Reduction of nitrogen oxides by carbon monoxide over an iron oxide catalyst under dynamic conditions

Harvey Randall, Ralf Doepper, Albert Renken[*]

Institute of Chemical Engineering, Federal Institute of Technology, 1015 Lausanne, Switzerland
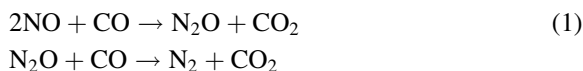
Abstract

The reduction of NO and N_2O by CO over a silica-supported iron oxide catalyst was investigated by the transient response method, with different initial oxidation states of the catalyst, i.e. completely reduced (Fe_3O_4), or oxidised (Fe_2O_3). The influence of CO pre-adsorption was also studied. From the material balance on the gas phase species, it was shown that the composition of the catalyst changes during relaxation to steady-state. The degree of reduction of the catalyst at steady-state could thus be estimated. During the transient period, CO was shown to inhibit N_2O as well as NO reductions by adsorption on reduced sites. The activity of the reduced catalyst was found to be substantially higher as compared to the oxidised catalyst for both reactions. On this basis, it was attempted to keep the catalyst in a reduced state by periodically reducing it with CO. As a result, a significant increase in the performance of the reactor with respect to steady-state operation could be achieved for N_2O reduction by CO. Finally, the dynamic behaviour of the N_2O–CO and NO–CO reactions made it possible to evidence reaction steps, the occurrence of which could not be shown during our previous investigations on the separate interactions of the reactants with the catalyst. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Transient kinetics; Nitrogen oxides; Carbon monoxide; Oxide catalyst
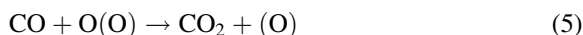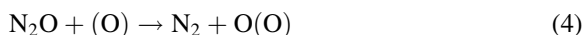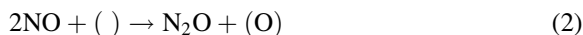
1. Introduction

Amongst oxide catalysts, transition metal oxides are of particular interest for the reduction of NO by CO, since they are the most active for this reaction [1–3]. On iron oxide, the reaction follows a consecutive reaction pathway wherein NO is first reduced to N_2O, which is then further reduced to N_2 [4]:

$$2NO + CO \rightarrow N_2O + CO_2 \qquad (1)$$
$$N_2O + CO \rightarrow N_2 + CO_2$$

In previous works [4–6], we studied the interactions of NO, N_2O and CO individually with the catalyst. It was shown that NO readily reacts with the reduced catalyst (Fe_3O_4). During this process (described in Eqs. (2) and (3)), N_2O and N_2 are formed by the reaction of NO and N_2O with surface oxygen vacancies, symbolised by ( ). The catalyst is thus reoxidised to Fe_2O_3. (O) stands for oxygen from the lattice of iron oxide [5,6]. The formation of atomic oxygen species adsorbed on Fe_2O_3, O(O), according to Eq. (4), was also established. On the oxidised catalyst, CO is oxidised to CO_2, and the catalyst is reduced to Fe_3O_4. CO was found to react with adsorbed oxygen species as well as oxygen from the lattice of iron oxide

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*Corresponding author. Tel.: 0041 21 693 3181; fax: 0041 21 693 3190; e-mail: renken@igcsun3.epfl.ch

(Eqs. (5)–(7)) [5].

$$2NO + (\ ) \rightarrow N_2O + (O) \qquad (2)$$

$$N_2O + (\ ) \rightarrow N_2 + (O) \qquad (3)$$

$$N_2O + (O) \rightarrow N_2 + O(O) \qquad (4)$$

$$CO + O(O) \rightarrow CO_2 + (O) \qquad (5)$$

$$CO + (O) \rightarrow CO(O) \qquad (6)$$

$$CO(O) \rightarrow CO_2 + (\ ) \qquad (7)$$

The aim of this work is to obtain more detailed information on the mechanism of the NO–CO reaction. For this purpose, we have applied the transient response method, which is suitable for heterogeneous catalytic reactions following a redox mechanism [8,9]. This method consists in creating a sharp change in gas phase composition at the reactor inlet, and measuring the responses of the gas phase components to this perturbation at the reactor outlet during relaxation to steady-state. From the qualitative analysis of the shapes of the responses of the products during the transient period, information on the rate-controlling step of product formation can be obtained [10,11]. Moreover, amounts of adsorbed intermediates can be determined [12]. Finally, changes in the catalyst composition can also be evidenced by this method, as shown for instance by Panayotov and Mehandjiev [9], who were able to determine the degree of reduction of a $CuCo_2O_4$ catalyst at steady-state during the NO–CO reaction.

In this work, we have applied the transient method to the N_2O+CO and the NO+CO reactions. We found it important to investigate these reactions with different initial states of the catalyst, in order to obtain a maximum of mechanistic information. Hence, both reactions were carried out on initially reduced (Fe_3O_4) and oxidised (Fe_2O_3) catalysts. The influence of CO pre-adsorbed on the reduced catalyst was also investigated.

2. Experimental

2.1. Gases and catalyst

High purity gases were used (>99.99%, except NO: >99.9%; Carbagas, Lausanne). Ar, which was used as the carrier gas, was further purified using a molecular sieve and an oxygen trap.

The catalyst consisted of Fe_2O_3 supported on SiO_2 prepared by iron nitrate impregnation. The catalyst support, consisting of SiO_2 particles ($200<d_p<250\,\mu m$, Grace GmbH, Worms) was impregnated in an aqueous solution of $Fe(NO_3)_3$ (1 $kmol/m^3$, >99% pure, Fluka, Buchs). It was then dried under vacuum at room temperature, and finally calcinated at $650°C$. The amount of Fe, determined by using a plasma emission spectrometer (Perkin–Elmer Plasma 2000, Le Mont-sur-Lausanne), after dissolution of the iron in concentrated hydrochloric acid (38% HCl at $60°C$ during 2 h) was 10.4 wt% Fe. The specific area and pore size distribution, determined via Micromeretics (type ASAP 2000, Norcross, GA) was $S_{BET}=252\,m^2/g$. 250 mg of the catalyst were used during experiments.

2.2. Apparatus

The flow-apparatus used for step-response analysis basically consisted of two feed sections converging to a four-way valve, a fixed-bed, tubular, glass reactor (i.d.: 5 mm) and a mass spectrometer (QMG 420, Balzers AG). It has previously been described in detail [4]. Due to adsorption of NO in the mass spectrometer, the concentration of NO was measured with an infrared analyser (Siemens AG, Karlsruhe).

