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Modified geopolymers as promising catalyst supports for abatement of dichloromethane

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ABSTRACT

Geopolymers have not been extensively employed as catalytic materials despite of their zeolite-resembling Si–Al structure. Geopolymerization offers a novel way for preparation of catalysts and possibility to use waste or industrial side-stream derived raw material as a resource for catalyst manufacturing. This work concentrates on metakaolin-based geopolymer materials that were prepared, characterized and tested as alternative environmentally benign catalyst supports for the oxidation of dichloromethane. The geopolymers with the Si/Al ratio of 1.5 were modified with HCl to increase their specific surface area, which is important in catalytic applications. Significant increase in specific surface areas was achieved via leaching of Na and Al from the geopolymer structure. Highest specific surface areas achieved for calcined geopolymers were over 500 m²g⁻¹. Use of acid concentrations higher than 1 M led to the dehydroxylation of the geopolymer. Dehydroxylation decreased the total acidity of geopolymer through the loss of the Brønsted acid sites, which are responsible for the adsorption of dichloromethane in the beginning of the catalytic reaction. Absence of Brønsted acid sites was observed by the formation of CH₂O as the only reaction intermediate. The best result in the dichloromethane oxidation was found with the geopolymer treated with 1 M HCl. Without using any additional active sites, the maximum dichloromethane conversion of 90% was reached at 525 °C with the maximum HCl yield of 83%. This result indicates the good potential of modified geopolymers to be used as catalyst supports in environmental applications.

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1. Introduction

Geopolymers (GPs) are amorphous inorganic materials prepared by the activation of aluminosilicate precursors with hydroxides, carbonates or silicates of alkali or alkaline earth metals. These materials are often projected as greener construction materials due to lower carbon emissions when compared to Ordinary Portland Cement and thus are widely investigated for the use in construction industry (Amran et al., 2020). Geopolymers are also considered to be used in solidification of hazardous chemicals (Jaarsveld et al., 1998), CO₂ capture (Papa et al., 2019), insulation (Novais et al., 2016), as well as fire resistant materials (Cheng, 2003) and water treatment adsorbents for heavy metal adsorption (Chen

et al., 2019). Since most of the aluminosilicate precursors are industrial side streams or waste materials, such as fly ash, volcanic ash, mine tailings, waste ceramics, blast furnace slag, utilization of geopolymers promote the concept of circular economy (Asim et al., 2019).

The structure of a geopolymer consists of three-dimensional network of SiO₄ and AlO₄ tetrahedra, with the negative charge of AlO₄ tetrahedra balanced by alkali or alkaline earth metals (Rožek et al., 2019). In terms of this local ordering, geopolymers resemble zeolites, thus bringing out potential substitution for zeolite materials. There has been a growing interest in the use of geopolymers as catalytic materials. Examples can be found especially in heterogeneous liquid-phase reactions such as, the Beckmann rearrangement (Alzeer et al., 2016), the Friedel–Crafts acylation (Al-Zeer and MacKenzie, 2019) and the biodiesel production (Sharma et al., 2015), while less information is available in heterogeneous gas-phase reactions. One good example on gas-

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phase reactions is presented by [Canadamaro et al. \(2015\)](#), where he used Ni-modified geopolymer catalysts in steam reforming, partial oxidation and autothermal steam reforming of ethanol to syngas. The results showed that the developed catalyst gave best results in steam reforming conditions resulting in complete conversion of ethanol and ~70 mol-% production of hydrogen. ([Canadamaro et al., 2015](#)). To improve the performance of the geopolymers in specific reactions, they have been modified by different post-treatments, e.g., to reach dealumination and desilication ([Alzeer et al., 2016](#)), by adding active metals such as Fe, Co, Cu ([Sazama et al., 2011](#)) and Ni ([Canadamaro et al., 2015](#)), by NH₃ ion exchange to modify acidity ([Al-Zeer and MacKenzie, 2019](#)), and calcium ([Sharma et al., 2015](#)) to modify the basic sites.

There are only few studies available on the utilization of geopolymers in the environmental catalysis field. A recent review by [Zhang et al. \(2020\)](#) summarizes that the geopolymer catalysts and photocatalysts have been applied especially in water treatment, e.g. in dye degradation, but considerably less studies are available on gas abatement applications. [Sazama et al. \(2011\)](#) prepared metakaolin-based catalysts by ion-exchanging Cu and Co and impregnating Fe and Pt on the geopolymer surface. These catalysts were applied in NH₃-SCR reaction (NO_x reduction) and total oxidation of n-decane (volatile organic compound included in the diesel fuel). Pt-geopolymer catalyst was able to oxidize 250 ppm of n-decane completely already at around 175 °C in presence of 6% of oxygen. They also demonstrated that Cu-geopolymer catalyst performed better than commercial V₂O₅/TiO₂ catalyst in NH₃-SCR reaction ([Sazama et al., 2011](#)).

