

# NO REDUCTION BY ACTIVATED CARBON. CATALYSIS BY TRANSITION METALS

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## Introduction

In previous studies we have observed that the temperature for NO reduction by carbon may be considerably decreased using catalysts such as potassium, calcium or iron, and that the effectiveness of those metals is determined by their capacity for the dissociative chemisorption of NO [1-4]. The aim of this study is to analyze some first series transition metals (Cr, Fe, Co, Ni and Cu) as catalysts of NO reduction by carbon.

## Experimental

An activated carbon sample (K-UA1), was chosen for this study [5]. The catalysts were introduced by impregnation. The NO-carbon reaction was studied in a fixed-bed flow reactor connected to a gas chromatograph. Two types of experiments were carried out: (i) temperature-programmed reaction (TPR), consisting of heating the sample at 5°C/min to 900°C in a NO/He mixture (0.4% NO, 60 mL/min); and (ii) isothermal reaction at 300, 400, 500 and 600°C for a period of 2h.

## Results and discussion.

Figure 1 compares the TPR curve for the K-UA1 carbon with those of the samples containing the different metals. All the curves show the catalytic effect of the metals, which causes a significant decrease both in the starting reaction temperature and the temperature required to reach 100% reduction ( $T_{100}$ ). However, the effect of each metal in these two parameters varies: i) regarding the temperature at which the reaction starts, Fe, Co and Ni are the metals that show the highest activity, and ii) in respect to the  $T_{100}$  value, Co and Cu show the lower temperature (500 and 520°C) followed by Ni (580°C), Cr (585°C) and Fe (600°C). In relation with the shape of the TPR curves, the following observations can be made: Cr and Cu do not modify significantly the TPR curve shape of the parent carbon, Co and Ni show a TPR profile different from that of the original carbon in which the two reactivity steps observed [5] cannot be

distinguished and Fe modifies noticeably the entire TPR profile.

The analysis of the evolved reaction products ( $N_2O$ ,  $N_2$ , CO and  $CO_2$ ) and of the reacting gas (NO) during the TPR experiments completes the data supplied by the reduction curves. The product emissions for iron-loaded carbon differs greatly from that of the parent free-metal carbon [5] and it is similar to that found for potassium-loaded carbon [1,2]. Four reaction stages can be described: the first consists of a NO dissociative chemisorption characterized by the evolution of  $N_2O$  and  $N_2$  and oxygen retention in the catalyst; in the second stage, only  $N_2$  is emitted and a loss of catalyst activity is observed; in the third  $CO_2$  release starts (showing an excess compared to  $N_2$ ) and the catalyst recovers its activity; finally, CO evolution starts in the last reaction step in which the  $N_2$  evolution becomes constant. With Co and Ni, the  $N_2O$  emission is also detected proceeding from NO dissociative chemisorption, but this process cannot be observed as a separate step from the beginning of the reaction (characterized by the onset of  $CO_2$  emission). Finally, with Cr and Cu, the product emission profile is similar to that of the parent carbon [5].

Isothermal reaction experiments were performed to obtain easily comparable catalytic activity data. The activity curves at 300 and 400°C exhibit a continuous decrease after which a constant level, different for each metal, is approached asymptotically. The extent of the activity decrease depends on both the nature of the catalyst and the temperature of the reaction. In the low temperature range it is observed that only the metals that chemisorb dissociatively NO (Fe, Co and Ni) show a remarkable activity, which decreases for approximately 20-30 min. The period of high activity becomes longer as the reaction temperature increases. Once the steady state is reached it can be observed that the activity increases with the reaction temperature. The analysis of the reaction products evolved during the isothermal experiments shows that the  $CO_2$  evolution is initially delayed with respect to the  $N_2$  evolution giving rise to a

negative oxygen balance. This behavior is largely observed in the presence of Fe and Co, Cu almost does not show this delay and Ni only slightly does it. This CO<sub>2</sub> delay agrees with previous results reported with K [1,2] and Fe[4] and confirms the above statement that Fe, Co and Ni (in a lesser extend) retain the oxygen from the dissociative NO chemisorption. Once CO<sub>2</sub> evolves, as a result of the reduction of the oxidized metal species by carbon, the catalytic redox cycle is closed and the steady state may be reached. However, the reduction of the intermediate oxidized metal species for Cu, Co and Ni cannot be the factor limiting the CO<sub>2</sub> evolution because the oxides of these three metals are easily reduced by carbon (T < 400°C). Thus, the formation of metal oxide from the oxygen originating in NO dissociative chemisorption on the metal, will be the factor limiting CO<sub>2</sub> evolution speed.

