

Two-dimensional magnesium phyllosilicate as a recyclable solid base catalyst for Knoevenagel condensation

Hunsoo Park

Chungbuk National University

Sungjoon Kweon

Incheon National University

Eun-Jeong Kim

SK biotek

Min Bum Park

`mbpark@inu.ac.kr`

Incheon National University

Jong-Ho Moon

Chungbuk National University

Hyung-Ki Min

Korea Research Institute of Chemical Technology

Research Article

Keywords: Delamination, Knoevenagel condensation, Layered zeolite, Magnesium, MWW

Posted Date: October 30th, 2024

DOI: <https://doi.org/10.21203/rs.3.rs-5123553/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

Version of Record: A version of this preprint was published at Journal of Porous Materials on November 8th, 2024. See the published version at <https://doi.org/10.1007/s10934-024-01710-9>.

Abstract

A zeolitic molecular sieve with two-dimensional (2D) morphology and basic properties is a promising catalyst material for organic synthesis owing to the ease access of reactant molecules to the basic sites exposed on the external surface. Here, we report the single step preparation of basic magnesium silicate delaminated MWW layer (Mg-DML) catalysts with 2D morphology by hydrothermal treatment of borosilicate MWW with magnesium nitrate aqueous solution at different hydrothermal temperatures. The resulting solid products exhibited delaminated nature and basic character originated from the framework-incorporated Mg^{2+} species. The formation of magnesium silicate in Mg-DML was confirmed by ultraviolet–visible diffuse reflectance spectroscopy, Fourier transform infrared spectroscopy, ^{29}Si magic angle spinning nuclear magnetic resonance, and X-ray photoelectron spectroscopy analyses. The basic character was measured by CO_2 temperature programmed desorption. The degree of delamination and boron substitution by magnesium increased with higher hydrothermal temperature. The basicity of Mg-DML was found to be a crucial factor in determining the catalytic activity for Knoevenagel condensation, and the Mg-DML-180 catalyst hydrothermally treated at 180°C exhibited the highest conversion of benzaldehyde.

1 Introduction

Knoevenagel condensation, creating a carbon–carbon bond from active methylenes and carbonyl compounds (aldehydes or ketones), is a key synthetic tool in modern organic chemistry [1]. This reaction proceeds through the nucleophilic addition of active hydrogen to a carbonyl group in aldehydes or ketones, followed by dehydration [2]. The resulting products, α,β -unsaturated carbonyl compounds, are widely used in the pharmaceutical and fine chemical industries, particularly for the synthesis of drugs, pigments, and flavorings [3, 4]. In academic research, this reaction has been often employed as a model reaction to evaluate catalyst basicity [5]. To date, homogeneous nitrogen-containing bases, such as pyridines, primary and secondary amines, and piperidines have been used as catalysts for Knoevenagel condensation [1, 6]. However, despite the excellent activities of the homogeneous catalysts, the need to separate catalyst from products stream adds the complexity of the process [1, 7, 8].

The use of solid bases, such as alkaline and alkaline earth metal oxides, alkali ion-exchanged or nitrated zeolites, supported alkali metal compounds, and clay minerals have offered several advantages over liquid bases, owing to the easiness of separation from the product [1, 7, 8]. However, the use of pure basic metal oxides (e.g., MgO , CaO , and BaO) in catalytic applications is limited by their intrinsic low surface areas [9]. As a result, porous materials, such as modified zeolites and mesoporous materials, were employed as catalytic supports [1, 10, 11]. For example, Otomo et al. reported the highest catalytic activity of Cs-exchanged beta zeolite among the alkali and transition metal ion-exchanged ones for Knoevenagel condensation owing to the increased basicity [11]. However, the findings of Zapelini and Cardoso highlighted the limited effectiveness of propylamine-grafted LTA zeolites as a catalyst for Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate owing to the restricted access of reactants to the active sites within the micropores [12].

A two-dimensional (2D) structure with basic property has several advantages as a catalyst for Knoevenagel condensation compared to a three-dimensional (3D) structure. These advantages include easier and faster diffusion of both reactants and products, unrestricted accessibility of reactants regardless of molecular size, and the prevention of catalyst deactivation due to pore blocking. Guo et al. reported a significantly higher yield of 2-benzylidenemalononitrile using 2D nanosheet MOF-5 (99%) compared to the 3D cube-shaped one (3%) in Knoevenagel condensation of benzaldehyde and malononitrile [13]. In our previous work, we also demonstrated the superior catalytic activity of 2D nitrated ITQ-2 in the Knoevenagel condensation of various aldehydes (benzaldehyde, 2-naphthaldehyde, phenanthrene-9-carbaldehyde, and pyrene-1-carbaldehyde) with different molecular sizes and ethyl cyanoacetate, compared to nitrated zeolites (MCM-22, ZSM-5, and Y) and mesoporous SBA-15 [14]. Kawano and coworkers also observed an increase in catalytic activity of nitrated MCM-22 zeolites in the Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate, which was found to be related to the extent of delamination [15].

In this study, we investigate the synthesis of magnesium silicate delaminated MWW layers (Mg-DMLs) using a hydrothermal process with magnesium nitrate and a borosilicate MWW precursor (B-MWW(P)), and their catalytic performances in the Knoevenagel condensation of benzaldehyde and malononitrile. The transition from 3D to 2D structural properties and the formation of Mg–O–Si bonds as a function of hydrothermal temperature were characterized by various analytical tools and correlated with the catalytic properties. In addition, the reusability and stability of the 2D basic catalyst were also confirmed through recycle experiments.

