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N_2O reduction by activated carbon over iron bimetallic catalysts

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Abstract

The kinetics of N_2O conversion with activated carbon impregnated with binary mixtures of Fe with Co, Cu, Mg, Ni, Pb and V was studied in the temperature range of 300–650 °C using a microbalance. Synergetic effects were found for the Fe binary mixtures. External diffusion limitations to mass transfer seem to take place in the reaction with N_2O above 600 °C. N_2O conversion was also followed and reaction products were identified as N_2 and CO_2 in a stoichiometry of 2:1. *In situ* XRD was carried out to identify the phases present during reactions. The ability of the catalysts to chemisorb N_2O dissociatively going through redox transference of oxygen to the carbon reactive sites seems to explain catalytic activity.

Keywords: Nitrous oxide (N_2O); Synergetic effect; Conversion; Kinetics; Catalysis; X-ray diffraction

1. Introduction

The contribution of nitrous oxide (N_2O) to pollution increase has been virtually ignored when compared to the attention given to NO. When NO emissions take place there can be a simultaneous production of N_2O, which was not considered until some years ago. N_2O is produced in many of the same processes that yield NO, including fossil fuel combustion (e.g. automobiles), adipic and nitric acid production and biomass conversion. Since this compound has a very long lifetime (about 150 years), it has a long duration effect in the depletion of the ozone layer, therefore its reduction is a topic of interest [1–9].

Since activated carbon is a reductor, it can be a cheap promising alternative to other methods that use external gaseous reducing agents for NO_x reduction [10]. Some studies were already published for the N_2O reaction with activated carbon [3,5,7–9,11–14], however its number is still very small when compared with the studies done with NO. For the uncatalysed reaction, several authors observed that the decomposition rate of N_2O on activated carbon is higher than that for NO decomposition on the same material [3,9,13,15]. Rodriguez-Mirasol et al. [3,13] showed that the obtained products are N_2 and CO_2 (with a stoichiometry of 2:1) according to the following mechanism:

$$N_2O_{(g)} + C_{(s)} \rightarrow N_{2(g)} + C(O)$$

$$N_2O_{(g)} + C(O) \rightarrow N_{2(g)} + CO_{2(g)}$$

N_2O seems to promote the formation of surface C(O) complexes. These more or less stable complexes can decompose and originate CO_2 and free sites [3,5,11,13].

For the catalysed reaction, the N_2O decomposition mechanism does not change in the presence of a catalyst. The role of the catalyst seems to be the decrease of the decomposition temperature, without changing the gas products distribution [4,7,9,11]. The catalyst chemisorbs N_2O dissociatively at a low temperature, which leads to an increase in the number of unstable surface oxygen complexes that, as shown in the above mechanism, react with N_2O to release CO_2 and create free sites. The presence of a catalyst seems to increase the production of these surface oxygen complexes, increasing N_2O decomposition [3–5,7,9,11,13]. A catalyst with a strong ability to transfer oxygen to carbon can also accelerate the release of

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C(O) complexes that might accept more oxygen from the oxidized metal, originating CO_2 [5].

The aim of this work was to obtain binary metal catalysts with improved catalytic activities for N_2O reduction. In earlier papers we reported on binary Ba [12] and Mn [9] mixtures as catalysts for the N_2O reduction by activated carbon. In the present paper we investigate the catalytic effect of Fe binary mixtures. The joint analysis of the results obtained by thermogravimetry, temperature programmed reaction (TPR) and *in situ* X-ray diffraction (XRD) will make possible to elucidate the mechanism of N_2O conversion.

2. Experimental

Charcoal-activated GR MERCK (particle size 30 μm, 1% ashes and 10% humidity) was used. Its characterization by adsorption of N_2 at 77 K (in an ASAP 2010 Micromeritics apparatus) revealed a surface area of 1289 m^2/g, a pore total volume of 0.67 cm^3/g and a micropore volume of 0.22 cm^3/g. This activated carbon was impregnated with solutions of acetates of Ba, Co, Cu, Fe, Mg, Mn, Ni, Pb and V using the incipient wetness method (metal salts were dissolved in a small amount of distilled water and the obtained solutions were added dropwise to the carbon, mixing thoroughly, and the product was evaporated in hot plate). Binary mixtures of 4% Fe with 4% of each of the other metals were also prepared.

