Journal of Thermal Analysis, Vol. 47 (1996) 357-364

THE THERMOCHEMICAL REACTIVITY OF SILICATE MINERALS IN HYDROGEN AND METHANE

U. Sazama and A. Reller

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

Abstract

The thermochemical reduction of transition metal silicates, i.e. garnierite $(Ni,Mg)_6[(OH)_8(Si_2O_7)]$, chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$, dioptase $CuSiO_3{\cdot}H_2O$, willemite Zn_2SiO_4, and hemimorphite $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$ has been studied. By means of combined thermogravimetric/mass spectrometric measurements, X-ray diffraction and analytical scanning electron microscopy it is shown that in a 5% H_2/95% N_2 or in a methane atmosphere the transition metals are selectively reduced at temperatures qualitatively corresponding to their electrochemical potential. Mixtures of elemental transition metals and quartz, SiO_2, are obtained as solid products. Depending on the nature of the parent mineral, different mixtures of volatile products are obtained. Principal volatile product, however, is water vapour. The reduction in methane leads to the formation of syngas.

Keywords: metal/silica products, syngas formation, thermochemical reduction, transition metal silicates

Introduction

The industrial production of metals is usually performed by carbothermal or electrochemical reduction of the corresponding ores. Considering the fact, however, that these processes lead to remarkable emissions of carbon dioxide as main product of the energy production using fossil fuels, alternate pathways using different reducing reactants are of interest. Apart of this rather ecological argument there is an economic one: in regions where metal ores are explored, but energy carriers have to be imported, the implementation of natural gas or regenerative energy systems, i.e. solar driven processes, may be developed successfully within a few decades. Finally, the implementation of hydrogen as reducing reactant appears to be a very attractive alternative. If such type of processes can become feasible, the thermochemical reactivity of ores in the corresponding atmospheres has to be tested. Therefore, we set out to investigate the thermochemical reactivity of the natural minerals and potential ores garnierite $(Ni,Mg)_6[(OH)_8(Si_2O_7)]$, chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$, dioptase $CuSiO_3{\cdot}H_2O$, willemite Zn_2SiO_4, and hemimorphite $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$ by combined thermogravimetric/mass spectrometric studies. All measurements were performed in a 5% H_2/95% N_2 atmosphere. Experiments in a methane at-

0368–4466/96/ $ 5.00

John Wiley & Sons, Limited
Chichester

mosphere were carried out in a separate furnace. Parent phases, intermediates and products were characterized by X-ray diffraction and analytical scanning electron microscopy.

Thermochemical reductions in a 5% hydrogen/95% nitrogen atmosphere

Reduction of garnierite $(Ni,Mg)_6[(OH)_8(Si_2O_7)]$

The TG-MS measurements (Fig. 1) reveal a two-step decomposition for the reduction of garnierite $(Ni,Mg)_6[(OH)_8(Si_2O_7)]$. The reduction starts above 500°C, reaches an intermediate stage at 600°C and is completed at ~900°C. As volatile product water is detected in both steps. The characterization of the intermediate solid products at 600°C proves to be difficult because they are formed as nanocrystalline, X-ray amorphous phases. At 900°C, elemental nickel can be identified. The by-products silica, magnesia and/or magnesium silicates are still X-ray amorphous. This result is explicable by the fact that the tendency of sintering and thus forming crystalline domains of the mentioned products is rather limited at the given reaction temperatures.