2 Experimental section

2.1 Catalyst preparation

The synthesis of B-MWW(P) with a Si/B ratio of 9.5 was conducted using hexamethyleneimine as a structure-directing agent (SDA). Sodium hydroxide (99%, Sigma-Aldrich) and hexamethyleneimine (99%, Sigma-Aldrich) were dissolved in deionized (DI) water, followed by the addition of boric acid (99.5%, Junsei). Fumed silica (Evonik) was then added, and the mixture was homogenized. The solution was then transferred to a Teflon-lined autoclave, heated at 175°C for 7 d with agitation, and filtered with DI water to produce a white solid powder.

Mg-DML was synthesized through a single-step hydrothermal treatment of B-MWW(P) with magnesium nitrate hexahydrate (99.0%, Sigma-Aldrich) solution with a concentration of 1.0 M at various temperatures (100–180°C) for 4 d. After the hydrothermal treatment, the solid products were recovered by filtration with DI water and dried at room temperature. The as-synthesized Mg-DML samples were calcined at 550°C for 8 h to remove the organic SDA and denoted as Mg-DML-*x*, where *x* represents the hydrothermal treatment temperature (100–180°C).

2.2 Characterization

All characterizations were performed using the calcined sample, unless otherwise stated. Powder X-ray diffraction (XRD) patterns were measured on a Rigaku SmartLab X-ray diffractometer using Cu-K α radiation in the 2θ range of 3–50° (scan rate = 4° min⁻¹). N₂ sorption experiments were performed on a Micromeritics Tristar II analyzer. Elemental analysis was performed on a PerkinElmer OPTIMA 7300DV inductively coupled plasma (ICP) spectrometer. The crystal morphology and average size were determined using a Hitachi SU8010 scanning electron microscope (SEM) operating with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) elemental mapping images were obtained using a FEI TALOS F200X operated at 200 kV.

The IR spectra in the structural region were collected on a Shimadzu IRTracer-100 Fourier transform infrared (FT-IR) spectrometer in attenuated total reflectance mode. The IR spectra in the hydroxyl region of 3000–4000 cm⁻¹ (OH-IR) were measured using the same equipment described above. First, a self-supporting solid disk of approximately 20 mg with a 1.3 cm diameter was placed inside a home-built IR stainless cell attached in IR spectrometer to remove the water adsorbed in the samples. Subsequently, the samples were heated at 450°C for 2 h under flowing He (30 mL min⁻¹), and the OH-IR spectra were recorded at the same temperature. Ultraviolet–visible diffuse reflectance spectroscopy (UV-DRS) was performed using a Shimadzu UV-2600 UV-Vis spectrophotometer. The UV absorption spectra were plotted using the Kubelka-Munk function. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI 5000 Versa Probe II with Al-K α radiation ($h\nu$ = 1,486.6 eV). The XPS samples were prepared with self-supporting solid wafers of approximately 20 mg weight with a 1.3 cm diameter in dry condition. The ²⁹Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded on a 500 MHz Avance III HD Bruker solid state NMR spectrometer at a spinning rate of 5 kHz, a ²⁹Si frequency of 99.36 MHz with a $\pi/2$ rad pulse length of 4 μ s, a recycle delay of 60 s, and an acquisition of ca. 300 pulse transients. The ²⁹Si chemical shift is reported relative to tetramethyl silane.

CO₂ temperature-programmed desorption (TPD) profiles were obtained using a homemade apparatus equipped with a thermal conductivity detector (TCD) and a Scion 456 gas chromatograph. A powder sample of 100 mg was placed in the furnace and pretreated under flowing N₂ (30 mL min⁻¹) at 550°C for 2 h. After then, pure CO₂ (30 mL min⁻¹) was passed through each sample at 30°C for 0.5 h. To remove physisorbed CO₂, the sample was flushed with flowing He (30 mL min⁻¹) for 1 h. CO₂ TPD was then carried out under flowing He at the same flow rate in the temperature range of 30–800°C with a ramping rate of 10°C min⁻¹. All the spectral decomposition and simulation operations were performed using the Origin 9.0 curve-fitting program.

2.3 Catalyst evaluation

The Personal Organic Synthesizer (ChemiStation, Eyela) with five independent reaction modules and reflux systems was used to perform the Knoevenagel condensation. In a typical procedure, the reaction mixture consisted of bezaldehyde (5 mmol) and malononitrile (5 mmol) in toluene (30 mL) was heated to 110°C, after which 200 mg of catalyst was added. Samples were periodically withdrawn (ca. 0.1 mL),

diluted in tetrahydrofuran, filtered, and analyzed using a gas chromatograph (Agilent 6890N) equipped with a HP-5 capillary column (30 m × 0.32 mm) and flame ionization detector. The reactions were repeated multiple times to ensure reproducibility, and the catalyst was recovered after 96 h of reaction, washed with excess acetone, dried at 80°C in a convection oven, and tested for reusability.