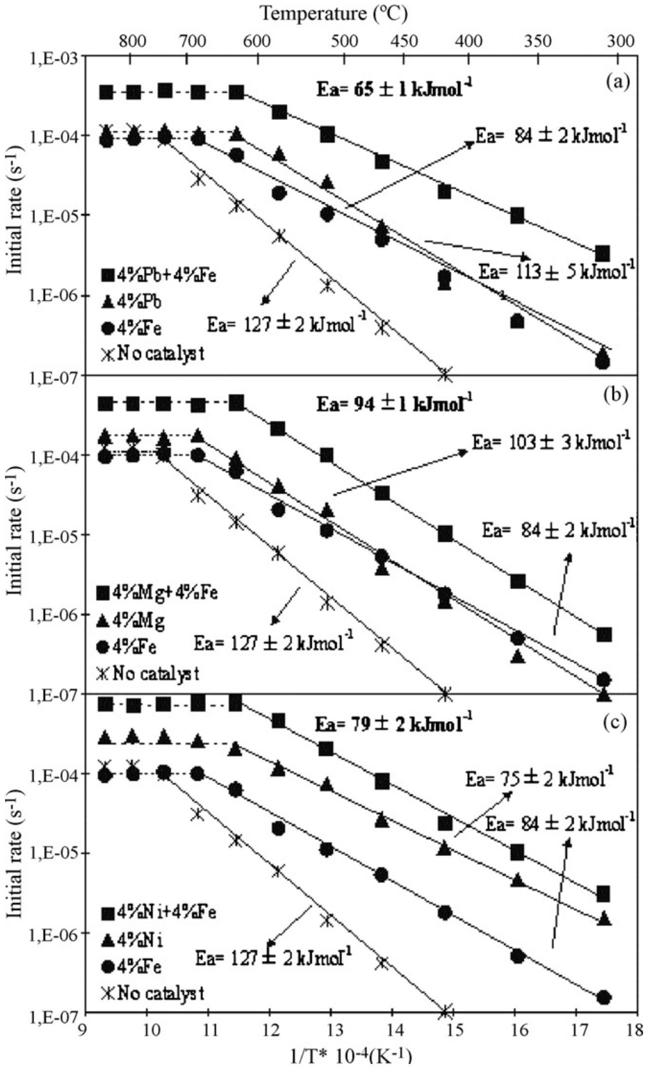

Fig. 1. Arrhenius plots for carbon gasification in N_2O for the carbon parent sample and samples doped with Pb, Fe and Pb + Fe mixture (a), the carbon parent sample and samples doped with Mg, Fe and Mg + Fe mixture (b) and the carbon parent sample and samples doped with Ni, Fe and Ni + Fe mixture (c).

In order to prevent diffusional limitations, the thermogravimetric sample weight was around 2–3 mg. Isothermal kinetic studies were carried out using a thermobalance system (CI Electronics MK II microbalance) with continuous recording of change in weight between 300 °C and 800 °C, with a mixture of Ar + 0.5% N_2O, and a flow rate of 3.3 cm^3/s. N_2O conversion was studied using a fixed bed reactor. The reactor effluents were analysed using a GC/MS (Fisons MD800) apparatus, equipped with a column of GS-Molesieve (30 m × 0.541 mm) type. These essays included heating of sample at 2 °C/min (TPR) to 950 °C in a mixture of 0.5% N_2O in He. The flow rate was 3.3 cm^3/s. All samples were pre-treated in He at 500 °C for 30 min.

In situ X-ray diffraction studies were conducted in a Rigaku D/max III C diffractometer with a Cu-Kα radiation source (50 kV, 30 mA), equipped with a high temperature special chamber. All the experiments were carried out at exactly the same experimental conditions as the thermogravimetric studies.

