



Article Pt-Modified Nano-Sized Mn₂O₃ Oxide Prepared from the Mn₃O₄ Phase with Tetragonal Symmetry for CO Oxidation

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Abstract: One of the current problems in the environmental catalysis is the design of an effective and less costly catalytic system for the oxidation of CO. The nano-sized α -Mn₂O₃ oxide has been prepared and modified with 0.5 wt.% Pt. The catalysts have been characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), temperature-programmed reduction (TPR) and diffuse-reflectance infrared spectroscopy (DRIFTS). Finely divided PtO and Pt(OH)₂ are being formed on the Mn₂O₃ surface as a result of the strong interaction between platinum and the nano-oxide. Based on DRIFTS investigations and the model calculations, a Langmuir–Hinshelwood type of mechanism is supposed for CO oxidation on Pt/Mn₂O₃. The CO and oxygen are adsorbed on different types of sites. The Mars–van Krevelen mechanism is the most probable one over pure Mn₂O₃, thus suggesting that CO₂ is adsorbed on the oxidized sites. The CO adsorption in the mixture CO + N₂ or in the presence of oxygen (CO + N₂ + O₂) leads to a partial reduction in the Pt⁺ surface species and the formation of linear Pt¹⁺–CO and Pt⁰–CO carbonyls. Both of them take part in the CO oxidation reaction.

Keywords: Pt-Mn₂O₃ catalyst; nano-sized Mn₂O₃ Mn₃O₄ phase; tetragonal symmetry; CO oxidation; reaction mechanism; in-situ DRIFTS of CO oxidation

1. Introduction

The main global environmental problems include air, water and soil contamination. Water pollution is caused by oil spills, acid rain and urban waste [1–3].

Air pollution is caused by various gases and toxins that are released by the industry and by burning fuels. The main air pollutants are PM (particulate matter), SO_2 , NH_3 , NOx, CO, volatile organic compounds (VOCs), and CH_4 . The abatement of volatile organic compounds (VOCs) and carbon monoxide (CO) in the waste gases is an important task in the areas of environmental protection and odor control.

One of the most dangerous air pollutants, CO, is due to its high toxicity. Long-term exposure should not exceed 25 ppm in 8 h or 50 ppm in 4 h [4].

Catalysis plays a key role in solving environmental problems by creating highly active and efficient catalytic systems for environmental protection and reducing greenhouse gas emissions from the industry. Designing an efficient and cheaper catalytic system for CO oxidation is an important problem of actual environmental catalysis. Low-temperature CO oxidation has attracted considerable attention due to its wide application in exhaust gas treatment, automotive emission control, and the preferential oxidation of CO (PROX) for proton exchange membrane fuel cell application [5,6].

According to the literature data, a single α -Mn₂O₃ phase has been demonstrated to display remarkable catalytic activity in different reactions, such as ethylene oxidation [7], methane oxidation [8,9] and carbon monoxide oxidation [10–12]. It has been established



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). that the order of reactivities for CO oxidation over various bulk MnOx is as follows: α -Mn₂O₃ > Mn₃O₄ > MnO₂ [13]. The α -Mn₂O₃ shows excellent thermal stability among all manganese oxides within the temperature interval 100–900 °C [13]. Below approximately 300 K, α -Mn₂O₃ transforms from a cubic to an orthorhombic structure with symmetrical *Pbca* [14]. The complex crystalline structure of α -Mn₂O₃ is responsible for its superior catalytic behaviour [15]. The α -Mn₂O₃ with orthorhombic symmetry crystallizes in a distorted bixbyite structure. The unique characteristic feature of α -Mn₂O₃ is that MnO6 octahedra can share 12 edges and six corners with neighbouring coordination units. Furthermore, α -Mn₂O₃ occupies two different types of coordination octahedra. Type I octahedra shows three pairs of Mn–O distances, varying from 1.955 to 2.067 Å, and in type II octahedra, all the distances are different, four short Mn–O bonds are located in a common plane with values ranging from 1.875 to 2.011 Å and two long bonds are found on each side of this plane forming the top of an elongated octahedron with distances varying from 2.192 to 2.306 Å. The α -Mn₂O₃ phase exhibits a very short O–O distance of 2.55 Å, which could facilitate the O₂ generation from these sites [13].