The geopolymers have certain advantages when used as catalysts including simple preparation procedure, flexibility of the modification of the catalytic properties for selected reaction, and thermal stability ([Rasaki et al., 2019](#)). Unique properties of geopolymers, such as oxidation-reduction properties, possibility to modify acidic/basic properties, reactive hydroxyl groups, ion exchange capacity etc., are beneficial in environmental applications, such as in the oxidation of chlorinated volatile organic compounds (CVOs), that has not been studied using geopolymer-based catalysts before.

Dichloromethane or methylene chloride (DCM, CH₂Cl₂) is an important commercial chemical used for example in degreasing, decaffeination, pharmaceuticals' production, and as propellants in aerosols ([National Toxicology Program, 1986](#); [Tlili and Schranck, 2017](#)). DCM is considered as a pollutant in indoor and outdoor air as well as in solid waste and water bodies. It is toxic and suspected to be a carcinogen ([ICSC, 2017](#)). The release of chlorinated volatile organic compounds into indoor air and atmosphere are strictly regulated and controlled ([EU, 2010](#)). Catalytic oxidation has proven to be an efficient abatement technology for the treatment of DCM emissions. The total oxidation of DCM has been studied over a wide range of catalytic materials. The most promising catalysts are noble metals, such as Pt, Pd, and Rh supported on γ-Al₂O₃, SiO₂, CeO₂, TiO₂, MgO, and mixed oxides ([El Assal et al., 2017](#); [Pitkäaho et al., 2013](#)).

It has been found that acidic and redox properties of the catalyst support will improve the DCM conversion. The role of the noble metal is mainly to improve the selectivity of the oxidation towards CO₂ ([Pitkäaho et al., 2013](#)). It is possible to prepare geopolymers with Brønsted acidity ([Alzeer et al., 2016](#)), which makes such materials very interesting in the total oxidation DCM. However, specific surface area of geopolymers, as prepared, are rather low for catalytic applications even when using Si/Al ratio <1.40 ([Duxson et al., 2005](#)). This is also probably one of the reasons why less studies on application of geopolymer-based catalysts in gas-phase reactions are found. There exist earlier studies where the porosity of geopolymer has been increased via foaming ([Lemoungna et al.,](#)

[2016](#)), using pore forming fibers ([Rasouli et al., 2015](#)) or different acid/base treatments ([Alzeer et al., 2016](#)). Dealumination by an acid treatment is one of the most known post-synthesis methods for zeolites to increase the porosity and to remove the extra framework aluminum. Removal of aluminum leads also to partial breakdown of zeolite structure and formation of vacancies. These events lead to improved meso- and microporosity ([Feliczak-Guzik, 2018](#)). Increasing specific surface area of geopolymer further would allow higher number of surface sites participating the catalytic events and enable higher dispersion of an active phase, which both affect the activity of the final catalyst. Adequately high surface area is especially important in gas-phase reactions, where shorter residence times in reactor require higher availability of active surface area of a catalyst.

Since the environmental catalytic applications of geopolymer-based catalytic materials are very scarcely studied, this work focuses first on increasing the geopolymer specific surface area by acid leaching up to a level necessary for gas-phase catalytic applications, and secondly, studying the performance of the modified geopolymer in DCM oxidative abatement in detail. Metakaolin (calcined anhydrous kaolinite clay) was selected as a raw material for geopolymer, since it is more homogeneous and purer than waste-based raw materials, such as fly ash or slag ([Duxson et al., 2005](#)). Using this model system minimizes the interference of impurities in the catalytic performance and allows understanding characteristics-performance relationships of the geopolymer better. The geopolymers prepared were characterized by N₂ physisorption analysis (BET-BJH), X-Ray diffraction (XRD), X-Ray fluorescence (XRF), thermogravimetric analysis (TGA-DTA/DSC), Raman spectroscopy as well as with temperature programmed reduction, oxidation and ammonia adsorption (H₂-TPR, TPO and NH₃-TPD) to discover the most important properties of the materials and evaluate their relationships on the material performance in oxidative abatement of DCM.

2. Materials and methods

Metakaolin (Metamax, BASF) was used as the precursor for the geopolymer synthesis. The composition of metakaolin is shown in [Table 1](#). A sodium silicate solution (refer [Table 1](#)) and sodium hydroxide pellets (with a purity >99%) were used for the activation (both obtained from Merck, Germany). Hydrochloric acid (37%, Sigma Aldrich) was used to prepare diluted solutions-(0.5 M, 1 M, 2 M and 3 M) for the acid treatment of geopolymers.

