Catalysis Science & Technology

PAPER



Cite this: Catal. Sci. Technol., 2021, 11, 1766

Received 29th October 2020, Accepted 11th January 2021

DOI: 10.1039/d0cy02112a

rsc.li/catalysis

Introduction

Hydrolysis of phosphodiester bonds (P–O) is important in many biological processes as information storage *via* DNA/RNA and energy transduction *via* ATP.¹ These reactions are also significant for the detoxification of pesticides, such as

Nanostructured manganese oxides as highly active catalysts for enhanced hydrolysis of bis(4nitrophenyl)phosphate and catalytic decomposition of methanol[†]

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Manganese oxide-based (MnO_x) catalysts have received increasing attention due to their low cost, low toxicity, and the ability to degrade organic molecules under mild conditions. In this work, several nanostructured MnO_x-based catalysts were prepared via redox reactions of manganese compounds in an aqueous solution and alkaline precipitation with aqueous ammonia. A wide arsenal of analytical techniques, including nitrogen physisorption (BJH and BET), X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), temperature-programmed reduction (H2-TPR), X-ray photoelectron spectroscopy (XPS), X-ray fluorescence (XRF), and Raman spectroscopy were applied for their characterization. The nanostructured MnOx exhibited high catalytic activity in hydrolysis of phosphate diester-based substrate bis(4-nitrophenyl)phosphate (BNPP) at 328 K. Furthermore, MnO_x specimens were also studied in decomposition of methanol to carbon monoxide and hydrogen as a potential alternative fuel. The results show high dependency of the materials catalytic properties on the synthesis method. It was found that the varying fractions of redox-active Mn²⁺/Mn³⁺/Mn⁴⁺ surface sites and the high proportion of oxygen species (such as O^{2-} or O^{-}) together with the particle dispersion and morphology are important for high catalytic activity of MnO_v in both investigated catalytic reactions. Based on the experimental data, possible mechanisms of BNPP hydrolysis and methanol decomposition were proposed and discussed in detail.

> organophosphorus insecticides,^{2,3} chemical warfare agents (typically soman, sarin, or VX agent),⁴ and their surrogates (DMMP)^{5,6} or newly in decontamination of cytostatic drugs (cyclophosphamide, ifosfamide).^{7,8} However, the phosphodiester bonds in these molecules are extremely resistant towards natural hydrolytic processes.^{9,10} In the absence of a catalyst and at room temperature, the half-life for phosphodiester bond hydrolysis has been estimated to be tens of million years for DNA at neutral pH.11 Several recent works reported on the assisted hydrolysis of these substances by their interaction with the active surfaces of nanostructured transition metal oxides, such as Fe₃O₄,^{12,13} Co₃O₄,¹⁴ NiO,¹⁵ or CeO₂,¹⁶ which exhibit high activities against organophosphates. It is believed that this effect is due to a large number of active sites (Lewis or Brønsted acid sites), high surface area, and a presence of dislocations and defects in the crystal lattice (Frenkel & Schottky defects) of metal oxide catalysts,¹⁷ which have been referred to as "reactive sorbents" or "inorganic enzymes (nanozymes)".18,19

> Similar to phosphatases, the active metal ions promote the cleavage of phosphodiester bonds.^{20,21} The nano-sized

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[†] Electronic supplementary information (ESI) available: Contains detailed material characterization along with ESI figures: XRD patterns, Raman investigations, H2-TPR profiles, adsorption/desorption measurements, XPS spectra, XRF investigations, LC ion chromatograms and the appropriate *m/z* spectra of BNNP and 4-NP molecules, and kinetic curves and kinetic parameters for the catalytic degradation of BNPP (4-NP) at different temperatures. Measurements of the methanol decomposition. See DOI: 10.1039/d0cy02112a

cerium oxide (nanoceria) has shown a great ability to degrade dangerous organophosphate pesticides (parathion-methyl) or chemical warfare agents (CWA's) under mild conditions. Janoš et al. (2017) synthesized a ceria-based reactive adsorbent by a conventional precipitation/calcination method for the fast degradation of thiamine pyrophosphate (TPP) and nicotinamide adenine dinucleotide (NAD) as model compounds.²² However, majority of biologically relevant substrates are huge biopolymers, of which separation, identification, and detection is not trivial. Therefore, to investigate catalytic activity, smaller substrates with reactivity as closely as possible corresponding to that of the biopolymers are used. Here, bis(4-nitrophenyl)phosphate (BNPP) is used to mimic a phosphodiester array of DNA and RNA, serving as a model simulant to study hydrolysis by catalytic interaction with phosphodiester bonds nanostructured metal oxides. The hydrolytic cleavage of this molecule in the presence of zero-valent iron nanoparticles,²³ metallomicelle catalysts containing Ce(III)²⁴ or Co(II),²⁵ or even a heterodinuclear Zn(II)/Pb(II) was reported.²⁶

In our previous works, we showed the activity of nanostructured manganese oxides (MnO_x) for the catalytic degradation of certain organophosphates, such as insecticides or CWA's under ambient conditions.^{27–29} Interestingly, the hydrolysis of BNPP on the surface of MnO_x has not yet been described in more detail.

In the last decades, the design and synthesis of nanostructured metal oxides has gained much attention due to their attractive physical, chemical, and catalytic properties.^{30–32}

Manganese oxides (MnO_x) have been used for a wide range of industrial catalytic applications, *e.g.*, methane³³ and carbon monoxide oxidation,³⁴ ozone decomposition,³⁵ selective reduction of nitric oxide,³⁶ and decomposition of hydrogen peroxide.³⁷

In particular, MnO_x specimens have been reported as efficient and environmentally friendly materials for catalytic decomposition of methanol at low temperatures.³⁸ Methanol is an efficient energy source³⁹ and a facile starting point for the preparation of a number of valuable chemicals, including synthesis gas and hydrogen.^{39,40}

Their catalytic performance is related to the varying valence of manganese and the participation of active oxygen species, oxygen vacancies, lattice oxygen, as well as morphological characteristics.^{41,42} An increase in catalytic activity was observed when Mn^{3+} and Mn^{4+} were present in the MnO_x structure.^{43,44} However, the catalytic activity of various types of MnO_x considerably varies depending on the method of their preparation.

In the present study, we selected robust and straightforward methods applicable in the large-scale production of nanocrystalline MnO_x . A series of five MnO_x based catalysts were prepared *via* 1) instantaneous redox reactions of manganese compounds in an aqueous solution and 2) alkaline precipitation with aqueous ammonia. The prepared samples were characterized by various physicochemical techniques, including nitrogen physisorption (BJH and BET), X-ray

diffraction (XRD), X-ray fluorescence (XRF), high-resolution transmission electron microscopy (HRTEM), temperatureprogrammed reduction (H_2 -TPR), and Raman spectroscopy. The resulting solids show different phases, crystallinities, and particle morphologies depending upon synthesis method. We compared their catalytic efficiencies towards the phosphate diester-based substrate (BNPP) and decomposition of methanol to carbon monoxide and hydrogen as a potential alternative fuel.

