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Synthesis of metakaolin-like aluminosilicates via sol-gel process and Pechini method

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Introduction

The varying morphology and chemical composition of metakaolin, even from the same mining site, can be a hinderance for comparative studies of additives for alkali activated binders (AAB) and geopolymers. Therefore, a reproducible synthetic metakaolin with adjustable chemical composition and no crystalline phases would be a good model-system for comparative studies on the behavior of additives for AAB and geopolymers. Metakaolin-like aluminosilicates can be synthesized from tetraethyl orthosilicate (TEOS) and aluminum nitrate nonahydrate (ANN) in a sol-gel-process [1]. An alternative synthesis method is the Pechini method, which is related to the sol-gel process, but utilizes the chelation of an hydroxycarboxylic acid with a cationic salt (**Fig. 1**) [2]. In both methods the resulting gels are then dried at 105 °C and dehydroxylated between 500 – 800 °C in an oven. In this study both methods were used to synthesize metakaolin-like aluminosilicates from TEOS and ANN, as well as iron doted aluminosilicates by addition of iron nitrate nonahydrate (INN). The gels were dried, dehydroxylated and then characterized by their chemical composition, morphology and pozzolanic reactivity.

Materials and Methods

Materials

TEOS - tetraethyl orthosilicate (≥ 99 %)

ANN - aluminum nitrate nonahydrate (≥ 98 %)

INN - iron(III) nitrate nonahydrate (≥ 96 %)

ultrapure water (≤ 0.05 µS/cm)

ethanol (≥ 96 %)

ethylene glycol (≥ 99 %)

citric acid (≥ 99.5 %)

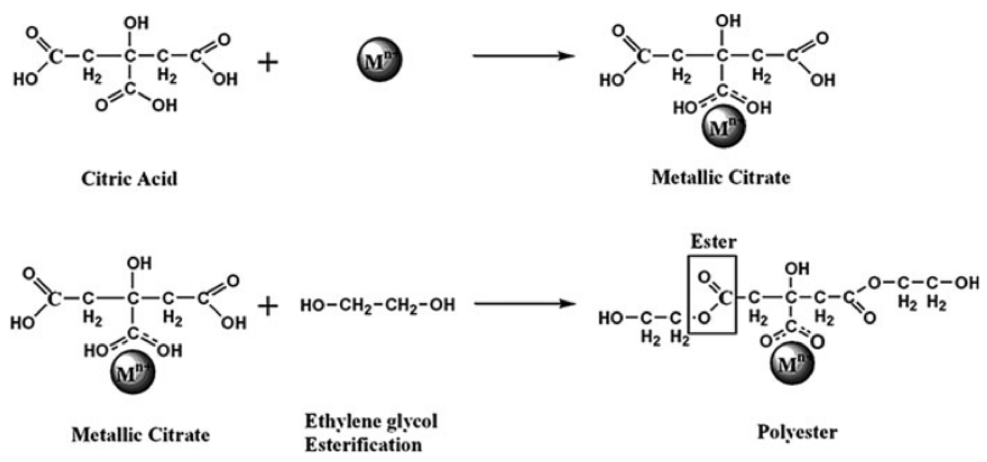

Fig. 1: Schematic of processes of the Pechini method [2]

sol-gel process

1. dissolution of TEOS in ethanol
2. dissolution of ANN in ethanol and water
3. mixing of both solutions
4. heating to 70 °C under constant stirring
5. gelation occurs

Pechini method

1. dissolution of citric acid in ethanol and water
2. addition and dissolution of ANN
3. addition of TEOS and ethylene glycol
4. heating to 150 °C under constant stirring
5. gelation occurs

Drying – 105 °C / 48 h → **Dehydroxylation** – 650/750 °C / 4 h → **Milling** – Vibratory Disk Mill

Investigations and Results

Pure aluminosilicates (MK) and aluminosilicates containing iron (MK-I) were synthesized and dehydroxylated at 650 °C and 750 °C. The analysis of phase content via XRD and Rietveld method shows (**Fig. 2**) that the Pechini method results in completely amorphous phases after dehydroxylation for three of four samples. Only traces of quartz can be found in the pure metakaolin-like aluminosilicate sample dehydroxylated at 650 °C. If iron is present crytalline hematite can be detected in amounts of 3 – 6 % if the samples derive from the sol-gel process.