It is well known that supported Au catalysts exhibit higher activity in CO oxidation at a low temperature, while supported Pt and Pd catalysts are quite active at higher temperatures [16]. The low reaction rate of CO oxidation on the supported Pt and Pd catalysts at a low temperature appears to be the result of the strong CO adsorption, which hinders the dissociative oxygen adsorption on the same sites [17]. Catalysts based on Pt have been of considerable interest due to their high efficiency as catalysts in some essential for the environment processes, such as the oxidation of CO and VOC [6,18], PROX [19,20], DeNox [21] and others.

Since Mn_2O_3 is the most stable oxide within the temperature interval of 100–900 °C and the crystalline Mn_2O_3 exhibits highest activity in CO oxidation among Mn_3O_4 and MnO_2 [13], as it was shown above, we directed our research efforts to shedding some more light on the behavior of the Pt phase supported on nanosized Mn_2O_3 during the CO oxidation.

The next purpose of our research work was to obtain more knowledge on the reaction mechanism of CO oxidation on crystalline Mn_2O_3 and platinum modified Mn_2O_3 . The most probable reaction mechanism of CO oxidation in the presence of non-modified manganese-based catalysts is that of Mars van Krevelen type (MVK) [12,22,23]. There are suggestions in the current literature that other mechanisms are also possible. For example, Wang et al [13] proposed Eley–Rideal (E-R), and Langmuir–Hinshelwood (LH) at temperatures up to 523 K, for CO oxidation over Mn_2O_3 and MnO_2 catalysts and Brooks [24] suggested an Eley–Rideal mechanism on a MnO_2 surface.

To elucidate the nature of the interaction between Pt and α - Mn₂O₃ and its possible influence on the CO oxidation reaction mechanism, nanosized α - Mn₂O₃ was modified with platinum by impregnation.

2. Materials and Methods

The Mn₂O₃ was prepared after the calcination of Mn₃O₄ for 2h at 450 °C in air. The nanosized Mn₃O₄ was prepared according to the procedure described in [24]. Aqueous solution of Mn(CH₃CO₂)₂·4H₂O was mixed with ethanol at a 1:3 ratio in a beaker. The solution was stirred for 3 h and then hydrothermally treated for 12 h at 100 °C. The obtained brownish red precipitate was washed with water and ethanol twice and finally dried at 70 °C [25].

The as-prepared Mn_2O_3 was modified with Pt (~0.5 wt.% Pt) by impregnation using the aqueous solution of Pt(NH₃)₄Cl₂. The solvent was evaporated quickly after the impregnation [26] in order to coat the oxide particles by a thin layer of Pt. In addition, the sample was calcined for 2 h at 450 °C in air.

The specific surface area of each sample was calculated by the Brunauer–Emmett– Teller (BET) method using a low temperature adsorption of nitrogen and Nova 1200 (Quantachrome) apparatus. The samples were degassed for 5 h at temperatures within the interval of 70–150 °C before the measurement Powder X-ray diffraction (XRD) patterns were collected at room temperature in a step-scan regime (step of 0.02° , 2θ) on a Bruker D8 Advance diffractometer using Cu K α radiation and a LynxEye detector. The XRD data processing was performed using the X'Pert HighScore program.

Electron spectrometer ESCALAB MkII (VG Scientific, now Thermofisher Scientific) was used for X-ray photoelectron measurements. The base pressure in the analysis chamber was 5×10^{-10} mbar. The spectrometer was equipped with a twin anode MgK α /AlK α X-ray source with excitation energies of 1253.6 and 1486.6 eV, respectively. The spectra were recorded at the total instrumental resolution of approximately 1 eV for both MgK α and AlK α excitation sources. The C1s line of adsorbed adventitious hydrocarbons with a binding energy of 285.0 eV has been used for energy calibration for the surfaces with electrostatic charging. Casa XPS software has been used for the processing of the measured spectra. Peak positions and areas were evaluated by a symmetrical Gaussian-Lorentzian curve fitting after a subtraction of X-ray satellites and Shirley-type background [27]. The relative concentrations of the elements, present on the surface, were determined based on the normalization of the peak areas to their photoionization cross-sections, calculated by Scofield [28].