2.1. Preparation of acid-modified geopolymers

The alkali activation procedure was modified from the procedure followed by ([Solismaa et al., 2018](#)). Activation solution was prepared by mixing 30 g of a sodium silicate solution, 7.5 g of NaOH pellets, and 13 g of water. The mixture was stirred for 24 h to ensure complete dissolution of the pellets. Metakaolin (30 g) was added to the prepared activation solution and mixed in a planetary centrifugal mixer (Thinky, USA) at 500 rpm for 3 min. The slurry was then introduced into cylindrical plastic molds (with 25 mm diameter and 25 mm height) and sealed in plastic bags for curing at 40 °C for

Table 1
XRF analysis of raw materials (% w/w).

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	Na ₂ O	TiO ₂	LOI
Metakaolin	53.0	44.5	0.4	0.1	0.3	1.4	5.9
Sodium silicate soln.	27.0	–	–	–	8.0	–	65.0

LOI: loss on ignition.

one day. After the curing, the samples with plastic bags were left at room temperature for seven days. The sample was then demolded and grinded with a vibratory disc mill (Retsch RS 200) at 700 rpm for 1 min.

The geopolymeric powder obtained was then modified with different concentrations of HCl. During the acid leaching, 10 g of the prepared geopolymer was mixed with 100 mL of HCl solution (with a series of concentrations) at 60 °C for 48 h. After leaching, the pH was adjusted to 8–9 under agitation. The slurry obtained was washed several times with deionized water and dried at 100 °C overnight. The dried, acid treated samples were finally calcined at 600 °C for 1.5 h. The nomenclature for various samples are shown in Table 2.

2.2. Characterization

X-ray diffraction patterns of the studied materials were recorded with a Rigaku SmartLab 9 kW XRD device. The analysis employed Co K α radiation ($K\alpha_1 = 1.78892 \text{ \AA}$; $K\alpha_2 = 1.79278 \text{ \AA}$; $K\alpha_1/K\alpha_2 = 0.5$), a scan rate of 3°/minute between 5° and 85° (2 θ) using 0.02° step size. “X’pert HighScore Plus” (PANalytical) software was used for the phase identification.

Thermal analysis of the non-calcined materials was performed with a Netzsch STA 449 F3 TGA-DTA/DSC analyzer (Selb, Germany). Specimen, about 20 mg, placed in a crucible was heated up to 700 °C with a heating rate of 10 °C min⁻¹ under the ambient atmosphere.

The chemical composition of the material was determined with the help of an XRF Spectrometer (PANalytical AXIOSmAX 4 kW PW2450) fitted with a Rh X-ray tube. The analysis was done with the loose powder method under He atmosphere. The analysis method used was “Omnian standardless” and the analysis software used was “SuperQ 5.3C”. The repeatability of the analysis is 3–5%.

The specific surface areas and pore volumes of all the prepared materials were determined by physisorption of nitrogen at -196 °C using a Micromeritics ASAP 2020 instrument. The specific surface areas were obtained using the BET (Brunauer-Emmett-Teller) method and pore size distributions using the BJH (Barrett-Joyner-Halenda) method. Prior to adsorption, the samples were degassed under vacuum at 100 °C for 1200 min. The error of the analysis is $\pm 5 \text{ m}^2\text{g}^{-1}$.

The total acidity and reducibility of the materials were determined by temperature-programmed methods using an AutoChem II 2090 equipment. Three measurements were done subsequently starting with H₂-TPR for the reducibility information, TPO for re-oxidation and NH₃-TPD for acidity determination. A sample of around 40 mg was pre-treated under an O₂ flow (50 cm³ min⁻¹) for 30 min at 500 °C and then cooled to room temperature under O₂ flow. Then, the sample was flushed with He for 30 min to remove excess oxygen. TPR was carried out under 10% H₂ in Ar. The heating

was done up to 500 °C with the heating rate of 10 °C min⁻¹. After TPR, the sample was flushed with He for 30 min, and 5% O₂ in He was introduced to re-oxidize the sample (TPO). The heating was done in a similar way than in the TPR experiment. After TPO, the sample was cooled down to 100 °C under a He flow. NH₃ adsorption was carried out at 100 °C during 60 min. Excess NH₃ was then flushed with He for 30 min. The NH₃ desorption (NH₃-TPD) was realized with the heating rate of 10 °C min⁻¹ up to 500 °C under a He flow.