3. Results and discussion

Thermogravimetric experiments were carried out at several temperatures for the binary Fe mixtures Co + Fe; Cu + Fe; Mg + Fe; Ni + Fe; Pb + Fe; V + Fe and the respective monometallic systems. All mixtures showed higher catalytic activity

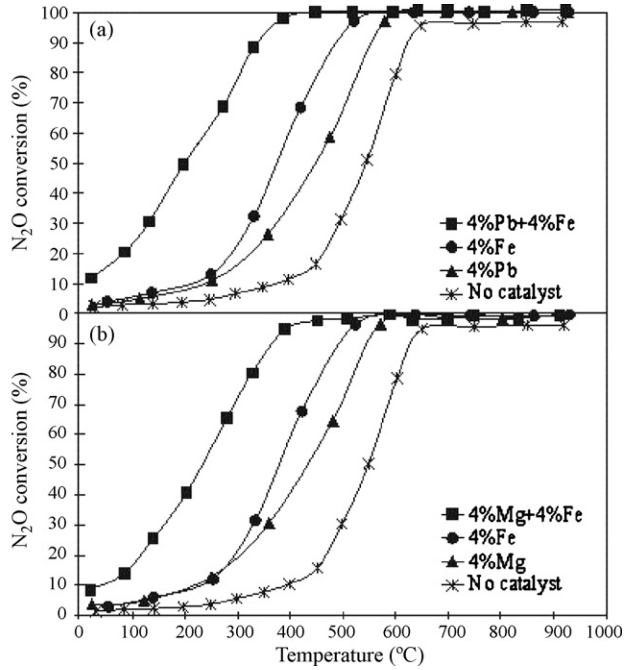

Fig. 2. N_2O conversion as a function of temperature (TPR) for the carbon parent sample and samples doped with Pb, Fe and Pb + Fe mixture (a) and the carbon parent sample and samples doped with Mg, Fe and Mg + Fe mixture (b).

than the monometallic systems. This effect is not only additive, as for the Pb + Fe, Mg + Fe and Ni + Fe mixtures, the reaction rate at low temperatures increases, approximately, between two and times more than the sum of the rates obtained for the individual components. At higher temperatures, the rate increases between two and four times. For other mixtures, these synergetic effects were more modest.

Fig. 1 shows the Arrhenius plots for the reaction with N_2O, using the mixtures Pb + Fe (a) and Mg + Fe (b) and Ni + Fe (c). Above 600 °C, all Arrhenius plots show the existence of external mass transfer limitations. A substantial decrease in the apparent activation energy for the catalysed reactions, in comparison with the uncatalysed was observed. The values obtained for the apparent activation energies range from $65\ \mathrm{kJ\ mol^{-1}}$ to $127\ \mathrm{kJ\ mol^{-1}}$ and are in agreement with those reported in literature for N_2O conversion over Co/C and Cu/C catalysts [5].

Ni showed to be the best catalyst among the monometallic systems studied (c), while Fe showed to be as good as Pb (a) and Mg (b). However, Pb + Fe (a) is the mixture that shows the highest synergetic effect at low temperatures. It is known that synergetic effects of binary mixtures can result from beneficial interactions between the mixture components and between reactants and the individual components [16].

Fig. 2 shows the TPR profiles for Mg + Fe (a) and Pb + Fe (b) mixtures. The results are in agreement with those obtained by thermogravimetry, since a higher conversion of N_2O at lower temperatures is observed for the binary mixtures. In fact, adding a metal catalyst to the activated carbon causes a decrease in the temperature required to reach ~100% N_2O conversion, from 650 °C to approximately 520 °C. Comparing the monometallic catalysts with the binary mixtures it is observed that higher conversions are reached at much lower temperatures. The binary mixtures Pb + Fe (a) and Mg + Fe (b) are more active since, at 350 °C, almost complete conversion is obtained. It is clear that the addition of Mg and Pb to Fe clearly enhances the activity showing the advantage of a bimetallic catalyst. Both the temperature at which the reaction starts and the temperature required for 100% N_2O reduction are lower for all Fe bimetallic catalysts than for Fe alone.