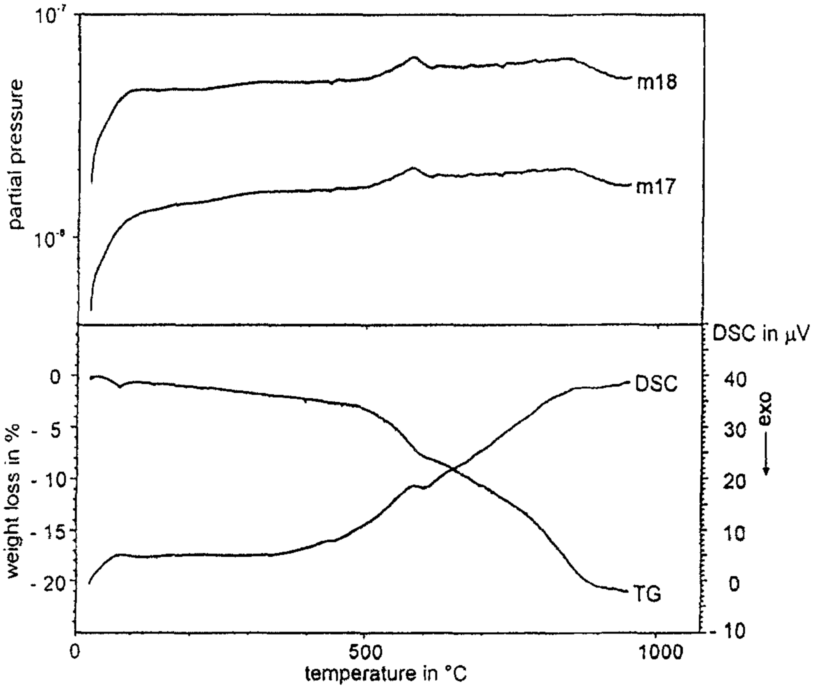

Fig. 1 TG-DSC-MS measurement of the thermochemical reduction of the natural mineral garnierite $(Ni,Mg)_6[(OH)_8(Si_2O_7)]$ in a 5% H_2/95% N_2 atmosphere (temperature range: 30 to 950°C; heating rate: 5°C min^{-1})

Reduction of chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$

This rather complex mineral chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$ undergoes reduction by a two-step process: the decomposition starts at relatively low temperatures by the evolution of water as confirmed by the TG-DSC-MS measurements (Fig. 2). The measured weight loss of the first step corresponds to the loss of 3 water molecules, i.e. one hydrate water and two hydroxide water molecules. For the second step starting at 280°C and being completed at 400°C the formation of two molecules of water per formula unit is registered. As solid products elemental copper and opal, $SiO_2{\cdot}nH_2O$ are identified by X-ray analysis. Eventual aluminum phases are nanocrystalline and thus X-ray amorphous. As SEM studies reveal copper is formed as microcrystalline spheres. This morphology can be explained by the high end temperature of the experiment, i.e. copper is melted and recrystallized. By interrupting the reduction at 500°C extremely small copper particles are observed (resolution limit of the SEM). As the DSC measurement reveals the formed elemental copper melts below 1100°C (literature value for the melting point: 1083°C). Detailed inspection of the evolved volatile products reveal (Fig. 3) that a mass peak $m/e=16$ is registered at a temperature of 440°C. The absence of peaks with $m/e=17$ and

