DeNO$_x$ Cu/Carbon Xerogels

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Abstract

Carbon materials with different pore texture have been prepared by evaporative drying and pyrolysis of resorcinol–formaldehyde aqueous gels. These carbon xerogels have been characterised and used as copper catalyst supports in the Selective Catalytic Reduction of NO by NH$_3$ at low temperature. Without metal, some activity is observed due to reaction between NO and NH$_3$, but the NO conversion is strongly enhanced after copper introduction. High deNO$_x$ efficiency was obtained on these Cu/carbon xerogels at very low temperature and some pore texture effect was observed. However, special cares have to be taken to avoid carbon consumption and preserve its surface by keeping reaction temperature below 215 °C.

INTRODUCTION

Selective catalytic reduction (SCR) of NO$_x$ using ammonia is commercially used to remove nitro oxide compounds from stationary sources by using conventionally V$_2$O$_5$–WO$_3$ (or MoO$_3$)/ TiO$_2$ catalysts [1], following the reaction:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

However, this kind of catalyst is efficient at temperature higher than 350 °C. For some applications, catalysts operating at low temperature (<350 °C) are required. Carbon supported materials are potential systems for low-temperature SCR processes [2].

Few studies concerning SCR of NO by NH$_3$ have been devoted to Cu/activated carbon catalysts (Cu/AC) [3, 4]. According to Singoredjo *et al.*, carbon supported copper oxides are more active than both titania supported vanadium and vanadium/tungsten oxide catalysts mainly in the low temperature region [5]. Working with a space velocity of 60 000 cm^3/(g · h) and using a reaction mixture of 3 % NO and 3.6 % NH$_3$, a NO conversion of 95 % is obtained on 21 mass % Cu at 200 °C. According to Shigemoto

and Moffat, the conversion of NO into N$_2$ increases linearly with the Cu loading of the catalysts with a maximum at 40 mass % Cu [3]. With 10 mass % Cu/AC, total conversion was obtained at 180 °C using high NO concentration (3 %) and a space velocity of 24 000 cm^3/(g · h). The influence of the metal content on SCR activity and selectivity was also reported by Pasel *et al.* [6]. The latter authors compared CuO and Fe$_2$O$_3$ loaded active carbons as catalysts with different metal content. Both 10 mass % oxide catalysts exhibit better activity and selectivity to N$_2$O at low temperatures than catalysts containing lower metal content. Nevertheless, Zhu *et al.* stressed that 5 mass % copper oxide content is sufficient for having the highest activity ([NO] = [NH$_3$] = 500 ppm, 3 % O$_2$, 36 000 cm^3/(g · h)) [7]. A metal loading lower than 5 mass % is too low but higher Cu loadings lead to aggregation of copper species and result in decreased NO conversions. Since the experimental conditions are very different, it is rather difficult to state conclusions from these studies. Nevertheless, it should be underlined that: *(i)* low space velocities are

usually used and *(ii)* studies with copper content above 15 mass % do not allow apprehending the effect of the support.

Obviously, the catalyst activity can be modified by changing the physicochemical and textural properties of the support. Recent works reported by Job *et al.* have shown that carbon materials with well definite textural properties can be obtained by simple evaporative drying and pyrolysis of resorcinol−formaldehyde gels, provided that the synthesis conditions are well chosen. They shaped the morphology of the porous carbon prepared by sol−gel process by varying the initial pH of the precursors solution [8, 9]. Therefore, the goal of this preliminary study was to evaluate the SCR activity of copper catalysts dispersed on supports prepared by sol−gel process and to examine the effect of the support texture on the catalyst performances.

EXPERIMENTAL

Support and catalyst synthesis

Carbon xerogels were prepared by evaporative drying and pyrolysis of aqueous resorcinol−formaldehyde gels. The dilution ratio, *i.e.* the solvent/(resorcinol + formaldehyde) molar ratio, was chosen equal to 5.7. The pore texture of the carbon materials was adjusted as desired by fixing the pH of the precursors solution to adequate values ranging from 5.25 to 6.25. After gelation (72 h at 70 °C), drying under vacuum and pyrolysis at 800 °C under N_2 flow, three supports with very different maximum pore sizes were obtained: one micro-mesoporous with small mesopores (10 nm), one micro-mesoporous with large mesopores (40 nm), and one micro-macroporous (80 nm).