Temperature-programmed reduction experiment was conducted by the method described in [29].

High resolution transmission electron microscopy (HRTEM) studies were carried out using the FEI Technai G2 20 (200 kV) instrument. The samples were prepared by dispersion in ethanol and loading on a holey copper grid.

The in situ diffuse–reflectance infrared Fourier transform spectroscopy was used to study CO adsorption on Pt/Me₂O₃-supported catalysts. The spectra were recorded on the Nicolet 6700 spectrometer (Thermo Electron Corporation, Madison, WI, USA), equipped with a high temperature/vacuum chamber installed in the Collector II accessory (Thermo Spectra-Tech, Thermo Electron Corporation, Madison, WI, USA). CO was adsorbed from the CO + N₂ or CO + O₂ + N₂ mixture. The experiments were carried out on oxidized ("as-prepared") catalysts, pretreated in N₂ for 1 h at 350 °C.

The following experimental testing conditions were applied: Catalyst bed volume of 0.3 cm^3 , irregular shaped particles having an average size of 0.2-0.4 mm, reactor diameter of 5.5 mm, quartz-glass, the catalyst bed volume was increased to 0.5 cm^3 with the same size of inert particles of crushed quartz glass. In order to minimize the external mass transfer limitations, the gaseous hourly space velocity (GHSV_{STP}) was fixed at 100,000 h⁻¹. The adiabatic effect of the reaction was compensated by keeping the catalyst bed temperature almost constant (the deviations did not exceed $+/-\pm 1$ °C). The pressure drop of the catalytic bed was established to be less than 2 kPa. The axial dispersion effect was not taken into account since the catalyst bed corresponds to a chain of more than 10 ideal-mixing cells. Thus, the geometric characteristics and the flow conditions of the catalytic reactor are similar to the case of the isothermal plug flow reactor (PFR), except for the effect of the radial velocity profile inside the catalyst bed that has been subtracted by mathematic modelling.

To obtain the experimental data, suitable for the fitting of the reaction parameters, the inlet concentrations of reactants were varied as follows: CO feed concentrations were set on the levels of 5×10^{-5} , 1.6×10^{-4} and 1.5×10^{-3} vol.%, oxygen had levels of 0.7, 7.0 and 20.0 vol.%. All gas mixtures were balanced to 100 % with nitrogen (4.0). The reproducibility of the measured conversion degrees was checked by preliminary tests under conditions similar but not identical to those represented in the study. The value of the standard deviation (+/ $-\pm$ 1.5%) was calculated using the data from six consecutive measurements at each experimental point. The represented results are based on the average values for the measured conversion degree within two parallel measurements. The gas analysis was performed using an on-line gas-analyzer of CO/CO₂/O₂ (FTIR, Horiba, HORIBA, Ltd., Tokyo, Japan).

3. Results and Discussion

Figure 1 illustrates the temperature dependencies of the conversion of CO to CO_2 . Obviously, the activity of the Mn-Pt-sample is higher than that of the pure Mn-catalyst.



Figure 1. Temperature dependencies of the conversion degree of CO oxidation for Pt/Mn_2O_3 (**a**) and pure Mn_2O_3 (**b**).

The XRD, IR, TEM data and surface area of as-prepared manganese oxide and after its calcination are discussed in [29]. According to these analyses, the formation of the Mn₃O₄ phase with tetragonal symmetry was suggested after synthesis following the procedure described above. The particles size is within the range ~15–20 nm and S_{BET} = 76 m²/g. Calcination for 2h at 450 °C leads to the transformation of Mn₃O₄ into α -Mn₂O₃ (bixbyite, PDF 01-071-0636). The transformation of Mn₃O₄ with tetragonal symmetry into α -Mn₂O₃ is accompanied by an increase in the particle size (30–40 nm) and a decrease in the surface area (20 m²/g) [29]. The form of α -Mn₂O₃ particles remains spherical (Figure 2A). The platinum loading and next calcination does not further change the manganese oxide phase, its symmetry and structure, surface area and manganese oxide particle size (Figure 2B).