3 Results and discussion

Figure 1 shows the powder XRD patterns of B-MWW(P) and the as-synthesized Mg-DML- x ($x = 100$ – 180) samples prepared in this study. The B-MWW(P) exhibited the low-angle XRD peaks at $2\theta = 7.4^\circ$, 8.1° , and 9.9° corresponding to (100), (101), and (102) reflections of MWW-type materials, respectively [16]. However, as the hydrothermal temperature increased to 140°C, the intensities of these characteristic peaks continuously decreased and broadened, which are similar to the XRD pattern of delaminated MWW analogue, such as ITQ-2 [17]. In addition, these MWW-type characteristic peaks were completely disappeared at higher temperatures of 160 and 180°C, and some other characteristic peaks at $2\theta = 36^\circ$ and 61° , which are in good agreement with the XRD pattern of magnesium silicate, were emerged [18, 19]. In all Mg-DML- x samples, however, the formation of MgO, represented by the intense XRD peaks at $2\theta = 42^\circ$ and 62° , was not observed [20].

The physical transformation from 3D MWW structure to 2D delaminated layers was further characterized by N₂ sorption experiments. As shown in Fig. 2a, the N₂ adsorption-desorption isotherms of calcined B-MWW were similar to those of type I microporous solids, while those of Mg-DML- x ($x = 100$ – 180) were changed to type IV mesoporous materials as the hydrothermal temperature increased. This is well corresponded to the appearance of an H3-type adsorption-desorption hysteresis loop of Mg-DML-180, indicating the generation of interparticle void spaces between parallel plates. In addition, the external surface areas of Mg-DML- x ($x = 100$ – 180) steadily increased with rising hydrothermal temperatures, which is also a typical characteristic of delaminated materials (Fig. 2b and Table 1) [21]. The delamination of MWW layers was also accompanied by the increase in average pore diameter and pore volume as shown in Fig. S1 and Table 1. In contrast to the increase of the external surface area, the micropore area of Mg-DML- x drastically decreased, reaching zero as the hydrothermal temperature increased to 180°C. This is consistent with the disappearance of XRD peaks corresponding to non-porous magnesium silicate as shown in Fig. 1.

Table 1
Physicochemical properties of B-MWW and Mg-DML-x (x = 100–180)

Catalyst	ICP elemental analysis				N ₂ sorption analysis			
	Si/Mg	Si (wt.%)	Mg (wt.%)	B (wt.%)	BET surface area (m ² g ⁻¹)			Total pore volume (cm ³ g ⁻¹)
					Total	Micropore	External	
B-MWW	-		-	1.8	477	452	25	0.364
Mg-DML-100	22	43	1.7	1.2	533	422	111	0.458
Mg-DML-120	36	44	1.1	1.1	475	360	115	0.538
Mg-DML-140	18	47	2.3	0.6	297	158	139	0.690
Mg-DML-160	11	48	3.7	0.1	143	4	139	0.679
Mg-DML-180	9	50	4.7	0.1	127	0	127	0.744

The transformation of MWW crystals to delaminated layers and magnesium silicate layers through the hydrothermal treatment was monitored in SEM images (Fig. 3). The thick and plate-like crystals of B-MWW were transformed to thinner layers-like crystals as the hydrothermal temperature increased. Meanwhile, very small and thin layers, likely corresponding to magnesium silicate, began to form on the surface of MWW crystals, becoming predominant at temperatures higher than 160°C [22, 23]. As shown in Fig. S2, the IR absorption band corresponding to terminal hydroxyls and defect hydroxyls on B-MWW increased as the hydrothermal temperature of Mg-DML-x increased. This also suggests the structural evolution of Mg-DML-x from 3D MWW to 2D layers having silanol groups on their surface. The transformation from B-MWW to magnesium silicate also further confirmed by the uniform distribution of Mg species on the STEM-EDS images of Mg-DML-x catalysts, whose Mg contents varied from 1.2 to 4.7 wt.% as hydrothermal temperature increases from 100 to 180°C (Fig. 4), which were closed to the values calculated from ICP elemental analysis (Table 1). However, the contents of Mg on Mg-DML-x were much lower than those of other transition metal-incorporated DMLs, such as Ni-, Co-, and Zn-DMLs reported in our previous works [24, 25].

The state of Mg species on Mg-DML-x (x = 100–180) were characterized by UV-DRS (Fig. 5a). The formation of magnesium silicates on Mg-DML-x was confirmed by the observation of UV absorption bands at 221 and 256 nm, whose intensity increases with the increase of hydrothermal temperature [26, 27]. Additionally, the broad UV absorption band at 340 nm also steadily increased and red shifted with the rise in the hydrothermal temperature, attributed to the formation of silica nanoparticles [28]. The chemical states of Mg in Mg-DML-x were further characterized by FT-IR spectroscopy in the structural

region of 500 to 1600 cm^{-1} (Fig. 5b). The IR absorption bands of B-MWW were observed at 560, 610, 810, 1085, 1250, and 1390 cm^{-1} , typical framework vibrations of the MWW-type structures [29]. The bands at 560 and 610 cm^{-1} , originated from the double six-ring in MWW structure, were continuously decreased as the increase of hydrothermal temperature [23]. Notably, these characteristic IR bands for MWW structure were not observed on Mg-DML-180, indicating that MWW framework had almost degraded to amorphous layer at this high temperature. Meanwhile, additional bands at approximately 667 and 1025 cm^{-1} , corresponding to Mg–OH and Si–O–Mg, respectively, were continuously increased. This also indicates the formation of magnesium silicates on the surface region of 2D Mg-DML-*x* as seen in SEM images (Fig. 3). In line with the observation of UV absorption band for silica nanoparticles on Mg-DML-160 and Mg-DML-180, the intensity of IR absorption band at 803 cm^{-1} , representing Si–O–Si symmetric stretching vibrations, also increased in these catalysts. The increase of silica nanoparticles on Mg-DML-160 and Mg-DML-180 was further corroborated by the generation of intense peak at 3671 cm^{-1} in Fig. S2, corresponding to the stretching mode of hydroxyl groups.