After crushing and sieving in order to prepare pellets with diameter ranging from 1250 to 1000 μm, the Cu/C catalysts were obtained by impregnation with $Cu(NO_3)_2$ solutions. Two impregnation methods were used: *(i)* the wet impregnation method (WIM), *i.e.* the immersion of the support in an excess of metal salt solution. The concentration is adjusted so that the volume of liquid entering into the pore network contains the metal amount to be deposited on the support; the procedure is

followed by filtration and drying; *(ii)* the impregnation (IMP) using an excess of solvent containing the exact amount of metal to be dispersed on the support, the solvent being removed by evaporation.

For comparison, two catalysts were prepared by impregnation (IMP) on commercial activated carbon (L3S) supplied by CECA: one with a low metal content labelled "Cu_l" and the other with a higher amount of copper, "Cu_h".

Support and catalyst characterization

Temperature programmed decomposition (TPDec) was performed onto carbon supports from room temperature up to 900 °C (5 °C/min) in helium flow (25 cm^3/min). The evolved gases were monitored on-line and analysed with an OMNISTAR Pfeiffer Vacuum mass spectrometer. The mass/charge (*m/z*) ratios 28 and 44, which correspond to CO and CO_2 respectively, were particularly followed.

The elemental analysis of the materials was performed using plasma atomic absorption spectroscopy at the Service Central d'Analyse du CNRS (Vernaison, France).

Catalytic tests

The reduction of NO by NH_3 was performed over a catalyst bed packed in a Pyrex tube 1.4 cm in diameter. The bed was constituted of 0.02 g of crushed catalyst pellets. A type K thermocouple was placed close to the bed for temperature measurements. Reactant gases (NO, NH_3, O_2) were fed to the reactor using mass flow controllers, and helium was added to make up a total flow rate of 138 cm^3/min with reactant content equal to 0.2, 0.2 and 3 % for NO, NH_3 and O_2, respectively. The SCR effluents composition was continuously monitored by sampling on-line to a quadruple mass spectrometer (OMNISTAR Pfeiffer Vacuum). The NO reduction experiments were decomposed into two successive and similar runs to study the influence of activation step. Each run consisted of: *(i)* a heating step, from 120 to 300 °C, and *(ii)* a plateau at 220 °C for 3 h to study the catalyst stability.
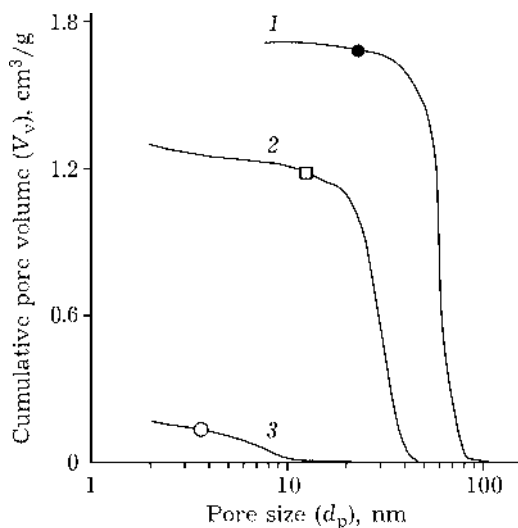
Fig. 1. Mesopore and macropore size distributions for the three carbon xerogel supports before impregnation: *1* − X-525, *2* − X-560, *3* − X-625.

RESULTS AND DISCUSSION

Characterization of carbon xerogels

The texture of the carbon xerogels was tailored by fixing the initial solution pH at an adequate value: the total pore volume, V_v, decreases from 2.1 to 0.41 cm^3/g while increasing the solution pH from 5.25 to 6.25. All samples contain approximately the same volume of micropores (0.25−0.26 cm^3/g). Figure 1 shows the mesopore and macropore size distribution of the

three supports. Sample X-525 is micro-macroporous with a maximum pore size close to 70 nm. X-560 is micro-mesoporous with large mesopores (maximum pore size is 40 nm) and X-625 is micro-mesoporous with small mesopores (maximum pore size is 10 nm). The micropore volume of the activated carbon L3S is close to that of carbon xerogels (0.25 cm^3/g) but its total void volume value (V_v) remains lower than that of the two most porous xerogels (0.79 cm^3/g).