The specific surface area determined by BET method can be seen in **Fig. 3**. If no iron is present, the samples derived from the Pechini method show a very large specific surface area of 340 – 380 m²/g, more then double the area compared to sol-gel derived samples. Typically, the specific surface area of metakaolin is in a range up to 30 m²/g. The rise of dehydroxylation temperature from 650 °C to 750 °C leads to an increase of specific surface area for sol-gel derived samples and a slight decrease for samples derived from Pechini method. If iron is present, a reduction can be seen regardless of synthesis method. While the Pechini method results in a bigger specific surface area for samples dehydroxylated at 650 °C, no difference can be seen for samples dehydroxylated at 750°C. The mean values of all samples were determined tri-fold and the Pechini method results in lower standard deviation for samples containing iron. The dehydroxylation process was investigated by ^{27}Al-NMR analysis on iron-free metakaolin-like aluminosilicates synthesized by the sol-gel process. The spectra (**Fig. 4**) show that the dehydroxylation leads to the formation of high amounts of Al(6)-species and low amounts of Al(4)-species compared to metakaolines from natural sources. The pozzolanic reactivity was investigated by the modified Chapelle test described in the french norm NF P 18-513, Annexe A. According to the norm, a metakaolin can be considered as pozzolanic if the amount of fixed $Ca(OH)_2$ is greater than 700 mg/g. All synthesized samples showed high pozzolanic reactivity with amounts of fixed $Ca(OH)_2$ greater than 1000 mg/g (**Fig. 5**). The Pechini method results in alumosilicates with higher pozzolanic reactivity regardless of the dehydroxylation temperature with amounts of fixed $Ca(OH)_2$ in between 1200 – 1350 mg/g. The sol-gel derived samples show results around 1050 – 1300 mg/g, with high standard deviation for the MK/750 sample.

