N_2O reduction by CO over Pt electrode in a solid oxide electrolyte cell

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The reduction of nitrous oxide by carbon monoxide in a cell with a solid oxygen-conducting electrolyte – $CO + N_2O$, Pt | $0.9ZrO_2 + 0.1Y_2O_3$ | $Pt + PrO_2$, air – was studied. Experiments were performed in the temperature range 410–670 °C. The reaction kinetics under open-circuit conditions and the effect of current passing through the cell on the reaction rate were found to depend on the gaseous composition. In particular: (i) for a reaction mixture rich in N_2O, in contrast to the reaction mixture rich in CO, the temperature steady-state multiplicity of the reaction was observed under open-circuit conditions; (ii) for the reaction mixture rich in CO, in contrast to the reaction mixture rich in N_2O, a slight non-Faradaic enhancement of the reaction rate upon cathodic current application was demonstrated.

Keywords: nitrous oxide, reduction, carbon monoxide, platinum, solid oxide electrolyte cell

1. Introduction

Much attention has been paid [1,2] to the study of different catalytic reactions over metal electrode-catalysts in a solid oxygen-conducting electrolyte cell:

gaseous reactants, metal catalyst |
ZrO_2 (8–10 mol% Y_2O_3) | metal, O_2

The current passing through the cell (a flow of O^{2-} ions through the electrolyte) was found to change remarkably and reversibly the activity of the metal catalyst. The induced change in the catalytic rate exceeded by several orders of magnitude the rate of oxygen flow through the electrolyte. This effect is of interest for heterogeneous catalysis; it was coined the non-Faradaic electrochemical modification of catalytic activity (NEMCA).

The reduction of N_2O by CO catalyzed by noble metals, including Pt, has been investigated extensively because of its importance for automotive exhaust emission control [3–7]. In a recent communication [8] the $CO + N_2O$ reaction on a Pd electrode in a solid oxide electrolyte cell was studied. The NEMCA phenomenon for this system was observed upon application of both cathodic and anodic currents. To our knowledge, there are as yet no reports in the literature of the effect of electrochemical oxygen pumping on reduction of nitrous oxide by carbon monoxide over Pt electrodes in a solid oxide electrolyte cell.

This paper presents the results of the $CO + N_2O$ reaction over a Pt electrode-catalyst in a cell with a solid oxygen-conducting electrolyte:

$$CO + N_2O,\ Pt \mid ZrO_2\ (10\ mol\%\ Y_2O_3) \mid Pt + PrO_2,\ air$$

under open- and closed-circuit conditions.

2. Experimental

The electrochemical cell design was similar to that used in [9]. It was a tube closed at one end made of yttria-stabilized zirconia (YSZ) electrolyte. The electrolyte tube was 100 mm in length, 10 mm in diameter and had a wall thickness of 0.6 mm. The Pt (working) electrode was supported on the inner surface of the tube. A reaction mixture of carbon monoxide, nitrous oxide and helium was fed inside. A Pt electrode containing praseodymium oxide (ca. 2 wt%) was deposited on the outer surface of the electrolyte tube and served as counter and reference electrode simultaneously. This electrode was blown with air. Note that it was practically nonpolarized, as was revealed by special experiments performed in a cell with a reference electrode. The geometrical area of the electrodes was 3 cm^2 and the amount of Pt was 10 mg/cm^2.

The principle of the experiments was as follows. With an open circuit a heterogeneous catalytic reaction of $CO + N_2O$ takes place on the Pt electrode-catalyst. Upon passing current through the cell, the electrode-catalyst can be either anode or cathode, depending on the polarity of the applied current. This results in oxygen pumping to or from the reaction zone through the electrolyte. The effect of electrochemical pumping of oxygen on the $CO + N_2O$ reaction is the subject of study in this paper.

The effect of current on the rate of catalytic reaction over the electrode deposited on YSZ is described by two parameters: $\rho = r/r^0$ and $\Lambda = (r - r^0)/(I/2F)$, where r^0 and r are rates of the catalytic reaction under open- and closed-circuit conditions, respectively; I is the current passing through the cell; F is Faraday's constant. Rate enhancement ratio ρ shows the current-induced variation in the reaction rate with respect to the open circuit. Enhancement factor, Λ,

reflects the change in the reaction rate ($r - r^0$) relative to the oxygen flow rate through the electrolyte ($I/2F$). $\rho \neq 1$ and $|\Lambda| \gg 1$ are characteristics of the systems exhibiting non-Faradaic catalysis or NEMCA effect.