Figure 2. TEM image of: (A) Mn₂O₃ after Mn₃O₄ calcination; (B) after Pt deposition figure.

Platinum or platinum oxide was not detected in Pt/Mn₂O₃ catalysts revealing a finely divided phase of Pt (XRD data are not represented here). Additional information concerning manganese oxide phases were obtained from the infrared spectroscopy. The

amorphous components and those with short-range order could be established by means of IR analysis [30]. Figure 3 exhibits the IR spectrum of pure Mn_2O_3 and Pt/Mn_2O_3 .



Figure 3. IR spectra of pure Mn₂O₃ and Pt/Mn₂O₃.

The characteristic IR bands of manganese oxides are appearing in the next three regions: 200–450, 450–600, and 600–750 cm⁻¹. They are related to spectral regions where wagging, bending and stretching vibrations are active [31]. Table 1 compares the IR bands of pure manganese oxide after calcination with those of various types of manganese oxides. As is visible in Figure 3 and Table 1, the IR spectrum of our mono-component manganese sample exhibits the bands characteristic of α -Mn₂O₃ and γ -Mn₂O₃, thus suggesting that, after calcination, a part of Mn₂O₃ is in the form of amorphous γ -Mn₂O₃.

Table 1. IR frequency vibrations of manganese oxides.

Samples		References					
Mn ₂ O ₃		668		602	575, 524	497, 445	
β -MnO ₂			618, 626				[29]
R-MnO ₂	740	687			589, 515		[29]
α -Mn ₂ O ₃				606	576, 533		[29]
γ -Mn ₂ O ₃		666			592, 533		[29]

The TPR patterns of pure Mn_2O_3 and after Pt deposition are represented in Figure 4. The reduction profile of Mn_2O_3 consists of two overlapping peaks with a maxima at 420 and 473 °C (Figure 4) [29]. They are related to a subsequent reduction of Mn_2O_3 to Mn_3O_4 and MnO. The reduction of Mn_2O_3 in hydrogen is influenced by the preparation procedure and the Mn_2O_3 of higher crystallinity is reduced at a higher temperature [32]. The reduction of Pt/Mn_2O_3 takes place at a significantly lower temperature. The hydrogen consumption is observed at the following temperatures in the TPR profile of Pt/Mn_2O_3: 144, 206 and 261 °C. The peak at 144 °C most likely result from the reduction in platinum oxide [33], and the other two peaks result from the promoted reduction of manganese oxide due to the presence of platinum. It is well known in the current literature that noble metals promote the reduction of oxides by supplying hydrogen via spillover from the pre-reduced noble metal particles to the oxides [33,34].

X-ray photoelectron spectroscopy was applied to study the chemical state of Pt and Mn and the atomic concentrations of the different elements on the catalytic surfaces (Figure 5). The binding energy of the Mn2p peak and the Pt/Mn₂O₃ samples is within the range of 641.3–641.9 eV, which is characteristic of Mn₂O₃ [35,36].



Figure 4. TPR profile of pure oxides and after Pt modification.



Figure 5. XPS spectra of Pt/Mn₂O₃ after calcination for 2 h at 450 °C: (a) Mn 2p region; (b) Mn3s region.

The Mn3s exchange splitting is accepted as a more precise means for determining the oxidation state of manganese ions [36,37]. According to the data in the literature, the exchange splitting of the 3s level is 6.5 eV for Mn^{2+} , 5.5 eV for Mn^{3+} and 4.5 eV for Mn^{4+} [38]. The Mn3s spectrum of Pt/Mn₂O₃ shows a broad 3s line at 83.8 eV and a satellite line at 89.3 eV, which is in accordance with the existence of Mn^{3+} (5.5 eV) species.