2.3. Procedures

CO and N_2 both generate an MS signal at m/z =28 amu. Moreover, CO_2 and N_2O give rise to an MS signal at m/z=44 amu. In order to distinguish between these species, a mixture of ^{13}CO, ^{12}CO and Ar (1:4:95) was used (Alphagas, Paris). The concentration of all species could then be determined, since ^{13}CO generates an MS signal at m/z=29 amu, and the product $^{13}CO_2$ at m/z=45 amu.

N_2O+CO as well as NO+CO concentration steps were performed by substituting, at the reactor inlet, a flow of pure Ar (flow-rate: 100 ml (NTP)/min) with a flow containing N_2O or NO and CO in Ar (same total pressure and flow-rate). Helium was always added to the feed containing the reactants as an inert tracer. The pressure in the reactor was 150 kPa. The inlet molar fraction of CO was always set to $y_{CO,0}=0.015$ (20% of which was ^{13}CO). N_2O and NO inlet molar fractions

were $y_{N_2O,0}$=0.004 or 0.008 and $y_{NO,0}$=0.004, respectively.

Step experiments were performed with three different initial states of the catalyst, the preparations for which are described below.

2.3.1. Reduced catalyst

The catalyst was reduced in a flow of CO ($y_{CO,0}$=0.015, T=310°C, flow-rate: 100 ml (NTP)/min) during 40 min (which assures total reduction to Fe_3O_4 as measured by the X-ray diffraction patterns carried out on a Siemens D500 ($\theta/2\theta$) diffractometer with Cu K_α monochromatic radiation [7]). Thereafter, the remaining CO adsorbed on the catalyst was desorbed in a flow of Ar at 450°C for 20 min. The desorbing CO was monitored by MS during this procedure to ensure its complete removal.

2.3.2. Reduced catalyst with adsorbed CO

The catalyst was reduced in a flow of CO as in Section 2.3.1. Contrary to the preparation of the reduced catalyst, the remaining CO was not desorbed.

2.3.3. Oxidised catalyst

The catalyst was oxidised in a flow of N_2O ($y_{N_2O,0} = 0.004$, T=310°C, flow-rate of 100 ml (NTP)/min) during 40 min (which assures total oxidation to Fe_2O_3 as measured by the X-ray patterns [7]).

3. Results and discussion

3.1. Reduction of N_2O by CO

3.1.1. Influence of the initial degree of reduction of the catalyst

Fig. 1 shows the transient responses of the products to a step change in N_2O and CO concentrations at 310°C over initially reduced and oxidised catalysts. Over the initially reduced catalyst, the N_2 molar fraction instantaneously reaches its maximum potential value, namely $y_{N_2} = 0.004$ (corresponding to total conversion of N_2O) and, after approximately 500 s, slowly decreases towards steady-state. The initial rise in CO_2 concentration is slower than that for N_2, due to the fact that surface oxidising species, which are not present at the beginning of the transient period, have to be formed through oxidation of the catalyst by N_2O for
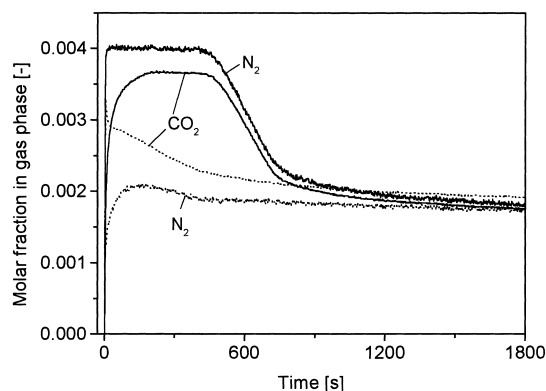

Fig. 1. Comparison between transient responses for the reduction of N_2O by CO over initially reduced and oxidised catalysts. Conditions: T =310°C; $y_{N_2O,0} = 0.004$; $y_{CO,0}$=0.015. Solid line: reduced catalyst; dots: oxidised catalyst.

CO oxidation to take place. The initial activity of the catalyst is higher than the activity at steady-state, since in the first part of the transient period, CO_2 and N_2 concentrations both go through a maximum. For times greater than 2000 s, the concentrations of CO_2 and N_2 become almost equal, as expected from the material balance, since these products are formed in equimolar quantities during the N_2O–CO reaction. The N_2 and N_2O as well as the CO_2 and CO responses were found to be complementary for all runs (i.e. the carbon and nitrogen mass balances were restricted to ±1–2%), indicating that no appreciable amounts of nitrogen or carbon containing species adsorb on the catalyst. The amount of N_2 produced over the whole experiment is substantially higher than the amount of CO_2 produced. Since no adsorption of reactants or products was observed, this indicates that the catalyst is reoxidised to some extent during the transient period, suggesting that the catalyst is more active when in a reduced state, since reoxidation occurs simultaneously, along with deactivation.

Over the initially oxidised catalyst, CO_2 and N_2 concentrations both show a maximum as a function of time, indicating a higher initial activity of the catalyst as compared to the steady-state. The maximum in N_2 concentration is not reached instantaneously, indicating that surface-reducing species are produced in the first part of the transient period, through reduction of the catalyst by CO. The amount of CO_2 formed over the whole experiment is higher than the amount of N_2.

As for step changes on reduced catalysts, the amount of adsorbed C- and N-containing species on initially oxidised catalysts was found to be negligible. Therefore, the difference between CO_2 and N_2 responses indicates that the catalyst has been reduced to some extent. The comparison between the responses of the oxidised and the reduced catalysts suggests that the reduced catalyst is more active, since higher average CO_2 and N_2 concentrations are obtained in this case. The higher activity observed for the reduced catalyst is in agreement with Mössbauer spectroscopic studies on the NO–CO reaction, by which it was shown that the reaction rate is proportional to the concentration of Fe^{2+} ions [13]. Moreover, by means of ESCA [14] and by applying the transient response method to the NO–CO reaction on iron oxide [15], it was shown that the reduction of the catalyst is accompanied by an increase in activity.

