Magnesium diolates as precursors for MgO: A low-temperature route[1]

Heiko Thoms, Matthias Epple, Armin Reller[*]

Inorganic and Applied Chemistry Institute, University of Hamburg, Martin-Luther-King-Platz 6, D-20146, Hamburg, Germany

Abstract

Six magnesium alcoholates from bifunctional alcohols $HO-(CH_2)_n-OH$, $n = 2\ldots6, 8$ were prepared and characterized. The thermal decomposition leads to magnesium oxide with a distinct particle size as a function of the alcohol chain length n. The final decomposition temperature to MgO is much lower as compared to inorganic precursors, for example, magnesium carbonate. It was shown for these diolates that the thermal decomposition under air most likely includes the formation of Mg–OH groups; the thermal intermediates can be described as alkoxy/hydroxy species.

1. Introduction

Metal oxides can be obtained in different ways. A classical route is the high-temperature decomposition of inorganic salts, for example, carbonates and nitrates. As an example, magnesium oxide (magnesia) is conventionally prepared by thermal decomposition of magnesium carbonate:

$$MgCO_3 \xrightarrow{800-900°C} MgO + CO_2 \qquad (1)$$
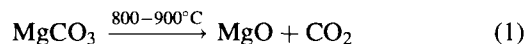
At these high temperatures usually only thermodynamically stable oxides are obtained. Using precursor substances containing organic groups, metal oxides can be synthesized at much lower temperatures; one may even obtain metastable phases.

A promising group of precursors are metal alcoholates of the general formula $M_x(OR)_y$ [1–5]. In the case of magnesium oxide (magnesia), the variability of the organic group R has been used to control morphology and particle size of the resulting magnesium oxide [6–9], which is important, for example, for an application as catalyst or catalyst support.

The decomposition of magnesium alcoholates to magnesium oxide occurs at around 500°C. Some alcoholates are volatile and can be used in MOCVD [10,11].

Here, we report on further magnesium alcoholates that were synthesized from five different diols $HO(CH_2)_nOH$ with $n = 2\ldots6, 8$. Since no single crystals could be obtained, we characterized these alcoholates by IR-spectroscopy, elemental analysis (C, H, Mg) and solid-state NMR spectroscopy. Their decomposition was followed by thermal analysis (combined thermogravimetry–differential thermal analysis–mass spectrometry; TG-DTA-MS). The

*Corresponding author. Tel.: 0049-40-4123-3103; fax: 0049-40-4123-6348; e-mail: reller@xray.chemie.uni-hamburg.de.
[1]Dedicated to Prof. Hans Paulsen on the occasion of his 75th birthday.

obtained magnesium oxides were characterized by scanning electron microscopy (SEM).

The much lower decomposition temperatures of magnesium diolates as compared to magnesium carbonate (800–900°C) are attractive for the preparation of MgO and mixed oxides with defined morphology and chemical structure. Such low-temperature syntheses become increasingly important in materials science [12,13].

2. Experimental

The low reactivity of the diols ethan-1,2-diol, propan-1,3-diol, butan-1,4-diol, pentan-1,5-diol, hexan-1,6-diol and octan-1,8-diol requires the reactive diethyl magnesium for the synthesis of the diolates which is prepared by standard methods [14]:

$$Mg(C_2H_5)_2 \xrightarrow[\text{diethylether}]{+\text{diol}}$$

$$Mg[O(CH_2)_nOH]_x[O(CH_2)_nO]_y + 2\,C_2H_6 \quad (2)$$
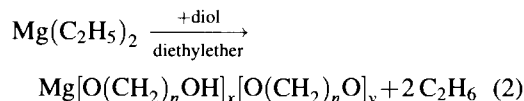
It is also possible to synthesize the magnesium diolates by alcoholate exchange, for example, by reacting $Mg(OCH_3)_2$ [6] with propan-1,3-diol:

$$Mg(OCH_3)_2 \xrightarrow{+\text{diol}}$$

$$Mg[O(CH_2)_3OH][O(CH_2)_3O]_{0.5} + 2\,CH_3OH$$
$$(3)$$
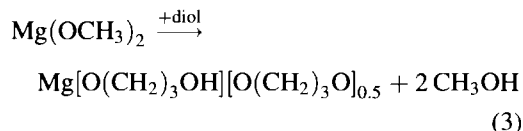
IR spectra were measured on a Perkin–Elmer FT-IR 1720. In all cases the samples were mixed with dry KBr under nitrogen and pressed at 125 bar.