The calcined materials were characterized by Time-gated Raman spectroscopy (PicoRaman and model M1 devices, Time-gate Instruments Inc.) equipped with a fiber coupled pulsed (532 nm) laser and a single photon counting CMOS SPAD matrix detector with $\sim 5 \text{ cm}^{-1}$ spectral resolution. The data were collected with the Raman shift range from 100 cm⁻¹ to 2000 cm⁻¹ and 3000 cm⁻¹ to 4000 cm⁻¹. The AirPLS method was used in the data treatment for background correction.

2.3. Dichloromethane oxidation

The DCM oxidation tests were performed in a continuous flow tubular quartz reactor operating under atmospheric pressure. Liquid DCM (Algol, 99.0 vol-%) and H₂O were fed with syringe pumps to the evaporator where they were mixed with a controlled amount of air to reach 500 ppm and 1.5 vol-% concentration for DCM and H₂O, respectively. The mass of the catalyst in each experiment was 500 mg and the particle sizes were between 100 and 315 μm . The gas hourly space velocity (GHSV) was 119 000 h⁻¹, except with G-0M-C, for which it was 80 000 h⁻¹. During the experiments, the oven was heated from 100 °C to 550 °C with a heating rate of 5 °C min⁻¹. Temperature was measured outside reactor right before the catalyst bed and corrected to represent the value inside the reactor. The concentrations of the feed and reaction products were measured with a Gasmeter Dx-4000 N FTIR analyzer. The experiments were repeated, and the accuracy of the indicated temperatures is $\pm 10 \text{ }^\circ\text{C}$. More detailed information on the experimental set-up can be found in the literature (Pitkäaho et al., 2012).

3. Results and discussion

3.1. Characterization of geopolymers

The results of the XRD characterization for the non-calcined samples are shown in Fig. 1(a). The sample G-0M (not acid treated), shows a broad hump centered at 32°, which is characteristics for the geopolymers (Duxson et al., 2007). Note that XRD analysis was performed with Co K α radiation and hence, the position of the hump is 4–5° higher than the values reported in the literature (where Cu K α radiation was employed). Upon acid treatment (G-0.5M to G-3M), there is a shift of the amorphous hump towards a lower theta value showing the formation of a new amorphous phase. Similar change in hump position was observed by Alzeer et al. (2016) after dealumination, and they explained it by removal of some crystalline phases and Al-rich residues. The center of the hump in acid-treated samples lies between 26° and 29° with a correlation to the acid concentration: the higher the concentration of the acid solution, the higher the position of the hump. Higher acid concentration made the hump also broader indicating a more amorphous nature of the geopolymer. The samples also show the crystalline peaks of anatase (JCPDF file: 04-014-5762), which is originally present in the metakaolin as an impurity (refer Table 1). The anatase phase is retained in all the acid-treated samples, which shows its chemical resistance and that only amorphous part of the geopolymer participates the reaction with acid. This behavior is similar than the behavior of raw materials in geopolymer

Table 2
Nomenclature used for the samples.

Sample code	Acid treatment		Calcination
G-0M	No		No
G-0.5M	0.5M	HCl	
G-1M	1M	HCl	
G-2M	2M	HCl	
G-3M	3M	HCl	
G-0M-C	No		Yes
G-0.5M-C	0.5M	HCl	
G-1M-C	1M	HCl	
G-2M-C	2M	HCl	
G-3M-C	3M	HCl	

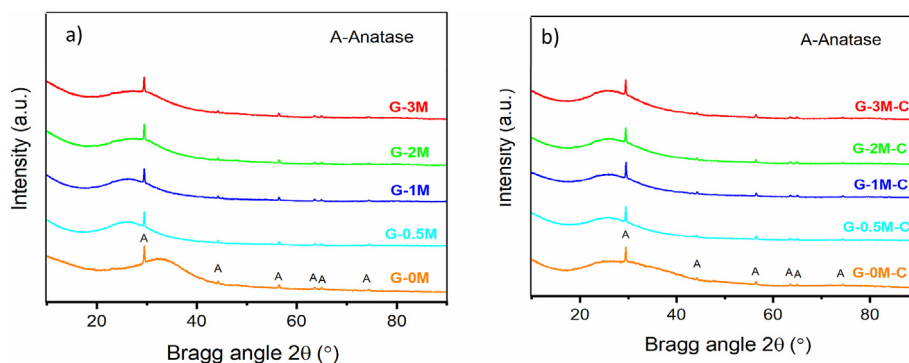


Fig. 1. XRD characterization of (a) non-calcined and (b) calcined acid-modified geopolymers. Please refer to Table 2 for the nomenclature of the samples.

preparation (Candamano et al., 2015). The crystallographic information of the calcined samples are shown in Fig. 1(b). There is a noticeable broadening and a small downward shift of the G-0M-C hump compared with the case of the untreated sample (G-0M) after calcination. In the cases of all acid treated samples, calcination leads to a noticeable compression and a small downward shift of the hump (especially with G-3M-C). This indicates a possible decrease in the amorphous nature of these samples.