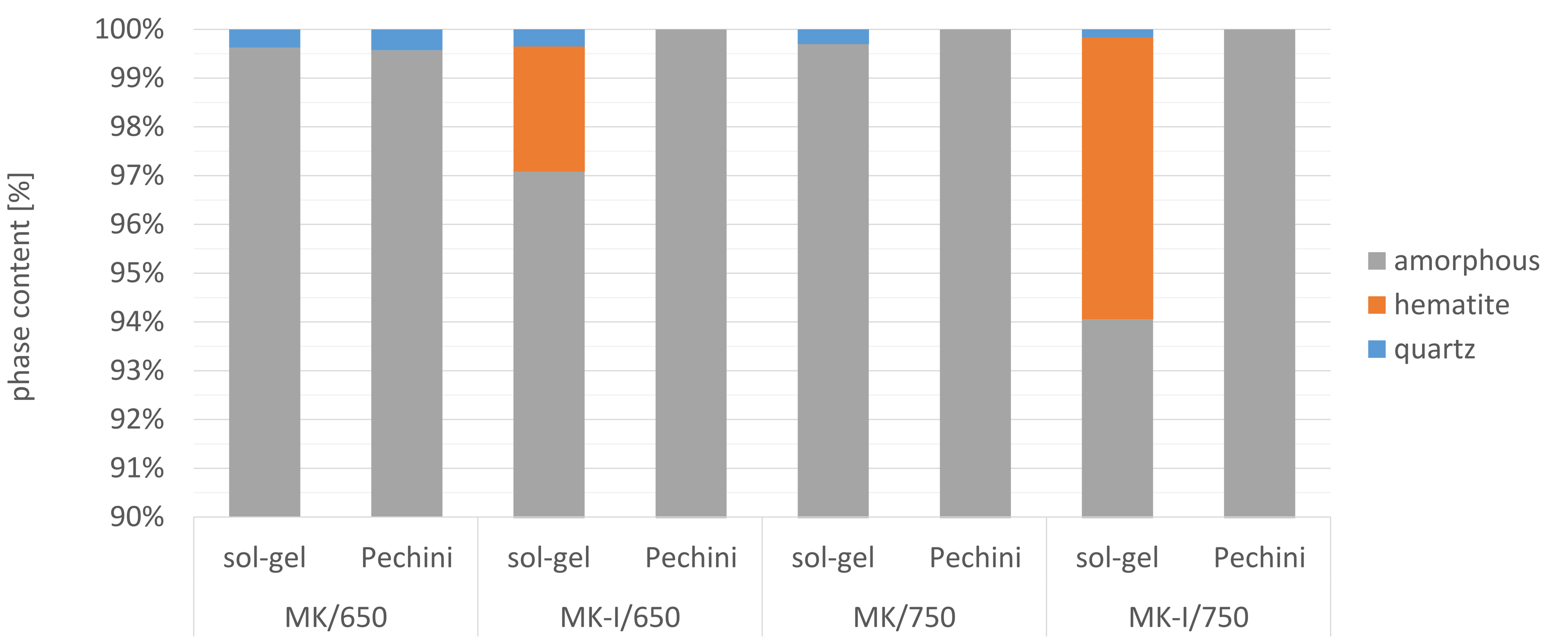

Fig. 2: Phase content of samples determined by XRD and calculation by Rietveld analysis

