Catalysis Letters 41 (1996) 7–11

Ion cyclotron resonance study of CO oxidation in the gas phase in the presence of rhenium cations with carbonyl and oxygen ligands. Comparison with heterogeneous catalysis

E.F. Fialko, A.V. Kikhtenko, V.B. Goncharov and K.I. Zamaraev

Boreskov Institute of Catalysis, Pr. Akademika Lavrentieva 5, 630090 Novosibirsk, Russia

Received 1 April 1996; accepted 11 June 1996

Gas-phase oxidation of CO in the presence of rhenium cations with carbonyl and oxygen ligands has been studied by Fourier transform ion cyclotron resonance (FT-ICR) spectrometry. Rhenium cations have been generated by the electron impact of $Re_2(CO)_{10}$ vapour. Contrary to the unreactive rhenium ions, rhenium monocarbonyl ions have been found to react with O_2 molecules yielding rhenium monoxide ions and CO_2 molecules. ReO^+ ions are subsequently oxidized with O_2 to di- and trioxide ions. The bond energies in rhenium oxide ions were estimated as $D^0(Re^+–O) = 104 \pm 14$, $D^0(ReO^+–O) < 118$, $D^0(ReO_2^+–O) = 122 \pm 4$ kcal/mol. Simultaneous addition of CO and O_2 molecules to the reaction volume leads to the gas-phase catalytic oxidation of CO with pairs of rhenium oxide ions ReO_3^+/ReO_2^+ serving as the oxidized and reduced forms of the catalyst. The mechanisms of the above reactions are discussed in connection with that for oxidation of CO over solid oxide catalysts.

Keywords: catalytic gas-phase CO oxidation; carbon monoxide; Fourier transform ion cyclotron resonance spectrometry; rhenium ion carbonyls; rhenium ion oxides

1. Introduction

Two different mechanisms of heterogeneous catalytic oxidation of CO are believed to exist: the stepwise and the concerted one [1–3]. In the stepwise mechanism reactants interact with the catalyst consecutively. In the concerted mechanism the reactants react with the catalyst and each other simultaneously, forming an active complex in which the reactants transform into products. Some reactions are believed to proceed over oxide catalysts via both mechanisms, high temperatures favouring the stepwise mechanism and low temperatures the concerted one [1–3].

While the pathway for the stepwise mechanism of CO oxidation over oxides is more or less clear [1–3], the detailed picture of the concerted mechanism of CO oxidation has not been elucidated so far.

For characterisation of catalytic reaction steps at the molecular level, ion cyclotron resonance (ICR) spectrometry may be used. This mass-spectrometric method provides an opportunity to investigate these steps in the gas phase, i.e. under the most pure conditions, where many complications induced by condensed phases are absent. Using the ICR method Kappes and Staley [4] have shown that oxidation of CO with N_2O in the gas phase is catalysed by Fe^+, Ti^+, Zr^+, V^+, Nb^+ and Cr^+ ions. In ref. [5] the catalytic oxidation of CO by N_2O in the presence of MoO_3^+/MoO_2^+ and WO_3^+/WO_2^+ ions was observed. In all these systems the catalytic reaction proceeds via the stepwise mechanism:

$$MoO_x^+ + CO \longrightarrow MoO_{x-1}^+ + CO_2 \qquad (1)$$

$$MoO_{x-1}^+ + N_2O \longrightarrow MoO_x^+ + N_2 \qquad (2)$$

$$CO + N_2O \longrightarrow CO_2 + N_2 \qquad (3)$$

Irikura and Beauchamp have studied the reactivity towards some organic compounds and oxygen of third-row transition metal ions produced with direct laser vaporization of a metal target [6]. They have found that the Re^+ ion does not react with O_2. In contrast, rhenium monoxide ion is oxidized by oxygen to di- and trioxide ions.

Also it was mentioned that rhenium ion has the smallest reactivity in comparison with other third-row transitional metal ions. In the ground state the Re^+ ion has the electron configuration d^5s^1 and a maximum spin–spin interaction. Bonding with e.g. an oxygen atom should lead to the loss of 58 kcal/mol due to the decrease of the energy of spin–spin interaction [7]. This could be a reason for the relative unreactivity of Re^+.

In this work the reactivity toward various oxidants and CO of Re^+ and $Re(CO)^+$ ions generated by the electron impact of the $Re_2(CO)_{10}$ vapour were studied using ICR spectrometry. The mechanisms of CO oxidation with O_2 in the gas phase are elucidated and compared with those over solid oxide catalysts.

