

VANADIUM MIXTURES FOR NO CONVERSION

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Introduction

NO removal from exhaust streams of various combustion sources has become increasingly important in the past few years [1-5]. Recently catalytic reduction of NO with carbons as reducing reagents has been intensively investigated [1-5]. The aim of the present work is to study the behaviour of several binary Vanadium mixtures for the C-NO reaction.

Experimental

Charcoal Activated GR MERCK (powder) was used to carry out isothermal kinetic studies of NO. The charcoal was impregnated with diluted solutions of Ba, Co, Cu, Fe, Mg, Mn, Ni, Pb and V precursors (acetates). The metal loading was 4 wt %. Binary Vanadium mixtures of these catalysts were also prepared. O conversion was studied using a fixed bed reactor and a GC/MS on line. Samples were heated at 2°C/min (TPR) to 950°C in a mixture of 0.5%NO in He. All samples were pre-treated in He at 500°C for 30 minutes. *In situ* XRD studies were conducted in a diffractometer with a Cu (K α) radiation source (50 kV, 30 mA), equipped with a high temperature special chamber.

Results and Discussion

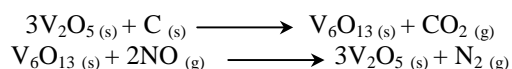
All mixtures showed to have higher catalytic activity than the individual catalysts and some had synergetic effects. Figure 1 shows the Arrhenius plots for NO reaction for the V+Cu mixture. The reaction rate of this mixture at 450°C and 800°C had a synergetic effect of 3 times at both temperatures.

Figure 2 shows the program temperature reaction profile for NO conversion. These results are in agreement with the kinetic ones, as the mixture converts the NO at lower temperature than the individual components. The analysis of the reaction products for the reaction with NO (Figure 3a) using a GC/MS *on line* show the presence of N₂O, N₂, CO₂ and CO together with some unreacted NO. Between 400°C and 500°C only CO₂, N₂O and N₂ were detected. CO was observed in minor quantities above 500°C. The greater the rate of CO₂ evolution the greater the NO conversion. The analysis of the reaction products for the uncatalysed reaction (Figure 3b) showed a similar trend, but in this case CO₂ evolution was observed at higher temperatures (above 500°C) and higher amounts of CO were detected above 550°C. The results obtained

suggest that dissociative NO chemisorption occurs and the catalyst enhances the formation of a carbon oxygen complex. Decomposition of these complexes leads to production of CO₂ and CO. Thus the catalytic effect observed with addition of Vanadium seems to be related with an enhancement of oxygen carbon complexes and CO₂ evolution. Similar results were obtained by other authors [2-4].

Active phases play also an important role on the catalytic conversion of NO [2-7]. Figure 4 shows XRD patterns obtained in NO at several temperatures for carbon doped with V+Cu mixture. The peaks show shifts to 2 θ with increasing temperature, which reflects expansion of the crystal lattices. Pt peaks appear in the spectra resulting from exposure of the sample holder to the X-ray beam as carbon burned away. *In situ* XRD shows that metal oxides are reduced to lower oxidation states such as V₂O₅, V₆O₁₃; CuO, Cu;. Same phases were detected in an inert atmosphere. No evidence of a new phase responsible for the synergetic effect was observed in the mixtures by *in situ* XRD, however the addition of vanadium seems to increase carbon reactivity at low temperatures.

The catalytic effect observed for the NO conversion can be explained by the occurrence of redox processes in which the oxides particles are reduced by reaction with the carbon at points of contact with the carbon substrate to form lower oxides according to a redox mechanism such as:



It is known that V₂O₅ is a good catalyst for carbon gasification because of its low Tamman temperature. Various authors reported that V₂O₅ has the ability to spread and wet carbon surfaces [8-11]. The reduction of V₂O₅ to V₆O₁₃ further reduces the melting point of the catalyst and could lead to more extensive spreading on carbon surface [8-11]. *In situ* XRD carried out both in NO and N₂ atmospheres showed that both V₂O₅ and V₆O₁₃ are present under reaction conditions and with increasing temperature the peaks become less intense to both oxides suggesting that the catalyst is spreading to form an amorphous thin film on carbon surface. It has been reported that melting of the catalysts improves wetting of the carbon surface promoting catalyst/carbon interaction [1, 6-9, 12]. Active catalysts seem to act as an oxygen acceptor from NO, transferring it to the carbon surface and recovering reduced state. Similar behaviour has been reported by several authors [1-3, 7-8].