The model in Eqs. (3)–(7) is consistent with the behaviour observed on initially oxidised catalysts. In this case, the maxima in N_2 and CO_2 responses is due to the fast redox reaction on the oxidised surface (Eqs. (4) and (5)), and relaxation towards steady-state at a lower activity arises from adsorption of CO on lattice oxygen (Eq. (6)). The model, however, does not account for the high initial activity encountered for initially reduced catalysts. The rate constant of Eq. (3) has to be rather small to describe the steady state, and therefore Eq. (3) cannot describe the fast initial rate. This behaviour can be explained by a fast redox reaction on reduced sites, ( ), by which a highly reactive surface oxygen species adsorbed on reduced sites is formed (O( )) (Eqs. (8) and (9)), which would be the precursor to the formation of lattice oxygen (Eq. (10)) – in this way, it is suggested that the oxidation of the catalyst (Eq. (3)) really takes place via a two step mechanism (Eqs. (8) and (10)).

$$N_2O + ( ) \rightarrow N_2 + O( ) \qquad (8)$$

$$O( ) + CO \rightarrow CO_2 + ( ) \qquad (9)$$

$$O( ) \rightarrow (O) \qquad (10)$$
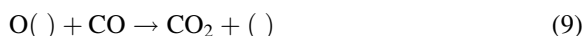
Such a precursor is known to exist in oxidation catalysis on solid oxides. For instance, Sokolovskii [17,18] has proposed a generalised scheme of the catalytic oxidation, by which in a first step, gas phase oxygen forms highly reactive surface oxygen species which can be transformed into less reactive oxygen of

the catalyst lattice. Adsorption of oxygen on a partially reduced surface may occur if there is only a partial charge transfer between the reduced surface cation to adsorbed oxygen or if the oxygen species occupies a site different from a surface lattice site [16].

The reactions in Eqs. (8)–(10), combined to reactions in Eqs. (4)–(7), are consistent with the gas phase responses to N_2O+CO concentration steps over initially reduced and oxidised catalysts. As a matter of fact, if reactions in Eqs. (8) and (9) are fast compared to the other reactions, the activity of the catalyst would be higher at the beginning of the transient period over the initially reduced catalyst with respect to the initially oxidised catalyst, as is observed experimentally. Over the initially reduced catalyst, N_2 and CO_2 responses would both go through a maximum at the beginning of the transient period, and subsequently decrease towards steady-state, due to the emergence of adsorbed oxygen into the lattice (reaction in Eq. (10)). The activity at steady-state depends on the ratio between the rates of consumption of O( ) by the two parallel reactions in Eqs. (9) and (10).

3.1.2. Influence of CO pre-adsorption

In Fig. 2, the transient responses of the products for step changes in N_2O and CO concentration over reduced catalysts, with or without pre-adsorption of CO, are compared. In both cases, there is a maximum in N_2 and CO_2 outlet molar fractions at the beginning
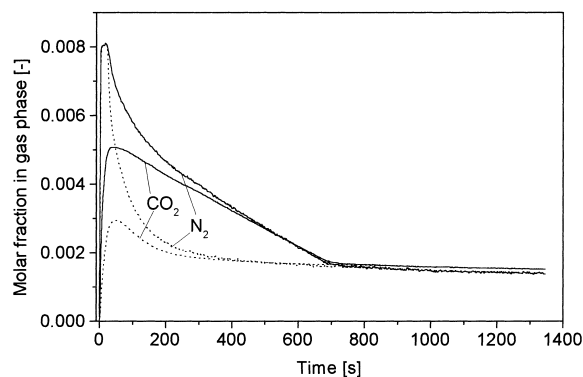

Fig. 2. Influence of CO pre-adsorption on the transient responses for the reduction of N_2O by CO over initially reduced catalysts. Conditions: T=290°C; $y_{N_2O,0} = 0.008$; $y_{CO,0}$ =0.015. Solid line: reduced catalyst without pre-adsorbed CO; dots: reduced catalyst with pre-adsorbed CO.
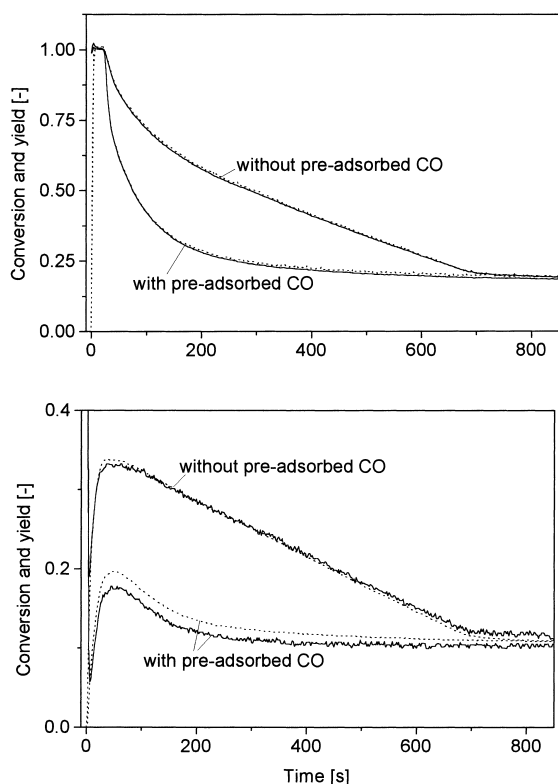
Fig. 3. Nitrogen and carbon balances during reduction of N_2O by CO over reduced catalysts with and without pre-adsorbed CO. Conditions: $T=290°C$; $y_{N_2O,0} = 0.008$; $y_{CO,0}=0.015$. Upper graph: N_2O conversion (solid line) and N_2 yield (dots); lower graph: CO conversion (solid line) and CO_2 yield (dots).

$$X_{N_2O} = 1 - \frac{y_{N_2O}}{y_{N_2O,0}}, \tag{11}$$

$$X_{CO} = 1 - \frac{y_{CO}}{y_{CO,0}}, \tag{12}$$

$$Y_{N_2} = \frac{y_{N_2}}{y_{N_2O,0}}, \tag{13}$$

$$Y_{CO_2} = \frac{y_{CO_2}}{y_{CO,0}}. \tag{14}$$

For both catalyst pre-treatments, the conversion of N_2O is equal to the yield of N_2, indicating that N_2O does not adsorb on the catalyst. For the catalyst without pre-adsorbed CO, the conversion of CO is equal to CO_2 yield, i.e., CO adsorption on the initially reduced catalyst is not observed. Upon pre-adsorbing CO, CO_2 yield is higher than CO conversion, due to the consumption of pre-adsorbed CO during the transient response.