The results of thermal analysis of non-calcined acid-treated samples are shown in Fig. 2. The two main processes that accompany heating are dehydration and dehydroxylation. The differential thermal analysis of the untreated sample (G-0M) shows two main peaks (Fig. 2(a)). The endothermic peak (ranging from 50 °C to 200 °C) corresponds to removal of free and physisorbed water from the surface or porous structure of the geopolymer (Sharma et al., 2015). The second peak (400 °C–700 °C) is assigned to the loss of hydroxyl groups or chemisorbed water (Sharma et al., 2015). Hydrochloric acid can cause both dehydration and dehydroxylation during acid treatment. The higher acid concentration leads to a smaller surface water release, which is visible in the case of G-2M and G-3M presented in Fig. 2(a). The effect of acid concentration in dehydroxylation is more complicated. HCl treatment creates hydroxyl groups in the GP structure explaining the increase in the hydroxyl release up to 1M. Then, higher HCl concentrations cause dehydroxylation of the formed hydroxyl groups leading to a decrease in the hydroxyl release (from 1M to 3M). A similar trend is observed in thermogravimetric analysis (Fig. 2(b)). The samples treated with high acid concentrations (greater than 2M) lose significantly less mass in regions corresponding to dehydration and dehydroxylation.

The results of the elemental analysis of the calcined acid-treated

geopolymers are shown in Table 3. There are three noticeable trends in the chemical composition of the geopolymers due to the acid treatment. The first is the selective leaching of aluminum while silicon is not leached. This has a profound impact on the overall Si/Al ratio, which almost becomes 10-fold when moving from G-0M-C to G-3M-C. Aluminum removal becomes more significant when the HCl concentration is increased to 2 M. The second trend is that the acid treatment leads to almost complete removal of sodium already at the concentration of 0.5 M, which indicates that proton can be present as charge balancer in these samples. The third trend is that TiO₂ (the anatase phase based on XRD) is highly resistant to the acid treatment (the slight increase in its concentration with acid treatment is due to the overall mass decrease with acid treatment).

The specific surface areas (S_{BET}) and pore sizes determined by N₂ physisorption are summarized in Table 4. The acid treated samples exhibited significantly higher S_{BET} values than the untreated samples. The S_{BET} 629 m²g⁻¹ achieved with 3M HCl is exceptionally high compared to those reported earlier (Al-Zeer and MacKenzie, 2019a; Sazama et al., 2011; Sharma et al., 2015). The increase in the specific surface area occurs due to significant dealumination and sodium

Table 3

Results of the XRF analysis of calcined acid-treated geopolymers calculated as oxides.

Sample	XRF Composition (wt-%)						Overall Si/Al (mole)
	Na ₂ O	Al ₂ O ₃	SiO ₂	K ₂ O	TiO ₂	Fe ₂ O ₃	
G-0M-C	18.5	28.5	51.4	0.1	1.2	0.3	1.51
G-0.5M-C	0.7	33.7	63.8	0.0	1.5	0.3	1.58
G-1M-C	0.0	26.7	70.6	0.0	1.8	0.3	2.22
G-2M-C	0.3	8.4	88.9	0.0	2.3	0.1	8.87
G-3M-C	0.4	5.2	92.3	0.0	2.1	0.0	14.88

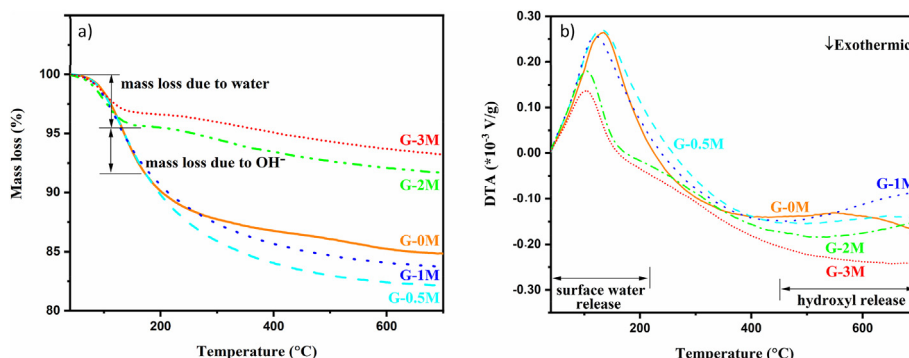


Fig. 2. Results of the thermal analysis of the non-calcined acid-treated geopolymers: (a) DTA; (b) TGA. Please refer to Table 2 for the nomenclature of the samples.

