

NO AND N₂O DECOMPOSITION ON ACTIVATED CARBON

J. Rodríguez-Mirasol, J.R.Pels, F. Kapteijn and J.A. Moulijn
*Chemical Process Technology, Delft University of Technology,
Julianalaan 136, 2628 BL Delft, The Netherlands.*

INTRODUCTION

The decomposition of NO and N₂O by chars prepared from different rank coals was studied in a previous work [1]. The apparent activation energies found for these chars were dependent on char structure and agreed reasonably well with the values given in the literature for both reactions. This was not the case for the reaction order. The reaction of NO and N₂O with chars and carbons, in general, have been reported to be first order (mostly assumed) with respect to partial NO and N₂O pressure, respectively. We found, however, fractional reaction orders for both NO and N₂O reaction over the chars studied, changing with temperature. In this regard, we suggested that other models, taking into account surface coverages, accounting for changing reaction orders should be evaluated. The higher reaction rates found for lignite chars for both NO and N₂O decomposition were attributed to the catalytic effect of Ca contained in the mineral matter, which produces a shift from CO production towards CO₂ production.

In the present work, we study in more detail the influence of temperature, inlet partial pressure and the catalytic effect of Ca and K on both NO and N₂O decomposition over a well characterized carbon. The presence of CO and the mutual influence of NO and N₂O have been also investigated.

EXPERIMENTAL

The catalytic decomposition of NO and N₂O have been studied over Norit RX1 Extra(Norit), an acid-washed, steam-activated peat char (3 wt% ash) with a high specific surface area (1360 m²/g, N₂ adsorption at 77 K; pore volume 0.76 ml/g) and of particle size 106-212 μm. Ca- and K-containing Norit RX1 Extra were also used (Ca/Norit and K/Norit, respectively). Catalyst addition was performed by pore volume impregnation with an aqueous metal carbonate solution of proper concentration to yield 2.9 wt% Ca and 5.6 wt% K loading, respectively. The experiment were carried out in a laboratory packed-bed reactor (5 mm I.D.), containing 20 mg of carbon diluted with 180 mg of SiC (106-212 μm), at steady state conditions. The inlet partial NO and N₂O pressure used in this study

were in the range of 0.5 to 2.5 mbar, at a total pressure of 2.5 bar and the space time for NO and N₂O (W/FNO(N₂O)) amounted to 15x10⁴ and 17x10⁴ g s/mol, respectively. The product gases were continuously analyzed for NO and NO₂ using a chemiluminescent analyzer and, discontinuously, for N₂O, N₂, CO₂, CO, and O₂ by GCs.

RESULTS AND DISCUSSION

Figure 1 shows the effect of temperature on NO and N₂O conversions for the three carbons studied. Under similar conditions, N₂O is more readily reduced on these carbons than NO. Ca and K clearly catalyze both NO [2-4] and N₂O [5] reduction by carbon. This catalytic effect was more pronounced in the case of N₂O reaction. The kinetic parameters for Norit, Ca/Norit and K/Norit are presented in Table 1. Activation energy values for N₂O decomposition were lower than those for NO decomposition and fractional reaction orders were found for both NO and N₂O decomposition on the three samples studied [1]. The main products for the NO decomposition on Norit are N₂, CO and CO₂, with a molar CO/CO₂ ratio of ~3. When Ca or K are present, the products for this reaction are N₂ and CO₂ and only at high temperature, when a complete conversion of NO is achieved, CO becomes the dominant oxygen-containing product. For the N₂O/Norit reaction, the gas products observed were N₂ and CO₂. CO was only detected at high temperature or at high inlet partial N₂O pressure. The presence of Ca or K decreased the decomposition temperature, but did not change the gas product distribution for this reaction. The catalytic effect of Ca and K, in the case of NO/carbon reaction, seems to be related not only to a faster NO dissociation and oxygen transfer to the carbon [3,4], but to a shift from CO production towards CO₂ production.