The electric current flowing through the cell was controlled by a potentiostat–galvanostat. Ohmic resistance of the cell was determined by the current interruption method. Since the counter electrode was practically nonpolarized in air atmosphere, the measured cell voltage minus ohmic loss was equal to the Pt working electrode-catalyst potential. The techniques used for the electrochemical measurements were presented in detail elsewhere [10]. The composition of the gas mixture before and after passing through the cell was analyzed by on-line gas chromatography with a molecular sieve and a Porapak-Q columns.

The experiments were performed at 410–670 °C, atmospheric pressure and a fixed rate of CO + N_2O + He flow of ca. 1 cm^3/s. Two reaction mixtures, viz. 2.5 vol% CO + 15.2 vol% N_2O + 82.3 vol% He and of 9.2 vol% CO + 3.8 vol% N_2O + 87 vol% He were used. The rate of CO + N_2O reaction was negligible in a blank test without deposition of Pt on the YSZ tube.

Pt electrodes were prepared from a Pt paste, containing 5 wt% of YSZ, according to the procedure described in [9]. Note that the counter electrode, which at the same time was the reference electrode, contained praseodymium oxide along with the Pt and YSZ. The PrO_2 was added to the Pt electrode by impregnation with a water solution of praseodymium nitrate. To obtain stable electrochemical characteristics of the cell, the electrodes were pretreated by applying both the anodic and cathodic currents in air at 850 °C for 20 h. SEM observations showed porous Pt electrodes with a thickness of ca. 10–15 μm.

3. Results and discussion

3.1. CO–N_2O reaction under open-circuit conditions

When the reaction mixture is fed to the Pt electrode-catalyst, the catalytic reduction of N_2O by CO occurs:

$$N_2O + CO \rightleftharpoons N_2 + CO_2 \qquad (1)$$

According to the results obtained, the rate of CO_2 formation was equal to the rate of N_2 formation under all experimental conditions in open circuit.

Figure 1 shows the N_2O conversion (X_{N_2O}) and open-circuit potential (E^0) versus temperature for the CO–N_2O reaction with a reaction mixture rich in CO. One can see that, when the temperature was increased from 500 to 670 °C, X_{N_2O} increased from 8 to 90% and E^0 increased slightly from -0.91 to -0.8 V. These high negative values of E^0 are typical of a reducing atmosphere and, in principle, evidence that the surface of the Pt electrode-catalyst was covered by CO. This conclusion seems natural, since the reaction mixture is rich in carbon monoxide.

Figure 2 (a) and (b) shows the CO conversion (X_{CO}) and E^0 versus temperature for the CO + N_2O reaction with

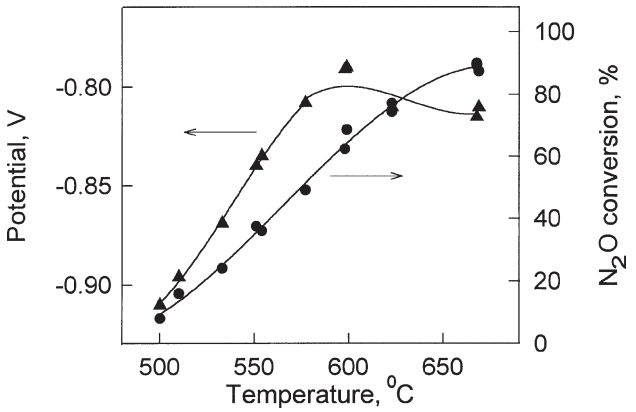

Figure 1. Effect of temperature on the N_2O conversion and Pt electrode potential at CO + N_2O reaction under open-circuit conditions. Inlet composition: [CO] = 9.2 vol%, [N_2O] = 3.8 vol%, [He] = 87 vol%.