The inhibiting effect of CO can be explained by adsorption of CO on reduced sites:

$$CO + (\ ) \rightarrow CO(\ ) \tag{15}$$

As a result, the concentration of reduced sites, $(\ )$, at the beginning of the transient response is lower in the case of CO pre-adsorption, leading to a lower activity during relaxation to steady-state, as compared to the initially reduced catalyst without pre-adsorbed CO. Consumption of adsorbed CO by N_2O (Eq. (16)) restores surface oxygen vacancies, such as, whether the activity at steady-state is the same, whether CO is pre-adsorbed or not. The reaction in Eq. (16) accounts for the fact that CO_2 yield is higher than CO conversion during the N_2O+CO concentration steps on reduced catalysts with pre-adsorbed CO (Fig. 3).

$$N_2O + CO(\ ) \rightarrow N_2 + CO_2 + (\ ) \tag{16}$$
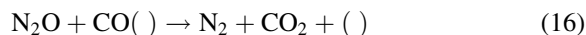
Evidence for the occurrence of reactions in Eqs. (15) and (16) has been shown previously by comparing the transient responses of initially reduced catalysts with and without pre-adsorbed CO to N_2O concentration steps [4].

3.1.3. Average degree of reduction of catalyst at steady-state

As seen in the previous sections for step changes in N_2O and CO concentration over oxidised and reduced catalysts with or without CO pre-adsorption, the relative amounts of N_2 and CO_2 produced during relaxa-

of the transient followed by relaxation to steady-state at lower values of outlet molar fraction. However, the effect of CO pre-adsorption is to decrease the activity of the catalyst during relaxation to steady-state: during this period, the average transient CO_2 and N_2 concentrations are lower than that for the catalyst without pre-adsorption of CO, indicating an inhibiting effect of CO.

Fig. 3 gives the conversions and yields of reactants and products referred to inlet N_2O and CO molar fractions (Eqs. (11), (12), (13) and (14)) for both experiments. The mean residence time of an inert gas in the reactor was found to be equal to 6 s [4], so that conversions and yields were considered only for times greater than 6 s, in order to eliminate hydrodynamic effects on conversions and yields.

tion to steady-state were found to be substantially different. The difference between CO_2 and N_2 responses was used to estimate the average degree of reduction of the catalyst at steady-state (ϕ_{ss}, Eq. (17)), which corresponds to the ratio between the average concentration of reduced sites at steady-state and the total concentration of sites (N_s). ϕ_{ss} thus determined from the CO_2 and N_2 molar fractions at the reactor outlet corresponds to an average value, since there is a gradient in N_2O and CO concentrations in the reactor, generating a gradient of the degree of reduction of the catalyst as well. The total concentration of sites (N_s) has been previously determined by measuring the amounts of N_2 and CO_2 formed, respectively, upon oxidising the reduced catalyst with N_2O and reducing the oxidised catalyst with CO [7]. An experimental value of N_s=0.33 mol/kg$_{cat}$ was obtained. The loading of the catalyst was 10.4%, calculated on Fe, as measured by atomic absorption. Therefore, 250 mg of catalyst contain 26 mg Fe, that equals 0.466 mmol Fe. The catalyst contains 0.698 mmol O in the case of Fe_2O_3 and 0.621 mmol O in the case of Fe_3O_4. The difference is 0.078 mmol, that becomes 0.31 mol/kg. The difference with the observed 0.33 mol/kg is in the range of experimental error.

$$\phi_{ss} = \begin{cases} 1 - \dfrac{\dfrac{\dot{n}_{TOT}}{m_{cat}} \displaystyle\int_0^\infty (y_{N_2} - y_{CO_2})dt}{N_s} & \text{(reduced catalyst)}, \\[4mm] \dfrac{\dfrac{\dot{n}_{TOT}}{m_{cat}} \displaystyle\int_0^\infty (y_{CO_2} - y_{N_2})dt}{N_s} & \text{(oxidised catalyst)}. \end{cases}$$

(17)

Fig. 4 gives the degree of reduction of the catalyst at steady-state at different temperatures and inlet molar ratios M ($M = y_{CO,0}/y_{N_2O,0}$) for initially reduced catalysts with or without pre-adsorbed CO. Almost the same values of ϕ_{ss} are obtained at M=1.88 for reduced catalysts with and without CO pre-adsorption. Thus, despite the different transient responses obtained for these initial states of the catalyst (Fig. 2) the same values of conversions, yields and reduction state of the catalyst are obtained at steady-state. With an inlet molar ratio of M=3.75, higher values of ϕ_{ss} are obtained, which is reasonable, since in that case the concentration of the gas phase reducing species (CO) is increased with respect to the oxidising species (N_2O).
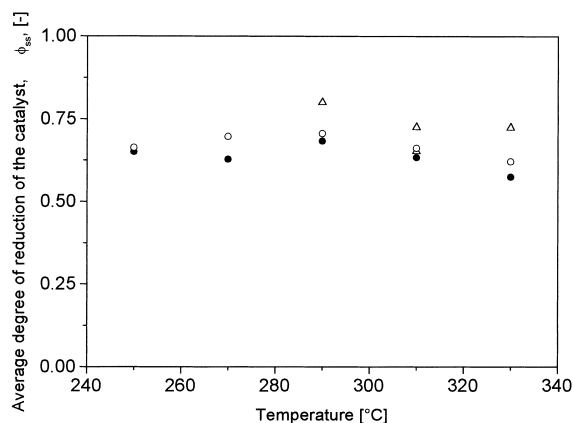

Fig. 4. Average degree of reduction of the catalyst at steady-state as a function of temperature for different values of the inlet molar ratio M=CO/N_2O: ($\triangle$) M=3.75, reduced catalyst, no pre-adsorbed CO; ($\bigcirc$) M=1.88, reduced catalyst, no pre-adsorbed CO; ($\bullet$) M=1.88, reduced catalyst, pre-adsorbed CO.

The values of ϕ_{ss} for the initially oxidised catalysts could not be determined, due to the fact that experiments with initially oxidised catalysts were stopped before CO_2 and N_2 concentrations attained equal values, owing to the high price of [13]CO (longer relaxation times are obtained with these catalysts).

In general, under the reported experimental conditions, the catalyst is rather reduced at steady-state (ϕ_{ss}>0.6). There is no significant effect of temperature on ϕ_{ss}, indicating that the values of the activation energies of reduction and oxidation of the catalyst are close to each other. This result is in accordance with previous studies on the reduction of hematite by CO [6] and oxidation of magnetite by N_2O [5]. As a matter of fact, reduction of hematite was shown to proceed through a three-step mechanism, the energies of activation of which are 75, 73 and 88 kJ/mol. For the oxidation of magnetite, a value of 72 kJ/mol was obtained, which is close to the values obtained for the reduction of the catalyst.