The formation of magnesium silicate in Mg-DML-*x* (*x* = 100–180) was investigated by ^{29}Si MAS NMR spectroscopy (Fig. 5c). The borosilicate B-MWW has distinct peaks at – 105 and – 112 ppm, corresponding to $\text{Q}^4(\text{nB})$ signals, which is similar to the spectrum of low silica (Si/Al = 9) aluminosilicate MCM-22 zeolite [30]. However, the intensity of these two peaks was gradually decreased with increasing hydrothermal temperature, while a new peak at – 98 ppm, corresponding to Q^3 signal of talc-like species, emerged [31]. This observation is consistent with the evolution of Si–O–Mg band in FT-IR spectra shown in Fig. 5b. Additionally, the Q^4 signal at – 112 ppm was still observed on the samples prepared at high temperature (140–160°C) of hydrothermal treatment. This also correlates well with the increase of IR absorption band (803 cm^{-1}) representing Si–O–Si symmetric stretching vibrations (Fig. 5b).

The valence state of the elements in Mg-DML-*x* (*x* = 100–180) was characterized by XPS analysis. As shown in Fig. 6a, Mg 2p signals were deconvoluted into two peaks (Peak I and II) at approximately 49.9 and 50.5 eV, corresponding to magnesium silicate and MgO, respectively [32]. In line with the elemental analysis results in Table 1, the overall intensity of Mg 2p signals increased proportionally with the hydrothermal temperature (Table S1), which is due to the increasing Mg contents in solid samples. Furthermore, while the proportion of magnesium silicate were grown until Mg-DML-160, Mg-DML-180 showed the highest proportion of MgO (Table S1). This can be explained by the higher thermodynamic stability of MgO at such high hydrothermal temperature. In Fig. 6b, the evolution of Peak I, assigned to Si–OH with the increase in intensity corresponding to hydrothermal temperature was observed in Si 2p region, which aligns with the OH-IR results mentioned above. Additionally, Peak II at 103.6 eV in Si 2p XPS and Peak III at 533.5 eV in O 1s XPS spectra, corresponding to Si^{4+} and O^{2-} in Si–O–Mg, respectively, both increased proportionally to hydrothermal temperature up to 160°C. However, in Mg-DML-180, the proportion of Si–O–Mg was lower than in Mg-DML-160, which is consistent with Mg 2p XPS results.

The basic properties of Mg-DML- x ($x = 100\text{--}180$) originating from the substitution of B by Mg were investigated by CO₂ TPD (Fig. 7). The CO₂ TPD profiles can be categorized into three temperature regions, i.e., 50–250°C, 250–550°C, and 550–800°C, corresponding to CO₂ desorption from weak, intermediate, and strong base sites, respectively. With the increase of hydrothermal temperature up to 160°C, the concentration of strong base sites increased. In addition, the desorption of CO₂ from weak base sites was shifted to higher temperature region, indicating the enhancement in the strength of weak base sites compared to the other Mg-DML samples. This can be attributed to the increased concentration of framework Mg species as discussed in structural IR and Mg 2p XPS (Figs. 5b and 6a). Unlike the other catalysts, Mg-DML-180 exhibited intermediate base sites, which is a typical base strength of MgO [14].

The catalytic properties of basic Mg-DML- x ($x = 100\text{--}180$) catalysts were investigated by Knoevenagel condensation of benzaldehyde with malononitrile as a test reaction. As shown in Fig. 8a, the conversions of benzaldehyde over all Mg-DML catalysts increased linearly as a function of reaction time, indicating that the product yield is not limited by the thermodynamic equilibrium of the reaction. Here, benzylidenemalononitrile was the only product observed in all experiments. The conversions of benzaldehyde at 96 h of reaction time increased following the hydrothermal temperature of Mg-DML- x ($x = 100\text{--}180$). Although Mg-DML-160 exhibited the higher conversion of benzaldehyde up to 48 h, Mg-DML-180 prevailed at the end of the reaction. This can be rationalized by the presence of intermediate base sites on Mg-DML-180, which is more favorable for catalyzing Knoevenagel condensation [33]. As shown in Fig. 8b, Mg-DML-180 exhibited good reusability as evidenced by the stable benzaldehyde conversion of 72–77% during 5 repeated uses after regeneration. This can be attributed by the 2D crystal morphology of this catalyst, which is favorable for removal of carbonaceous deposits through simple washing with organic solvent.