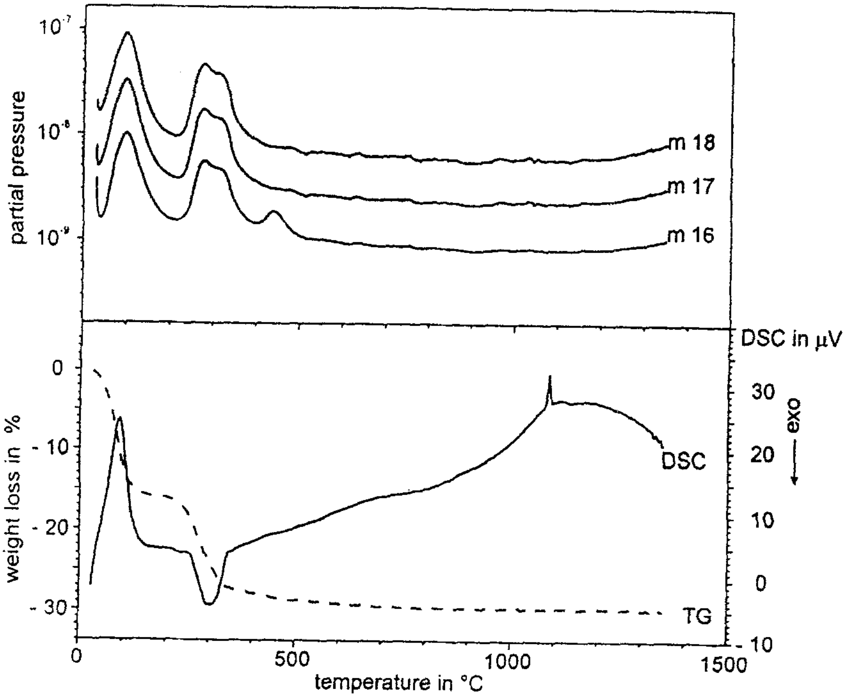

Fig. 2 TG-DSC-MS measurement of the thermochemical reduction of the natural mineral chrysocolla $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$ in a 5% H_2/95% N_2 atmosphere (temperature range: 30 to 1350°C; heating rate: 5°C min^{-1})

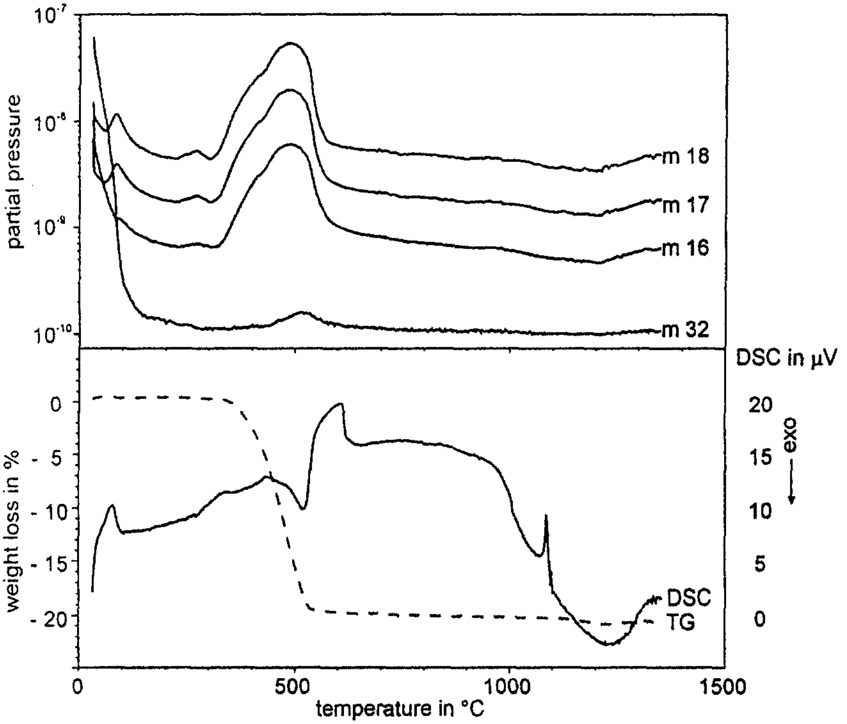

Fig. 3 TG-DSC-MS measurement of the thermochemical reduction of the natural mineral dioptase $CuSiO_3 \cdot H_2O$ in a 5% H_2/95% N_2 atmosphere (temperature range: 30 to 1350°C; heating rate: 5°C min^{-1})

$m/e = 18$ prove that this signal cannot be attributed to H_2O. Additional experiments gave evidence that small amounts of methane, CH_4, are formed by the decomposition of carbonate constituents. It has been shown in earlier studies that in reducing atmosphere the decomposition of mixed transition metal carbonates leads to the formation of catalytically active metal particles. They lead to the *in-situ*-conversion of CO_2 and CO into CH_4 [1].

Reduction of dioptase $CuSiO_3 \cdot H_2O$

The bottle-green mineral dioptase $CuSiO_3 \cdot H_2O$ does not belong to the industrially explored copper ores. It is rather used as semi-precious stone for jewelry. However, its comparably simple composition is well suited for the study of the thermochemical reduction in various atmospheres (see also following chapter). The TG-DSC-MS measurements (Fig. 3) give evidence for a single-step decomposition in the temperature range of 350 to 530°C. The volatile product water and the solid products silica and elemental copper are formed. The weight loss is in agreement with the theoretical value. Again, below 1100°C the melting of the formed copper is observed by DSC.