The XPS spectra of the calcined Pt/Mn₂O₃ sample in the region of Pt4f (Figure 6a) show a peak at 74.6 eV attributed to Pt²⁺ and another peak at 72.8 eV assigned to Pt(OH)₂ [39–41]. Obviously, during the calcination, both Pt(OH)₂ and PtO are being formed. According to the data for thermal decomposition of [Pt(NH₃)₄]Cl₂ above 320 °C [42], the main decomposition product is Pt⁰. The formation of platinum in an oxidized state only on the surface of Mn₂O₃ could be associated with the interaction between the Pt(II)tetraamine complex and the



 Mn_2O_3 surface. A similar phenomenon was observed by the deposition of platinum from $[Pt(NH_3)_4]Cl_2$ on hexaniobate nanoscrolls [43] and Pt on SnO₂ [44].

Figure 6. XP Spectra of Pt4f core level (**a**) and of the O1s core level (**b**) of the 0.5%Pt/Mn₂O₃ sample as prepared. Legend: (**a**) dots-represent the experiment; red color is used for resultant; grenn line–Pt²⁺; blue line–Pt⁴⁺; (**b**) dots–experiment; red line–resultant; blue and green lines–lattice oxygen; magenta line–OH⁻ groups.

The O1s spectrum is shown in Figure 6. It contains a main peak at ca. 529.4 eV, which is characteristic of the lattice oxygen (O^{2-}) [27] along with a distinct shoulder at ca. 531.5 eV, which is assigned to the OH⁻-groups, and 532.1 eV is assignable to a mixture of C-H-O groups, residues from the preparation procedure, and adsorbed water on the surface of the catalysts [44–46].

In situ DRIFTS was used to acquire some additional information about the type, stability and reactivity of the active sites, chemical state of the surface under static and dynamic conditions. Since the v(C-O) vibration is sensitive to the chemical state of the metal atom(s), to which the CO molecule is coordinated, it is the most used probe molecule for studying supported catalysts. IR spectra can provide information on the relative strength of the adsorption of the reactants, whose strength is closely related to the catalytic activity of the respective sites, and it allows information to be gained regarding the mechanism of the CO adsorption on the surface of Pt supported on manganese oxide and the behavior of adsorbed CO surface species in feed flow mixtures of CO, N₂ and O₂. The IR spectra of adsorbed CO from CO + N₂ flow on the calcined sample are represented in Figure 7.

The CO gas is demonstrated by a doublet with a minimum centered at 2142 cm^{-1} [49]. It is visible that the wing of the CO gas phase at higher wavenumbers overlaps with the band at 2119 cm^{-1} , attributed to the linear CO species adsorbed on Pt¹⁺ [50]. The occurrence of such species was confirmed after CO gas removal by a short purge with nitrogen (Figure 7d,e). Low intensive shoulder at 2080 cm⁻¹ is visible after 10 min in a nitrogen flow as well. It is ascribed to the Pt⁰–CO species [50].



Figure 7. DRIFTS spectra of Pt/Mn_2O_3 after: a-in N_2 flow; b-10 min in a flow mixture 10% CO in N_2 , at T_{room} ; c-stay 21 h in the mixture 10% CO in N_2 at T_{room} ; d-5 min desorption of CO in N_2 flow; e-10 min desorption in N_2 flow.

Considering the XPS results (see Figure 6a), the Pt/Mn_2O_3 sample initially contains Pt^{2+} surface species only. The formation of Pt^{1+} –CO and Pt^0 –CO linear carbonyls proves the reduction of the platinum surface as a result of CO adsorption.

The IR spectra of Pt/Mn_2O_3 were also recorded after exposure to CO/O_2 mixture at different temperatures (Figure 8). The formation of Pt^{1+} –CO and Pt^0 –CO linear carbonyls at room temperature is seen as well. As a result of a further increase in the temperature, the band at 2078 cm⁻¹ related to linearly adsorbed CO on metallic Pt increases, thus showing a gradual reduction in the platinum surface.



Figure 8. Adsorption of CO on 0.5% Pt/Mn₂O₃ from a mixture of 4% CO + 10% O₂ + N₂ at different temperatures: $a-T_{room}$; b-100 °C; c-cooling after reaction at 100 °C; d-150 °C; e-cooling after reaction at 150 °C; f-200 °C; g-cooling after reaction at 200 °C; h-67 h in mixture.