It was found that the varying fractions of redox-active $Mn^{2+}/Mn^{3+}/Mn^{4+}$ surface sites and the high proportion of oxygen species (such as O^{2-} or O^{-}) together with the particle dispersion and morphology are important for high catalytic activity of MnO_x in catalytic degradation of both molecules. Based on detailed analyses of the experimental data, possible mechanisms of the BNPP hydrolysis and decomposition of methanol were proposed and discussed in detail.

Materials

All chemical compounds were obtained from commercial sources and used without pre-treatment. Bis(4-nitrophenyl) phosphate (BNPP) and its hydrolysis product 4-nitrophenol (4-NP) were obtained from Sigma-Aldrich as chromatographic standards. HPLC-grade organic solvents and deionized water were used to prepare the solutions and mobile phases for liquid chromatography. $MnSO_4$ ·H₂O, KMnO₄, $Mn(NO_3)_2$ ·4H₂-O, HCl solution, NH₃ solution (25%), and *N*-cetyl-*N*,*N*,*N*-trimethyl ammonium bromide (CTAB) were supplied by penta Chemicals.

Experimental

Materials preparation

Sample MnO_1 was prepared by a modified procedure described elsewhere⁴⁵ using a redox reaction of $Mn(NO_3)_2$ and $KMnO_4$ without any surfactants. 5.2 g $KMnO_4$ was dissolved in 4 l distilled water, and 23.8 g of $Mn(NO_3)_2$ ·4H₂O was carefully added. The reaction mixture was adjusted to the pH ~ 4 by adding 10 ml hydrochloric acid and heated at *ca.* 363 K under vigorous stirring for six hours. Thus, the asprepared suspension was cooled, decanted with distilled water, filtered off, and dried at 378 K in the oven.

Sample MnO_2 was prepared by redox reaction of KMnO₄ and MnSO₄, as described in our previous work.²⁸

Sample MnO_3 was prepared *via* precipitation of KMnO₄ and concentrated HCl. In this procedure, 5 g of KMnO₄ was dissolved in distilled water, and the as-prepared solution was made up to 300 mL in a beaker and boiled at *ca.* 363 K for 30 minutes under vigorous stirring. After that, 2 M HCl solution was slowly added dropwise until a brown precipitate formed (MnO_x formation). The mixture was stirred for 2 hours at *ca.* 363 K. After the reaction time, it was allowed to cool, decanted several times, filtered off, and dried at 378 K.

Sample MnO_4 was prepared *via* precipitation of $Mn(NO_3)_2$ and NH_3 solution. In this procedure, 1.5 g of $Mn(NO_3)_2 \cdot 4H_2O$

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was dissolved in 100 ml of water under vigorous stirring. Next was added of a 25% aqueous NH_3 diluted in water (1:1) dropwise until the pH of the solution reaches 8.5. The mixture was stirred at this pH until a light brown precipitate form (manganese hydroxide was formed). After the reaction time, it was decanted several times, filtered off, and dried at 378 K.

Sample Mn_xO_y -HT was synthesized by a template-assisted technique using CTAB as a template and hydrothermal treatment at 373 K.⁴⁶ 12.0 g CTAB was dissolved in 100 ml distilled water, and then slowly, and under vigorous stirring, a solution of MnCl₂·4H₂O (5.8 g) in 50 ml distilled water was added. Then, the temperature was raised to 323 K, and the reaction mixture was stirred for 30 min before adding dropwise 20 ml aqueous NH₃ (25%). The resulting mixture was stirred overnight at 323 K and then treated at 373 for 24 h. The obtained material was filtered, washed with distilled water, dried at room temperature, and annealed at 773 K for 10 h.

Further details are given in Section S1 of the ESI.†

Catalytic hydrolysis of BNPP

The kinetics of the BNPP hydrolysis was examined as follows. Constant amounts (0.1 g) of the powder catalyst were weighed into a dark glass vial (Supelco, 4 ml) and dispersed in 2.0 ml of TRIS buffer (pH = 7) using an ultrasonic bath (DT-100, BANDELIN electronic GmbH & Co. KG, Berlin -Germany) for 10 minutes. Then an exact volume (2.0 ml) of the BNPP solution (50 mg dm⁻³) in TRIS buffer (pH = 7) was added. The thus prepared mixture in the vial was shaken by thermo-shaker LAB MARK at constant temperature (298, 308, 318, or 328 K). At pre-determined time intervals (5, 10, 20, 30, 50, 70, 90, and 120 minutes), a small amount (100 μ l) of the reaction suspension was removed and acidified with 1 ml of formic acid (0.1%), thereby stopping the reaction. Catalyst powder was separated by centrifugation (18000 rpm, 2 min), and the supernatants were analyzed by two HPLC systems: a) HPLC with a diode array detector (DAD) and b) HPLC system coupled with mass spectrometry (HPLC-MS). Detailed chromatographic conditions are given in Section S1 of the ESI.†

Catalytic decomposition of methanol

Methanol decomposition was carried out in a flow type microreactor (0.055 g of catalyst diluted with crash glass in a weight ratio of 1:3), particle size of 0.3–0.6 mm, and catalytic bed volume of about 0.5 cm³ at 1.57 kPa partial pressure of methanol and weight hourly space velocity (WHSV) of 100 h⁻¹. Methanol dosage was achieved by a saturator kept at 273 K using argon as a carrier gas. The experimental data were collected under a thermoprogrammed regime of the heating rate of 2 K min⁻¹ within the temperature range of 350–700 K. Before the catalytic test; the samples were pre-treated *in situ* for 1 h at 373 K in argon. The on-line GC analyses were performed on HP 5890

apparatus equipped with TCD and FID detectors. The results were calculated using a method of absolute calibration on the base of carbon material balance. The methanol conversion was calculated as $X = ((C_{\text{ini}} - C_{\text{cur}})/C_{\text{ini}}) \times 100$, where C_{ini} and C_{cur} were the initial and current detected amounts of methanol. The selectivity to i product from methanol conversion was calculated as $Y_i/X \times 100$, where Y_i was its yield determined from $C_i/C_{\text{ini}} \times 100$ (C_i was the amount of i product). The selectivity (S) to CO, CO₂, CH₄, methyl formate (MF), and C₂–C₃ hydrocarbons was calculated as $S_i = Y_i/X \times 100$, where Y_i was the yield of (i) product and X was the conversion (30%). The specific catalytic activity (SA) was calculated as SA = X/A, where X was the conversion at 700 K and A was the specific surface area (m² g⁻¹).

The carbon balance (BC), representative of the converted methanol into by-products, CH_4 , CO, CO_2 , methyl formate (MF), and C_2 - C_3 hydrocarbons, was determined from the sum of the selectivities (S_i) according to eqn (1):⁴⁷

BC (%) =
$$\sum S_i$$
 (1)

Results and discussion

Material characterization

Many studies have focused on preparing nanostructured manganese oxides, including sol-gel,^{48,49} co-precipitation method,⁵⁰ hydrothermal synthesis,⁵¹ sonochemical synthesis,⁵² and solid-state reactions.⁵³ However, most of these methods are expensive and often produce non-uniform particles. In the present study, nanocrystalline MnOx with controlled particle size and shape are prepared via 1) the rapid redox reactions of manganese precursors in an aqueous solution at low temperature and 2) alkaline precipitation with aqueous ammonia followed by drying at 378 K without further annealing of the material (except for the template-assisted technique using CTAB). The resulting materials show distinct phases, crystallinity, and particle morphologies depending on the synthesis procedure. Additionally, the choice of manganese precursor allows activating some oxygen species of the catalyst, which play an important role in the catalytic process.