The thermochemical behaviour of all samples was studied with a simultaneous thermal analyser (Netzsch STA 409C/MS) which simultaneously measures DTA, thermogravimetry and evolved reaction gases by mass spectrometry (Balzers QMS 421). The samples were heated in open alumina crucibles in dynamic air atmosphere (50 ml min^{-1}) with a heating rate of 10 K min^{-1}. The typical sample mass was 10–100 mg.

SEM analyses of magnesium oxide samples were performed using a Philips 515 scanning electron microscope.

High-resolution solid-state CP/MAS NMR was carried out on a Bruker MSL-300 NMR spectrometer (75.5 MHz; ^{13}C). The alcoholate sample was put into a 7 mm ZrO_2 rotor under argon atmosphere and spun with 4 kHz.

3. Results and discussion

The six moisture-sensitive magnesium diolates (Table 1) were characterized by elemental analysis (Mg, C, H), IR spectroscopy and thermogravimetry. All were white insoluble substances that did not form single crystals.

The IR spectra of all six magnesium diolates show the typical C–H (ca. 2900 cm^{-1}), C–O (ca. 1200 cm^{-1}) and Mg–O vibration bands (500–400 cm^{-1}), but also a strong O–H band at ca. 3400 cm^{-1}. This leads to the assumption that hydroxy groups are left in the structure (despite thorough moisture exclusion). This interesting result stands in contrast to the analysis of Maleki [15], who prepared some magnesium diolates from $Mg(OCH_3)_2$ via alcoholate exchange. He found no O–H absorption in the IR spectra and proposed the following two structures:

—Mg—O—R—O—Mg—O—R—O—
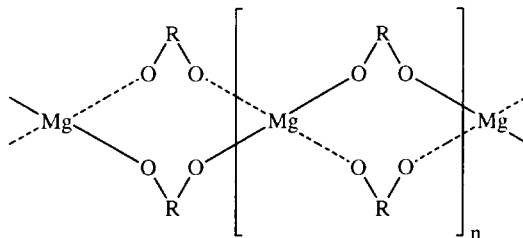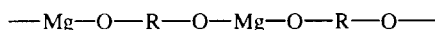
We were not able to determine the crystal structures of the diolates because their insolubility in organic

Table 1
The six prepared magnesium diolates

Alcoholate	Formula
1. Magnesium ethan-1,2-diolate	$Mg[O(CH_2)_2OH][O(CH_2)_2O]_{0.5}$
2. Magnesium propan-1,3-diolate	$Mg[O(CH_2)_3OH][O(CH_2)_3O]_{0.5}$
3. Magnesium butan-1,4-diolate	$Mg[O(CH_2)_4OH]_2$
4. Magnesium pentan-1,5-diolate	$Mg[O(CH_2)_5OH][O(CH_2)_5O]_{0.5}$
5. Magnesium hexan-1,6-diolate	$Mg[O(CH_2)_6OH][O(CH_2)_6O]_{0.5}$
6. magnesium octan-1,8-diolate	$Mg[O(CH_2)_8OH][O(CH_2)_8O]_{0.5}$

solvents prevented the preparation of single crystals. We assume that the magnesium diolates have a polymeric structure which is known from most magnesium alkoxides [1–5]. The combination of elemental analysis, IR spectroscopy and thermogravimetry led to the following formal formula and a proposed structural element for the diolates 1, 2, 4, 5 and 6:

$$Mg_2(OROH)_2(ORO)$$
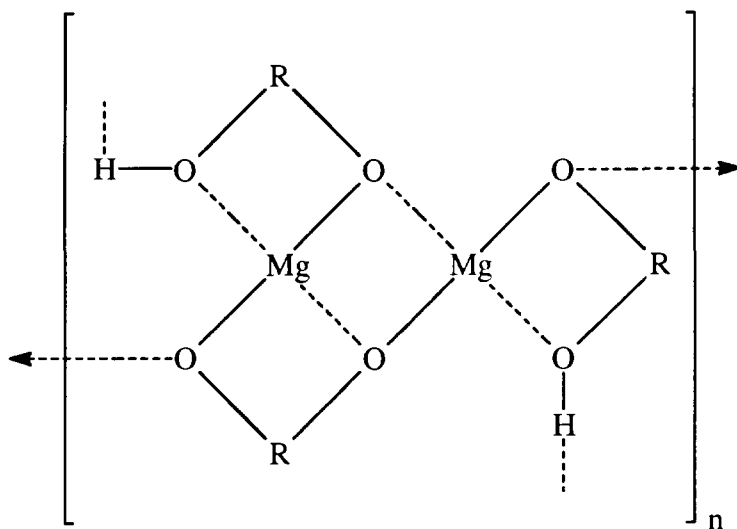
For magnesium butan-1,4-diolate 3 we obtained the formal formula $Mg[O(CH_2)_4OH]_2$ and propose the following structural element:
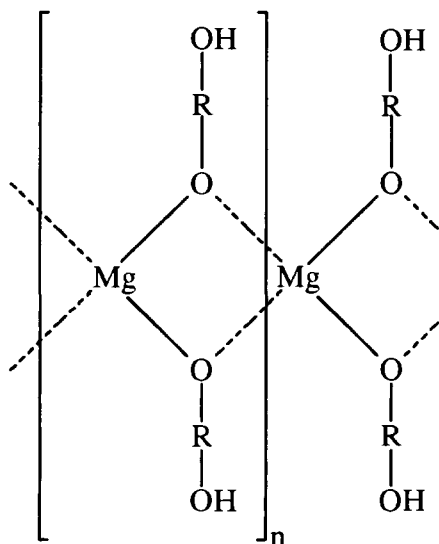
The IR spectra of the six magnesium diolates show significant differences in the Mg–O absorption band. The Mg–O absorption wavenumber increases with increasing carbon chain length (Fig. 1). Pure MgO shows absorption at the lowest wave number at ca. $425\ cm^{-1}$. This means that with increasing carbon chain length more energy is required to excite the Mg–

O vibration. MgO crystallizes in the NaCl structure, a well-ordered structure. We assume that the magnesium diolates have increasingly disordered structures with increasing length of the carbon chain which require more energy to excite the Mg–O vibration.
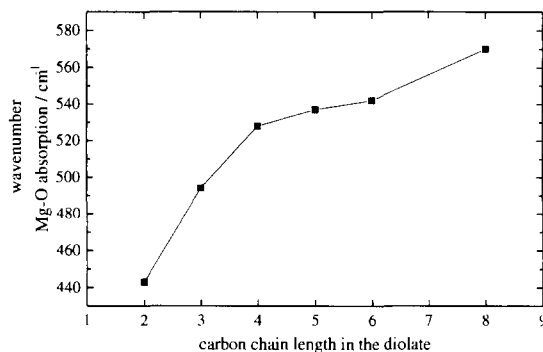

Fig. 1. The change of the Mg–O absorption band with increasing carbon chain length in the IR spectra of the six magnesium diolates.

It could also be a sign for an increasingly covalent character of the Mg–O bonding in comparison to the more ionic pure magnesium oxide.

Another way to study the molecular structure of the non-crystalline-magnesium diolates is solid-state NMR spectroscopy. We measured the ^{13}C solid-state NMR spectrum of magnesium pentan-1,5-diolate 4. The spectrum shows five peaks indicating five different carbon atoms in the diolate ($\delta = 22.50$, 32.75, 36.64, 62.12, 64.12 ppm). The peak at 64 ppm can be attributed to the CH_2-group bonded to –O–Mg, the peak at 62 ppm represents the CH_2-group bonded to – O–H. These results are in agreement with the structure proposed above. The ^{13}C solid-state NMR spectrum of magnesium hexan-1,6-diolate 5 shows six different peaks ($\delta = 26.01$, 26.03, 33.03, 37.11, 62.06, 63.83 ppm) with the CH_2-group bonded to –O–Mg at 64 ppm and the CH_2-group bonded to –O–H at 62 ppm.

The thermal decomposition of the magnesium diolates leads to MgO at comparatively low temperatures (Fig. 2). These are much lower than the decomposition temperature of $MgCO_3$.