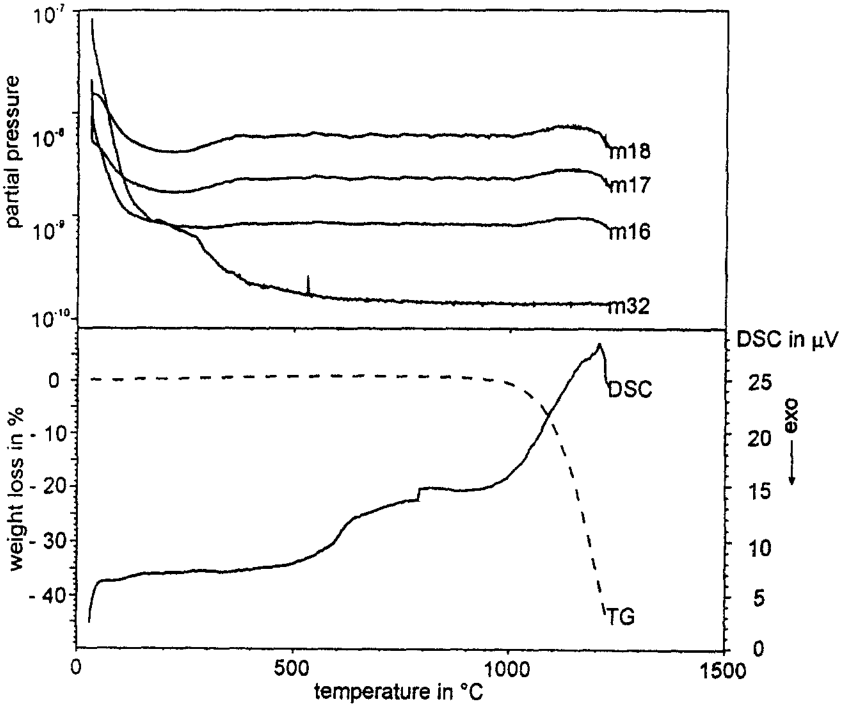

Fig. 4 TG-DSC-MS measurement of the thermochemical reduction of the natural mineral willemite Zn_2SiO_4 in a 5% H_2/95% N_2 atmosphere (temperature range: 30 to 1230°C; heating rate: 5°C min^{-1})

Reduction of willemite Zn_2SiO_4

Willemite Zn_2SiO_4 is found in Australia. It belongs, as hemimorphite (see below) to the metal silicates which are explored industrially. Owing to its 'simple' composition, a one-step reduction is expected. The thermoanalytical/mass spectrometric measurements confirm this assumption. The reduction, however, only starts above 1000°C (Fig. 4). At this temperature elemental zinc exhibits a considerable volatility. Therefore it is evolved and it can be easily condensed and collected at any cooled device. Accordingly, under the given conditions the TG curve does not reach weight stability. This specific feature of the reduction process is remarkable: it proves that the thermochemical reduction in hydrogen includes a combined reduction/refinement step. The technical feasibility is under consideration.

Reduction of hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$

Finally, the reduction of hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ is presented. This mineral undergoes a multi-step thermochemical degradation: in a first step around 500°C one molecule of water ('crystal water') per formula unit is