Fig. 3a–h shows that the reaction products are N_2 and CO_2, as referred in literature [3,7,9,11,13,17]. For the mixtures, high selectivity towards N_2 is obtained at very low temperatures (below 200 °C). The onset temperature for N_2 and CO_2 evolution is lower for the single and binary catalysts than the one shown for the uncatalysed system. Also the onset temperature for CO_2 evolution is much lower for the binary

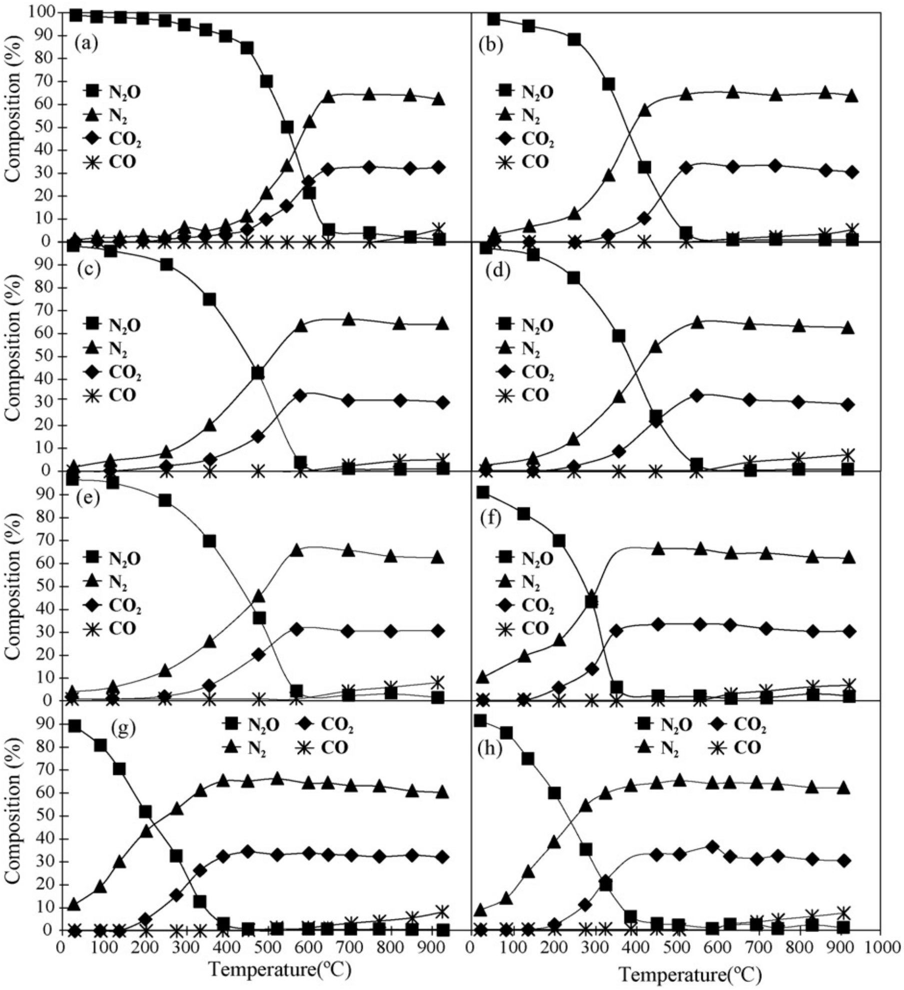

Fig. 3. Reaction products in TPR for the carbon parent sample (a) and samples doped Fe (b), Pb (c), Ni (d), Mg (e) and the Ni + Fe (f), Pb + Fe (g) and Mg + Fe (h) binary mixtures.

mixtures when compared with the single catalysts (ca. 120–200 °C). Interestingly, N_2 was detectable already below 100 °C for all the catalytic systems, but the onset temperature of CO_2 evolution was delayed with respect to N_2 and depends on the catalyst.

As referred in literature, catalysts chemisorb N_2O dissociatively at low temperatures. That leads to an increase of unstable surface oxygen complexes that react with N_2O to release CO_2 and create free sites [3–5,7,9,11,13]. Fig. 3 shows that, with CO_2 emission, N_2O conversion began to increase quickly along with an evolution of N_2. This reveals the importance of oxygen transfer from metal to carbon. The delay observed on CO_2 evolution seems to indicate retention of oxygen on metal or lower valence metal oxides. The stronger ability of the catalysts to transfer oxygen to carbon and recover the reduced state might explain the decrease in the onset temperature of CO_2 evolution for the mixtures. N_2 and CO_2 stabilise around 550 °C for the monometallic systems, and at 350 °C for the mixtures. According to the mechanism referred in the introduction, the stoichiometry of products is approximately 2:1. After product stabilisation, above 750 °C, some CO is detected, as referred by Rodriguez-Mirasol et al. [3]. This can be formed by the reaction with carbon, according to the Boudouard inverse reaction, which is favoured at high temperatures [7,18].