As a summary, Figure 2, shows the steady state activity of the transition metals at 300, 400 and 500°C. The histogram stresses the importance of reaction temperature in the activity sequence for this metal series. At low temperatures, Fe, Co and Ni are the most effective, as they are metals able to chemisorb NO dissociatively; at high temperatures they are Co and Cu, metals whose oxides are reduced by carbon at a lower temperature; and Cr is the less active metal. This order of activity seems to indicate that, at low temperatures (T < 400°C), the controlling step in the process is NO chemisorption, whereas at high temperatures (T > 500°C), the reduction of the intermediate oxidized metal species is the rate-limiting step in the reaction sequence.

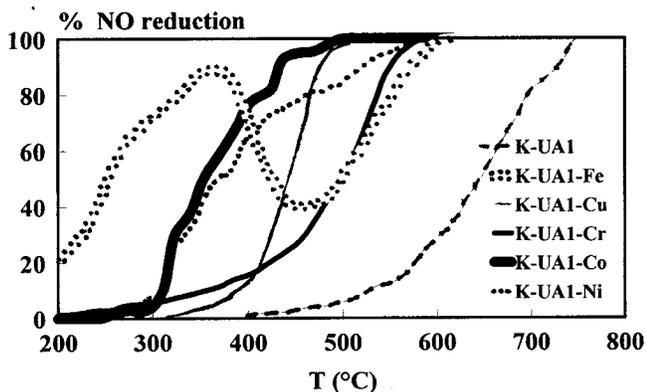


Fig. 1. TPR profiles of NO reduction for sample KUA1 and metal-impregnated carbons.

## Conclusions

The study of the catalytic activity of Cr, Fe, Co, Ni and Cu in the NO carbon reaction has allowed us to draw the following conclusions. All the metals studied catalyze the NO-carbon reaction, causing a substantial shift toward lower temperatures of the NO reduction by carbon. Both dissociative chemisorption of NO, associated to the oxygen acceptor capacity of the metal, and the ease of the reduction of the metal oxide formed by the carbon are important steps.

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## References

1. Illán-Gómez, M. J.; Linares-Solano, A.; Radovic, L. R.; Salinas-Martínez de Lecea, C. *Energy Fuels* 1995, 9, 97.
2. Illán-Gómez, M. J.; Linares-Solano, A.; Radovic, L. R.; Salinas-Martínez de Lecea, C. *Energy Fuels* 1995, 9, 104.
3. Illán-Gómez, M. J.; Linares-Solano, A.; Radovic, L. R.; Salinas-Martínez de Lecea, C. *Energy Fuels* 1995, 9, 112.
4. Illán-Gómez, M. J.; Linares-Solano, A.; Radovic, L. R.; Salinas-Martínez de Lecea, C.; "NO reduction by activated carbon. 5. Catalysis by iron", *Energy Fuels*, in press
5. Illán-Gómez, M. J.; Salinas-Martínez de Lecea, C.; Linares-Solano, A.; Calo, J. M. *Energy Fuels* 1993, 7, 146.

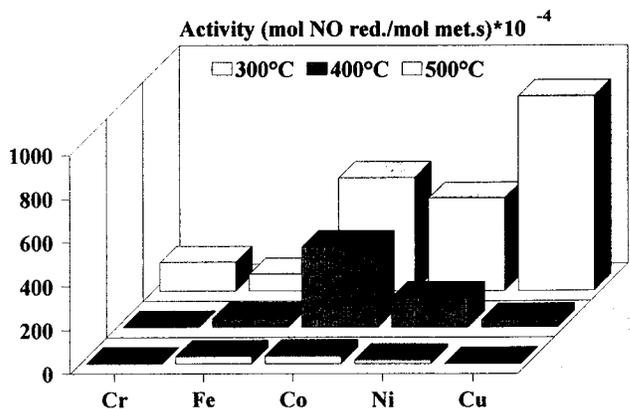


Fig. 2. Isothermal reduction activity at 300, 400, 500 °C for metal-impregnated carbons.