The reactivity of the different carbonyl species was studied after adsorption of CO at a longer contact time. The spectra in oxygen flow at elevated temperatures are shown in Figure 9.



Figure 9. FTIR spectra during oxidation of CO adsorbed on 0.5% Pt/Mn₂O₃: a–CO adsorption from a flow mixture (4% CO + 10% O₂)/N₂ at T_{room}, waiting 67 h at T_{room} and desorption in: b–10 min N₂; c–30 min at T_{room} in N₂ + O₂; d–30 min at 50 °C in N₂ + O₂; e–30 min at 100 °C in N₂ + O₂ flow; f–30 min at 150 °C in N₂ + O₂ flow; g–30 min at 200 °C in N₂ + O₂ flow; h–30 min at 250 °C in N₂ + O₂ flow;

The highest initial rate of depletion was observed in case of the Pt^0 –CO species and the band intensity decreases to zero after 30 min in N₂ + O₂ flow at 100 °C. The high frequency band at 2117 cm⁻¹, assigned to Pt^{1+} –CO species decreased in intensity more slightly and it disappeared completely after 30 min in a He + O₂ flow at 250 °C.

The DRIFTS of CO adsorption from the mixtures 10 vol.% CO in N₂ and 1 vol.% CO + 10 vol.% O₂ in N₂ indicates that: (i) CO linear carbonyls, formed on Pt/Mn₂O₃, are stable at ambient temperature in N₂ and O₂; (ii) under oxidation conditions part of the platinum is in the reduced (Pt⁰) state.

The Langmuir–Hinshelwood mechanism regarding the reaction between the adsorbed CO and oxygen species was well established as the main reaction pathway over the platinum catalysts [51]. As was mentioned above, the linear Pt^{1+} –CO and Pt^0 –CO carbonyls were observed in the IR spectra during the CO oxidation. The CO adsorbed on Pt^0 is stable up to 100 °C and Pt^{1+} –CO up to 250 °C. Based on this, it is possible to assume that the reaction mechanism below 100 °C involves both types of linear carbonyls (Pt^{1+} –CO and Pt^0 –CO), while at temperatures higher than 100 °C, the reaction pathway most likely involves the CO linear carbonyl adsorbed on the oxidized sites (Pt^{1+} –CO). Due to the fact that the CO species are not stable at higher temperatures, the great part of the Pt surface will be accessible for O₂ adsorption and dissociation. This allows the pre-adsorbed oxygen atoms to react with gaseous CO via the Eley-Rideal (denoted "E-R") mechanism. A so-called bifunctional reaction pathway involving the interaction between CO adsorbed on the noble metal and oxygen from the oxide is also possible, due to the high oxygen storage capacity of the manganese oxides [29].

In searching for the most probable mechanism, kinetic experiments were performed. The corresponding kinetic parameters were obtained by applying the method described by Duprat [52]. More details on the calculation procedure were reported in earlier publications [53–55]. The method consists of a direct integration of the reaction rate when operating at conversions higher than the limits of 5–8%, which is typical of the case for a differential type of reactor. The kinetic parameters fitting was performed by applying an integrated computer program for the simultaneous solving of the material balance in an isothermal reactor and numerical nonlinear optimization procedure. Residuals squared sums (RSS) between the experimental data and the model predictions are minimized and the square of correlation coefficient (\mathbb{R}^2) was calculated. The optimization procedure was carried out by different sets of starting conditions in order to find the global minimum.

Power-law kinetic model (PWL) was applied as a first approach for further selection among the chosen mechanistic models.

The value for the reaction order towards CO is relatively close to unity in the case of MnOx catalysts, which supposed the inclusion of the consideration of Eley–Rideal mechanism. The negative reaction order towards the CO_2 shows an inhibition effect and it is the highest in the Mn-bulk sample. It should be pointed out that the impact of the CO_2 formed during the reaction is only taken into account. The consumption of oxygen is also accounted for along the reactor length.

