H₂S, which did not appear with the mixture NO-SO₂, in the absence of CO. The balance for nitrogen and sulfur is almost closed. However, the presence of sulfates and sulfides on the carbon surface, observed by XPS analysis, confirms the beginning of the poisoning of the catalysts as reaction takes place. Nevertheless, the presence of CO clearly seems to delay the poisoning of the catalyst due to the formation of mainly COS.

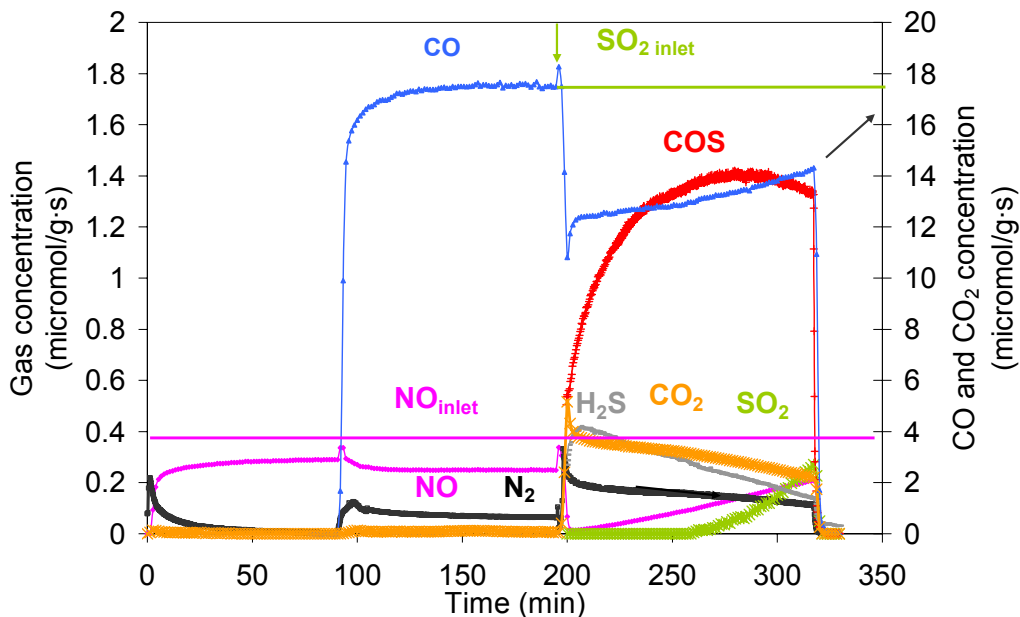


Figure 5. Outlet gas concentration as a function of the reaction time for the NO reduction by CO on SC-G in the presence of SO₂ at 375° C (200ppm NO, 1%CO, 1000ppm SO₂).

The reduction of NO by propylene was also studied on SC-G activated carbon at the same range of temperatures and different propylene concentrations. However, propylene did not increase significantly the NO activity on this activated carbon.

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