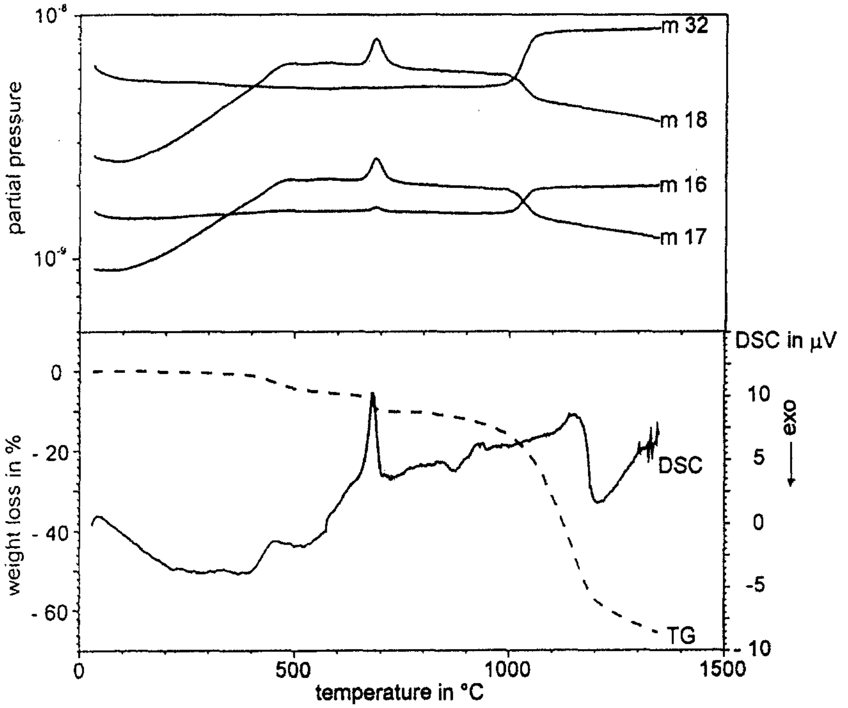

Fig. 5 TG-DSC-MS measurement of the thermochemical reduction of the natural mineral hemimorphite $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ in a 5% H_2/95% N_2 atmosphere (temperature range: 30 to 1350°C; heating rate: 5°C min^{-1})

evolved. During the second step around 700°C two molecules of water per formula unit are evolved. X-ray diffraction of this intermediate product confirms the formation of willemite Zn_2SiO_4. The subsequent course of the reduction is slightly different to the one observed for the parent willemite. The evolution of oxygen as volatile product as well as the reaching of weight stability may be explained by the high reactivity of the microcrystalline particles formed by the decomposition of hemimorphite. The final products are again silica and elemental, 'refined' zinc.

Thermochemical reductions in a methane and a methane/steam atmosphere

Methane is a cheap and readily available reducing reactant. Thus, preliminary investigations have been performed on the reducibility of zinc and copper silicates in a methane and in a methane/steam atmosphere. The methane/steam mixture has been chosen in order to get insights into the role of the water vapour pressure as well as with respect to the applicablity of this pathway to the reduction of ores or minerals with different chemical composition such as oxides or sulfides. Owing to the problems caused by the methane atmosphere, the experiments could not be performed in the thermobalance but in a specially designed furnace equipped with gas atmosphere, gas flow and temperature control.

For the reduction of willemite Zn_2SiO_4 in methane, elemental zinc, silica and syngas, i.e. a mixture of carbon monoxide and hydrogen are obtained. The formation of intermediate metal oxides and subsequent reduction has to be suggested. The formal processes can be summarized as follows:

$$Zn_2SiO_4 \longrightarrow 2ZnO + SiO_2 \quad (1)$$

$$ZnO + CH_4 \longrightarrow Zn^\circ + CO + 2H_2 \quad (2)$$

Process (2) and similar processes using metal oxides such as iron oxides or manganese oxides have been recently investigated with respect to their implementation into regenerative, i.e. solar driven energy systems [2–4]. Moreover it