Table 4Textural properties of the calcined and non-calcined GP samples obtained by N₂ adsorption using BET/BJH -method.

Sample Code	Specific surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
G-0M	17	0.04	9.46
G-0.5M	105	0.12	4.47
G-1M	329	0.22	2.65
G-2M	678	0.42	2.41
G-3M	629	0.58	3.50
G-0M-C	17	0.03	7.64
G-0.5M-C	56	0.09	6.08
G-1M-C	181	0.13	2.84
G-2M-C	523	0.30	2.30
G-3M-C	564	0.48	3.42

removal from the geopolymer. It has been reported before, that higher than 1.40 Si/Al ratio leads to a less porous and mechanically stronger GP (Duxson et al., 2005). The result is opposite in this case, since increasing Si/Al ratio is caused by leaching out aluminum, which leads to the higher porosity and specific surface area of the samples.

The acid leaching affects also the pore size distribution. It has been earlier reported that dealumination adds mainly mesoporosity of the microporous zeolites (Feliczak-Guzik, 2018), which was also expected in case of geopolymers. The number of larger pores was decreased significantly already with 0.5M HCl, and smaller pores appeared. There were two ranges of smaller pores: one between ~10 nm and ~5 nm (mesoporosity), and the other one being less than ~5 nm (microporosity < 2 nm). In the case of 3M HCl, only pores below ~5 nm was observed. Higher acid concentration led to smaller pores and improved microporosity, while lower acid concentrations resulted in higher mesoporosity of the geopolymer.

Calcination decreased the specific surface areas of the materials. The pore size distributions remained similar, however, the numbers of pores were decreased. The G-3M kept the porous structure well even after calcination, and hence, the decrease in the specific surface area after calcination was less significant than in the case of G-2M. The acid leaching had a more significant effect on the specific surface area and pore size distribution than the sintering caused by calcination. Pore size distribution figures are presented in supplementary material.

Strong TiO₂ signals (anatase) for all the calcined samples were visible in Raman analysis despite of the low content of TiO₂ observed in elemental analysis. The used Raman technique is very sensitive to TiO₂ and can detect it at very small concentrations, which explains why the signal of TiO₂ (impurity of metakaolin) was strong in the measured samples. It was also possible to observe that phase transition from anatase to rutile did not appear in our case, even if it typically starts slowly at around 600 °C (calcination temperature of the samples). Raman investigation between the spectral range of 4000 cm⁻¹ – 3000 cm⁻¹, revealed that all the materials retain a small amount of physisorbed water. The strongest signals representing the OH stretching of hydrogen bonded water between 3400 cm⁻¹ and 3700 cm⁻¹ (Beta et al., 2004) were observed for G-0.5M-C and G-1M-C. Based on TGA the release of hydroxyls was highest for G-0.5M-C and G-1M-C above 500 °C. Related Raman spectra are presented in supplementary material.

All the prepared geopolymers showed two low-temperature reduction peaks below 150 °C in TPR analysis. There were no major differences between the samples in the consumption of hydrogen and the values between 0.022 mmol H₂g⁻¹ – 0.036 mmol H₂g⁻¹ were observed. The TPR analysis was carried out up to 500 °C, and below that temperature other reduction peaks were not observed. The low-temperature peak is caused most probably by

the residual moisture remaining in the samples after calcination. Similar results have been reported earlier for metakaolin-based geopolymers (Candamano et al., 2015). During TPO also O₂ consumptions remained low, which is in accordance with the results of TPR. The materials displaying a bit higher H₂ consumption were showing also a bit higher O₂ consumption. These results demonstrate that geopolymers prepared are not easily reduced and their oxidic structure is stable. The samples G-0.5M-C and G-1M-C showed the highest amounts of acid sites in the temperature range from about 140 °C to 450 °C. In both materials, weak acid sites were more prominent. The total NH₃ quantities adsorbed were 0.15 mmol g⁻¹ and 0.40 mmol g⁻¹ for G-0.5M-C and G-1M-C, respectively. The observed value for NH₃ adsorption for G-1M-C is close to the value for 5% SiO₂–Al₂O₃ catalyst observed earlier (El Assal et al., 2018).