There is no significant change in the product distribution with temperature, independent of the catalysts used. Those results suggest that the role of the catalysts is to decrease the decomposition temperature without changing the gas products distribution. Similar results were obtained by Rodriguez-Mirasol et al. using other activated carbon supported catalysts [4,13]. The decomposition of N_2O in the catalyst active centres is generally envisaged as a charge donation from the catalyst into the antibonding of N_2O, destabilising the N–O bond and leading to scission [4,6,7,17]. The catalysts chemisorb N_2O dissociatively and, apparently, enhance the production of less stable surface oxygen complexes, which in turn decompose, yielding CO_2 and vacant sites, thus increasing N_2O decomposition [3–9,11,13–15,17].

The nature and the structure of the catalysts have an important role in the catalytic conversion of N_2O, CO_2 and NO [7,9,12,16,17–21]. Zhu et al. claim that the catalytic conversion of N_2O can be explained by an oxidation/reduction cycle of the catalysts [5]. Figs. 4–6 show the *in situ* XRD data and include the diffractograms obtained during the pre-treatment of the samples, at 500 °C, in inert atmosphere. In the diffractograms obtained for the activated carbon samples impregnated with the precursor salts (acetates), at 25 °C, only the carbon peak (C) is visible. The oxidation states before pre-treatment were (+2) for Ni, Fe, Mg

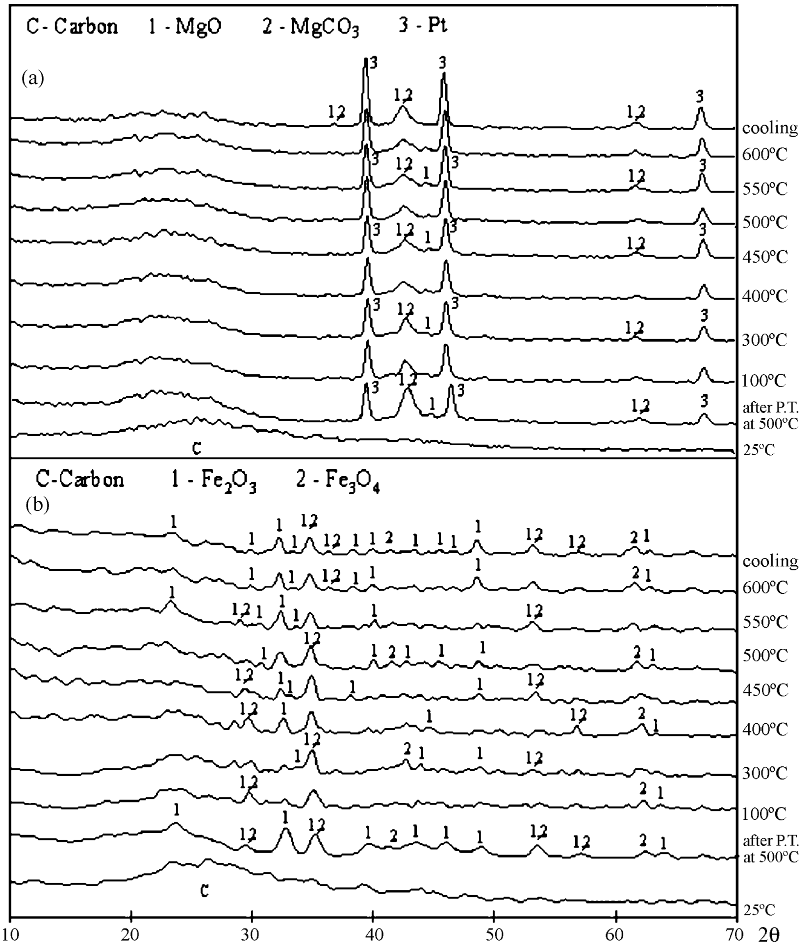

Fig. 4. *In situ* XRD data obtained in N_2O on heating samples doped with Fe (a) and Mg (b) at several temperatures. Spectra at room temperature and after pre-treatment (PT) measured in inert atmosphere, at 500 °C, also included for comparison.