Based on the values of the observed reaction orders given by the PWL model, one could suggest to evaluate several mechanistic models for their consistence with the obtained experimental results, i.e., the following specification could be given:

- Langmuir-Hinshelwood (LH-D-DS-1), adsorption of CO and oxygen on different types of sites (DS), dissociative (D) adsorption of oxygen, CO₂ molecules compete with oxygen molecules for the same type of adsorption sites [56].
- Langmuir-Hinshelwood (LH-D-DS-2), adsorption of CO and oxygen on different types of sites (DS), CO₂ molecules compete with CO molecules for the same type of adsorption sites [56].;
- Mars-van Krevelen [57] (MVK-1), CO2 molecules compete with the CO molecules for the oxidized adsorption sites;
- Mars-van Krevelen (MVK-2), CO₂ molecules compete with oxygen molecules for the reduced adsorption sites
- Eley-Rideal mechanism, CO₂ molecules compete with the oxygen molecules for the same type of adsorption sites, O₂ reacts directly from gas phase.

The calculated kinetics parameters (pre-exponential factor, activation energy, heat of adsorption and reaction order) are represented in Tables 2–5.

Table 2. Reaction rate expressions and kinetics parameters for the applied power-law kinetic model.

Model: PWL	Catalyst	ko	Ea	m (CO)	n (O ₂)	p (CO ₂)	RSS	R ²
$r = k D^m D^n D^p$	MnOx-bulk	79.9	$7.80 imes10^6$	0.73	0.34	-0.08	1.5	0.987
$r = \kappa P_{CO} P_{O_2} P_{CO_2}$	Pt/MnOx	107.7	$7.72 imes 10^3$	-0.29	0.86	-0.98	2.9	0.973

* Legend: $k_{oi,pwl}$, mol.s⁻¹.atm^{-[1-(m+n+p)}; E_{ai} , kJ/mol; ...

Table 3. Reaction rate expressions and kinetics parameters for the applied Mars-van Krevelen models.

Model: MVK–1 CO2 Adsorbed on Oxidized Sites	Catalyst	k _{o,ox}	E _{a,ox}	k _{o,red}	E _{a,red}	k _{o,CO2}	$-\Delta H_{CO2}$	RSS	R ²
$r = \frac{k_{red}k_{ox}P_{CO}P_{O_2}}{\gamma} = 0.5$	MnOx-bulk	$4.39 imes10^{0}$	40.5	$6.95 imes 10^8$	86.1	$4.43 imes 10^{-2}$	35.1	1.1	0.998
$\gamma k_{red} P_{CO} + k_{ox} P_{O_2} \left(1 + K_{CO_2} \cdot P_{CO_2} \right) $	Pt/MnOx	$8.44 imes 10^{-1}$	39.3	$2.92 imes 10^{10}$	45.1	$5.16 imes10^{0}$	69.4	2.3	0.968
Model: MVK–2 CO ₂ adsorbed on reduced sites	MnOx-bulk	$1.80 imes 10^{-3}$	12.3	$1.73 imes 10^{10}$	96.6	$9.67 imes 10^{-3}$	24.5	0.4	0.997
$r = \frac{k_{red}k_{ox}P_{CO}P_{O_2}}{\gamma k_{red}P_{CO}(1+K_{CO_2}\cdot P_{CO_2})+k_{ox}P_{O_2}}$ $\gamma = 0.5$	Pt/MnOx	$5.71 imes 10^{-1}$	36.5	$1.39 imes 10^6$	54.9	$1.61 imes 10^{-5}$	63.8	1.8	0.973

Legend: γ -stoichiometric coefficient for the reaction (mol O₂/mol of CO); E_{ai} , kJ/mol; k = k_o. exp(-E_a/RT); $K_{i(co,ox,co2)} = k_{o,(co,ox,co2)}$. exp(- $\Delta H_{i,co,ox,co2}/RT$); ΔHi , kJ/mol $\Delta H_i = E_{ad} - E_{des}$;