All magnesium diolates decompose in a dynamic air atmosphere in two main steps with an intermediate at ca. 330°C (e.g. magnesium pentan-1,5-diolate: Fig. 3). The two TG steps are connected with exothermic DTA peaks. In the first step leading to an intermediate the gaseous reaction products are mainly carbon fragments; the second TG step that leads to magnesium oxide shows mainly water and carbon dioxide as released gases. The IR spectra of the
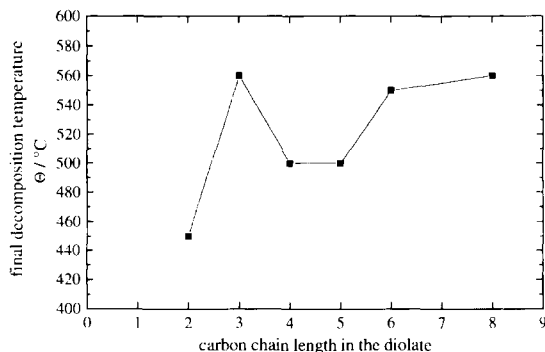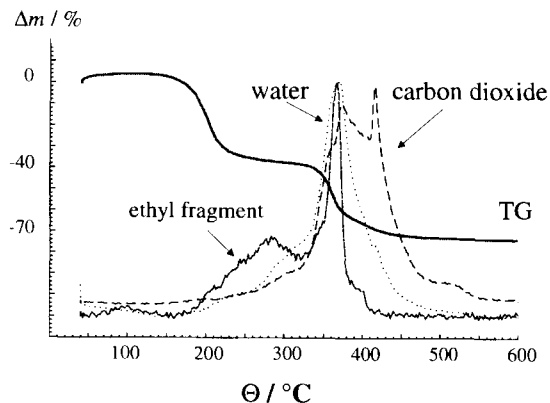

Fig. 3. TG-MS-diagram of magnesium pentan-1,5-diolate in O_2 (18.27 mg); heating rate 10 K min^{-1}.

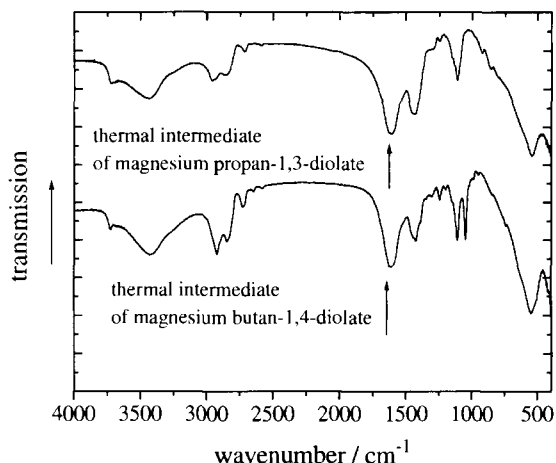
Fig. 4. IR spectra of thermal intermediates of magnesium propan-1,3-diolate at 325°C and magnesium butan-1,4-diolate at 320°C.

Fig. 2. The final decomposition temperatures to MgO of the six magnesium diolates.

moisture-sensitive, yellowish intermediates show a large absorption band at ca. 1620 cm^{-1} which can be attributed to (bridging) O–H-groups in the solid-state structure (Fig. 4). This was also found for the decomposition of magnesium methanolate [6] and other magnesium alcoholates [16]. This suggests that all magnesium alcoholates decompose in air via intermediates with mixed alkoxy-hydroxy-groups Mg(OR-O)$_x$(OH)$_y$.

We were interested in using magnesium diolates as precursors for MgO with defined morphology. SEM
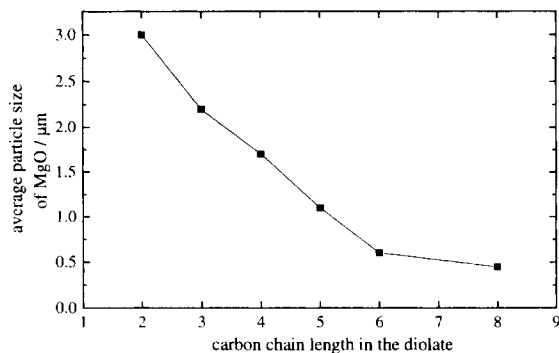
Fig. 5. The decrease of the average particle size of MgO with increasing carbon chain length in the precursor diolate.

analysis of the magnesium oxides prepared by thermal decomposition of the magnesium diolates in air shows significant differences in morphology and particle size. Fig. 5 gives the results of a visual particle size analysis.