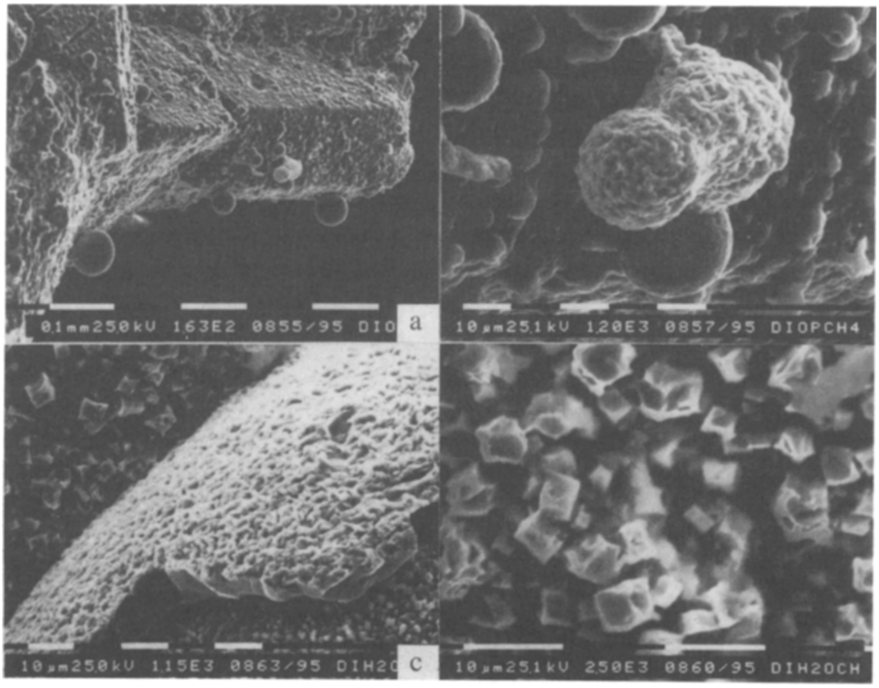

Fig. 6 Scanning electron micrographs of Cu°/SiO_2 products obtained by the reduction of dioptase $CuSiO_3 \cdot H_2O$ in a methane atmosphere (micrographs a and b) and in a methane/water vapour atmosphere (micrographs c and d). It is clearly visible that the shape of the Cu° particles is remarkably influenced by the composition of the reducing atmosphere

has been confirmed experimentally, that metals like zinc or iron, but also the slightly non-stoichiometric iron(II) oxide FeO may split water into hydrogen and oxygen, which is incorporated by the formation of the corresponding metal oxide ZnO or Fe_3O_4. Such cyclic processes are investigated with respect to their feasibility as future systems for the conversion of solar energy into useful chemicals or fuels.

In order to further study the influence of the partial pressure of water vapour on the formation of the products, reductions of the above mentioned mineral dioptase $CuSiO_3 \cdot H_2O$ in methane as well as in a mixture of methane/water vapour were performed. In both cases elemental Cu° and silica are obtained as solid products. The morphology of the products, however, is remarkably influenced by the actual gas atmosphere: in pure methane Cu° spheres are obtained, in a mixture of methane/water vapour, however, cube-like Cu° is formed (Fig. 6).

Discussion

Our investigations reveal that the reduction of various silicate ores or minerals using hydrogen or methane as reducing agents represent an attractive alternative to the carbothermal or electrochemical pathway. One obvious advantage of this approach can be ascribed to the metal selectivity, with which the separation of metals from polyphasic, multi-component ores can be achieved. In the case of hydrogen reduction, the problem of possible critical carbon compound emissions is omitted. The technical and economic feasibility of these processes, however, depends on the availability of the reducing reactants hydrogen and methane as well as on the engineering problems. With regard to future energy systems, especially with regard to regenerative energy carriers such as hydrogen, the described processes represent potential pathways to the production of necessary basic chemicals.

* * *

The authors acknowledge the financial support of the Schweizerisches Bundesamt für Energiewirtschaft as well as the Fonds der Chemischen Industrie.

References

1 A. Reller, C. Padeste and P. Hug, Nature, 329 (1987) 527.
2 P. Kuhn, A. Steinfeld and A. Reller, Proc. 7th Int. Symp. on Solar Thermal Concentr. Technol., Moscow, Russia, Vol. 3, 1994, p. 557.
3 A. Steinfeld, A. Frei, P. Kuhn and D. Wuillemin, Int. J. Hydrogen Energy (in press).
4 P. Kuhn, E. Steiner, K. Ehrensberger and J. Ganz, Int. J. Hydrogen Energy (in press).