	Model: LH-DS-D-1 CO ₂ Competes with O ₂	Catalyst	ko	Ea	k _{o,CO}	$-\Delta H_{c}$	CO k _{o,ox}	$-\Delta H$	ox k _{o,CO2}	$-\Delta H_{CO}$	D2 RSS	R ²
* _	kK _{CO} P _{CO} K _{0x} ^{1/2} P _{O2} ^{1/2}	MnOx-bulk	4.77×10^{10}	120.5	$1.76 imes 10^{-3}$	45.8	$7.03 imes 10^{-7}$	49.5	$1.00 imes 10^{-20}$	96.0	3.0	0.977
r =	$(1+K_{CO}P_{CO})(1+K_{ox}^{1/2}P_{O_2}^{1/2}+K_{CO_2}P_{CO_2})$	Pt/MnOx	$5.78 imes 10^3$	65.0	$1.87 imes 10^{-8}$	80.4	$7.81 imes 10^{-8}$	46.5	$1.00 imes 10^{-2}$	38.2	0.1	0.999
	Model: LH-DS-D-2 CO ₂ competes with CO	MnOx-bulk	4.77×10^{10}	120.5	$2.28 imes 10^{-3}$	45.0	$2.37 imes 10^{-6}$	45.0	$1.00 imes 10^{-20}$	96.0	2.9	0.977
<i>r</i> =	$\frac{{}^{kK_{\rm CO}P_{\rm CO}K_{O_2}^{1/2}p_{O_2}^{1/2}}}{{}^{(1+K_{\rm CO}P_{\rm CO}+K_{\rm CO_2}p_{\rm CO_2})(1+K_{O_2}^{1/2}p_{O_2}^{1/2})}}$	Pt/MnOx	$4.96 imes 10^2$	60.3	1.17×10^{13}	89.4	$1.89 imes 10^{-7}$	51.6	$1.00 imes 10^5$	48.9	0.2	0.997

Table 4. Reaction rate expressions and kinetics parameters for the applied Langmuir-Hinshelwood models.

Table 5. Reaction rate expressions and kinetics parameters for the applied Elley-Rideal model.

Model: ER	Catalyst	ko	Ea	k _{o,voc}	$-\Delta H_{voc}$	k _{o,CO2}	$-\Delta H_{CO2}$	RSS	R ²
$r = \frac{k^{P} CO^{K} CO^{P} O_{2}}{\frac{1}{1 + k^{P} CO^{K} CO^{P} O_{2}}}$	MnOx-bulk	$2.20 imes 10^7$	61.3	$2.00 imes10^{0}$	180.4	$7.01 imes 10^{-7}$	45.1	19.5	0.900
$^{1+K}CO^{P}CO^{+K}CO_{2}^{P}CO_{2}$	Pt/MnOx	3.13×10^{11}	69.8	$2.62 imes 10^4$	106.0	$1.00 imes 10^{-12}$	67.6	5.1	0.947

Regarding the Mn-bulk sample, the best fit was achieved when using the MVK-1 model, suggesting that CO_2 is adsorbed on the oxidized sites. In the case of the Pt/MnOx sample, the most probable mechanism is LH-DS-D-2, where the adsorption of CO and oxygen proceed on different types of sites (DS), the CO_2 molecules being in competition with CO molecules for the same type of adsorption sites. Regarding the Eley–Rideal mechanism, the probability is relatively lower, and the Pt/Mn₂O₃ sample still cannot be excluded.

4. Conclusions

The deposition of platinum on the surface of nanosized Mn_2O_3 having cubic symmetry leads to the formation of finely divided PtO and Pt(OH)₂. The CO adsorption in an inert atmosphere or in the presence of oxygen leads to a partial reduction in the Pt²⁺ surface species and the formation of linear Pt¹⁺–CO and Pt⁰–CO carbonyls.

Based on the combination of the experimental results and model calculations, we can conclude that the Mars–van Krevelen mechanism is the most probable over pure Mn_2O_3 , thus suggesting that CO_2 is adsorbed on the oxidized sites. The addition of platinum to Mn_2O_3 changes the reaction mechanism to the Langmuir–Hinshelwood type, where the adsorption of CO and oxygen proceeds on different types of sites, CO_2 molecules being in competition with CO molecules for the same type of adsorption sites. The results, obtained by the DRIFTS of CO adsorption from the mixtures CO in N_2 and $CO+O_2+N_2$, revealed that both linear carbonyls, formed on Pt^{1+} and Pt^0 centers took part in the reaction on the surface of Pt/Mn_2O_3 .

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