The particle size decreases with increasing length of the carbon chain in the precursor. SEM analyses of the resulting magnesium oxides show interesting results. MgO prepared from magnesium ethan-1,2-diolate shows large and very irregular particles; MgO from the hexan-1,6-diolate and octan-1,8-diolate gives smaller and mostly spherical particles. Thus particle size and morphology of the magnesia can be controlled by choice of the appropriate diolate as precursor.

The shape of the magnesia particles is controlled by different aspects: (i) the use of precursor samples of variable shape and size, for example, powder, bulk material or crystals; (ii) the route of the thermal decomposition of the alcoholate, especially heating rate, final temperature and sample annealing time; and (iii) the molecular size of the alcoholate group. It is conceivable that the molecular size of the alcoholate group plays an important role for the size of the MgO particles: when a larger alcoholate group is completely removed from the structure by thermal treatment of the precursor, the remaining MgO domains are smaller and the particle size decreases. These results were found for the simple magnesium alcoholates [6] and are another example of the use of magnesium alcoholates as precursors for the preparation of magnesia in different forms, morphologies and porosities for a wide range of applications.

It is known that the properties of magnesia can be controlled by different methods. Choudhary et al. [7] prepared MgO with different surface properties and catalytic activities from inorganic precursors (e.g. $MgCO_3$, $Mg(NO_3)_2$, $Mg(OH)_2$). The particle sizes decrease from ca. 3 μm (precursor $Mg(NO_3)_2$) to ca. 300 nm (precursor $Mg(OH)_2$). Klabunde et al. [8] demonstrated that it is possible to prepare MgO particles from $Mg(OCH_3)_2$ with a crystalline size of 4.5 nm by supercritical drying. Chhor et al. [9] prepared submicron MgO powders by thermal decomposition of magnesium chelates and acetates in liquid alcohol or supercritical alcohol/CO_2 mixtures. It is underscored that it is possible to influence the properties of oxides by varying the precursor substances and the way of precursor decomposition.

4. Conclusion

This work has shown that magnesium diolates are useful precursors for magnesia because morphology and particle size can be controlled by variation of the carbon chain length in the alcoholates. The alcoholates can be prepared by direct reaction of diethyl magnesium and the corresponding diol.

All magnesium diolates decompose in air to MgO at comparatively low temperatures (450–560°C) via alkoxy/hydroxy intermediates; the final decomposition temperature is much lower than the decomposition temperature of $MgCO_3$ (800–900°C) which is the conventional way to magnesia.

Acknowledgements

References

[1] D.C. Bradley, Prog. Inorg. Chem., 2 (1960) 303.
[2] N.Y. Turova and A.V. Novoselova, Russ. Chem. Rev., 34 (1965) 161.
[3] R.C. Mehrotra, Inorg. Chem., 1 (1967) 99.

[4] D.C. Bradley, Adv. Chem. Radiochem., 15 (1972) 259.

[5] D.C. Bradley, R.C. Mehrotra and D.P. Gaur, Metal Alkoxides, (Academic Press, London, 1978).

[6] H. Thoms, M. Epple, H. Viebrock and A. Reller, J. Mat. Chem., 5 (1995) 589.

[7] V.R. Choudhary, V.H. Rane and R.V. Gadre, J. Catal., 145 (1994) 300.

[8] S. Utamapanya, K.J. Klabunde and J.R. Schlup, Chem. Mater., 3 (1991) 175.

[9] K. Chhor, J.F. Bocquet and C. Pommier, Mat. Chem. Phys., 40 (1995) 63.

[10] K.G. Caulton and L.G. Hubert-Pfaltzgraf, Chem. Rev., 90 (1990) 969.

[11] W.A. Herrmann, N.W. Huber and O. Runte, Angew. Chem., 107 (1995) 2371.

[12] D.C. Bradley, Chem. Rev., 89 (1989) 1317.

[13] A. Stein, S.W. Keller and T.E. Mallouk, Science, 259 (1993) 1558.

[14] E. Weiss, J. Organomet. Chem., 4 (1965) 101.

[15] P. Maleki, Ann. Chim., 2 (1977) 167.

[16] H. Thoms, M. Epple, A. Reller, Solid State Ionics (1997) (in press).