METAL CATALYZED NO_X REDUCTION BY ACTIVATED CARBONS

E. Raymundo-Piñero, M.J. Illán-Gómez, A. Linares-Solano and C. Salinas-Martínez de Lecea.
Departamento de Química Inorgánica. Universidad de Alicante. Spain.

Introduction

The catalytic activity of first series transition metals for carbon gasification reaction is well known [1-3]. In these reactions, the metal oxidation state determines its performance, since, the catalyst participates in an oxygen transfer mechanism that implies a redox cycle involving metal species with different oxidation state [2,4]. In a previous publication [5], the catalytic effect of first series transition metals for the NO reduction by carbon, in the absence of oxygen, was shown. The presence of oxygen in the reaction atmosphere could modify the state of metals and consequently their catalytic activity. The objective of the present paper is to study the catalytic properties of first series transition metals and potassium (for comparative purposes) in the NO_x reduction by carbon.

Experimental

An activated carbon (A3), with a high surface area (S_{CO2}= 1285 m^2/g and S_{N2}=1417 m^2/g), prepared by chemical activation with potassium hydroxide [6], was selected for this study. Sample preparation was previously described [5]. The catalysts were introduced by excess-solution impregnation using nitrates as metal precursors.

Samples characterization was accomplished by physical adsorption of N_2 at 77K and CO_2 at 273K in an automatic system (Autosorb-6, Quantachrome); metal species identification, before and after NO_x /carbon reaction, was carried out using XRD (Seifert, JSO Debye-Flex 2002) and XPS (Perkin Elmer PHI ESCA 5600).

The NO_x/carbon reaction was studied at atmospheric pressure in a fixed bed flow reactor (15mm id; ca 300 mg sample) connected to a gas chromatograph (Hewlett Packard Model 5892A) to analyze N_2, CO_2, CO and N_2O using a multicolumns system (Porapak Q 80/100 and Molecular Sieve 5A) with a thermal conductivity detector, and a chemiluminiscence analyzer (Thermo Environmental Mod. 42H) to analyze the nitrogen oxides (NO and NO_x).Two types of experiment were carried out using fresh samples : i) temperature programmed reaction (TPR) and ii) isothermal reaction. Experimental details were previously described [5].

Results and discussion

Figure 1 shows the TPR curves (%NOx reduction versus reaction temperature) for activated carbon A3 and samples containing different metals. (Metal content –in weight percentage- is included in the sample nomenclature). Two stages are observed in the TPR profile:

i) At temperature lower than 150°C, the NO_x reduction percentage decreases with reaction temperature, even reaching negative values.

ii) At temperature higher than 200°C, NO_x reduction increases with reaction temperature.

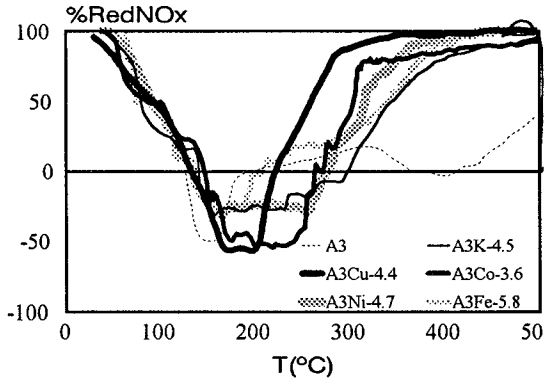

Figure 1. TPR profiles of samples

No effect of metals is observed at the low temperature stage, the curves for % NO_x reduction are very similar for all samples. However, at the high temperature stage the catalytic effect of metals is clearly shown, being copper the most active one. Yamashita et al. [7] also observed the high activity of copper in comparison to others transition and alkaline earth metals.

The analysis of products evolved during TPR helps to understand the TPR behavior:

i) At low temperature stage, no reaction products (N_2, N_2O, CO_2 and CO) are evolved which seems to indicate that NO_x adsorption in the carbon (all samples have similar surface area) is the main phenomena [8]. It is well known the NO_x adsorption

capacity of activated carbon [9], that will decreases with temperature and even a desorption step from 150 to 200°C would appear.

ii) At high temperature stage, the evolution of products, mainly N_2 and CO_2, indicates the NO_x reduction by carbon.