4 Conclusions

The basic magnesium silicate Mg-DML catalysts were prepared through single-step hydrothermal treatment of borosilicate MWW with aqueous magnesium nitrate solution at different temperatures. The resulting solid products exhibited delaminated structure with framework incorporated magnesium species and the degree of delamination and boron substitution by magnesium were dependent on hydrothermal temperature. The proportion of magnesium silicate in Mg-DML increased with hydrothermal temperature up to 160°C, with MgO formation becoming dominant at higher temperature. The formation of Si–O–Mg bond in Mg-DML was confirmed by XPS, FT-IR, and ²⁹Si MAS NMR and the basic properties were measured by CO₂-TPD. The proportion of strong basic sites in Mg-DML, evidenced by the CO₂ desorption at 600–750°C in CO₂-TPD, increased following the increase of hydrothermal temperature up to 160°C and intermediate strength basic sites (CO₂ desorption at 250–550°C) basic sites were observed at higher temperature of 180°C. Although the initial benzaldehyde conversions of Mg-DML were increased in line with the proportion of strong basic sites, the final conversions were

proportional to the total contents of base site. Mg-DML-180 catalyst exhibited benzaldehyde conversions of 72–77% during the five repeated cycles, indicating the high stability for Knoevenagel condensation.

Declarations

Acknowledgments

This study was supported by the Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (2520000248).

Author contributions Hunsoo Park: Data curation, Formal analysis, Investigation, Writing—original draft. Sungjoon Kweon: Formal analysis, Investigation. Eun-Jeong Kim: Formal analysis, Investigation. Min Bum Park: Conceptualization, Funding acquisition, Supervision, Writing—review & editing. Jong-Ho Moon: Conceptualization, Supervision, Writing—review & editing. Hyung-Ki Min: Conceptualization, Funding acquisition, Supervision, Writing—original draft. Writing—review & editing.

Competing Interests The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this study.

References

1. J.N. Appaturi, R. Ratti, B.L. Phoon, S.M. Batagarawa, I.U. Din, M. Sevaraj, R.J. Ramalingam, A review of the recent progress on heterogeneous catalysts for Knoevenagel condensation. *Dalton Trans.* **50**, 4445–4469 (2021)
2. J. Ortiz-Bustos, P. Cruz, Y. Pérez, I. Hierro, Prolinate-based heterogeneous catalyst for Knoevenagel condensation reaction: Insights into mechanism reaction using solid-state electrochemical studies. *Mol. Catal.* **524**, 112328 (2022)
3. R.H. Vekariya, H.D. Patel, Recent advances in the synthesis of coumarin derivatives via Knoevenagel condensation: A review. *Synth. Commun.* **44**, 2756–2788 (2014)
4. R. Tokala, D. Bora, N. Shankaraiah, Contribution of Knoevenagel condensation products toward the development of anticancer agents: An updated review. *Chem. Med. Chem.* **17**, e20210073 (2022)
5. B. Siebenhaar, B. Casagrande, M. Studer, H.-U. Blaser, An easy-to-use heterogeneous catalyst for the Knoevenagel condensation. *Can. J. Chem.* **79**, 566–569 (2001)
6. J. Stec, W.H. Witola, Alternatives to piperidine in Knoevenagel condensation of 2-cyanoacetamide with benzaldehyde. *Results Chem.* **6**, 101212 (2023)
7. G. Li, J. Xiao, W. Zhang, Efficient and reusable amine-functionalized polyacrylonitrile fiber catalysts for Knoevenagel condensation in water. *Green. Chem.* **14**, 2234–2242 (2012)
8. K.M. Parida, D. Rath, Amine functionalized MCM-41: An active and reusable catalyst for Knoevenagel condensation reaction. *J. Mol. Catal. A: Chem.* **310**, 93–100 (2009)