The first reaction route (sample MnO_1) is based on the rapid redox reaction of KMnO₄ with Mn(NO₃)₂ in acidic solution at a temperature below the boiling point water according to reaction (2). This reaction can lead to the formation of MnO₂ with the birnessite phase (δ -MnO₂),⁵⁴ or a mixture of akhtenskite (ϵ -MnO₂) and ramsdellite (γ -MnO₂) polymorphs, as shown by the XRD results (see S1.1. part of ESI[†]).

$$2KMnO_4 + 3Mn(NO_3)_2 + 2H_2O \rightarrow 5MnO_2 + 4HNO_3 + 2KNO_3$$
(2)

The comparative samples of MnO_x were prepared by the redox reaction of $KMnO_4$ and $MnSO_4$ (see eqn (3)) or *via* redox precipitation of $KMnO_4$ and concentrated HCl,

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respectively (see eqn (4)). The samples were denoted MnO_2 and MnO_3 .

Manganese oxides with the structure of birnessite, cryptomelane, or pyrolusite can be obtained depending on the molar ratio of $KMnO_4$ and $MnSO_4$.⁵¹ In our case, crystalline cryptomelane (α -MnO₂) was obtained (see S1.1. part of ESI†).

On the contrary, redox precipitation of $KMnO_4$ with concentrated HCl leads to the formation of birnessite-type manganese oxide (δ -MnO₂), as evidenced by some previously published works^{55,56} and XRD results (see S1.1. part of ESI[†]).

 $2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$ (3)

$$2KMnO_4 + 8HCl \rightarrow 2MnO_2 + 2KCl + 3Cl_2 + 4H_2O \qquad (4)$$

Sample *MnO_4* was prepared *via* precipitation of manganese nitrate and ammonia solution.

The reaction of an aqueous solution of $Mn(NO_3)_2$ and ammonia solution results in rapid precipitation of Mn^{2+} species. It is believed that hydrolysis of Mn^{2+} leads to amorphous $Mn(OH)_2$, according to eqn (5). A part of this precipitate can undergo oxidation in air, which causes a change of color from light brown into dark brown,⁵⁷ as described by eqn (6). In other words, the resulting precipitate thus consists of amorphous $Mn(OH)_2$ and amorphous $Mn(OH)_3$. Aging of these precipitates leads to further oxidation in air, resulting in crystallization of hausmannitetype manganese oxide Mn_3O_4 (see eqn (7)), as confirmed by XRD analysis (see S1.1. part of ESI[†]).

 $Mn(NO_3)_2 + 2NH_4OH \rightarrow Mn(OH)_2 + 2NH_4NO_3$ (5)

$$4Mn(OH)_2 + O_2 + 2H_2O \rightarrow 4Mn(OH)_3$$
 (6)

$$Mn(OH)_2 + 2Mn(OH)_3 \rightarrow Mn_3O_4 + 4H_2O$$
(7)

Similarly, the sample Mn_xO_y _HT was prepared *via* precipitation of manganese chloride and ammonia solution and subsequent hydrothermal treatment. Ammonia solution was added to aqueous manganese chloride, leading to the manganese hydroxide precipitation as a white precipitate (see eqn (8)). The white precipitate changes into dark brown upon being exposed to air, as described by eqn (6). Annealing at 773 K results in multi-phased Mn_xO_y (see S1.1. part of ESI†).

Hydrothermal synthesis in the presence of structuredirecting agents (template) is the conventional procedure which can control the particle size, structure, and morphology of materials.⁴⁶ Hydrothermal treatment in the presence of templates will result in materials with mesoporous structure and thicker walls, making them significantly more stable and improving their catalytic activity by forming a large and wellexposed active surface and hence to facilitated access of the reactants to the active catalytic sites.

$$MnCl_2 + 2NH_4OH \rightarrow Mn(OH)_2 + 2NH_4Cl$$
(8)

Different phases were found in the individual materials depending on the method of preparation. The detailed phase analysis results are given in sections ESI† S1.1. (X-ray powder diffraction, XRD) and S1.2. (Raman investigations), respectively. Temperature-programmed reduction (H_2 -TPR) was used to study the reducibility of the MnO_x samples in hydrogen as a temperature function, and the results are discussed in detail in section S1.3.† The surface area and porosity of samples were determined using the nitrogen physisorption that proved the mesoporous character of MnO_x samples (see section S1.4.†).

The surface-sensitive XPS technique was used to study chemical states of Mn and O on the surface of MnO_x (see Fig. S7 and S8 and Tables S3 and S4†). In order to obtain detailed information on the chemical states of Mn, the curve fitting was performed on the Mn $2p_{3/2}$ peaks in spectra (see Fig. S7a–e†).

As shown in Fig. S7a–e,† each chemical state of Mn $2p_{3/2}$ peak was deconvolved into sets of multiple peaks at BE 639.2 \pm 0.2 eV, 640.2 \pm 0.2 eV, 641.1 \pm 0.2 eV, 642.1 \pm 0.2 eV, and 643.2 \pm 0.2 eV, corresponding to Mn^{2+,58–60} Than, the set of peaks at BE 640.7 \pm 0.2 eV, 641.4 \pm 0.2 eV, 642.2 \pm 0.2 eV, 643.2 \pm 0.2 eV, and 644.6 \pm 0.2 eV were assigned to Mn³⁺ ions.^{60,61} And similarly, the set of peaks at BE 641.6 \pm 0.2 eV, 643.2 \pm 0.2 eV, 643.2 \pm 0.2 eV, 643.2 \pm 0.2 eV, 643.2 \pm 0.2 eV, 643.9 \pm 0.2 eV, 644.7 \pm 0.2 eV, and 645.8 \pm 0.2 eV were assigned to Mn⁴⁺ ions.^{60,61} The area of each individual peak in the spectra decomposition model assigned to each oxidation state was set as in the literature.⁶⁰

The content of surface Mn^{n+} (n = 2, 3, and 4) and their molar ratios were calculated by a quantitative analysis method on the Mn $2p_{3/2}$ XPS spectra, as shown in Table S3.† The results show that the sample *MnO_1* shows the absence of Mn⁴⁺ on the surface, and the main manganese species are Mn²⁺ and Mn³⁺. Contrary, mainly Mn⁴⁺ (~66%) was formed in the *MnO_2* sample, which correlates well with the phase found by XRD (see Fig. S1†). The proportions of Mn²⁺, Mn³⁺, and Mn⁴⁺ species on the surface of manganese oxides impact the surface oxygen species. Generally, for MnO_x, a higher manganese oxidation state (Mn⁴⁺) will produce more surface adsorbed oxygen species, such as O²⁻ or O⁻. On the other hand, a lower manganese oxidation state (Mn²⁺) will produce an oxygen vacancy, which will promote the lattice oxygen mobility.⁶²