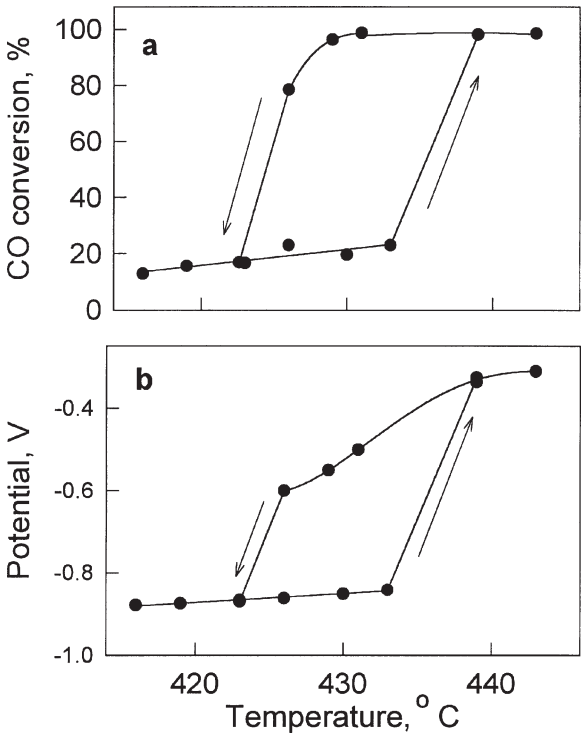

Figure 2. Effect of temperature on the CO conversion (a) and Pt electrode potential (b) at CO + N_2O reaction under open-circuit conditions. Inlet composition: [CO] = 2.5 vol%, [N_2O] = 15.2 vol%, [He] = 82.3 vol%.

reaction mixture rich in N_2O. Obviously, for this reaction mixture, in contrast to the reaction mixture rich in CO, there is a hysteresis in X_{CO} and E^0 versus temperature or temperature steady-state multiplicity of the reaction. The hysteresis occurs at temperatures ranging from 423 to 437 °C. Low X_{CO} values (ca. 20%) correspond to the low values of E^0 (ca. -0.85 V) and high X_{CO} values (ca. 100%) correspond to the high values of E^0 (ca. -0.35 to -0.6 V). In other words, it means that the surface covered with CO corresponds to a low X_{CO}, and the surface practically free of CO corresponds to a high X_{CO}.

In recent papers [3,4], the kinetics of the CO + N_2O reaction on an alumina-supported platinum catalyst has been

studied in detail. The concentration steady-state multiplicity of the reaction or hysteresis in the reaction rate versus the inlet concentration of reagents was observed. A Langmuir–Hinshelwood-type mechanism was proposed:

$$CO_{gas} \rightleftharpoons CO_{ads} \quad (2)$$

$$N_2O_{gas} \rightleftharpoons O_{ads} + N_{2\,gas} \quad (3)$$

$$CO_{ads} + O_{ads} \rightleftharpoons CO_{2\,gas} \quad (4)$$

It was shown that the mechanism incorporating the CO self-exclusion effect provides an excellent description of the concentration steady-state multiplicity of the reaction. This mechanism seems to account for the kinetic behavior of the reaction revealed in the present paper.

3.2. CO–N_2O reaction under closed-circuit conditions

For the reaction mixture rich in N_2O, the effect of polarization of the Pt electrode-catalyst (or electrochemical oxygen pumping) on the $CO + N_2O$ reaction rate was studied over the temperature range 415–430 °C when X_{CO} was low under open-circuit conditions (see figure 2(a)). The ohmic-drop-free Pt electrode-catalyst potential (φ) changed from 2 to -2 V leading to a change in current passing through the cell from 1.4 to -0.06 mA; table 1 exemplifies the experimental results. The rates of CO_2 and N_2 formation are seen to be practically unchanged upon applying both cathodic and anodic currents with respect to their open-circuit values. Thus, electrochemical oxygen pumping does not effect the reaction rate for the reaction mixture rich in N_2O.

Recently [8], the $CO + N_2O$ reaction has been studied over a Pd electrode in YSZ cell. The experiments were performed at 400 °C with a reaction mixture rich in N_2O. Non-Faradaic behavior was demonstrated upon the application of both cathodic and anodic potentials. The reaction rate was doubled with $\Lambda \approx 20$. These results can be explained in terms of the NEMCA concept reported in [1,2,11]. The cathodic current effect on the reaction rate was attributed to an enhanced N_2O dissociation as the cathodic potential increased (or work function of the electrode decreased), while the anodic current effect on the reaction rate was attributed to a decrease in CO inhibition as the anodic potential (or work function of the electrode) increased.

For the Pt electrode, in contrast to the Pd electrode, there was no effect of current on the reaction rate with a reaction mixture rich in N_2O (see table 1). This can be explained by the fact that there is no influence of either anodic or cathodic Pt electrode potential on CO inhibition and N_2O dissociation.