2. Experimental

All experiments were carried out on a standard Bruker-Spectrospin CMS-47 ion-cyclotron resonance spectrometer, equipped with 33 mm cubic trapping cell and an Oxford Instruments vertical type superconducting magnet maintained at 4.7 T [8]. The warm bore of the magnet was 89 mm. The vacuum system was evacuated by means of an ionic pump with a capacity 160 ℓ/s. Background pressure was about 3×10^{-9} mbar. A Bayard-Alpert ionization gauge was used to monitor the pressure. Partial pressure of rhenium pentacarbonyl was $(1-6) \times 10^{-8}$ mbar. In this work a $Re_2(CO)_{10}$ sample with the natural isotopic ratio (abundance $^{185}Re = 37.40\%$, $^{187}Re = 62.60\%$) was used to generate Re^+ and $ReCO^+$ ions. Pressures of the oxidants (NO, O_2, N_2O) and CO were $(1-7) \times 10^{-7}$ mbar. All reagents were commercial ("Reachim") ones. Gaseous reagents were used without additional purification. An FTICR spectrum was excited by pulse sequences, which were repeated in each experiment for several dozen times to obtain a better signal-to-noise ratio. All experiments were carried out at ambient temperature.

A double resonance technique, described in ref. [9], was used in some experiments. In this technique suppression of the daughter ions is sought by ejection of the supposed parent.

To determine the metal–ligand bond energies the kinetic method or method of destructive ligand addition was used. Since the FTICR method allows one to observe only exothermic reactions, occurrence of the reaction

$$M^+ + L_1L_2 \longrightarrow ML_1^+ + L_2 \qquad (4)$$

establishes the bottom limit of the metal–ligand bond energy $D^0(M^+-L_1) > D^0(L_1-L_2)$, where M^+ denotes the metal ion, L_1L_2 the neutral molecule.

However, the absence of the products of reaction (4) should not be considered as the top limit of $D^0(M^+-L_1)$ because of a possible energy barrier.

3. Results and discussion

The ionization of $Re_2(CO)_{10}$ by electron impact results in formation of Re^+, $ReCO^+$, as well as $Re(CO)_n^+$, $Re_2(CO)_n^+$, and $Re_2(CO)_n^{2+}$ ions:

$$Re_2(CO)_{10} + e^- \rightarrow Re^+ + Re(CO)_n + (10-n)CO + 2e^- \qquad (5)$$

$$Re_2(CO)_{10} + e^- \rightarrow Re(CO)_n^+ + Re(CO)_m + (10-n-m)CO + 2e^- \qquad (6)$$

$$Re_2(CO)_{10} + e^- \rightarrow Re_2(CO)_n^+ + (10-n)CO + 2e^- \qquad (7)$$

$$Re_2(CO)_{10} + e^- \rightarrow Re_2(CO)_n^{2+} + (10-n)CO + 3e^- \qquad (8)$$

In the presence of oxygen in the reaction medium rhenium oxide ions ($ReO_x^+, x = 1-3$ and $Re_2O_y^+$, $y = 1-6$) were found. Since the behaviour of rhenium oxide ions containing two rhenium atoms occurred rather complicated, their reactivity is not described in this contribution and will be discussed in detail in a subsequent publication. However, it should be mentioned that the chemistry of cluster ions did not affect the chemistry of species containing one rhenium atom. Double resonance experiments showed that in the reactions of $Re_2(CO)_n^+$ and $Re_2O_y^+$ ions the Re–Re^+ bond did not break.

The kinetic behaviour of Re^+, $Re(CO)^+$, ReO^+, ReO_2^+ and ReO_3^+ ions is presented in fig. 1. It can be seen that concentration of rhenium ion changes insignificantly in comparison with the increase in the rhenium oxide ion concentration. So reaction (9) of Re^+ with O_2 does not occur and the rhenium ion was not supposed to be a precursor of the rhenium oxide ion:

$$Re^+ + O_2 \rightarrow \text{no reaction} \qquad (9)$$

This could be taken to employ reaction endothermicity. The absence of reaction (9) was confirmed with the use of the double resonance technique. Ejection of Re^+ ions did not lead to significant changes in the concentration of ReO^+ ions (fig. 2). Whereas, the ejection of $Re(CO)^+$ ions was accompanied with nearly total disappearance of ReO^+ ions (fig. 2c).