From the heating of activated carbons under inert atmosphere, CO, CO$_2$ and H$_2$O emissions evolve [10]. The CO and CO$_2$ profiles of the carbon supports free of metal are reported in Fig. 2. The desorption temperatures of CO (see Fig. 2, *a*) and CO$_2$ (see Fig. 2, *b*) are characteristic of specific oxygenated surface groups [10]. CO emission at 600−700 °C results from the dissociation of phenol and ether groups, while carbonyl and quinone functions are stable up to 700 °C. The tailing of CO$_2$ desorption peak between 200 and 400 °C corresponds to decomposition of carboxylic acids. Carboxylic anhydride and lactone groups are thermally more stable and usually decompose at higher temperature (400−600 °C). Note that the presence of anhydride groups can be due to the in situ condensation of vicinous carboxylic acids [11]. Quantitative results are given in Table 1. The amount of oxygenated functional groups detected in carbon xerogels is in the range of the non-
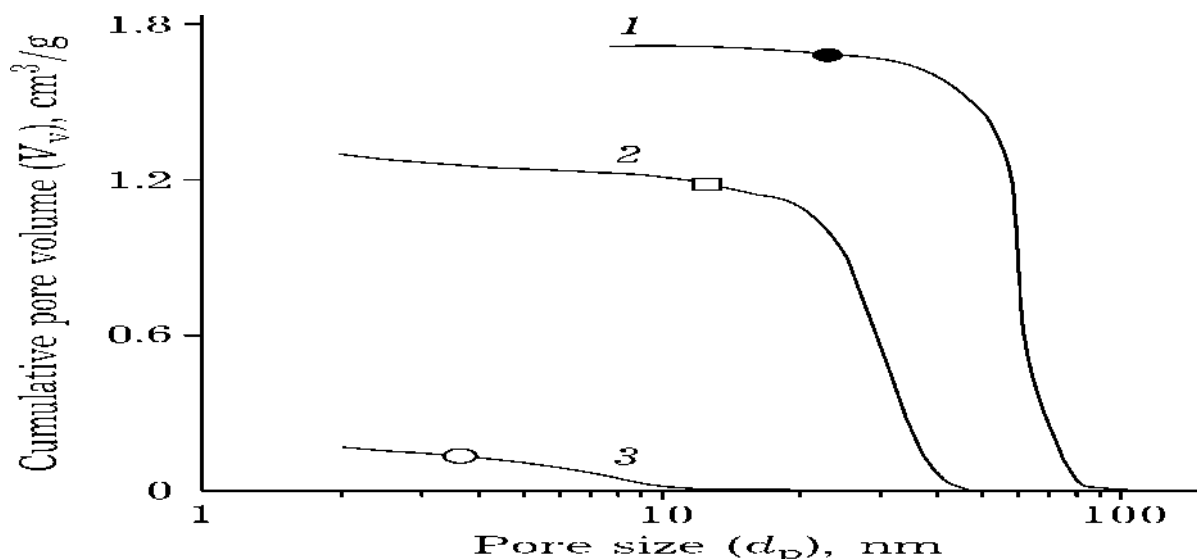

Fig. 2. Thermodecomposition profiles: CO$_2$ (*a*) and CO emission (*b*) on X-525 (*1*), X-560 (*2*), X-625 (*3*) and L3S (*4*).

TABLE 1

Characteristics of the activated carbon and carbon xerogels: Cu loading and SCR results

Support	S_{BET}, m^2/g	V_v, cm^3/g	$V_{\mu p}$, cm^3/g	CO_2, μmol/g	CO, μmol/g	Cu/C catalyst	Method	Cu, mass %	NO* conversion, %
L3S	900	0.79	0.25	70	440	Cu$_l$/L3S	IMP	2.8	–
						Cu$_h$/L3S	IMP	4.2	–
X-525	645	2.1	0.26	119	530	Cu1/X-525	IMP	3.6	48
						Cu2/X-525	WIM	4.8	62
X-560	615	1.29	0.25	177	447	Cu1/X-560	IMP	3.2	47
						Cu2/X-560	WIM	5.0	63
X-625	600	0.41	0.25	192	374	Cu1/X-625	IMP	2.9	29
						Cu2/X-625	WIM	4.2	28

*NO conversion at 220 °C (conditions: see Fig. 3).

oxidized L3S activated carbon. The amount of CO and CO_2 released from each support per gram of carbon, n_{CO} and n_{CO_2}, respectively, are very close and very low whatever the support: n_{CO} ranges from 374 to 530 μmol/g$_C$ and n_{CO_2} ranges from 79 to 192 μmol/g$_C$. Variations observed between the supports are very slight and the surface composition can be considered as quasi constant.