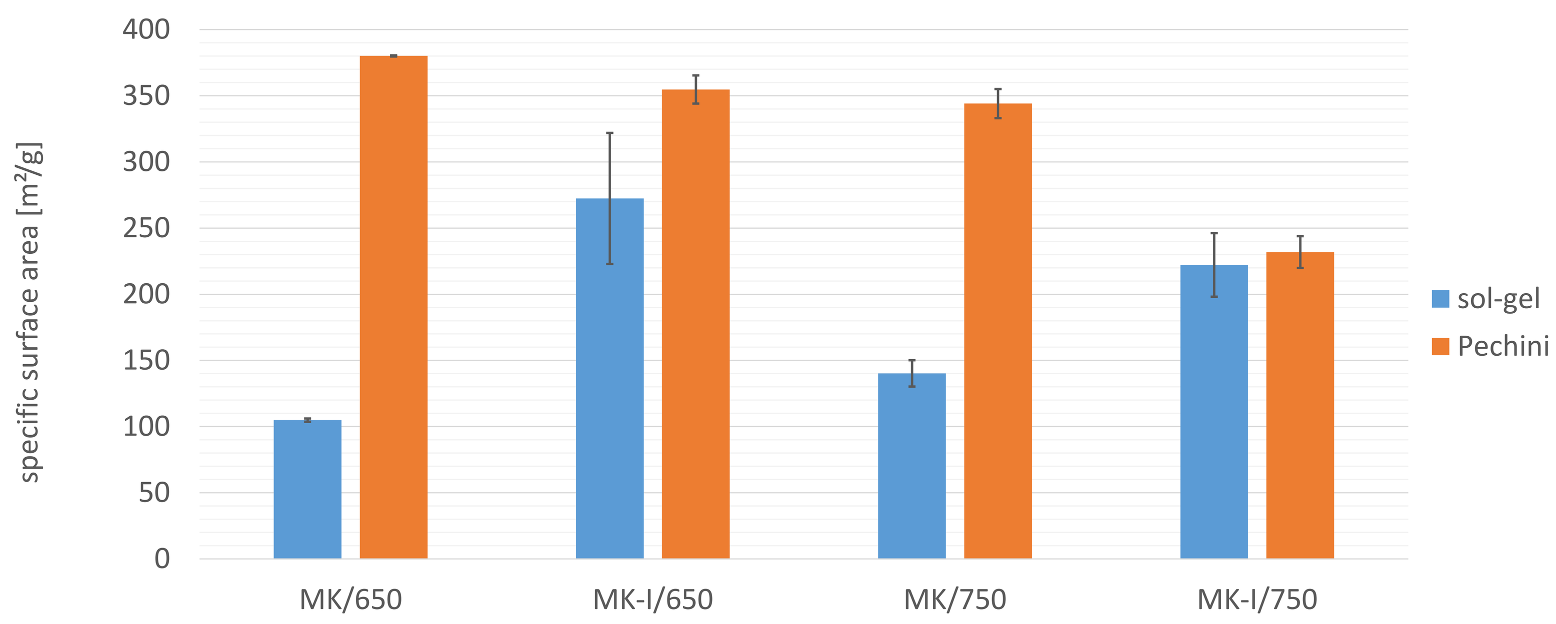

Fig. 3: Specific surface area determined by BET method

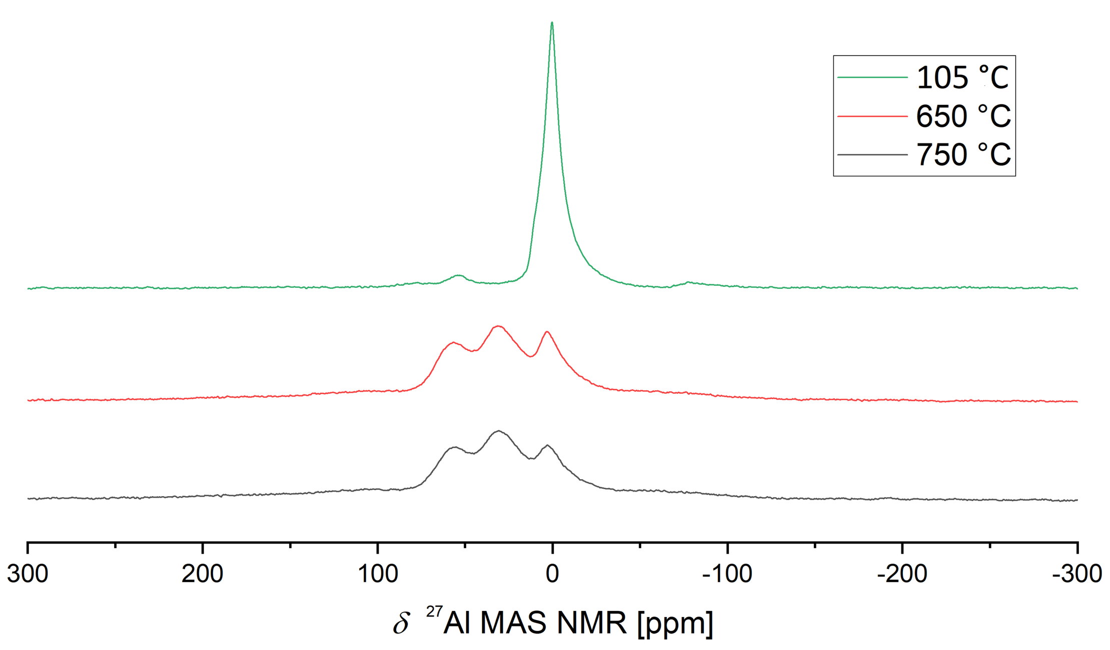

Fig. 4: ^{27}Al-NMR spectra of pure metakaolin-like aluminosilicates before and after dehydroxylation