For the reaction mixture rich in CO, the effect of electrochemical oxygen pumping on the catalytic properties of the Pt electrode for the $CO + N_2O$ reaction was investigated over the temperature range of 500–670°C. Figure 3 shows a typical galvanostatic transient rate of CO_2 formation at 500 °C when applying anodic currents of 6.7 and 10.3 mA. One can see that the current leads to reversible enhancement of CO_2 formation rate and does not change the N_2 formation rate. However, the factor Λ is ca. 1 for r_{CO_2}. Thus, electrochemical oxygen pumping to the Pt electrode-catalyst causes no effect on the rate of the $CO + N_2O$ reaction and results in purely Faradaic enhancement in CO_2 formation rate via the electrochemical reaction

$$CO + O^{2-} \rightleftharpoons CO_2 + 2e^- \quad (5)$$

where O^{2-} is electrochemically pumped oxygen.

The observed phenomenon may be accounted for by the assumption that the catalytic (equation (1)) and electrochemical (equation (5)) reactions proceed independently of each other at different sites of the electrode. The electrochemical reaction occurs at a three-phase boundary (gas–Pt–YSZ), whereas the catalytic reaction occurs at the platinum surface.

It is most probable that for a reaction mixture rich in N_2O, the electrochemical oxidation of CO also occurred with anodic polarization of the Pt electrode catalyst. In this case, there is no change in r_{CO_2} due to the low anodic current of 1.4 mA (see table 1). In fact, the current of 1.4 mA corresponds to an oxygen flow rate of 0.21 μmol O_2/min through the electrolyte. As a result, r_{CO_2} increases by 0.42 μmol CO_2/min; this value is within experimental error.

Thus, the $CO + N_2O$ reaction under anodic polarization of the Pt electrode-catalyst can be explained by both ordinary catalytic steps (equations (2)–(4)) occurring at the

Table 1
Influence of cathodic and anodic polarizations on the rate of $CO + N_2O$ reaction over Pt electrode-catalyst.[a]

Current (mA)	Electrode-catalyst potential (V)	r_{CO_2}/r_{N_2} (μmol/min)
0	-0.87	$11.2 \pm 0.3/11.2 \pm 0.3$
-0.03 to -0.06	-1.4 to -2.0	$11.3 \pm 0.3/11.2 \pm 0.3$
1.4	2.0	$11.5 \pm 0.3/11.2 \pm 0.3$

[a] Temperature and inlet composition: $T = 423$ °C; [CO] = 2.5 vol%; [N_2O] = 15.2 vol%, [He] = 82.3 vol%.

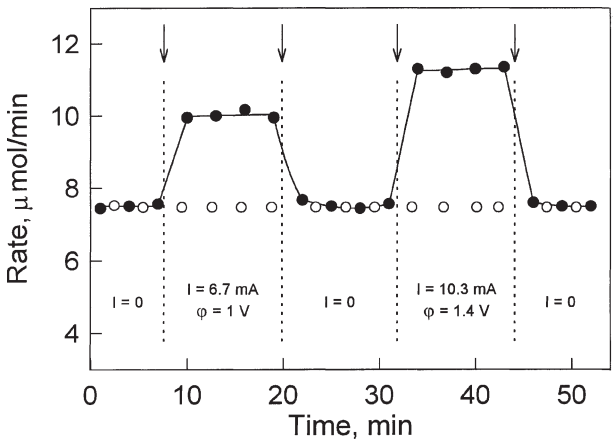

Figure 3. Effect of anodic current on the rates of CO_2 and N_2 formation at $CO + N_2O$ reaction over Pt electrode-catalyst. Temperature and inlet composition: $T = 500$ °C; [CO] = 9.2 vol%, [N_2O] = 3.8 vol%, [He] = 87 vol%. (•) Rate of CO_2 formation, (○) rate of N_2 formation.

platinum surface and the electrochemical step (equation (5)) occurring at the three-phase boundary.

For the reaction mixture rich in CO, the effect of cathodic current on the reaction rate was observed at an ohmic-drop-free Pt electrode-catalyst potential lower than −1.5 V. That was a reversible effect. It was found that the cathodic current led to a slight increase in r_{CO_2} and r_{N_2} against their open-circuit values. As an example, figure 4 shows the galvanostatic transient rates of CO_2 and N_2 formation at 550 °C on applying a cathodic current of −0.6 mA ($\varphi = -1.7$ V). One can see that the current causes an enhancement of r_{CO_2} and r_{N_2}. The ratio ρ and the factor $|\Lambda|$ were 1.1 and ca. 20, respectively. Thus, for the reaction mixture rich in CO, in contrast to the reaction mixture rich in N_2O, electrochemical oxygen pumping from the Pt electrode-catalyst causes a slight NEMCA effect on the rate of the $CO + N_2O$ reaction.