Thus, in our system the formation of ReO^+ proceeded

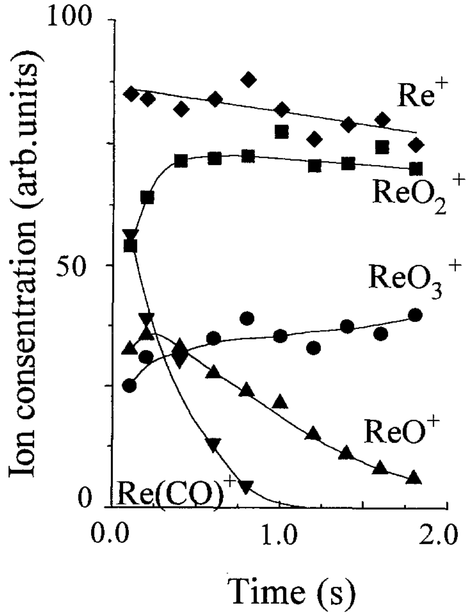


Fig. 1. Kinetic curves for the oxidation of the ions formed during the electron impact ionization (70 eV) of the rhenium pentacarbonyl vapours, $Re_2(CO)_{10}$, with O_2. $P(O_2) = 5.6 \times 10^{-7}$ mbar, $P(Re_2(CO)_{10}) = 6 \times 10^{-8}$ mbar. $[^{187}ReO_2^+]/[^{187}ReO_3^+] = 2$.

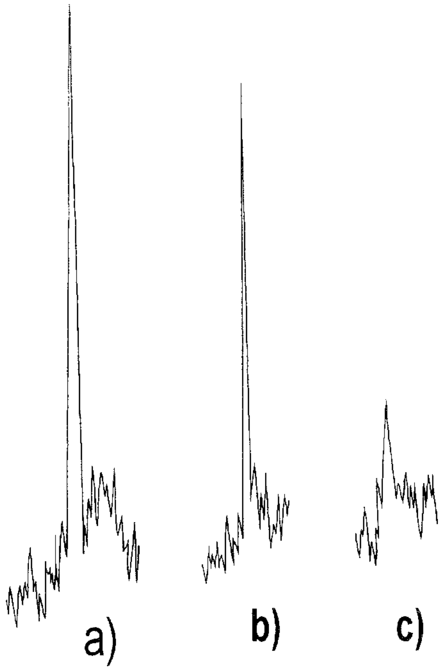


Fig. 2. Mass spectrum of $^{187}ReO^+$ ion generated in reaction (6) (a), and the same spectrum recorded after the ejection of $^{187}Re^+$ ion (b) and $^{187}Re(CO)^+$ ion (c).

during the interaction of rhenium monocarbonyl $Re(CO)^+$ with oxygen:

$$Re(CO)^+ + O_2 \rightarrow ReO^+ + CO_2 \qquad (10)$$

Reaction (10) should be very exothermic. Taking into consideration that the typical bond energies in metal monocarbonyl ions are 20–40 kcal/mol [10] and the energy of abstraction of one oxygen atom in CO_2 is $D^0(CO\text{–}O) = 127$ kcal/mol, the energy gain for the reaction (10) should be about 87–107 kcal/mol. In ref. [11] Kappes and Staley mentioned that the oxidation reaction with great exothermicity can lead to the formation of oxide cations in the excited states. These excited cations in some cases are more reactive in comparison with the same ions formed in reactions with lower exothermicity.

The formation of the rhenium oxide ions is not observed in the reaction of Re^+ with N_2O and NO. Rhenium monocarbonyl ion readily reacts with these oxidizers by CO_2 formation:

$$Re(CO)^+ + N_2O \rightarrow Re^+ + N_2 + CO_2 \qquad (11)$$

$$Re(CO)^+ + NO \rightarrow ReN^+ + CO_2 \qquad (12)$$

Reaction of ReO^+, formed in reaction (10), with oxygen yields di- and trioxide ions:

$$ReO^+ + O_2 \rightarrow ReO_2^+ + O \qquad (13)$$

$$ReO_2^+ + O_2 \rightarrow ReO_3^+ + O \qquad (14)$$

These results are in a good agreement with the data of ref. [6].

As seen from fig. 1, the ratio of the concentrations of ReO_2^+ and ReO_3^+ ions is nearly constant. Apparently, this is due to the reduction of ReO_3^+ back to ReO_2^+ by background CO molecules:

$$ReO_3^+ + CO \rightarrow ReO_2^+ + CO_2 \qquad (15)$$

According to our measurements, this background CO pressure reached 4×10^{-8} mbar when only rhenium carbonyl $Re_2(CO)_{10}$ evaporized in the vacuum system. The additional inlet of CO molecules ($P_{CO} = 1.2 \times 10^{-7}$ mbar) to the reaction medium was accompanied by an increase of the ratio of the concentrations $[ReO_2^+]/[ReO_3^+]$ from 2 to 3.2 (fig. 3).