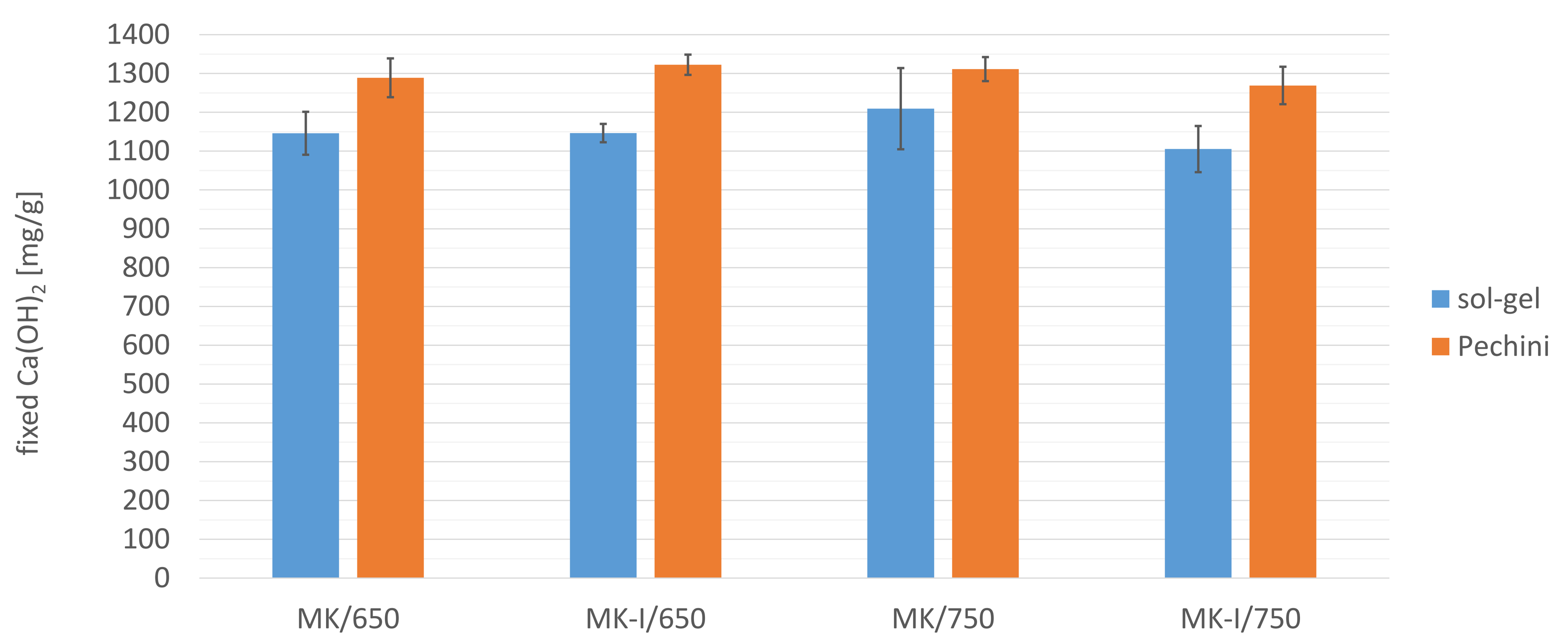

Fig. 5: Amount of fixed $Ca(OH)_2$ per gram of sample determined by modified chapelle test

Conclusion

Both synthesis methods result in alumosilicates with high pozzolanic reactivity. The Pechini method, in contrast to the samples derived from the sol-gel process, results in a higher pozzolanic activity, a much higher specific surface area for iron-free samples and in 100 % amorphous phases if iron is present. The morphology of the samples needs to be further investigated in further research.

References

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[2] Dimesso, L. (2016) Pechini Processes: An Alternate Approach of the Sol–Gel Method, Preparation, Properties, and Applications in: Klein, L.; Aparicio, M.; Jitianu, A. [Publisher] Handbook of Sol-Gel Science and Technology. Cham: Springer International Publishing, P. 1–22.

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