In a previous study, in an oxygen free atmosphere [5], the high activity of copper was observed a temperature higher than 500°C. The ease reduction of copper by carbon, during the heat treatment before reaction (a heating in helium till 900°C), as well its facility to be reduced by carbon, at the reaction temperature, was used to explain its high activity. In this work, samples are not thermally treated before TPR experiment, but some metal reduction by carbon, during the preparation step, has been observed by XPS.

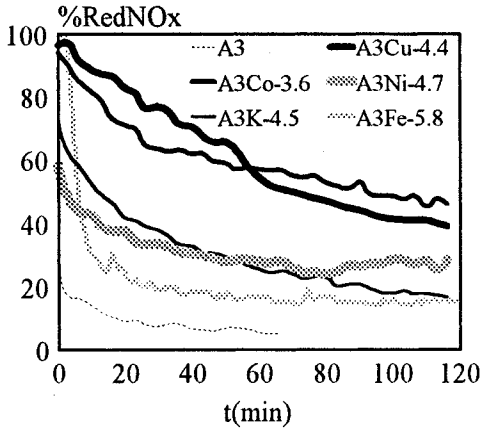

Figure 2. Isothermal reaction curves at 300°C.

Isothermal reaction experiments at 300°C have been performed for the activated carbon and samples with catalysts. Figure 2 shows the % of NO_x reduction versus time. The results prove the catalytic effects of metals for NO_x reduction by carbon in the presence of oxygen. If these results are compared to those in the absence of oxygen, it is interesting to note that the activity of potassium is only slightly increased by the presence of oxygen. However, in the case of copper and cobalt the activity a 300°C is much higher for NO_x than for NO reduction. A 50% NO_x conversion is maintained at two hours of reaction that is the highest found for any metal at this temperature. The observed sequence, Cu=Co>Ni>K>Fe, could be explained regarding the temperature of metal oxide reduction by carbon as also was concluded at reaction temperatures higher than 500°C in the absence of oxygen [5]. XRD and XPS have been used to characterize the metals species in some samples previous to the reaction (after a thermal treatment in an inert gas at 300°C). No diffraction peaks were observed probably due to the small particle size. The XPS results show that a higher fraction of reduced metal was for copper in comparison to a less active catalyst as iron.

The XPS analysis of copper sample after 2 hours of reaction reveals that a fraction of copper is still in the reduced state (Cu (0) or Cu (I)).

Conclusions

TPR and isothermal reaction experiments of NO_x reduction by carbon in the presence of metals allow the following conclusions to be drawn. Bellow 150°C a NO_x adsorption process on the carbon occurs. The reduction of NO_x, in presence of metal catalysts, starts at temperatures as low as 200°C. The first series transition metals studied are active catalysts for NO_x reduction by carbon in the presence of oxygen. Copper and cobalt exhibit the largest activity, which is highly enhanced in the presence of oxygen. The activity of copper, during isothermal reaction, may be due to the presence of reduced copper species as shown by XPS analysis.

Acknowledgment. This study was made possible by financial support from OCICARBON (C-23-435) and CICYT (AMB96-0799)

References

1. Mckee, D.W. *In Chemistry and Physics of Carbon*, Vol. 16, ed. P.L. Jr Walker, P.A. Thrower, New York, 1988, p.1.
2. Kasaoka, S., Sakata, Y. Yamashita, H., Nishimo, T. *Int. Chem. Eng.* 1981, 21, 419
3. Yamada, T., Tomita, A., Homina, T. Fuel, 1982, 63, 246.
4. Illán-Gómez, M.J., Linares-Solano, A., Radovic, L.R. and Salinas-Martínez de Lecea, C. *Energy Fuels*, 1996, 10, 158.
5. Illán-Gómez, M.J., Linares-Solano, A. And Salinas-Martínez de Lecea, C. *Energy Fuels*, 1995, 9, 976.
6. Illán-Gómez, M.J., García-García, A. Linares-Solano, A. and Salinas-Martínez de Lecea, C. *Energy Fuels*, 1996, 10, 596.
7. Yamashita, H., Yamada, H., Tomita, A. *Appl. Catal.* 1991, 78, L1.
8. Illán-Gómez, M.J., Linares-Solano, A, Phillips, J., Salinas-Martínez de Lecea and Radovic, L.R., in *Carbon'96 (Ext. Abstr. European Carbon Conf.)*, New Castle, 1996, p. 703.
9. Rubel, A., Stewart, M.L., and Stencel, J.M. *J. Mater. Res.*, 1995, 10, 562.