9. L.G. Possato, E. Pereira, R.G.L. Goncalves, S.H. Pulcinelli, L. Martins, C.V. Santilli, Controlling the porosity and crystallinity of MgO catalysts by addition of surfactant in the sol-gel synthesis. *Catal. Today*. **344**, 52–58 (2020)
10. J.N. Appaturi, T. Pulingam, J.R. Rajabathar, F. Khoerunnisa, T.C. Ling, S.H. Tan, E.-P. Ng, Acid-base bifunctional SBA-15 as an active and selective catalyst for synthesis of ethyl α -cyanocinnamate via Knoevenagel condensation. *Microporous Mesoporous Mater.* **320**, 111091 (2021)
11. R. Otomo, R. Osuga, J.N. Kondo, Y. Kamiya, T. Yokoi, Cs-Beta with an Al-rich composition as a highly active base catalyst for Knoevenagel condensation. *Appl. Catal. Gen.* **575**, 20–24 (2019)
12. I.W. Zapelini, D. Cardoso, Amine-grafted Na-LTA zeolite precursors as basic catalysts for Knoevenagel condensation. *Microporous Mesoporous Mater.* **324**, 111270 (2021)
13. C. Guo, Y. Zhang, L. Zhang, Y. Zhang, J. Wang, 2-Methylimidazole-assisted synthesis of a two-dimensional MOF-5 catalyst with enhanced catalytic activity for the Knoevenagel condensation reaction. *CrystEngComm*. **20**, 5327–5331 (2018)
14. H.-K. Min, S.H. Cha, S.B. Hong, Nitrided ITQ-2 as an efficient Knoevenagel condensation catalyst. *Chem. Commun.* **49**, 1115–1117 (2013)
15. A. Kawano, T. Moteki, M. Ogura, Effect of delamination on active base site formation over nitrided MWW-type zeolite for Knoevenagel condensation. *Microporous Mesoporous Mater.* **299**, 110104 (2020)
16. W.J. Roth, D.L. Dorset, Expanded view of zeolite structures and their variability based on layered nature of 3-D frameworks. *Microporous Mesoporous Mater.* **142**, 32–36 (2011)
17. A. Corma, V. Fornés, S.B. Pergher, T.L.M. Maesen, J.G. Buglass, Delaminated zeolite precursors as selective acidic catalysts. *Nature*. **396**, 353–356 (1998)
18. E. Bernard, B. Lothenbach, C. Chlique, M. Wyrzykowski, A. Dauzères, I. Pochard, Cau-Dit-Coumes, Characterization of magnesium silicate hydrate (M-S-H). *Cem. Concr. Res.* **116**, 309–330 (2019)
19. D.R.M. Brew, F.P. Glasser, Synthesis and characterisation of magnesium silicate hydrate gels. *Cem. Concr Res.* **35**, 85–98 (2005)
20. A. Ansari, A. Ali, M. Asif, Shamsuzzaman, Microwave-assisted MgO NP catalyzed one-pot multicomponent synthesis of polysubstituted steroidal pyridines. *New. J. Chem.* **42**, 184–197 (2018)
21. J. Přeck, P. Pizarro, D.P. Serrano, J. Čejka, From 3D to 2D zeolite catalytic materials. *Chem. Soc. Rev.* **47**, 8263–8306 (2018)
22. Q. Lu, Q. Li, J. Zhang, J. Li, J. Lu, Facile mesoporous template-assisted hydrothermal synthesis of ordered mesoporous magnesium silicate as an efficient adsorbent. *Appl. Surf. Sci.* **360**, 889–895 (2016)
23. Z. Sun, Y. Liu, W. Hong, Facile synthesis of porous hydrated magnesium silicate adsorbent from ordinary silica gel. *Mater. Lett.* **272**, 127886 (2020)
24. H.-K. Min, S. Kweon, Y.W. Kim, H. An, D. Jo, E.D. Park, C.-H. Shin, M.B. Park, Atomically dispersed nickel species in a two-dimensional molecular sieve: Origin of high activity and stability in dry

- reforming of methane. *Appl. Catal. B-Environ.* **298**, 120627 (2021)
25. H.-K. Min, S. Kweon, S. Oh, H. An, Y. Cho, H. Min, D. Jo, J.F. Kim, C.-H. Shin, S.B. Kang, M.B. Park, Single-step preparation of zinco- and aluminosilicate delaminated MWW layers for the catalytic conversion of glucose. *Green. Chem.* **23**, 9489–9501 (2021)
26. K. Mondal, J. Manam, Optical properties of novel Sm^{3+} activated distrontium magnesium disilicate phosphor. *J. Mater. Sci: Mater. Electron.* **28**, 8793–8802 (2017)
27. M.A. Alnassar, A. Alshehri, K. Narasimharao, Visible light active magnesium silicate–graphitic carbon nitride nanocomposites for methylene blue degradation and Pb^{2+} adsorption. *Catalysts.* **12**(10), 1256 (2022)
28. H.R. Ghorbani, The formation of silica nanowires using green beans. *Rev. Roum Chim.* **63**, 55–58 (2018)
29. M. Marosz, B. Samojeden, A. Kowalczyk, M. Rutkowska, M. Motak, U. Díaz, A.E. Palomares, L. Chmielarz, MCM-22, MCM-36, and ITQ-2 zeolites with different Si/Al molar ratios as effective catalysts of methanol and ethanol dehydration. *Materials.* **13**, 2399 (2020)
30. C. Delitala, M.D. Alba, A.I. Becerro, D. Delpiano, D. Meloni, E. Musu, I. Ferino, Synthesis of MCM-22 zeolites of different Si/Al ratio and their structural, morphological and textural characterization. *Microporous Mesoporous Mater.* **118**, 1–10 (2009)
31. G. Rim, A.K. Marchese, P. Stallworth, S.G. Greenbaum, Park, ^{29}Si solid state MAS NMR study on leaching behaviors and chemical stability of different Mg-silicate structures for CO_2 sequestration. *Chem. Eng. J.* **396**, 125204 (2020)
32. J. Zhang, L. Dang, M. Zhang, Q. Lu, S. Zhao, Characterization of mesoporous magnesium silicate with hierarchical structure and its adsorption performance for dye and lead ion. *Surf. Interfaces.* **8**, 112–118 (2017)
33. A. Corma, V. Fornés, R.M. Martín-Aranda, F. Rey, Determination of base properties of hydrotalcites: Condensation of benzaldehyde with ethyl acetoacetate. *J. Catal.* **134**, 58–65 (1992)

