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Nanostructured MnO_x as highly active catalyst for CO oxidation

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ABSTRACT

Non-stoichiometric Mn-oxides (MnO_x and MnO_y) were prepared by temperature-programmed oxidation (TPO) of Mn-oxalates, $MnC_2O_4{\cdot}3H_2O$ and $MnC_2O_4{\cdot}2H_2O$. Both oxides provide high specific surface areas ($525\ m^2\ g^{-1}$ and $385\ m^2\ g^{-1}$, respectively) and identical CO oxidation reaction rates of 10^{-2} molecules $nm^{-2}\ s^{-1}$ ($0.017\ \mu mol_{CO}\ m^{-2}\ s^{-1}$) at 298 K. A “spinodal” transformation of oxalates into oxides was observed by transmission electron microscopy (TEM). The quantitative evaluation of TPO and temperature-programmed reduction with CO allowed x-values of 1.61,…,1.67 to be determined for MnO_x. The Mn oxidation state in MnO_x was found to be 3.4 ± 0.1 by X-ray absorption near-edge structure analysis and X-ray photoelectron spectroscopy. In accordance with the high specific surface area and mixed-type I/IV adsorption isotherms of MnO_x, high resolution TEM demonstrated the occurrence of nested micro-rod features along with nanocrystalline particles in the endings of the rods. After CO oxidation MnO and Mn_3O_4 phases were able to be identified in the regions between rods.

1. Introduction

The oxidation of carbon monoxide (CO) is one of the “evergreens” in catalysis research. The continuing interest in this reaction is, on the one hand, sparked by environmental concerns since gaseous CO is toxic and harmful to human beings and animals. On the other hand, there are still unanswered questions of a more fundamental nature, like the low-temperature activity of certain 3d metal-oxides. While it is generally accepted that a Langmuir–Hinshelwood type mechanism (LH) between molecular CO and atomic oxygen leads to carbon dioxide (CO_2) formation on the surface of metals or metals supported by oxides, a Mars–van Krevelen type mechanism (MvK) is frequently suggested for pure metal-oxides. One of the consequences in moving from an LH to an MvK mechanism is the essential absence of CO inhibition effects for metal oxides, which is of considerable importance for achieving low-temperature activity. For example, the kinetic order dependence becomes positive in both CO and oxygen when running the reaction over spinel-type Co_3O_4 which is one of the most thoroughly studied 3d metal-oxides [1]. The high CO oxidation activity of Co_3O_4 is frequently related to the simultaneous presence of tetrahedral Co^{2+} and octahedral Co^{3+} sites [1–7]. Similarly high activity has also been reported for Mn-oxides; however, no such site requirement has ever been claimed to exist for these oxides. This is probably due to the structural flexibility of Mn-oxides which exist in a number of different stoichiometric (as MnO, Mn_2O_3, Mn_3O_4 Mn_5O_8 and MnO_2 along with their polymorphs) and non-stoichiometric phases, with the Mn valence varying smoothly between +4, as in MnO_2, and +2, as in MnO. Most of the studies on CO oxidation were performed with stoichiometric Mn-oxides. In early works, Klier and Kuchynka [8] and Kanungo [9] found high catalytic activity over bulk MnO_2 at 293 K and 353 K. Liang et al. [10] synthesized MnO_2 catalysts with nanorod morphology and found their catalytic activity to change according to α- $\cong$ δ- > γ- > β-MnO_2. The variation of the catalytic activity with the polymorphism of the sample at otherwise identical bulk composition can only be explained by assuming that the specific surface termination and, consequently, the Mn–O bond strength are the determining factors. For commercially available manganese oxides the following trend of CO oxidation activity (at 523 K) has been reported by Ramesh et al. [11] and Wang et al. [12]: $MnO \leqslant MnO_2 < Mn_2O_3$. In the present study, non-stoichiometric MnO_x ($x = 1.61,\ldots,1.67$) is prepared via temperature-programmed oxidation of Mn-oxalates [13]. This oxide demonstrates even higher CO oxidation activity, with an onset far below room

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temperature. A micro-structural correlation with this activity is subsequently established and has identified MnO_x to exhibit structural features reminiscent of those of Mn_5O_8. In addition, nanocrystals are found in the endings of micro/nanorods and confer on MnO_x its unusually high specific surface area and catalytic activity. The "oxalate route" to high surface area metals and metal oxides was previously applied to produce Ni [14] and Ag on TiO_2 [15], or metal mixtures such as CoCu [16]. The present work provides the first nanostructural characterization of a highly reactive metal-oxide system prepared via oxalate precipitation.

2. Experimental section

2.1. Catalyst preparation

Catalysts were prepared in a two-step procedure. First, Mn-oxalate was precipitated from an aqueous solution of oxalic acid by adding $Mn(NO_3)_2{\cdot}4H_2O$ at room temperature while stirring continuously and adjusting the pH value to between 6 and 9 using ammonia. Precipitation was gradual with an induction period of 3–5 min. The precipitation times were 40 min and 24 h for producing $MnC_2O_4{\cdot}3H_2O$ and $MnC_2O_4{\cdot}2H_2O$, respectively, after filtration, washing and drying overnight at 343 K (see Ref. [13] for details). The as-prepared Mn-oxalates were subsequently transformed into manganese oxides using temperature-programmed oxidation (TPO) in a U-type glass reactor with a frit to deposit the sample. The decomposition/oxidation performed in a mixture of 10% oxygen in Ar with a total flow rate of 50 mL min^{-1} was followed by a quadrupole mass spectrometer (Balzers QMS 200) using a calibrated flow-through capillary while heating from room temperature to 633 K at a rate of 3 K min^{-1}. Samples were kept for 20 min at the maximum temperature before cooling them to ambient temperature in pure Ar using the same gas flow rate. In addition, for comparison purposes, a "calcined MnO_x" sample was prepared by heating $MnC_2O_4{\cdot}3H_2O$ in a crucible under the same TP conditions but using air rather than O_2/Ar.