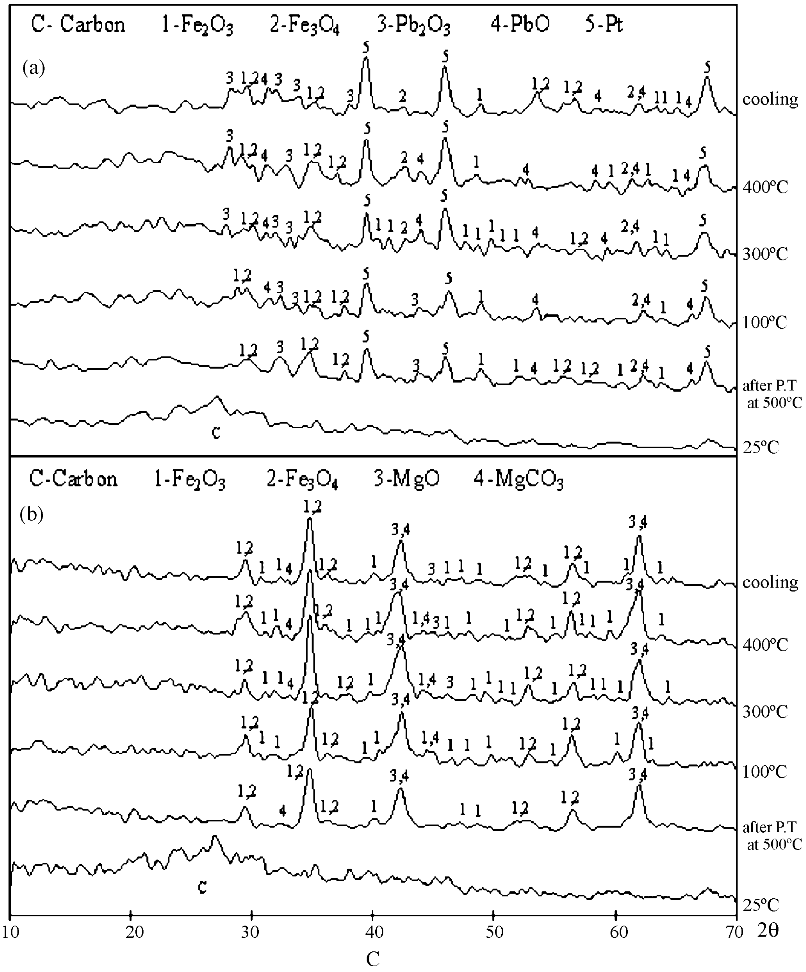

Fig. 5. *In situ* XRD data obtained in N_2O on heating sample doped with the Pb + Fe (a) and Mg + Fe (b) mixtures at several temperatures. Spectra at room temperature and after pre-treatment (PT) measured in inert atmosphere, at 500 °C, also included for comparison.

and (+4) for Pb. After pre-treatment at 500 °C, in inert atmosphere, Fe_2O_3, Fe_3O_4 ($FeO{\cdot}Fe_2O_3$), MgO, PbO, Pb_2O_3, NiO and Ni were detected. The precursor salts were probably decomposed to Fe_2O_3, MgO, NiO, and Pb_2O_3 which were partially reduced by carbon to Fe_3O_4 ($FeO{\cdot}Fe_2O_3$), Ni and PbO.

Fig. 4 shows the *in situ* XRD patterns obtained in N_2O at several temperatures for carbon doped with Fe (a) and Mg (b) while Fig. 5 shows the XRD data for the Pb + Fe (a) and Mg + Fe (b) mixtures. In some cases, the peaks show shifts to higher 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. It can be seen that, at the beginning of the reaction with N_2O, the catalysts are present as a mixture of oxides with two oxidation states. In the case of Mg, it is possible that $MgCO_3$ is formed by reaction of MgO with release of CO_2, as reported by Illán-Gómez et al. for NO reduction using Ca as catalyst [22]. The oxide is thought to participate in a catalytic redox cycle analogous to that proposed for carbon–oxygen gasification:

$$CaO \rightarrow CaO(O)$$

The oxygen is transferred to the carbon surface with formation of C(O) surface complexes. As CO_2 is evolved it is probably trapped on the surface by chemisorption on CaO, forming $CaCO_3$.which may inhibit the reaction at intermediate temperatures [22]. It can be possible that the same mechanism takes place with Mg in N_2O. The only phase clearly detected under the reaction conditions was MgO, but also some carbonate may be present because some of the peaks may be overlapped with the MgO peaks.