Figures

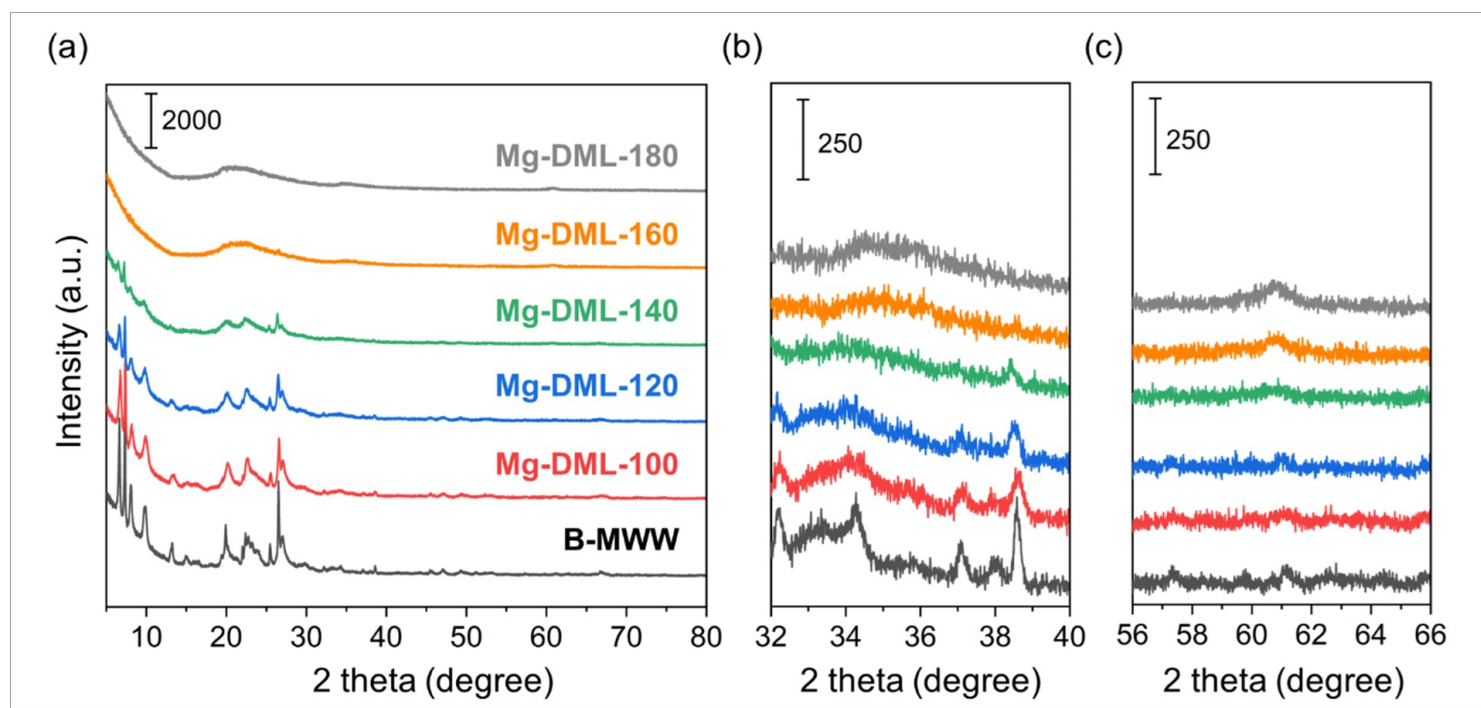


Figure 1

(a) Powder XRD patterns of B-MWW(P) and as-synthesized Mg-DML- x ($x = 100-180$). Magnified XRD patterns at (b) $2\theta = 32-40^\circ$ and (c) $2\theta = 56-66^\circ$