3.1.4. Reduction of N_2O by CO under periodic conditions

In the previous section, it was shown that the reduced catalyst has a higher activity for the reduction of N_2O by CO than the oxidised catalyst. On this basis, it was attempted to keep the catalyst in a reduced state
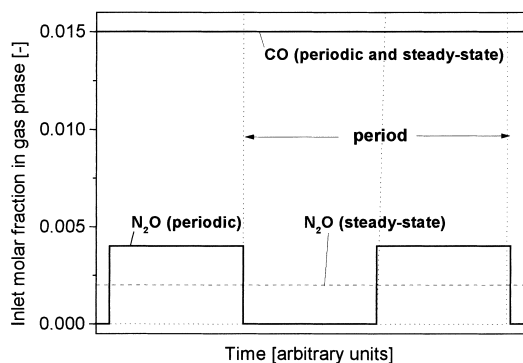
Fig. 5. Inlet molar fractions as a function of time for periodic and steady-state operation.

Fig. 6. Reduction of N_2O by CO under periodic inlet conditions at cycle-invariance. Conditions: $T=310°C$; upper graph: period $=32$ s; lower graph: period=720 s.

by periodically substituting the feed containing N_2O and CO with a feed containing only CO. Furthermore, this periodic situation was compared to steady-state operation, where CO and N_2O inlet molar fractions were set to the time-average molar fractions applied during periodic operation. This is depicted in Fig. 5, where the inlet molar fractions of N_2O and CO for periodic and steady-state operation as a function of time are shown.

During periodic experiments, the half-period under N_2O and CO was always set equal to the half-period under CO. The total period was varied between 32 and 4320 s. The dynamic responses of reactants and products at cycle-invariance for two different periods (a short and a long period) are given in Fig. 6. During the half-cycle under CO, CO_2 is still produced, due to reduction of the catalyst. At the lower period of 32 s, during the period under N_2O and CO, N_2O conversion rapidly decreases due to an insufficient reduction time under CO. On the other hand, at the higher period of 720 s, during the N_2O+CO half-cycle, N_2O is totally converted during approximately 80 s, but reaches a higher concentration at the end of the half-cycle than that noted for the lower period of 32 s.

In Fig. 7, the time-average reactor performance with respect to reactants and products over several periods at cycle-invariance, as calculated with Eqs. (18), (19), (20) and (21), are compared to the values obtained at steady-state. These reactor performances correspond to the time-average molar flow rates of products and of converted reactants, respectively.
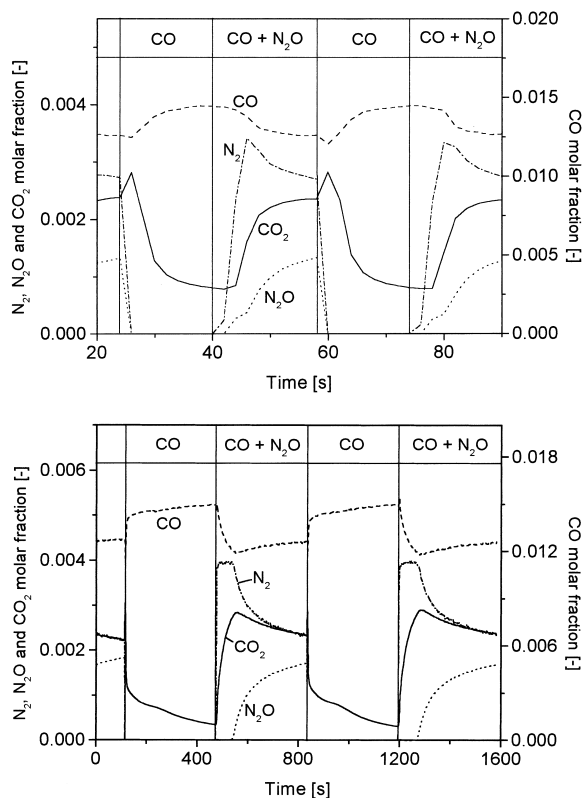
$$L_{p,N_2} = \dot{n}_{TOT}\, \overline{y_{N_2}}, \qquad (18)$$

$$L_{p,N_2O} = \dot{n}_{TOT}\, (\overline{y_{N_2O,0}} - \overline{y_{N_2O}}), \qquad (19)$$

$$L_{p,CO_2} = \dot{n}_{TOT}\, \overline{y_{CO_2}}, \qquad (20)$$

$$L_{p,CO} = \dot{n}_{TOT}\, (\overline{y_{CO,0}} - \overline{y_{CO}}), \qquad (21)$$

where $\overline{y_{N_2}}$, $\overline{y_{N_2O}}$, $\overline{y_{CO_2}}$ and $\overline{y_{CO}}$ are the time-average molar fractions during periodic operation, whereas $\overline{y_{N_2O,0}}$ and $\overline{y_{CO,0}}$ represent the average inlet molar fractions of the reactants (see Fig. 5).

As can be seen in Fig. 7, concentration cycling with short periods of about 30–60 s led to an increase in reactor performance with respect to N_2O, and N_2 yield of approximately 30%, which presumably arises from a higher time-average degree of reduction of the catalyst as compared to the steady-state situation. The values at quasi steady-state (QSS), i.e. for an infinite period [19,20], were calculated as follows: at
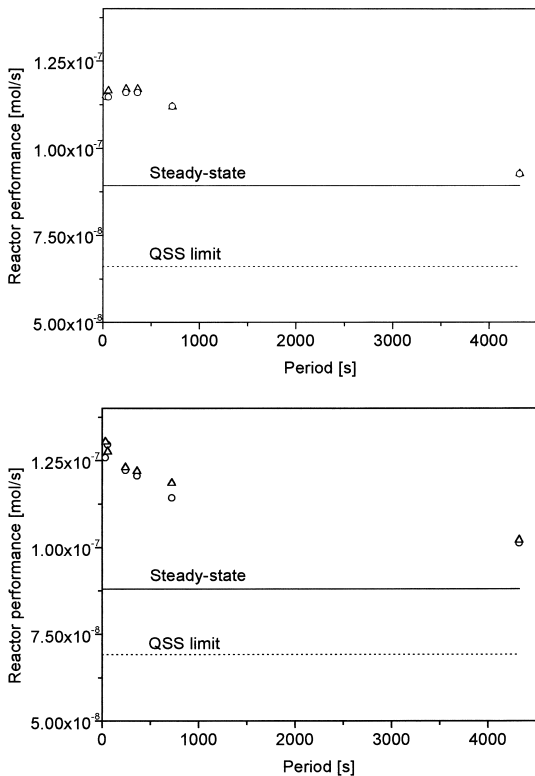
Fig. 7. Time-average reactor performance as a function of period. Comparison between periodic operation and steady-state. Upper graph: N_2O (○) and N_2 (△); lower graph: CO (○) and CO_2 (△).