These effects can be proved by investigating O 1s XPS spectra. As presented in Fig. S8a–e,† the asymmetrical O 1s peak can be fitted by two components: the first peak at low binding energy ~529.6 eV, which can be assigned to the lattice oxygen (O^{2-} ; denoted as O_{α});⁶³ and a broad peak centered at 531.3 ± 0.2 eV that can be attributed to the surface chemisorbed oxygen species (O^- , O_2^- , and O_2^{2-}) in the vicinity of the surface defects (denoted as O_{β}).⁶⁴

The content of O_{α} can be calculated according to eqn (9).⁶⁵

$$X_{\mathrm{O}\alpha} = (A_{\mathrm{O}\alpha}/S) / [\sum A (\mathrm{O}_{\alpha} + \mathrm{O}_{\beta})/S] \times 100 \ (\%) \tag{9}$$

where $X_{O\alpha}$ is the percentage content of $O\alpha$, *A* is the integrated area of characteristic peak in the XPS pattern, *S* is a sensitivity factor (*S* = 0.711).



Fig. 1 TEM (a) and HRTEM (b) micrographs of *MnO_1* nanoparticles; the intensity of electron diffraction pattern of the akhtenskite and ramsdellite-type structures (c) with SAED pattern (inset), and FFT pattern (d) obtained from (b).

The content of O_{α} species in prepared samples is summarized in Table S3.† As can be seen, the samples with a high amount of surface lattice oxygen O^{2^-} (*MnO_2*, *MnO_4*, and *Mn_xO_y*-*HT*) have a higher proportion of Mn⁴⁺ state and also better catalytic activity for BNPP hydrolysis that will be discussed in detail in Section S3.4.†

Fig. 1–5 show the TEM micrographs of prepared MnO_x . As shown in Fig. 1a, sample MnO_1 consists of spindle-like



Fig. 3 TEM (a) and HRTEM (b) micrographs of *MnO_3* flower-like nanoparticles; the intensity of electron diffraction pattern of birnessite structure (c) with SAED pattern (inset), and FFT pattern (d) obtained from (b).

particles with a length of ~100 nm and 20 nm width. From the fast Fourier transform (FFT) analysis of the particle shown in Fig. 1d, were found the (100), (110), and (200) planes of akhtenskite structure (done on flat particles). On the other hand, the selected area electron diffraction (SAED) pattern (see inset in Fig. 1c) revealed the structure of akhtenskite and ramsdellite-type MnO_x , which is consistent with the XRD results (see Fig. S1†).



Fig. 2 TEM (a) and HRTEM (b) micrographs of MnO_2 nanorods; the intensity of electron diffraction pattern of the cryptomelane structures (c) with SAED pattern (inset), and FFT pattern (d) obtained from (b).



Fig. 4 TEM (a) and HRTEM (b) images of MnO_4 irregularly shaped nanoparticles; the intensity of electron diffraction pattern of hausmannite structure (c) with SAED pattern (inset), and FFT pattern (d) obtained from (b).



Fig. 5 TEM (a) and HRTEM (b–b") images of Mn_xO_y -HT irregularly shaped nanoparticles, and FFT pattern (c–c") obtained from (b–b").

MnO_2 sample (Fig. 2a–d) is formed by cryptomelane nanorods with a diameter from 10 to 45 nm and a length from 300 nm to 1 μ m. The corresponding FFT pattern (Fig. 2d) shows that the diffraction spots are projected by the (211) crystal plane of ammonium manganese oxide and cryptomelane, respectively, and (310) of ammonium manganese oxide.

As can be seen from Fig. 3a, MnO_3 consists of flower-like nanoparticles typical for birnessite-type MnO_2 with an average particle size from 300 to 400 nm. The corresponding FFT pattern (Fig. 3d) shows that the diffraction spots are projected by the (006) crystal plane of pure birnessite.

 MnO_4 sample (Fig. 4a) consisted of irregularly shaped nanoparticles with diameters ranging from 20 to 125 nm. FFT pattern (d) of HRTEM micrograph (b) and SAED pattern (see inset in Fig. 4c) reveal the structure of hausmannite.

Similarly, the Mn_xO_y -HT sample showed irregular nanoparticles with a size of about 100–400 nm. Although three phases were identified (corresponding to Mn_2O_3 , Mn_5O_8 , and Mn_3O_4) based on FFT, the sample showed very low electron diffraction intensities, so these measurements were not included in Fig. 5.

Influence of acid-base properties

In general, the environmental behavior of metal oxides is given by their surface charge. The surface charge is most often determined by the surface hydroxyl groups chemically attached to the metal atom in the crystal lattice of oxides. In an aqueous environment, the surface becomes charged due to surface chemical reactions with H^+ or OH^- ions.

Depending on the pH of the environment, protonation or deprotonation reactions can take place on the S–OH sites, as described by eqn (10) and (11), respectively.^{66,67}

$$S-OH + H^{+} = S-OH_{2}^{+} (protonation)$$
(10)

or

$$S-OH + OH^{-} = S-O^{-} + H_2O$$
(deprotonation) (11)

As can be seen from eqn (10) and (11), in an acidic solution, the surface of the catalyst is more positively charged, so it can easier adsorb a negatively charged substrate. Conversely, in a basic solution, the surface is negatively charged, and adsorption of the positively charged adsorbate is preferred. The pH at which the concentrations are equal $[S-O^-] = [S-OH_2^+]$ is called the point of zero charge (pHPZC).⁶⁸ The pHPZC can be determined through potentiometric titration (PT).

In this work, the *pHPZC* values for MnO_x have been evaluated from titration curves, which have been transformed into curves corresponding to the total concentration of protons consumed in the titration process (TOTH), as described by eqn (12):⁶⁹

$$\text{FOTH} = \left[\left(V_{\text{NaOH}} - V_{\text{EP1}} \right) \cdot c_{\text{NaOH}} \right] / m \left[\text{mol } g^{-1} \right]$$
(12)

where c_{NaOH} represents the concentration of NaOH [mol dm⁻³], V_{EP1} represents the volume of first equivalent point [L⁻¹], V_{NaOH} [L⁻¹] represents the consumption of NaOH at individual titration points, *m* is the amount of sample used for the titration [g].

The amount of surface hydroxyl groups (*q*-OH) per solid weight was calculated from the two equivalence points on the titration curve (V_{EP1} and V_{EP2}) by the following formula (see eqn (13)):

$$q_{-\rm OH} = \left[\left(V_{\rm EP2} - V_{\rm EP1} \right) \times c_{\rm NaOH} \right] / m \tag{13}$$

The amount of surface hydroxyl groups (q-OH) and pHPZC values are summarized in Table 1.

The titration curves of TOTH vs. pH calculated according to eqn (12) for MnO_x are shown in Fig. 6. From Fig. 6, it can be seen that at pH < 4.0, the surfaces of MnO_x were positively charged, and at pH > 4.0, the surfaces of MnO_x were negatively charged.