The influence of CO on NO and N₂O decomposition was studied for Norit and Ca/Norit. Addition of CO to a reference flow of constant concentration of NO in He (Fig. 2 a) very slightly decreased the NO conversion for Norit. However, CO enhanced the NO decomposition for Ca/Norit. Similar results were found for the N₂O decomposition on Norit and

Ca/Norit. The presence of Ca on the surface of the carbon seems to favor the production of surface-oxygen, which can easily be scavenged by CO to produce CO₂ and vacant sites, enhancing thus the NO and N₂O decomposition. The oxygen scavenging effect of CO did not take place on Norit. The mutual influence of N₂O on NO decomposition was studied for Norit and Ca/Norit in a similar way as for CO (Fig.3). The decomposition of N₂O over Norit is enhanced by NO. At the same time, the presence of N₂O results in the decomposition of NO, even at temperatures at which NO is not converted in the absence of N₂O. The presence of NO did not affect the N₂O decomposition on Ca/Norit. The enhancement of the NO decomposition by N₂O seems to be due to the production of a more active oxygen surface complex [6], i.e., N₂O can easily provide oxygen to a C_f(O) surface complex producing a less stable oxygen surface complex C(O)C_f(O), which decomposes as CO₂ leaving vacant sites. The fact that this behavior does not take place on Ca/Norit confirm that the catalytic effect of Ca is, indeed, due to a shift from CO production towards CO₂ production.

CONCLUSIONS

Under similar conditions, N₂O is more readily reduced on activated carbon, Norit RX1 Extra, than NO. Ca and K are relatively good catalysts for NO and N₂O decomposition by carbon, decreasing the

decomposition temperature. This effect is accompanied by a shift from CO production towards CO₂ production. The oxygen scavenging effect of CO to produce CO₂ and vacant sites enhanced both NO and N₂O decomposition for Ca/Norit. CO had no effect on these reactions in the case of Norit. The mutual influence of NO and N₂O is to enhance both reaction rates on Norit, which may be ascribed to the formation of a more active oxygen surface complex by N₂O. Such effect was not observed for Ca/Norit.

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Table 1. Kinetic parameters for the NO- and N₂O-carbon reaction

	NO reaction			N ₂ O reaction		
	E _a (kJ/mol)	ln k (k in mol/g s bar ⁿ)	reaction order, n	E _a (kJ/mol)	ln k (k in mol/g s bar ⁿ)	reaction order, n
Norit	146	6.1	0.42	119	6.7	0.54
Ca/Norit	136	7.0	0.56	101	5.6	0.50
K/Norit	149	7.8	0.40	101	4.9	0.45

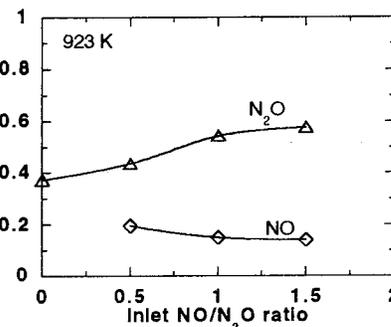
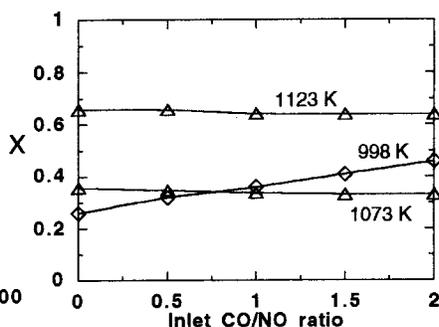
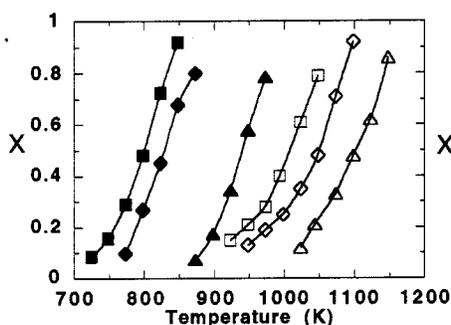


Figure 1. Observed conversions of NO and N₂O as a function of temperature for Norit (Δ), Ca/Norit (\diamond) and K/Norit (\square), at inlet partial NO and N₂O pressure of 1 mbar. Open symbols: NO conversion; closed symbols: N₂O conversion.

Figure 2. Observed NO conversion as a function of the inlet CO/NO ratio for Norit (Δ) and Ca/Norit (\diamond), at inlet partial NO pressure of 1 mbar.

Figure 3. Observed NO and N₂O conversions as a function of the inlet NO/N₂O ratio for Norit, at inlet partial N₂O pressure of 1.5 mbar and space time of 77×10^4 g s/mol.