Fig. 8. Transient responses for the reduction of NO by CO over an initially reduced catalyst. Conditions: $T=310°C$; $y_{NO,0}=0.004$; $y_{CO,0}=0.015$.

QSS, the transient period (which lasts less than two hours) can be neglected with respect to the period at steady-state (an infinite time), so that the time-average molar fractions of the reactants and products correspond to half of their values at steady-state during the half-period under N_2O+CO, since during the half-period under CO, the average molar fractions are equal to 0. That the QSS limit is lower than the steady-state ensures that the observed increase in reactor performance is not due to any concentration effect but is actually due to an oxidation state of the catalyst which cannot be achieved under steady-state conditions.

3.2. Reduction of NO by CO

3.2.1. Influence of the initial degree of reduction of the catalyst

Fig. 8 shows the transient response of the reduced catalyst to a step change in NO and CO con-
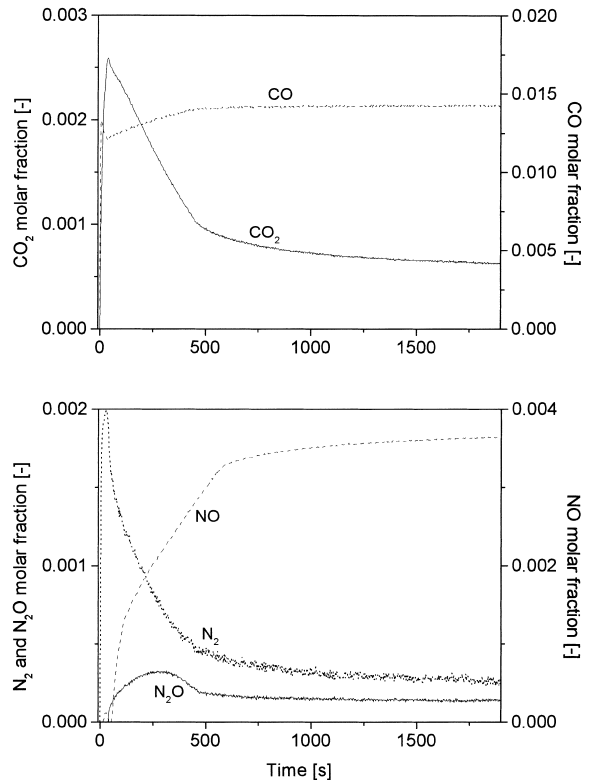
centrations at 310°C. N_2, N_2O as well as CO_2 molar fractions all go through a maximum at the beginning of the transient response, indicating that the initial state of the catalyst has a higher activity as compared to steady-state. The maximum in N_2O concentration is delayed with respect to N_2. This phenomena has already been observed in a previous work on oxidation of magnetite with NO [4], and was attributed to the consecutive reduction of NO to N_2, with N_2O as the intermediate product by reaction of NO and N_2O with reduced surface sites and simultaneous oxidation of the surface (Eqs. (2) and (3)).

The following dynamic material balances (nitrogen and carbon balances) were applied to calculate CO and NO molar fractions from inlet CO and NO molar fractions as well as from CO_2, N_2O and N_2 outlet

molar fractions.

$$y_{CO,mb} = F y_{CO,0} - y_{CO_2}, \qquad (22)$$

$$y_{NO,mb} = [\Delta_N]_{IR}, \qquad (23)$$

where

$$\Delta_N = F y_{NO,0} - 2(y_{N_2O} + y_{N_2}). \qquad (24)$$

F represents the experimental cumulative residence time distribution function (F-curve) of the catalytic reactor, i.e. the response of the reactor to a concentration step input function of an inert tracer (He in our case) normalised by dividing the output concentration by the inlet concentration of the tracer [21]. In the right term of Eq. (23), in square brackets, appears the difference between $F y_{NO,0}$ and the molar fraction of nitrogen atoms in the products, Δ_N, as measured by mass spectrometry. The subscript IR in the right term of Eq. (23) means that Δ_N was transformed into the values of Δ_N that would be measured in the infra-red analyser, in order to compare NO molar fraction thus calculated ($y_{NO,mb}$) to NO molar fraction measured at the same place, i.e. in the infra-red analyser. This transformation was performed by using Δ_N as inlet function to the infra-red analyser, and by solving the dynamic material equations describing the hydro-dynamics of the infra-red analyser, which leads to $[\Delta_N]_{IR}$. Fig. 9 shows that the responses of NO and CO calculated from Eqs. (22) and (23) are almost super-imposed to the measured responses, indicating that no notable adsorption of carbon- or nitrogen-containing species takes place on the reduced catalyst.

At steady-state, for the NO–CO reaction, the following relation exists between CO_2, N_2 and N_2O molar fractions:

$$y_{CO_2,mb} = y_{N_2O} + 2y_{N_2}. \qquad (25)$$

In Fig. 9, it can be seen that during the first 1000 s approximately, the molar fraction of CO_2 calculated according to Eq. (25) is higher than the experimental response of CO_2. Since adsorption of C- or N-containing species is not observed, this effect indicates that the catalyst has been oxidised to some extent during the transient period. As for the reduction of N_2O by CO (previous section), oxidation of the catalyst occurs simultaneously, along with deactivation, indicating that the catalyst has a higher activity when reduced.
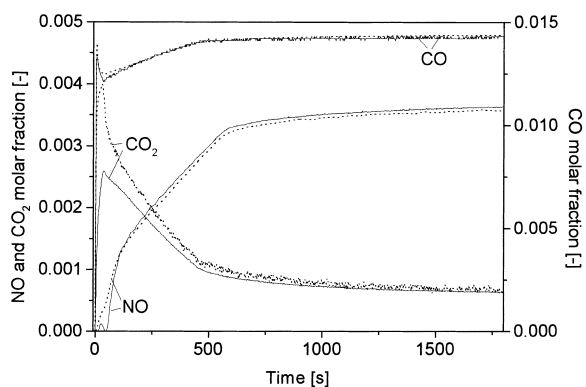

Fig. 9. Transient carbon and nitrogen balances for the reduction of NO by CO over an initially reduced catalyst. Conditions: T=310°C; $y_{NO,0}$=0.004; $y_{CO,0}$=0.015. Solid line: measured; dots: calculated from material balance.
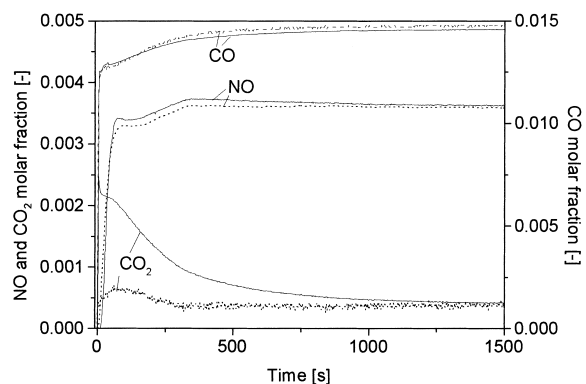

Fig. 10. Transient carbon and nitrogen balances for the reduction of NO by CO over an initially oxidised catalyst. Conditions: T=310°C; $y_{NO,0}$=0.004; $y_{CO,0}$=0.015. Solid line: measured; dots: calculated from material balance.