The *pHPZC* values of the individual manganese oxides ranged from 4.14 (Mn_xO_y -HT) to 5.28 (MnO_4), which corresponds to some previously published values obtained by PT.^{70,71}

In general, manganese oxides have relatively low PZC values and therefore possess a relatively high negative charge at normal pH values. For this reason, they have an important

Table 1 The amount of hydroxyl groups (q-OH) and pHPZC calculated from the TOTH curves

Sample	$\frac{q\text{-OH}}{\text{mmol g}^{-1}}$	pHPZC
MnO 1	0.145	4.80
MnO_2	0.322	4.64
MnO_3	0.585	4.55
MnO_4	2.096	5.28
Mn_xO_y -HT	0.792	4.14

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Fig. 6 TOTH curves of the prepared MnO_x samples as a function of pH.

role in controlling the concentration of trace metal ions in soils or natural water systems.⁷⁰

Catalytic hydrolysis of BNPP at various temperatures

The MnO_x samples were tested for promoting BNPP hydrolysis at various temperatures. Generally, all MnO_x reveal high activity towards the BNPP hydrolysis. Kinetic tests were done in triplicate with a maximum error of 5%.

The process of surface hydrolysis can be expressed using the pseudo-first-order kinetic eqn (14):

$$[BNPP]_{\tau} = [BNPP]_0 \times e^{-k\tau}$$
(14)

where parameter $[BNPP]_r$ is the residual concentration of bis(4-nitrophenyl)phosphate (BNPP) in the reaction time τ [min], $[BNPP]_0$ represents the initial concentration of BNPP, and k is the pseudo-first-order rate constant for the hydrolysis of BNPP [min⁻¹].

Similarly, for the formation of 4-nitrophenol (4-NP) as a degradation product, the time dependence of this process can be expressed similarly to eqn (14) using the kinetic eqn (15) describing the increase of normalized concentration of 4-NP at time τ :

$$[4-NP]_{\tau} = 1 - [4-NP]_0 \times e^{-k\tau}$$
(15)

with a similar meaning of the symbols. The model fitted parameters obtained by non-linear regression (OriginPro 9.0) are listed in Table S5 (for BNPP) and S6⁺ (for 4-NP), respectively.

The half-life of the reaction was then calculated from the rate constant k (see eqn (16)):

$$T_{1/2} = \ln(2)/k \tag{16}$$

For all degradation experiments, the initial rate of conversion $v_i \, [\mu \text{mol dm}^{-3} \, \text{min}^{-1} \, \text{g}^{-1}]$ was calculated (see eqn (17)):^{72,73}

$$p_{i} = (C_{(0)} - C_{(5)})/(t \cdot m)$$
(17)

where $C_{(0)}$ [µmol dm⁻³] is the initial concentration of the substance (BNPP, 4-NP) in the reaction system; $C_{(5)}$ [µmol dm⁻³] is the concentration of the substance in the reaction system after 5 minutes of hydrolysis reaction; m [g] is the catalyst load (typically 0.1 g), and t [min] is the reaction time of 5 minutes.

The BNPP hydrolysis was measured by following the decrease of BNPP monitored by HPLC-DAD. Only 4-nitrophenol (4-NP) was observed as a primary hydrolysis product under the HPLC conditions used. Integrations for BNPP and 4-NP, respectively, were compared to standards.

It is well known that the temperature is one of the most important factor to affect the reaction rate according to the *Arrhenius equation* (see eqn (18)):⁷⁴

$$k = A e^{-Ea/RT}$$
(18)

In this work, reaction kinetics was studied for the temperature range from 298 to 328 K at pH = 7.0 to investigate the effect of temperature on the hydrolysis of BNPP. Pseudo-first-order normalized degradation curves for BNPP at different temperatures are given in ESI[†] in Fig. S9a–S13a. Appropriate normalized kinetic curves for the formation of 4-NP as a primary hydrolysis product of BNPP hydrolysis are given in Fig. S9b–S13b.[†]

Based on HPLC data, it was possible to determine the pseudo-first-order kinetic parameters, such as the rate constants for BNPP hydrolysis (see Table S5†) and 4-NP formation (see Table S6†), the initial rate of conversion, and the degree of conversion for BNPP and 4-NP.

Table S5[†] gives the experimentally measured activation energy, as deduced from the linear fitting of the *Arrhenius plot* based on eqn (19).

$$-\ln k = \mathrm{Ea}/RT - \ln A \tag{19}$$

As expected, at higher temperatures, increased rates have been observed, as shown in Fig. 7a.

The plots of $\ln k vs. 1/T \times 10^3$ (K) were drawn (as shown in Fig. 7b) using the Arrhenius eqn (15) to calculate apparent activation energy (Ea) of BNPP catalytic hydrolysis.

As shown in Table S5,† Ea values of the hydrolysis of BNPP using manganese oxides were found in the range from 10.9 $(Mn_xO_y$ -HT) to 34.5 kJ mol⁻¹ (*MnO_1*), respectively. These values of Ea are in close correspondence to the values previously reported for the hydrolysis of BNPP, catalyzed by various metal complexes, such as cobalt(π), zinc(π), or copper(π) complexes.^{25,75,76} Most of them exhibit good catalytic activity and catalytic character similar to the natural phosphatase enzymes. The highest activities were observed for the *Mn_xO_y*-HT sample prepared by the template method.

As shown in Table S5,† the rate constant k for BNPP hydrolysis at 328 K on the most active sample (Mn_xO_y -HT) was ~0.230 min⁻¹, which corresponds to reaction half-time



Fig. 7 Plots of the relationship between environment temperature (K) and the hydrolysis rate (min^{-1}) of BNPP (a), and Arrhenius plots for Ea calculations of BNPP hydrolysis (b).

 $(\tau_{1/2})$ *ca.* 3 min. The relatively high activity was also observed for *MnO_2* sample (~0.200 min⁻¹), which corresponds to reaction half-time ($\tau_{1/2}$) *ca.* 3.4 min. The highest initial rate of BNPP conversion was observed on the samples *Mn_xO_y*-*HT* (~42 µmol dm⁻³ min⁻¹ g⁻¹) and *MnO_2* (~34 µmol dm⁻³ min⁻¹ g⁻¹) at 328 K, respectively. In addition, both samples showed the highest degrees of BNPP conversion after 60 minutes approaching 100%.

Kinetic measurements indicate that the sum of BNPP is completely hydrolyzed to 4-NP, which has a lower affinity for the MnO_x surface⁷⁷ and can be determined in the supernatant. Furthermore, the kinetic curves of 4-NP formation (see Fig. S9b–S13b†) show that during the hydrolysis of BNPP, two 4-NP molecules are released in all cases (normalization to 1 corresponds to twice the molar concentration of the 4-NP standard against BNPP). The occurrence of 4-NP in solution is related to surface hydroxyl groups and O²⁻ lattice oxygen species, respectively, acting as strong nucleophiles in the hydrolysis mechanism, as discussed in detail below. This is an analogous process to that observed for the intramolecular hydrolysis of phosphate esters in the presence of some metal complexes.⁷⁸

The degrees of BNPP conversion after 60 minutes are compared for each sample at different temperatures, as

shown in Fig. 8. The results show a high activity of all samples, which can be attributed to more abundant surface oxygen species. These characteristics are related to the oxygen mobility and the reducibility of the catalyst, which is significantly influenced by the manganese oxide crystal structure depending on the hydrolytic decomposition temperature of BNPP and the method of MnO_x preparation.