3.2. Dichloromethane oxidation

In the dichloromethane (DCM) total oxidation, the desired reaction products are CO₂, H₂O and HCl. The HCl production is ensured with the help of a hydrogen source (1.5 vol-% water) (Pitkäaho et al., 2013). The complete DCM oxidation reaction can be described as Equation (1):



and the unwanted Cl₂ production as Equation (2):



The reaction over a heterogeneous catalyst is expected to start with the adsorption of DCM on the support material and end up with the desorption of reaction products from the noble-metal active sites. It is suggested that the adsorption of DCM is intensified by the presence of the acid sites on the support. Thus, increased acidity could potentially lead to a better conversion of DCM. In addition, the presence of H₂O in the feed of the reactor increases the amount of surface OH –groups that may act as weak Brønsted sites (Ausavasukhi and Sooknoi, 2009).

According to the experiments, the DCM conversions observed (Fig. 3) over the prepared materials were quite similar, except with G-0M-C. The results achieved with G-0M-C were close to the results of non-catalytic experiment. The low activity of G-0M-C can be connected to its very low specific surface area of 17 m²g⁻¹. The best conversion was observed for G-1M-C and increasing the acid concentration during leaching did not improve the DCM conversion further. The very high surface area to mass ratio of G-2M-C and G-3M-C did not improve the DCM conversion at high temperatures, and the maximum conversion with all the materials remained below 100%. Higher acid concentrations in leaching also led to

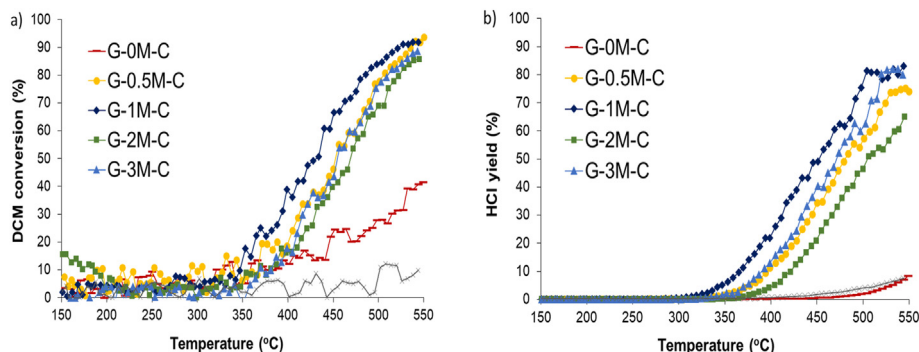
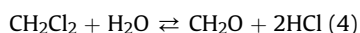
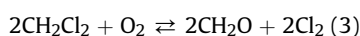


Fig. 3. The (a) activity and the (b) HCl yields of all the samples; -x- represents a thermal oxidation test with quartz wool (DCM 500 ppm, water 1.5 vol-%, GHSV 119 000 h⁻¹, except with G-0M-C the GHSV was 80 000 h⁻¹).

higher Si/Al ratios, which typically should lead to lower acidity (Sivasankar, 2008), and thus decrease in the DCM adsorption efficiency of the materials. Lower acidity of G-2M-C and G-3M-C was also observed in NH₃-TPD. Lack of acid sites was probably the main reason why the significantly higher surface area was not improving DCM conversion further in the cases of G-2M-C and G-3M-C. When DCM conversion is compared with the earlier results obtained for the γ -Al₂O₃ support alone, quite similar outcomes can be observed, however, 100% conversion of DCM was reached over the γ -Al₂O₃ support at the temperature range used in the current work (El Assal et al., 2017).

The best yield of HCl was observed with G-1M-C reaching the maximum of ~80% at 500 °C. The least active material, G-0M-C, did not show any improvement in the HCl production compared with the thermal experiment. The DCM oxidation is not complete at 550 °C based on the observed reaction products in the cases of all the geopolymer materials used. The first reaction intermediate appearing already at 300 °C is formaldehyde. It can be formed via the reactions 3 and 4:



Reaction 3 is thermodynamically favored at lower temperatures (below ~200 °C), after which also Reaction 4 becomes more important. At temperatures higher than 600 °C Reaction 4 is thermodynamically more favored. Since the formation of HCl is observed in the same range with the formaldehyde formation, Reaction 4 is more prominent when the DCM reaction is carried out over G-1M-C.