The results of the copper chemical analysis of the catalysts are reported in Table 1. Except for Cu1/L3S, a 5 mass % copper content was

expected. The best copper deposition procedure is the Wet Impregnation Method. The objective was reached for supports X-525 and X-560: since these carbon xerogel supports contain large pores, the impregnation is easier. Moreover, with this method, the filling of the pores with the copper solution is better monitored than in the classical impregnation method (IMP). With this latter method, some copper deposition was observed on the glass vessel and copper diffusion through the pores is probably hampered.
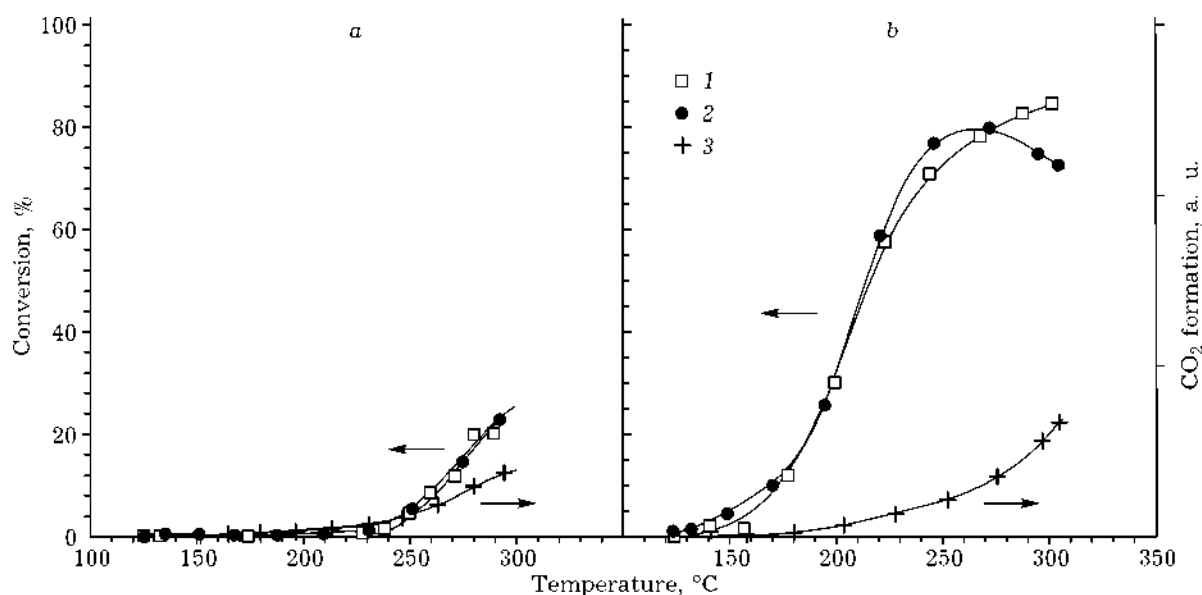

Fig. 3. NO and NH$_3$ conversion profiles and CO_2 formation obtained on X-525 (a) and Cu2/X-525 (b): 1 − NO, 2 − NH$_3$, 3 − CO_2. Conditions: [NO] = [NH$_3$] = 0.02 %, [O$_2$] = 3.00 %, [He] = 96.60 %, sample amount is 0.02 g, total flowrate is 138 cm^3/min.

SCR of NO by NH$_3$

Without metal, some catalytic activity is observed (Fig. 3, *a*). The reduction of NO begins above 215 °C. The profile of NH$_3$ conversion superimposes very well with that of NO, which means that the reaction proceeds *via* the equation (1). During this process, CO$_2$ emission is observed. This emission could be due to the oxidation of the carbon species at the surface of the material. Nevertheless, in our conditions, the NO conversion on carbon xerogel supported catalysts does not exceed 30 % at 300 °C. The introduction of copper on the carbon supports strongly enhances the reduction of NO by NH$_3$ (see Fig. 3, *b*). For all samples, the NO conversion begins at lower temperature (about 125 °C), increases with the reaction temperature, and reaches an optimum (≈80 %) at 270 °C. Most of the conversion profiles are volcano-type curves, and the decrease of activity appears above 270 °C. The NO consumption falls while NH$_3$ conversion continues to increase, suggesting that a side reaction, ammonia oxidation, starts to become significant. This behaviour is characteristic of the presence of copper oxide species [12, 13]. The oxidation of the carbon surface into CO$_2$ is also observed while using supported metal catalyst and a small increase is noticed.