The small non-Faradaic change in the $CO + N_2O$ reaction rate under cathodic polarization of the Pt electrode-catalyst is due to the reduction of the YSZ electrolyte. In fact, a NEMCA effect for this reaction was observed for the reaction mixture rich in CO at high values of cathodic potential ($\varphi < -1.5$ V). Under these conditions, reduction of the electrolyte, namely the formation of F centers and oxygen vacancies in the sub-surface region, can take place [12–14]. According to [13,14], F centers and oxygen vacancies on the electrolyte surface formed by an applied high cathodic potential are responsible for enhancement of the catalytic rate of nitric oxide decomposition over Pt and Au electrodes in a solid oxide electrolyte cell. F centers have also been proposed to explain the catalytic activity of oxides on N_2O decomposition [15].

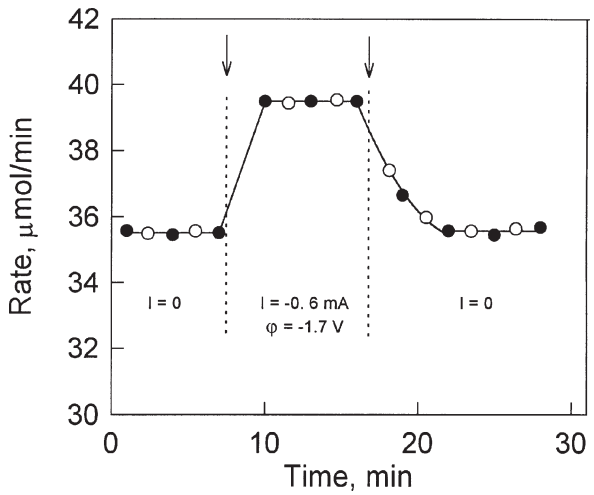

Figure 4. Effect of cathodic current on the rates of CO_2 and N_2 formation at $CO + N_2O$ reaction over Pt electrode-catalyst. Temperature and inlet composition: $T = 550$ °C; [CO] = 9.2 vol%, [N_2O] = 3.8 vol%, [He] = 87 vol%. (•) Rate of CO_2 formation, (○) rate of N_2 formation.

So, we think that for the reaction mixture rich in CO (reducing atmosphere) at high cathodic polarization of the Pt electrode, new catalytically active sites (F centers and oxygen vacancies) are formed in the sub-surface region of the YSZ electrolyte. This would explain why the non-Faradaic enhancement of reaction rate is observed for the reaction mixture rich in CO. For the reaction mixture rich in N_2O (oxidative atmosphere), the same cathodic polarization of the Pt electrode did not lead to reduction of YSZ electrolyte or to a change in the reaction rate (see table 1). This may relate to the fact that experiments were carried out at the values of temperature and cathodic current lower than those for the reaction mixture rich in CO.

4. Conclusion

According to [1,2,11] which deal with the NEMCA effect, the expected value of factor Λ can be estimated by the equation

$$\Lambda_{max} = 2Fr^0/I_0,$$

where r^0 is the rate of a catalytic reaction under open-circuit conditions and I_0 is the exchange current. This equation was used to estimate Λ_{max} for the systems under study. The exchange current was calculated as

$$I_0 = RT/nFR_\eta,$$

where n is a small number, supposedly 1, R_η is the polarization resistance determined from current–voltage curves at a small (⩽10 mV) deviation of the electrode potential from its open-circuit value. The values of r^0, I_0 and Λ_{max} for the CO–N_2O reaction are presented in table 2. One can see that Λ_{max} was ca. 10^3, and for this reason we expected the non-Faradaic effect of current on the rate of the CO–N_2O reaction.

However, the $|\Lambda|$ values observed for the CO–N_2O reaction over a Pt electrode-catalyst were essentially lower than those predicted by the above theoretical considerations. This inconsistency suggests that the NEMCA effect

Table 2
Experimental conditions, rates of $CO + N_2O$ catalytic reaction over Pt electrode-catalyst under open circuit of the cell (r^0), exchange currents (I_0) and theoretical magnitudes of the enhancement factor ($|\Lambda|_{max}$).

Feed composition (vol%)			T	r^0	I_0	$\|\Lambda\|_{max}$
[CO]	[N_2O]	[He]	(°C)	(μmol/min)	(mA)	
2.5	15.2	82.3	423	11.2	0.008	4.5×10^3
9.2	3.8	87	500	7.6	0.03	8×10^2
9.2	3.8	87	550	35.6	0.08	1.4×10^3

is not universal (see also [16–19]) and that the theory discussed in [1,2,11] needs some improvement.

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