Reactions (14) and (15) present the catalytic cycle of CO oxidation by oxygen in the presence of rhenium oxide ions. Catalytic oxidation in the studied system closely resembles a stepwise mechanism of CO oxidation over the oxide catalysts. For the latter catalysts such mechanism is proposed to dominate at high temperatures [1]. Our metal oxide ions ReO_2^+/ReO_3^+ can be considered as a model of the active site of the oxide catalysts. The reagent molecules CO and O_2 react with this active site consecutively. Note however, that in the gas-phase reaction (14) the oxygen atom O is formed in the free state, while in the reaction over oxide catalysts it is formed in an adsorbed state.

There is also the other pathway of CO_2 formation in our system, namely via reaction (10). In this case the synchronous mechanism of CO molecule oxidation occurs in the coordination sphere of rhenium. Monocarbonyl

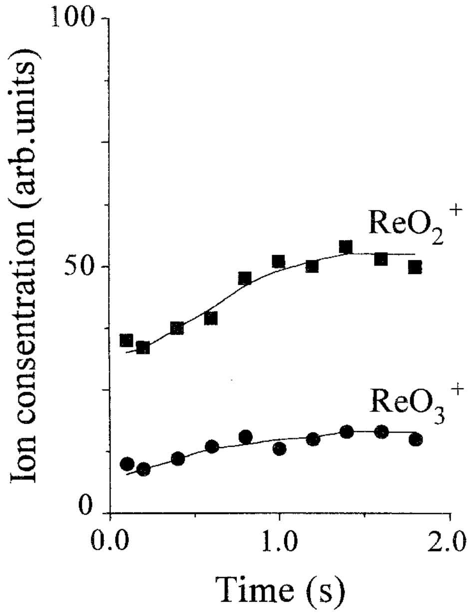
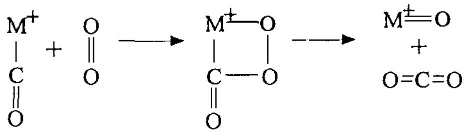


Fig. 3. Kinetic curves for the oxidation of the ions formed during the electron impact ionization (70 eV) of the rhenium pentacarbonyl vapours, $Re_2(CO)_{10}$, with O_2 in the presence of CO molecules. $P(O_2) = 4.8 \times 10^{-7}$ mbar, $P(Re_2(CO)_{10}) = 6 \times 10^{-8}$ mbar, $P(CO) = 1.2 \times 10^{-7}$ mbar. Kinetic curves for Re^+, $Re(CO)^+$ and ReO^+ are omitted since they are the same as in fig. 1. $[^{187}ReO_2^+]/[^{187}ReO_3^+] = 3.2$.



Scheme 1.

ions of other transition metals, such as Fe, Co, Mn [12], undergo the same reaction:

$$M(CO)^+ + O_2 \rightarrow MO^+ + CO_2 \qquad (16)$$

A possible mechanism of this reaction is shown in scheme 1. Reaction occurs via a supposed four-centered intermediate. Its decomposition leads to the formation of MO^+ ions.

This reaction could be a model of the interaction of oxygen molecule from the gas phase with CO absorbed on an oxide surface. With the metal ion M^+ as a model of a reduced active site of an oxide catalyst, the interaction of CO and O_2 over this site is seen to occur simultaneously. So, reaction (16) may be considered as a model of the concerted mechanism of CO oxidation. Thus, in the gas phase elementary reaction of both the stepwise and the concerted mechanisms of CO oxidation with O_2 are observed. However, the whole closed cycle for the concerted mechanism of CO oxidation is not realized in our gas-phase ICR study.

A number of thermochemical limits and rate constants were determined for the reaction observed. These are summarized in tables 1 and 2, respectively.

The top and the bottom limits for metal–oxygen bond energies in rhenium mono-, di- and trioxide ions were estimated using the kinetic method described above.

Rate constants were determined from the experimental curves of $ReCO^+$ decay and ReO_x^+ formation and decay at various partial pressures of O_2 and CO using a computer program [13] for solving the inverse kinetic problems. Reactions (10) and (13)–(15) were taken into account in these calculations. The rate constants are presented in table 2 together with the values calculated using the Langeven–Gioumousis–Stevenson model (LGS) [14]. The experimental rate constants are significantly smaller than the calculated values. It means that in the gas phase not every collision leads to the reaction. Note also that nonideal trapping of ions in the ICR cell could slightly influence the values of the experimental rate constants.