In Fig. 10, the CO, NO and CO_2 responses calculated from Eqs. (22), (23) and (25) are compared to the measured responses for a step change in NO and CO concentrations at 310°C over an oxidised catalyst. CO_2 molar fractions measured and calculated from Eq. (25) show a maximum at the beginning of the experiment, indicating a higher activity of the catalyst in its initial state. Thereafter, the molar fractions of products decrease towards steady-state. The slight differences between experimental and calculated CO and NO responses lie within the uncertainty range for NO and CO concentrations (±5%), so that adsorp-

tion of CO or NO can be considered negligible. During the first 1000 s approximately, the calculated response of CO_2 is lower than the measured response of CO_2. Since C and N adsorption do not occur to an appreciable extent, this indicates that the catalyst has been reduced during this period. The activity of the oxidised catalyst is considerably lower than that for the reduced catalyst, as can be seen by comparing Figs. 9 and 10: the molar fractions of all products are higher at the beginning of the transient response for the initially reduced catalyst than for the initially oxidised catalyst.

3.2.2. Influence of CO pre-adsorption on reduced catalysts

In Fig. 11, the transient responses of the products (CO_2, N_2O and N_2) to a step-change in NO and CO
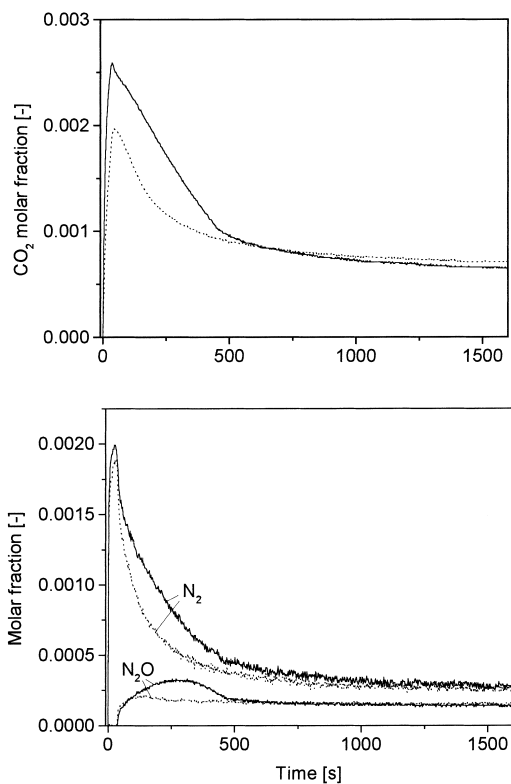

Fig. 11. Transient responses of products for the reduction of NO by CO over initially reduced catalysts with and without pre-adsorbed CO. Conditions: $T=310°C$; $y_{NO,0}=0.004$; $y_{CO,0}=0.015$. Solid line: reduced catalyst without preadsorbed CO; dots: reduced catalyst with preadsorbed CO.

concentrations at $310°C$ for initially reduced catalysts with and without pre-adsorbed CO are compared. As for the reduction of N_2O by CO, the effect of CO pre-adsorption is to decrease the activity of the catalyst during relaxation to steady-state: the molar fractions of the products during this period are lower upon pre-adsorbing CO. However, the same molar fractions are obtained at steady-state. Again, inhibition by CO can be explained by adsorption of CO on reduced sites (reaction in Eq. (15)); consumption of adsorbed CO by N_2O (reaction in Eq. (16)) accounts for the fact that activity at steady-state does not depend on CO pre-adsorption.

3.2.3. Average degree of reduction of catalyst at steady-state

As seen in the previous sections, the degree of reduction of the catalyst changes during relaxation to steady-state, whether the catalyst is initially reduced or oxidised. Thus, the average degree of reduction of the catalyst at steady-state (ϕ_{ss}) was calculated for all experimental conditions, according to Eq. (25).

$$\phi_{ss} = \begin{cases} 1 - \dfrac{\dfrac{\dot{n}_{TOT}}{m_{cat}} \displaystyle\int_0^\infty (2y_{N_2} + y_{N_2O} - y_{CO_2})dt}{N_s} & \text{(reduced catalyst),} \\[4mm] \dfrac{\dfrac{\dot{n}_{TOT}}{m_{cat}} \displaystyle\int_0^\infty (y_{CO_2} - 2y_{N_2} - y_{N_2O})dt}{N_s} & \text{(oxidised catalyst).} \end{cases}$$

(26)

The results are given in Fig. 12 for the three investigated temperatures and initial states of the catalyst. For initially reduced catalysts, the values obtained for ϕ_{ss} are the same, whether CO is pre-adsorbed or not. At $T=340°C$, ϕ_{ss} for the initially oxidised catalyst is close to the values obtained for reduced catalysts. At the lower temperatures, ϕ_{ss} for the initially oxidised catalyst could not be determined, due to the fact that experiments were stopped before the steady-state was reached, owing to the high price of ^{13}CO (longer relaxation times are observed for the initially oxidised catalyst).

Under the investigated reaction conditions, the catalyst, at steady-state, is almost reduced ($\phi_{ss} \cong 0.85$), and ϕ_{ss} is independent of temperature, indicating that the apparent activation energies for reduction and oxidation of the catalyst are comparable.