BNPP degradation mechanism. The kinetics of hydrolysis of BNPP have been extensively studied in the catalytic systems containing various types of metals, such as zero-valent iron nanoparticles,²³ Ce(m) complex,⁷⁹ or U(r) nanoparticles.⁸⁰ These studies indicated that the Lewis acidities of these metals and the presence of bound hydroxide (Me–OH) are crucial for stabilizing the transition state of phosphodiester hydrolysis. Similarly, we have studied the mechanism of BNPP hydrolysis on materials prepared in this study.

To identify BNPP hydrolysis products, time-resolved supernatants were collected and scanned by the UV-vis spectrophotometry and chromatographic methods (HPLC-DAD, LC-MS). Spectral analysis and liquid chromatography are effective methods for analyzing the reaction and have been used for analysis of supernatants in the BNPP catalytic hydrolysis. As shown in Fig. S14,† the maximum absorbance of the characteristic spectrum of p-nitrophenol was observed at 325 nm, and the characteristic spectrum of the BNPP solution appeared at 282 nm. It is apparent from the timeresolved UV-vis spectrum that the characteristic maximum of BNPP gradually decreased in intensity with increasing time and changes to the maximum of 4-NP. This shows that the product of the catalytic hydrolysis of BNPP contains p-nitrophenol. To identify other potential hydrolysis products, the LC-MS system was used. The results indicate that no other products, such as 4-nitrophenyl phosphate (NPP), were detected (see Fig. S15 and S16[†]). Based on this knowledge, we assume that the BNPP hydrolysis occurs



Fig. 8 The degree of BNPP conversion after 60 min at different temperatures.

through the P–O bonds breaking-off under the action of the MnO_x nanoparticles. Similarly to other nanostructured metal oxides, the molecule is decomposed into the *p*-nitrophenol and phosphate residue is immobilized on the surface.

It is well known that the catalytic activity of transition metal oxides is determined by several factors, such as lattice oxygen, oxygen vacancy, surface area, and metal oxidation state.⁸¹ In the case of MnO_x, we assume that the co-existence of various manganese oxidation states (Mn4+, Mn3+, and Mn2+) play an important role in improving catalytic activity. The individual states contribute to the formation of various oxygen species, including adsorbed oxygen, oxygen vacancy, and lattice oxygen, which are formed by redox reactions on the surface. Because Mn has a very strong ability to give electrons, the adsorbed oxygen $O_{2(g)}$ on the surface would be impelled to turn into O_2^{-1} or O^- species, respectively, and finally $O^{2-}_{(latt)}$. The course of oxygen adsorption on the MnO_x surface is as follows: $O_{2(g)} \rightarrow$ $O_2^- \rightarrow O_2^{2^-} \rightarrow O^-$, and $O_{(latt)}^{2^-}$ The adsorbed species stayed on the catalyst surface, where they can vary in strength participated in the hydrolysis of BNPP. Their character can be read from the XPS O1s spectra. While the positions of O1s lines at low binding energy (~529.6 eV) point to strong nucleophilic oxygen species (O^{2-}_{latt}) , broad peaks at 531.3 \pm 0.2 eV correspond to electrophilic oxygen species, which can be collectively referred to as defective oxygen species. It can be assumed that nucleophilic oxygens are important for the catalytic hydrolysis of BNPP substrate.

As indicated by XPS results (see Fig. S7 and S8†), samples with a higher proportion of Mn^{4+} on the surface (samples MnO_2 , MnO_4 , and Mn_xO_y -HT) showed a higher proportion of unsaturated $O^{2-}_{(latt)}$ (labeled as O_{α} ; see Table S3†) and hence higher activity towards BNPP hydrolysis.

However, as shown by the results of BNPP hydrolysis, a higher proportion of Mn^{2+} and Mn^{3+} on the surface can significantly affect the catalytic activity of the resulting material due to the creation of oxygen vacancy that can act as an important active site. The low-charged $Mn^{2+,3+}$ can generate relatively stable oxygen vacancies (V_o), which will promote the mobility of lattice oxygen, as shown in the scheme in Fig. 9.⁸³ In this proposed scheme, new active sites are formed for the catalytic decomposition of the BNPP substrate.

The highest activity observed in the Mn_xO_y -HT sample may be due to the ideal ratio of all manganese states in the

new active site



oxvgen vacancy

Fig. 9 Formation of active sites on the surface of a manganese oxidebased catalyst.

surface layer and higher content of lattice oxygen (O^{2^-}). The interplay of these factors can contribute to the overall activity of the sample. Moreover, the free unsaturated O^{2^-} ions in the crystal lattice are strongly basic and cannot exist separately in the aqueous environment in this form. When the O^{2^-} ion interacts with the aqueous medium, it is neutralized, and two hydroxide ions are formed, according to eqn (20).

$$O^{2^-} + H_2 O \rightarrow 2OH^-$$
(20)

The formation of negatively charged hydroxyls (-OH⁻) from the surface may result in increased metal oxide activity during the nucleophilic attack on the central phosphorus atom during cleavage of the phosphodiester bond in the substrate molecule, as shown in the proposed scheme in Fig. 11.⁸⁴ In the proposed scheme, the hydrolysis reaction path starts with the activation of the BNPP substrate by manganese ions (Mn^{n+} ; where n = 2, 3, and 4), which act as Lewis acid (electron-accepting). The positively charged Mn ions stabilize the negative charge on the oxygen atom of BNPP, which has the effect of increasing the dipole moment of the P-O bond. This binding results in a more positive charge on the P atom of BNPP, which thus become prone to undergo a nucleophilic attack by unsaturated lattice oxygen ions (O²⁻), or/alternatively formed OH⁻ ions according to eqn (20), and the hydrolysis product is desorbed (4-NP) from the surface. In principle, the release of two 4-nitrophenol (4-NP) units may occur from BNPP, as shown by kinetic measurements.