CH₃Cl is another common reaction intermediate that is typically observed during DCM total oxidation (El Assal et al., 2017). Both intermediate products are formed on the acid sites of a catalyst. CH₂O is typically formed on the Brønsted acid sites, which is a proton donor site, while CH₃Cl is formed on the Lewis acid sites, which is an electron acceptor site (Pinard et al., 2004). The absence of CH₃Cl in the analyzed gas mixture at the reactor outlet allows us to conclude, that the acid sites present on G-1M-C are mainly the Brønsted sites (Fig. 4). In the case of the G-0M-C catalyst, this would practically lead to the formation of Cl₂ during the reaction, since HCl formation was very low compared with the observed DCM conversion. Another possibility is that chlorine stays on the material structure. CH₃Cl was not observed in the product gas mixture of the tested materials, and highest CH₂O formation was observed with G-0.5M-C and G-1M-C. These results are consistent with the results of Raman and TGA-DSC. It has been reported earlier that the

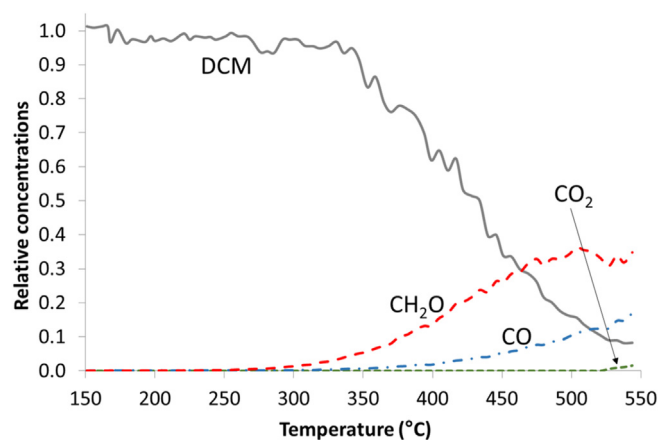


Fig. 4. Relative amounts of DCM, CH₂O, CO and CO₂ during the oxidation of DCM over G-1M-C (DCM 500 ppm, water 1.5 vol-%, GHSV 119 000 h⁻¹).

Lewis sites present in geopolymer are mainly due to the presence of extra framework aluminum. The preparation of geopolymers from metakaolin results typically in complete reaction and only the presence of tetrahedral aluminum is observed based on the NMR studies (Duxson et al., 2005). Furthermore, the acid leaching of the geopolymer would remove the rest of the extra framework aluminum (Al-Zeer and MacKenzie, 2019b). These results explain well the absence of Lewis acid sites and CH₃Cl in the product mixture. They also show how the geopolymer selectivity towards CH₂O or CH₃Cl formation could be improved.

At around 300 °C, carbon monoxide appears as a product of incomplete oxidation of either DCM or intermediate formaldehyde, and finally a small amount of CO₂ appears at around 525 °C. Since the relative amount of CO₂ remains very low, the reaction of DCM over G-1M-C is not total oxidation. As it was explained earlier, total oxidation of DCM could be improved for example by incorporating a small amount of noble metal on the GP surface (Pitkäaho et al., 2013).

4. Conclusions

High surface area geopolymers suitable as catalyst support materials were prepared successfully via alkali activation and HCl leaching. While high concentration (2 M and 3 M HCl) leads to specific surface areas over 500 m²g⁻¹, the catalytic activity is better for the geopolymers prepared with lower concentration of HCl. At the optimal HCl concentration (1 M), the hydroxyl groups are

remaining on the material surface resulting in a higher Brønsted acidity and formation of CH_2O as a reaction intermediate. Higher acidity of the geopolymer enhances also the DCM adsorption as an initial step of the reaction. Maximum conversion of about 90% for DCM at 550 °C was observed with the geopolymer treated with 1M HCl. By modifying the acid properties of the material (quantity and quality), it is possible to direct the reaction via the CH_3Cl reaction route or the CH_2O route, since CH_3Cl is formed on the Lewis acid sites that are connected to extra framework aluminum present in the geopolymer. The question remains, which route is more beneficial to avoid possible Cl-deactivation of the materials. Even though the addition of noble metals like Pt is necessary for the total oxidation of DCM, the geopolymer materials showed to be very promising alternative supports.

CRediT authorship contribution statement

Prem Kumar Seelam: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Harisankar Sreenivasan:** Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Satu Ojala:** Formal analysis, Investigation, Methodology, Supervision, Visualization, Writing - original draft, Writing - review & editing, Funding acquisition. **Satu Pitkäaho:** Formal analysis, Investigation, Methodology, Visualization, Writing - review & editing. **Tiina Laitinen:** Formal analysis, Investigation, Methodology, Visualization. **He Niu:** Formal analysis, Investigation, Methodology, Visualization. **Riitta L. Keiski:** Formal analysis, Validation, Writing - review & editing, Supervision. **Mirja Illikainen:** Formal analysis, Validation, Writing - review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2020.124584>.

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