Conclusions

This study has indicated that kinetic measurements combined with *in situ* XRD are useful tool for interpreting catalyst behaviour. In the C-NO reaction a reduced catalyst surface is required to NO reduction. The ability of the catalyst to chemisorb NO going through redox transference of oxygen to the carbon reactive sites seems to explain catalytic activity. The synergetic effect observed with addition of vanadium seems to be related with its ability to wet and spread on carbon surface.

References

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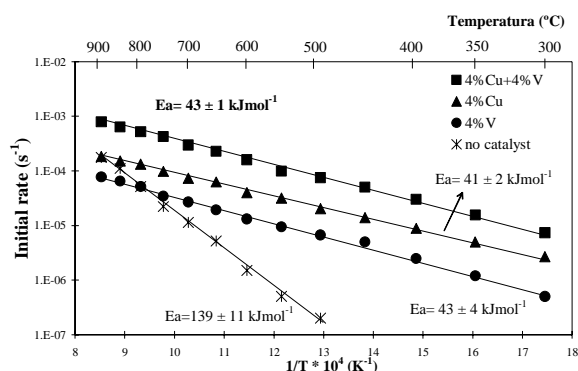


Figure 1 – Arrhenius plots for carbon gasification in NO for carbon parent sample and samples doped with V, Cu and V+Cu mixture.

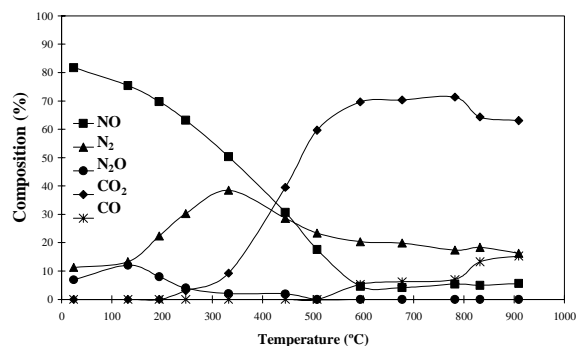


Figure 3 – Reaction products (TPR) for carbon sample doped with the Cu+V mixture (a) and carbon parent sample (b).

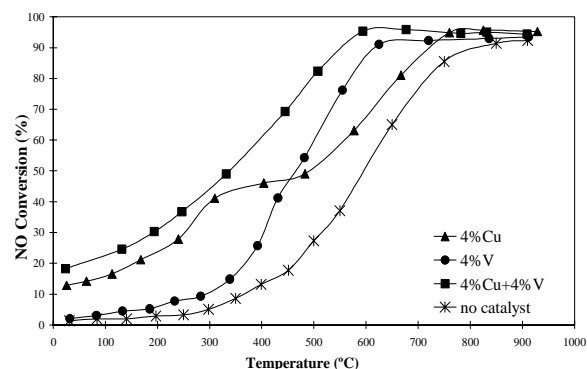


Figure 2– NO conversion as a function of temperature (TPR) for samples doped with V, Cu and V+Cu mixture.

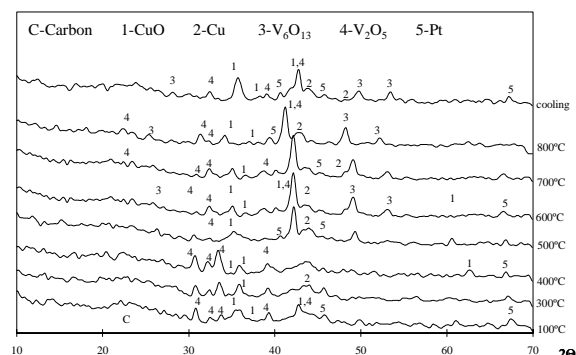


Figure 4 – *In situ* XRD data obtained in NO on heating sample doped with Cu+V mixture at several temperatures.