Likewise, the morphology and crystallinity of the prepared MnO_x cannot be ignored. Catalytic activity depends on the morphology, and there is a strong relationship between shape and its properties. It seems that good crystallinity with a structure of nanorods (MnO_2) or nanoparticles of irregular shapes (MnO_4 and Mn_xO_y -HT) is preferred for the reaction with the BNPP substrate. Among the MnO_x , cryptomelane with nano rod-like morphology is considered very interesting by its open 2 × 2 tunnel structure, mixed-valence of manganese, and high mobility of lattice oxygen.⁸⁵

Similarly, high activities against BNPP were also observed for Mn_xO_y -HT and MnO_4 samples, which can be due to the presence of a hausmannite (Mn₃O₄). A unit cell of spinel structure Mn₃O₄ contains 32 oxygen and 24 mixed valences of manganese cations. The good catalytic properties of Mn₃O₄ is due to the tetragonal distorted spinel structure (due to the Jahn–Teller distortion of the Mn³⁺ centered polyhedron).⁸⁶

Catalytic decomposition of methanol

Fig. 10a presents temperature dependencies of methanol conversion in the 550–770 K region for all materials. Methane (CH₄), carbon monoxide (CO), carbon dioxide (CO₂), methyl formate (MF), and C_3 – C_4 hydrocarbons in different proportions were detected as by-products, and their yield

(in%) is listed in Table S9.† Temperature-dependent selectivity of main by-products is listed in Table S8.†

For simplicity, only the selectivity to CO is presented in Fig. 10b because this product is directly related to the ability of catalysts to release hydrogen during the methanol decomposition to syngas.38,46 In all cases, methanol decomposition was initiated above 600-650 K (see Fig. 10a). MnO 2 and MnO 3 exhibited the lowest catalytic activity, and the maximum conversion of about 60% was detected at about 750 K. All other oxide materials demonstrated higher catalytic activity. The use of an ammonium precursor leads to the presence of more active sites in MnO_4 and Mn_xO_v_HT.^{97,98} Besides CO, which was the most important product (~45-80%) related to the release of hydrogen from methanol, methane (\sim 5–11%) and CO₂ (\sim 6–8%) as by-products were detected as well (see Table S9[†]). Other intermediates were detected in small amounts ($\sim 2\%$), such as methyl formate (samples MnO_1, MnO_2, and MnO_3) and C₃-C₄ hydrocarbon fragments (sample MnO 4).

In order to ignore the impact of the differences in the specific surface area of the samples, the specific catalytic activity SA as conversion per unit BET was calculated. It was the highest for Mn_xO_y -HT (6.89 mol m⁻²) and MnO_-4 (3.79 mol m⁻²), while for all other materials varied between 0.25–1.52 mol m⁻². The 30% conversion temperature ($T_{30\%}$) of these catalysts is summarized in Table S7.†



Fig. 10 Decomposition of methanol (a) and CO selectivity (b) on various MnO_{x} .

In accordance with the XRD and XPS data, we attribute the high specific activity of MnO_4 and Mn_xO_v -HT to the better exposure of large MnO_x particles, including a high amount of Mn⁴⁺ ions on the surface, which provides higher content of lattice oxygen (O²⁻). Considering the methanol decomposition is a particle-size-dependent reaction,^{98,99} and according to the TEM data, we can speculate that this effect is due to the homogeneous distribution of irregularly shaped manganese nanoparticles in these samples and their better accessibility to the methanol molecules (see Fig. 4a). At the same time, the MnO_2 and MnO_3 samples possess the lowest specific catalytic activity. In order to find the cause of the observed catalytic behavior, we performed an additional XRD analysis of these samples after reduction with hydrogen (see Fig. S3[†]). The results showed that in the case of both samples, the cubic manganosite phase (MnO; JCPDS card No. 00-007-0230; space group: facecentered $Fm\bar{3}m$) was formed with a high degree of crystallinity (142 nm for MnO 2 and 135 nm for MnO 3 samples; see Table S2[†]).

To elucidate the cause of the low catalytic activity of both samples, the effect of potassium ions (K^+) was studied since both materials were prepared from the KMnO₄ precursor. XPS and XRF detected the surface/bulk K^+ content in the samples; the results are shown in Table S4.†

Comparing the results measured by XPS and XRF, the surface K atomic concentration was very close to the corresponding bulk K concentration, indicating that K was uniformly dispersed in both samples.

The reduced catalytic activity of both samples for the decomposition of methanol may be due to the poisoning of the catalyst surface by the presence of potassium. The poisoning mechanism occurs *via* chemical bonding of the K^+ cation to the -M-OH (Brønsted acid sites), as well as K^+ can easily occupy the oxygen vacancy, as described in ref. 87.

Hence, the observed extremely low SA for these materials is probably due to the adhesion of large MnO_x particles in low oxidation state on the oxide surface, which leads to agglomeration⁸⁸ and a significant decrease in catalytic decomposition of methanol. As a result of the accumulation of large particles, a small specific surface is formed containing a low number of active centers.35 Moreover, according to TEM data, the presence of particles with high length and small diameter with the morphology of the nanorods (MnO_2) and flower-like nanoparticles (MnO_3) with thick walls indicate the low availability of the methanol molecule.⁸⁹⁻⁹¹ Note the significant low-temperature effect in the TPR-DTG profile (see Fig. S5[†]) for these oxides could be assigned both to the elimination of unsaturated hydrocarbons⁹² under the reductive medium and to changes in the dispersion and/or oxidative state of manganese ions.

The catalytic behavior of the catalysts strongly depends on the manganese-containing precursor used. Based on the registered differences in the initial reduction temperature of different manganese samples prepared using sulfate, ammonium, chloride, and nitrate precursor, a difference in the state of the active manganese particles could be concluded, including a different manganese-containing phase.

Summary of methanol conversion, by-products selectivities, and carbon balance calculated for 660 and 720 K temperatures is presented in Table S10.⁺

Mechanism of methanol decomposition

Several different types of metal oxide catalysts have been studied for methanol decomposition to CO and H₂. Among these, copper oxide,⁹³ nickel supported on silica,⁹⁴ zinc oxide,⁹⁵ or alumina⁹⁶ are reported to be effective materials for decomposing methanol to CO and H₂.

However, the mechanism of methanol decomposition on the surface of MnO_x is still not fully understood.

We expect that the mode and the strength of methanol interaction with the manganese oxides and the relation with this catalytic activity and selectivity are controlled by the changes in the lattice parameters during the $Mn^{4+}/Mn^{3+}/Mn^{2+}$ transformation, as well as by the variations in the acid properties due to the generation of oxygen vacancies in the lattice. The registered differences in the distribution of the by-products in the tested catalysts may be due to the course of the reaction along different routes. Based on the analyses above, the decomposition mechanisms of methanol on the MnO_x surface are proposed in Fig. 11.

 MnO_x -Based catalysts presented here are active for methanol decomposition at temperatures between 600–750



Fig. 11 The proposed mechanism of catalytic hydrolysis of BNPP (A) and methanol decomposition (B) on the MnO_x surface.

K. However, the reaction yield a mixture of by-products, including CO, CO₂, and methane (CH₄), and in small amounts also methyl formate (CH₃OCHO) and hydrocarbons (C_3-C_4).

It is believed that the decomposition of methanol on transition metal oxide catalysts generally goes through three stages:^{97–99} adsorption of methanol to form surface methoxy groups;⁹⁷ decomposition of methoxy groups to surface CO and H_2 intermediates⁹⁸ and subsequent desorption.