The comparison between Cu2/X-525 dried at 100 °C (run 1) and activated at 300 °C (run 2) is reported in Fig. 4. The NO conversion profiles are quite similar. With Cu(NO$_3$)$_2$ as metal precursor and using the impregnation preparation method, activation is not a
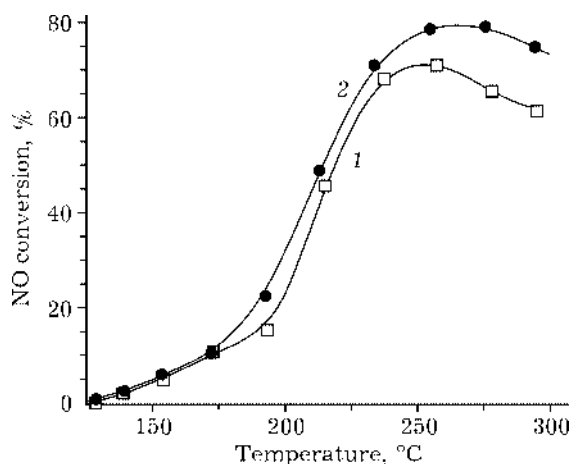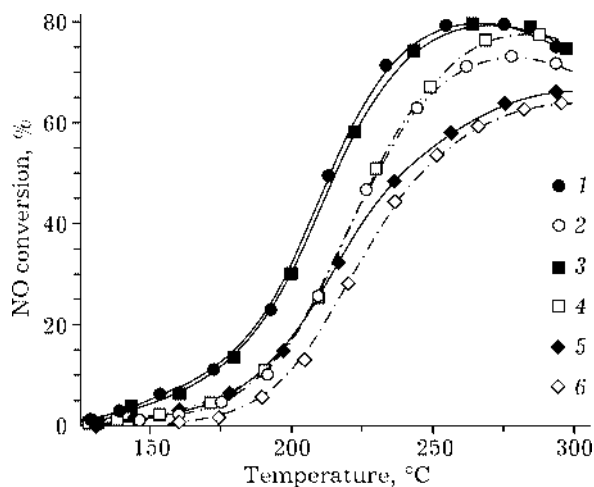
Fig. 5. NO conversion profiles obtained on Cu2/X-525 (*1*), Cu1/X-525 (*2*), Cu2/X-560 (*3*), Cu1/X-560 (*4*), Cu2/X-625 (*5*), Cu1/X-625 (*6*). Conditions: see Fig. 3.

determining step. All catalysts exhibit the same behaviour (not shown).

The conversion profiles of the different Cu/carbon xerogels prepared for this study are reported in Fig. 5. Some observations are noticeable: (*i*) the wet impregnation method leads to most efficient catalysts and (*ii*) carbon xerogels with large meso- or macropores are better supports for copper catalysts. These peculiar behaviours could be due to better dispersion obviously induced by the preparation method. The increase in activity could also be ascribed to a difference in copper content as mentioned before [7]. However, two catalysts containing 2.8 and 4.0 mass % copper deposited on L3S commercial activated carbon support were compared to each other (Fig. 6).
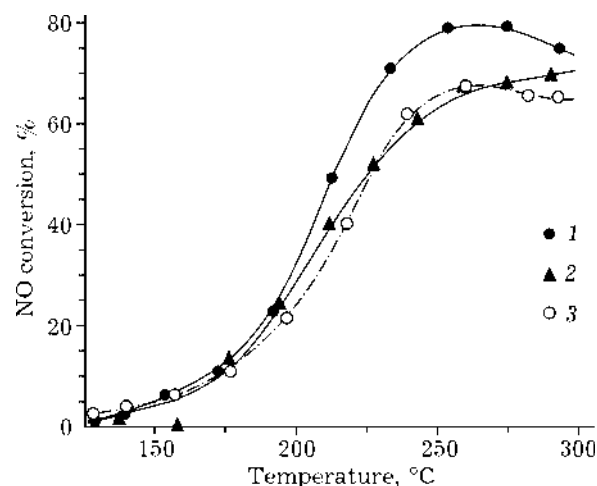
Fig. 4. NO conversion profiles obtained on Cu2/X-525: *1* − run 1, *2* − run 2. Conditions: see Fig. 3.

Fig. 6. NO conversion profiles obtained on Cu2/X-525 (*1*), Cu$_h$/L3S (*2*), Cu1/L3S (*3*). Conditions: see Fig. 3.

No significant difference in SCR of NO by NH_3 was observed. Below 200 °C, Cu/X-525 (or Cu/X-560) exhibits NO reduction activity similar to that of Cu/L3S catalysts. Above this temperature, Cu/carbon xerogels with the largest pores are more active.

The stability of the catalyst was studied at 200 °C with a plateau of several hours. No significant diminution in NO conversion was noticed. The values are reported in Table 1. After 3 h of reaction, the same conclusions as above can be done: the larger the pores, the more active the catalyst.

CONCLUSION

This preliminary study on the $deNO_x$ catalytic activity of Cu/carbon xerogels is very promising. It shows that it is possible to prepare carbon supports with a well defined pore texture and that the method of copper deposition on these materials is important in order to obtain well dispersed catalysts. With a very high space velocity (414 000 cm^3/g), a NO conversion of 60 % is obtained at 220 °C on the two materials containing the largest pores, which highlights some pore texture effect.

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