2.2. Catalytic activities

TPO-treated samples (140 mg) were tested for their CO oxidation activity in the same apparatus. The gas flow was switched to a mixture of CO and O_2 (2% each) in Ar as vector gas using a flow rate of 50 mL min^{-1} at overall atmospheric pressure. The down-stream gas composition was analyzed mass spectrometrically. The purity of the gases was as follows: O_2 (99.995%), CO (99.997%), and Ar (99.999%). The CO conversion was calculated from the measured CO_2 formation.

2.3. Catalyst characterization

Temperature-programmed reaction studies in the presence of CO (CO-TPR) were performed to demonstrate the CO oxidation activity of MnO_x in the absence of gas phase oxygen. Manganese oxides with stoichiometric composition (Mn_2O_3 and Mn_3O_4), which can also be prepared via the oxalate route (see Ref. [13]), were subjected to the same reactivity test for comparison purposes. Samples (140 mg) were heated to 773 K in 1% CO/Ar at 3 K min^{-1} using a flow rate of 30 mL min^{-1}. The BET surface areas of manganese oxides were determined subsequent to both TPO and CO oxidation, i.e. before and after the reaction studies. The surface area measurements were performed using Ar at 77 K according to an in-situ dynamic method developed in our laboratory [17]. For comparison purposes, the MnO_x catalyst was also characterized with a TriStar 3000 instrument (Micromeritics Co.) using the N_2 adsorption/desorption method at 77 K to determine the specific surface areas as well as the pore size distribution.

XRD patterns were obtained with a Philips instrument PW 3710 equipped with a PW 1050 Bragg–Brentano parafocusing goniometer, using monochromatized Cu Kα radiation. The XRD scans were digitally recorded with steps of 0.04° in the 2θ range from 4 to 70°.

The crystal structure and morphology of the samples were investigated by using TEM. Conventional TEM analysis was performed in a PHILIPS CM20 microscope at an electron acceleration voltage of 200 kV, and HRTEM was carried out in a JEOL 3010 instrument operated at 300 kV with a resolving power of 0.17 nm. The samples for the TEM measurements were prepared by ultrasonic dispersion in distilled water and subsequent deposition of a droplet of the suspension onto a carbon-coated copper grid. The HRTEM micrographs were evaluated using Fast Fourier Transformation (FFT).

X-ray absorption near-edge structure (XANES) experiments were performed at the fluorescence beamline L of the DORIS III synchrotron ring operated by HASYLAB at the German Electron Synchrotron DESY (Hamburg, Germany). The white beam of the bending magnet was monochromatized by a Si(1 1 1) double monochromator. A polycapillary half-lens (X-ray Optical Systems, E Greenbush, NY, USA) was employed for focusing a beam of 1×1 mm^2 down to a micrometer-sized spot (20 μm at 10 keV, 30 μm at 6.5 keV – micro-XANES mode). The absorption spectra were recorded in a fluorescence mode tuning the excitation energy near the K absorption edge of Mn (6539 eV) by stepping the Si(1 1 1) monochromator. The X-ray fluorescence photons were detected by a silicon drift detector with a 50 mm^2 active area (Radiant Vortex). The used step size varied between 0.5 (edge region) and 2 eV (more than 50 eV above the edge). The acquisition time per energy point was set to 5 s. For comparison purposes, powdered standards of pro-analysis-grade $MnCO_3$, $MnSO_4$, Mn_3O_4, MnOOH and MnO_2 with known Mn oxidation states were also investigated. In order to minimize the difference of self-absorption, microscopic grains of similar size were selected for the measurements in both the standards and the MnO_x catalyst.

X-ray photoelectron spectroscopy (XPS) measurements were performed in a combined ToF-SIMS/XPS/STM apparatus at a base pressure of 5×10^{-10} mbar using non-monochromatic Al Kα-radiation with a power of 130 W. Prior to analysis, manganese oxide samples prepared as described above were degassed in a preparation chamber (2×10^{-9} mbar) for 40 h. Photoelectron spectra were acquired with a hemispherical analyzer in the constant pass energy mode at $E_p = 50$ eV. After subtraction of the Shirley-type background the core-level spectra were decomposed into components with mixed Gaussian–Lorentzian (G/L) lines using a non-linear least-squares curve-fitting procedure. Similar to the micro-XANES studies, MnO_x was investigated along with pro-analysis-grade standard oxides MnO, Mn_3O_4, Mn_2O_3 and MnO_2. Emphasis was laid on analyzing the magnitude of the multiplet splitting of the Mn 3s photoelectron line in these samples. The carbon C 1s peak at 284.5 eV was used as reference energy for charge correction.

3. Results

As outlined in the Introduction, the thermal decomposition of Mn-oxalates in either the presence or absence of oxygen provides a convenient route to produce a variety of Mn-oxides. Crystalline and largely stoichiometric oxides as well as non-stoichiometric MnO_x are accessible in this way. According to our recent investigation, MnO_x ($x = 1.61, \ldots, 1.67$) is particularly active in the catalytic CO oxidation [13]. To recall, complete CO conversion was typically obtained at room temperature or slightly below. This is shown once again in Fig. 1. In addition, to allow comparison with