Table 1
Oxygen bond energies (kcal/mol) in rhenium oxide ions

$D^0(Re^+{-}O)$	$90 < D^0 < 118$	ref. [6], reaction (9)
$D^0(ReO^+{-}O)$	$D^0 < 118$	reaction (13)
$D^0(ReO_2^+{-}O)$	$118 < D^0 < 127$	reactions (14), (15)

Table 2
Rate constants ($\times 10^{-10}$ cm^3/s).
$Re(CO)^+ \xrightarrow{k_{10}, +O_2} ReO^+ \xrightarrow{k_{13}, +O_2} ReO_2^+ \underset{k_{15}, +CO}{\overset{k_{14}, +O_2}{\rightleftarrows}} ReO_3^+$

	k_{10}	k_{13}	k_{14}	k_{15}
experimental	0.49	0.14	0.20	0.17
theory	7.16	7.18	7.15	7.55

4. Conclusion

In this work it was found that carbonyl ligand greatly enhances the reactivity of Re^+ ion in reactions with oxidants. The reaction proceeds due to a great gain of energy upon CO_2 formation. The elementary reaction of gas-phase oxidation of rhenium monocarbonyl cation by O_2 molecule was found. This reaction may be considered as a model of an elementary step through which the postulated concerted mechanism of CO oxidation over oxide catalysts proceeds.

It should be mentioned that although the relationship between reactivity observed in the gas phase and that in the real catalytic system is not simple, according to our mind, the ion–molecular reactions observed with ICR method in the idealized gas-phase system can be considered as models of the elementary steps of the catalytic reactions over the active sites of oxide catalysts.

Note that the rate constants for gas-phase reactions studied in this work in comparison with the ones for the solid state are extremely high (table 2). There seem to exist two reasons for this. First, the activation energy for the gas-phase reactions is significantly lower than for those in the condensed phase, since for the ion–molecular reactions in the gas phase a much lower reorganization energy is required. Second, due to very low pressure, under conditions of the ICR experiment the eliminated energy is not dissipated completely, e.g. a part of exothermic effect of a reaction can be conserved in the reaction intermediate in the form of transitional, vibrational or electronic excitation. This excitation can be used to accelerate the subsequent slow step. In contrast to this, on solid surfaces energy relaxation processes are very fast, so it is typically impossible to use the energy evolved in one reaction step to accelerate directly the subsequent slow step [15].

Thus, we believe that CO oxidation with O_2 in the gas phase in the presence of metal cations and over metal oxide heterogeneous catalysts proceeds via similar elementary reactions. However, these elementary reactions have substantially different rate constants.

Acknowledgement

This work was supported by the International Science Foundation, Grant RBG 300.

References

[1] G.K. Boreskov, in: *Catalysis, Science and Technology*, Vol. 3, eds. J.R. Anderson and M. Boudart, (Springer, Berlin, 1982) p. 39.

[2] B.P. Bruns, Zh. Phiz. Chim. 14 (1947) 1337.

[3] S.Z. Roginsky and Y.B. Zeldovich, Acta Physicochim. URSS 1 (1934) 554.

[4] M.M. Kappes and R.H. Staley, J. Am. Chem. Soc. 103 (1981) 1287.

[5] A.V. Kikhtenko, V.B. Goncharov and K.I. Zamaraev, Catal. Lett. 21 (1993) 353.

[6] K.K. Irikura and J.L. Beauchamp, J. Phys. Chem. 95 (1991) 8344.

[7] K.K. Irikura and J.L. Beauchamp, J. Am. Chem. Soc. 113 (1991) 2769.

[8] M. Alleman, Hp. Kellerhals and K.-P. Wanczek, Chem. Phys. Lett. 75 (1980) 328.

[9] M.V. Comisarov, G. Parisod and V. Grassi, Chem. Phys. Lett. 357 (1978) 413.

[10] G.P. Smith, Polyhedron 7 (1988) 1605.

[11] M.M Kappes and R.H. Staley, J. Phys. Chem. 85 (1981) 942.

[12] V.B. Goncharov, unpublished.

[13] A. Yermakova, P. Valko and S. Vajda, Appl. Catal. 2 (1982) 139.

[14] G. Gioumousis and D.P. Stevenson, J. Chem. Phys. 29 (1958) 294.

[15] V.P. Zhdanov and K.I. Zamaraev, Catal. Rev. Sci. Eng. 24 (1982) 373.