No evidence of a new phase was observed for the mixtures (Fig. 5), which could be considered responsible for the synergetic effect, as the same phases were observed in the X-ray spectra of the monometallic catalysts. The XRD patterns obtained in N_2 for Ni (Fig. 6a), clearly show that carbon is a reductor and that metals oxides are partially reduced to lower oxidation states. Ni is formed at approximately 500 °C, which is in agreement with the temperature of reduction of NiO by carbon, as deduced from the Ellingham diagram [23]. Above that temperature NiO peaks are no longer detected showing that it was totally reduced to Ni.

In situ XRD patterns for Pb in N_2 (Fig. 6b), show that above 400 °C the peaks corresponding to Pb_2O_3 and PbO disappear completely. This observation suggests that all the oxides were probably reduced to Pb (melting point: ~327 °C), which on its turn would melt. Besides, according to the Ellingham diagram

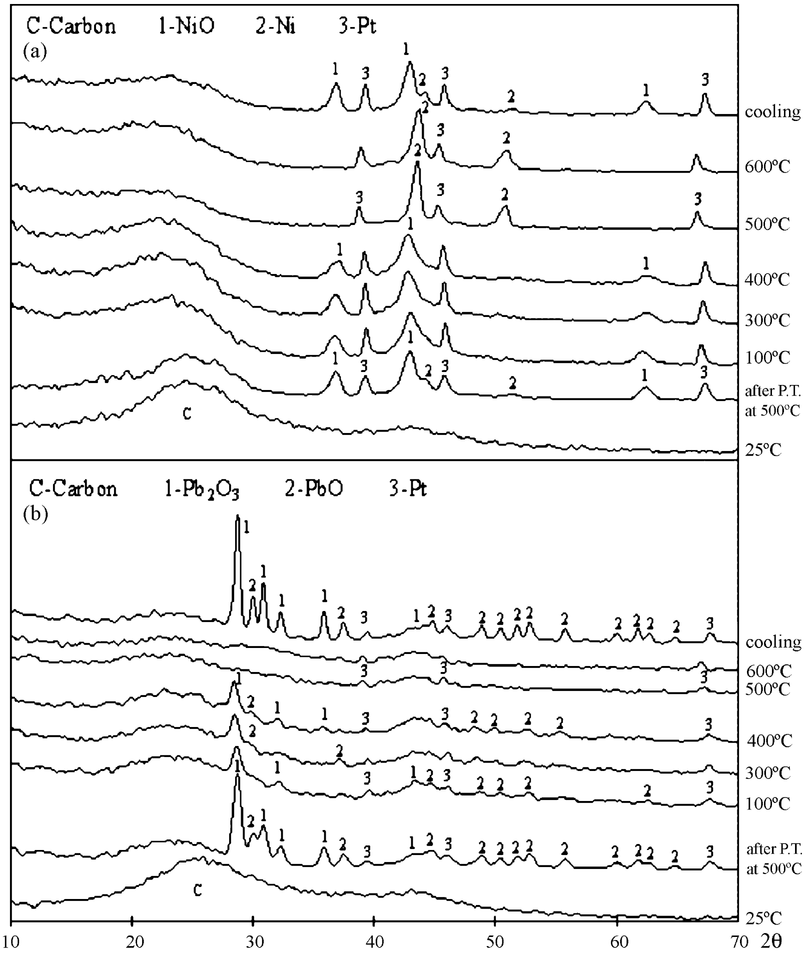

Fig. 6. *In situ* XRD data obtained in N_2 on heating samples doped with Ni (a) and Pb (b) at several temperatures. Spectra at room temperature and after pre-treatment (PT) at 500 °C also included for comparison.

[23], PbO is reduced by carbon to Pb at 327 °C. After cooling, the peaks attributed to Pb_2O_3 and PbO are again clearly visible. In other catalytic systems and other atmospheres (NO, CO_2, N_2O and air) the total disappearance of some peaks and their reappearance after cooling was also observed [12,17,21]. This behaviour suggests that the catalyst is going through a phase transition and thus is spreading on the carbon surface. In previous studies, using *in situ* ESEM, it was also possible to observe the melting of catalysts on the carbon surface [12]. Melting of the catalysts wets the carbon surface, promoting the distribution of active catalyst particles over a wider area [7,9,12,17,18,20,21,24–27]. For other catalysts and mixtures, melting was not clearly observed as with the Pb sample (Fig. 6b).