In general, methanol binds to the surface of metal oxides in two different ways. First, the methoxyl group of methanol can coordinate with a Lewis acid cation surface site (M^{n+}) via the methanol oxygen lone electron pairs (methanol acts as a base), or the adsorbed methanol may also act as an acid toward a basic surface hydroxyl (or surface oxygen ions) to form the dissociated methoxy surface species. However, many metal oxide surfaces can accommodate both types of adsorbed methoxy surface species simultaneously.¹⁰⁰

We suppose that the initial adsorption of methanol on the catalysts realizes *via* basic surface hydroxyl to form the dissociated methoxy surface species.

The results of potentiometric titrations confirm this assumption (see Table 1). The *pHPZC* values of MnO_x vary from 4.14 to 5.28. In this case, the hydroxyl groups on the surface of the MnO_x will be deprotonated $(Mn^{n+}-O^{-})$. Thus, MnO_x tends to have a more negative charge. This can result in different binding of methanol to the MnO_x surface, especially during the formation of methoxy groups at the beginning of the reaction (see Fig. 11, M1 reaction).

For all emerging products, it can be seen that their yield (%) increases with increasing temperature, as can be seen from the graphs in Fig. S17.† The highest yields were observed for CO, as shown in Table S9,† wherein the MnO_4 sample showed the highest yield of CO (~80%), as well as for CO₂ (~8%) at 725 K. At the same temperature, this sample showed the highest activity (~100%) for the decomposition of methanol, as described above.

We assume that with increasing temperature, the basic lattice oxygen ions (O^{2-}) present on the surface of MnO_x promote dehydrogenation of the surface methoxide intermediates to the surface formate species, which decompose to formaldehyde, and then to CO or CO₂ with the simultaneous formation of H₂ (see Fig. 11, M2 and M4 reaction).^{101,102}

On the contrary, no CO_2 formation was observed for the Mn_xO_y -HT sample, as shown in the graph in Fig. S17b.[†]

Methane can be formed in relatively-high selectivity (up to 13%) at 721 K (sample Mn_xO_y -HT; see Table S8†) in the reaction between CO and H₂, so-called methanation (see Fig. 11, M3 reaction), although it is possible to form together with CO₂ by decomposition of methyl formate intermediates.^{98,101,102} The observed relatively-high selectivity to methane on all materials (Table S8†) reveals that this process is facilitated by simultaneous presence of strong basic (lattice oxygen ions) and Lewis acidic sites (lattice oxygen vacancies).¹⁰³ Thus, the observed increase in the CH₄

yield for all materials, particularly for the MnO_4 and Mn_xO_y -HT, could be due to the increase of the basicity of the oxygen ions in the Mn–O–Mn structures.¹⁰⁴

At higher temperatures, dissociation of C-H bond in methyl group could occur, leading to the formation of hydrocarbons C_3 - C_4 with very low yield (~2%), as can be seen from Table S8† for the *MnO_4* sample.

As shown in Table S9,† a small yield (2%) of methyl formate (CH₃OCHO) was observed for the *MnO_1*, *MnO_2*, and *MnO_3* samples. Methyl formate is produced at low temperatures and low conversions, according to the following reaction (21):^{105,106}

$$2CH_3OH \rightarrow CH_3OCHO + 2H_2$$
(21)

At higher temperatures, methyl formate is further decomposed into CO by the following reactions (22) and (23), respectively:^{105,106}

$$CH_3OCHO \rightarrow CO + CH_3OH$$
 (22)

 $CH_3OCHO \rightarrow 2CO + 2H_2$ (23)

These reactions may increase the CO yield (~80%) for the MnO_4 sample.

The absence of any simple relation between the catalytic behavior of the oxides and the preparation procedure urged the authors to assume that their catalytic activity results from the superposition of the structural, surface, textural, and redox effects, which according to XPS data, are due to the simultaneous presence of manganese ions in variable oxidation states and ratios.

Conclusion

In summary, a series of nanocrystalline manganese oxidebased catalysts were prepared *via* 1) instantaneous redox reactions of manganese compounds in an aqueous solution and 2) alkaline precipitation with aqueous ammonia. The products were characterized by a wide arsenal of analytical techniques and showed distinct crystal structures and particle sizes and shapes in the individual specimens. The nanostructured MnO_x exhibited high catalytic activity in hydrolysis of phosphate diester-based substrate at 328 K. The Mn_xO_y -HT sample prepared by a template-assisted technique showed the best catalytic activity in BNPP hydrolysis at 328 K due to the ideal ratio of all manganese states in the catalyst surface layer and higher content of lattice oxygen (O^{2–}).

The MnO_x -based catalysts were also tested for methanol decomposition to CO and hydrogen as a potential alternative fuel. MnO_4 sample showed the best activity in methanol decomposition due to the better exposure of large MnO_x particles, including a high amount of Mn^{4+} ions on the surface.

Hence, the catalytic activity and selectivity of the synthesized MnO_x materials were successfully controlled by

the preparation procedure and the specific characteristics of the acidic and redox-active sites in them. Depending on the catalytic reaction mechanism, the catalytic activity is in a complex relation to the oxidative state, particle dispersion, and morphology, which are controlled by the preparation procedure and the precursor used.

It has been shown that the catalytic decomposition of both molecules is induced by the action of surface catalytic sites of different strengths. The individual findings can be summarized as follows:

• Catalytic hydrolysis of BNPP substrate is supported by a higher fraction of Mn^{4+} and thus a higher amount of lattice oxygen species (O^{2-}), which act as strong nucleophilic agents.

• However, the lower manganese states (Mn^{2+}, Mn^{3+}) present on the catalyst surface promote the formation of oxygen vacancies and promote the formation of new active sites for the further decomposition of the BNPP substrate.

• Catalytic decomposition of methanol proceeds faster on samples with the presence of crystalline manganese oxide phases possessing Mn^{3+} and Mn^{4+} ions (Mn_2O_3 and Mn_5O_8), which are most beneficial for the studied reaction. In addition, the catalytic activity of MnO_x increases with increasing amounts of surface deprotonated hydroxyl groups, which are essential for the first step of methanol chemisorption.

• Catalytic decomposition of both examined molecules also depends on the structure of the material. It appears that higher crystallinity and more regular shape of particles (nanorods) are more advantageous for the decomposition of BNPP. In contrast, the decomposition of methanol is supported by finely dispersed manganese particles with a low degree of crystallinity, which provides a greater amount of Mn^{4+} or Mn^{3+} vacations. On the other hand, the presence of particles of the nanorods with thick walls indicates the low availability of the methanol molecule.

• It has been found that in the case of methanol decomposition, the catalytic activity of MnO_x prepared from $KMnO_4$ can be reduced due to the presence of K^+ , which causes catalyst poisoning.

• It has been observed that the size of the specific surface area is not a determining parameter for the catalytic decomposition of both molecules.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Czech Academy of Sciences-Bulgarian Academy of Sciences bilateral project (BAS-20-11) and financial support of Project No. KP-06-PM-39/1/2019 are acknowledged. The authors acknowledge the assistance provided by the Research Infrastructure NanoEnviCz, supported by the Ministry of Education, Youth and Sports of the Czech Republic under Project No. LM2018124. The authors thank to Dr. Darina Raman spectroscopy, and XRF measurements.

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