By comparing Fig. 12 with Fig. 4, it appears that with same molar ratio in the feed (i.e., $M=3.75$) ϕ_{ss} is
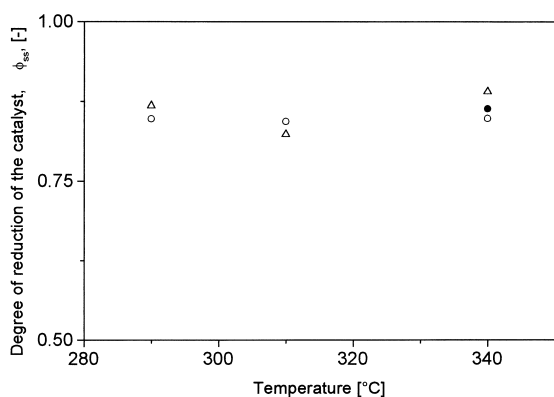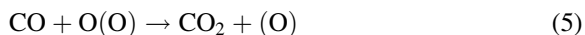
Fig. 12. Average degree of reduction of the catalyst at steady-state as a function of temperature for different initial states of the catalyst for the NO–CO reaction: ($\triangle$) reduced catalyst, no preadsorbed CO; ($\bigcirc$) reduced catalyst, preadsorbed CO; ($\bullet$) oxidised catalyst.
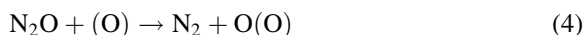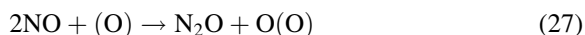
higher for the NO–CO reaction than for the N_2O–CO reaction, suggesting that the rate of oxidation of the catalyst by NO is lower than the rate of oxidation of the catalyst by N_2O. This observation is consistent with our previous kinetic investigations on the reduction of NO and N_2O with CO under steady-state conditions [4,7], during which it was found that the rate constant for surface oxidation by NO is lower than the rate constant for surface oxidation by N_2O.

The main features of the transient responses during the reduction of NO by CO are essentially the same as those for the reduction of N_2O by CO: the catalyst is more active when in a reduced state, there is an inhibition by CO and the catalyst is rather reduced at steady-state. The following reaction mechanism (which, in addition to the elementary steps proposed in the previous section for the N_2O–CO reaction, includes two additional steps for NO reduction, i.e. reactions in Eqs. (2) and (27) is consistent with the observations made during the investigation of N_2O+CO and NO+CO reactions:
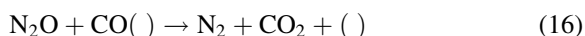
Reduction of the catalyst:

$$CO + O(O) \rightarrow CO_2 + (O) \tag{5}$$

$$CO + (O) \rightarrow CO(O) \tag{6}$$

$$CO(O) \rightarrow CO_2 + (\ ) \tag{7}$$

$$CO + O(\ ) \rightarrow CO_2 + (\ ) \tag{9}$$

Oxidation of the catalyst:

$$2NO + (\ ) \rightarrow N_2O + O(\ ) \tag{2}$$

$$N_2O + (\ ) \rightarrow N_2 + O(\ ) \tag{8}$$

$$O(\ ) \rightarrow (O) \tag{10}$$

$$2NO + (O) \rightarrow N_2O + O(O) \tag{27}$$

$$N_2O + (O) \rightarrow N_2 + O(O) \tag{4}$$

CO adsorption on reduced sites:

$$CO + (\ ) \rightarrow CO(\ ) \tag{15}$$

Consumption of adsorbed CO:

$$N_2O + CO(\ ) \rightarrow N_2 + CO_2 + (\ ) \tag{16}$$

The fast redox reaction on the reduced surface in Eqs. (9) and (2) explains the high initial activity observed for NO+CO concentration steps on initially reduced catalysts (Fig. 8). Deactivation by emergence of adsorbed oxygen into the lattice (Eq. (10)) leads to a lower activity at steady-state. The higher initial activity with respect to steady-state observed on initially oxidised catalysts (Fig. 10) can be explained by the occurrence of the redox reaction on the oxidised surface in Eqs. (5) and (27). The following decrease in activity is due to CO adsorption on lattice oxygen (Eq. (7)), which leads to a lower activity at steady-state, since CO reactive desorption (Eq. (7)) is slower than the reaction between CO and excess oxygen (Eq. (5)). The inhibiting effect of CO, which has been evidenced by comparing the initial activities during NO+CO concentration steps on initially reduced catalysts with and without pre-adsorbed CO (Fig. 11), can be explained by the adsorption of CO on reduced sites (Eq. (15)), which leads to lower rates of reactions in Eqs. (9) and (2). The consumption of adsorbed CO (Eq. (16)) explains that the same activity and selectivity are reached as steady-state, whether CO is pre-adsorbed or not.

4. Conclusions

By investigating the reduction of N_2O and NO by CO under transient conditions, it was shown that the composition of the catalyst changes during relaxation to steady-state, where it reaches a rather reduced state, close to Fe_3O_4. The activity of the reduced catalyst (Fe_3O_4) for both reactions was found to be signifi-

cantly higher than the activity at steady-state. This phenomenon was explained by a fast redox reaction of N_2O, NO and CO on the reduced surface, involving atomic oxygen species adsorbed on reduced surface sites. Periodic operation of the catalytic reactor resulted in a substantial increase in the performance of the reactor with respect to the steady-state situation for the N_2O–CO reaction. This effect is presumably due to the achievement of higher time-average degrees of reduction of the catalyst. The activity of the catalyst oxidised by N_2O is higher than the activity at steady-state for N_2O–CO and NO–CO reactions, due to the redox reaction of N_2O, NO and CO on the oxidised surface, involving excess surface oxygen, i.e. atomic oxygen species adsorbed on oxidised surface sites. CO was shown to inhibit both reactions by adsorption on reduced sites. Finally, the present study made it possible to evidence reaction steps, the occurrence of which could not be shown during our previous investigations [4–7] on the separate interactions of the reactants with the catalyst.

5. Nomenclature

d_p	diameter of particles (m)
F	cumulative residence time distribution function (F-curve) of the catalytic reactor
$L_{p,j}$	reactor performance with respect to species j (mol/s)
M	molar ratio in feed
m_{cat}	amount of catalyst (kg)
m/z	specific mass (amu)
n_{TOT}	total molar flow rate (mol/s)
N_s	total concentration of sites (=0.33 mol/kg_{cat} [7])
NTP	normal conditions of temperature and pressure (0°C, 1.013×10^5 Pa)
S_{BET}	BET specific area of catalyst (m^2/g)
T	temperature (K)
y	molar fraction
$\overline{y_j}$	time-average molar fraction for species j
y_j	molar fraction in gas phase for species j
$y_{j,0}$	molar fraction in feed for species j
( )	lattice oxygen vacancy
(O)	lattice oxygen
O(O)	oxygen adsorbed on oxidised site
O( )	oxygen adsorbed on reduced site
CO(O)	CO adsorbed on oxidised site
CO( )	CO adsorbed on reduced site

Greek letters

ϕ	degree of reduction of the catalyst

Subscripts

0	inlet
IR	at outlet from infra-red analyser
j	index for gas phase species (CO, CO_2, N_2, N_2O)
mb	calculated from material balance
ss	steady-state

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