In situ XRD patterns for Pb in N_2O (not shown) showed the presence of broader peaks for temperatures up to 400 °C, which might correspond to partial melting of the particles. McKee observed, using a hot stage microscope in flowing oxygen, for graphite oxidation catalysed by lead oxide, at temperatures below 500 °C, moving catalyst particles resembling liquid droplets, which coalesced with other particles [24].

Comparing the data obtained by TPR and *in situ* XRD at the same temperatures, the results suggest that evolution of N_2, at low temperatures (100–300 °C), seems to be due to dissociative chemisorption of N_2O on the reduced phase. According to a redox cycle:

$$M_x + yN_2O_{(g)} \rightarrow M_xO_y + yN_{2(g)}$$

$$M_xO_y + \frac{y}{2}C_{(s)} \rightarrow M_x + \frac{y}{2}CO_2$$

CO_2 evolution allows the catalyst to continue transferring oxygen to carbon and therefore close the redox cycle, generating new active sites on the carbon surface. The reduction temperature of the metal oxide by carbon seems to be a key factor controlling the activity of the catalyst. The reduction temperatures deduced from the Ellingham diagram [23] are ca. 350 °C for Fe_2O_3 to Fe_3O_4, ca. 490 °C for NiO to Ni and ca. 327 °C for PbO to Pb. Therefore, the onset temperatures of CO_2 in the TPR experiments are close to the oxide reduction temperatures.

For the mixtures, it is clear from thermogravimetric and TPR that addition of a second catalyst to Fe, decreases the temperature of 100% conversion of N_2O from ~50 °C to 350 °C. According to the TPR data for the mixtures, the onset of CO_2 evolution starts at lower temperature than the monometallic catalysts. It seems that the addition of another catalyst to Fe reduces the temperature of decomposition of the C–O complexes that lead to the production of CO_2 [4,6,10,16–21]. The decrease in the onset temperature of CO_2 emission observed when comparing the bimetallic catalysts with the monometallic, suggests that the temperature necessary for reduction by carbon seems to be lower for the bimetallic catalysts. These results agree with the conclusions of other authors [10]. Wang et al. [10,28,29] deduced from XPS studies that the presence of Cu favoured the partial reduction of Fe from α-FeOOH, explaining the increase in NO uptake observed for Cu doped α-FeOOH supported on activated carbon fibers. They explained the easier reduction as an increase in the electrical conductivity of α-FeOOH due to Cu doping. It has been reported that the addition of K (as K_2CO_3) to Fe or other supported transition metals produces an electron transfer to the metal and an easier metal reduction on the surface, which was evidenced by FTIR experiments of CO and NO adsorption [10,29,30]. For practical applications, the carbon loss has to be minimized, which can be achieved using the most active catalyst (Fe + Pb) that, at 200 °C, converts ca. 60% of N_2O with 100% selectivity towards N_2.

4. Conclusions

The use of bimetallic Fe catalysts presents a synergetic effect. Both the temperature at which the reaction starts and the temperature required for 100% N_2O reduction are lowered from ca. ~500 °C to 350 °C for Fe bimetallic catalysts, relatively to the monometallic Fe catalyst.

Reaction products are N_2 and CO_2 in a stoichiometry of 2:1. CO was detected at high temperatures (above 750 °C). The onset temperature for N_2 and CO_2 evolution is lower for single and binary catalysts than the one shown for the uncatalysed system. The onset temperature for CO_2 evolution is much lower for the binary mixtures than for single catalysts. It seems that the addition of another catalyst to Fe reduces the temperature of decomposition of the C–O complexes that lead to the production of CO_2. Also 100% of selectivity to N_2 is obtained below 200 °C, showing the advantage of a binary mixture.

The ability of the catalyst to chemisorb N_2O, going through redox transference of oxygen to the carbon reactive sites, might explain the catalytic activity, as observed previously in other atmospheres and other binary mixtures.

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