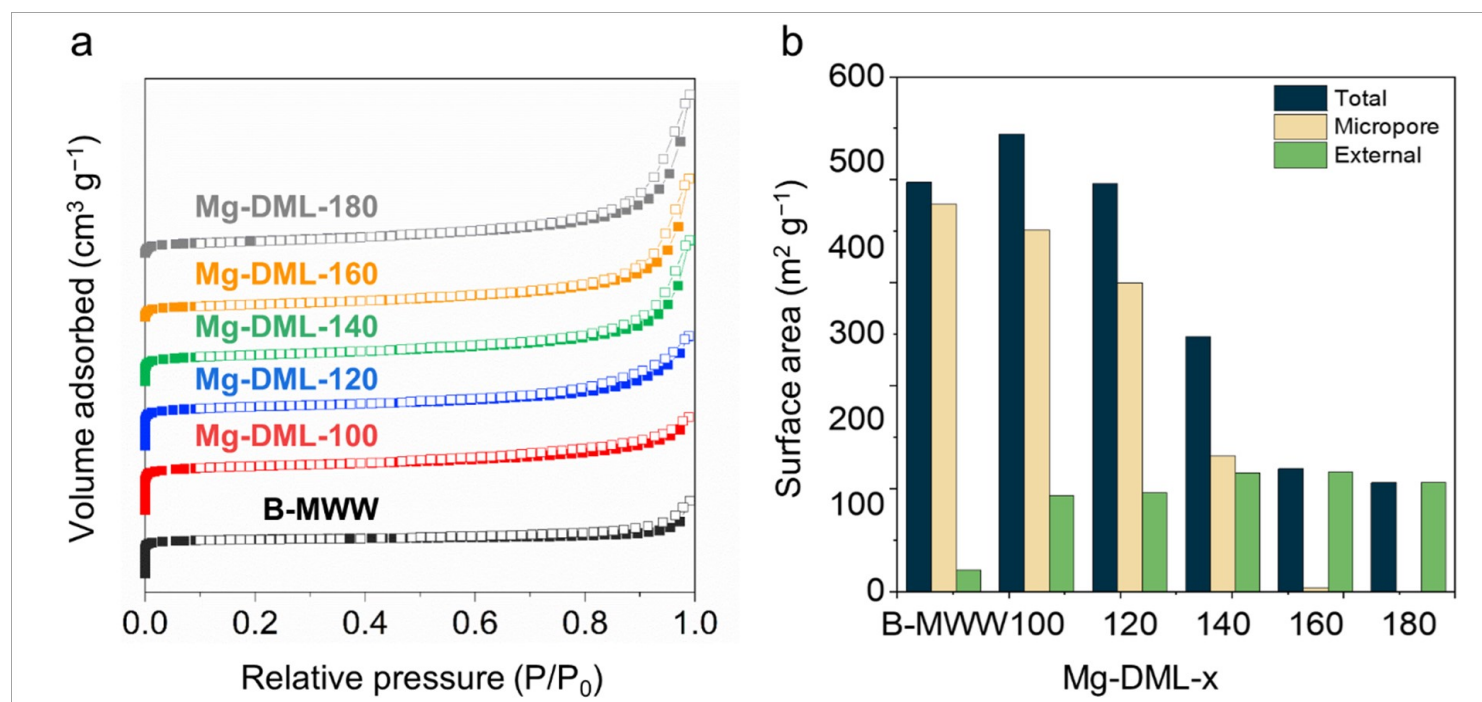


Figure 2

(a) N_2 sorption isotherms and (b) BET surface areas of B-MWW and Mg-DML- x ($x = 100-180$) catalysts

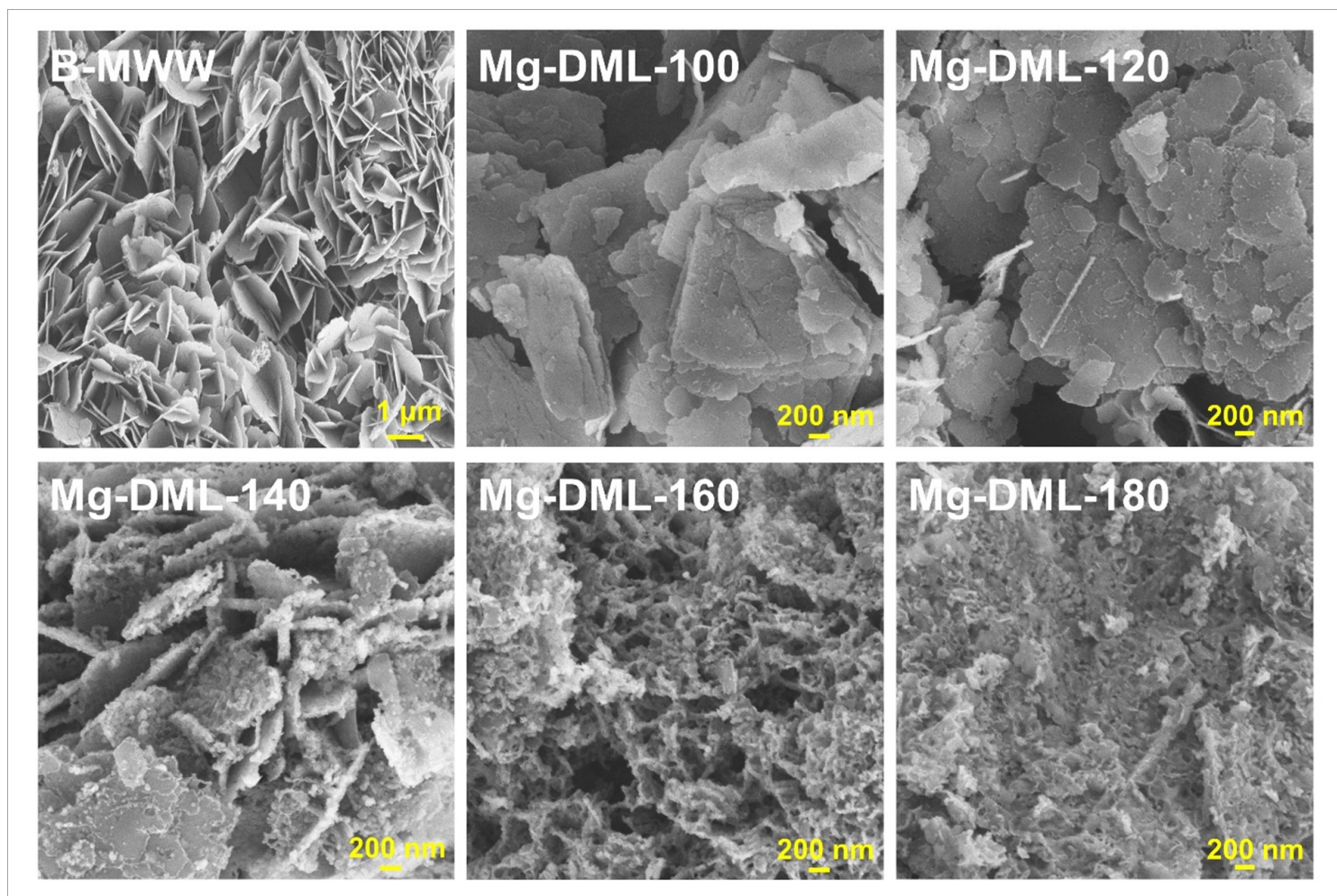


Figure 3

SEM images of calcined B-MWW and Mg-DML- x ($x = 100-180$) catalysts

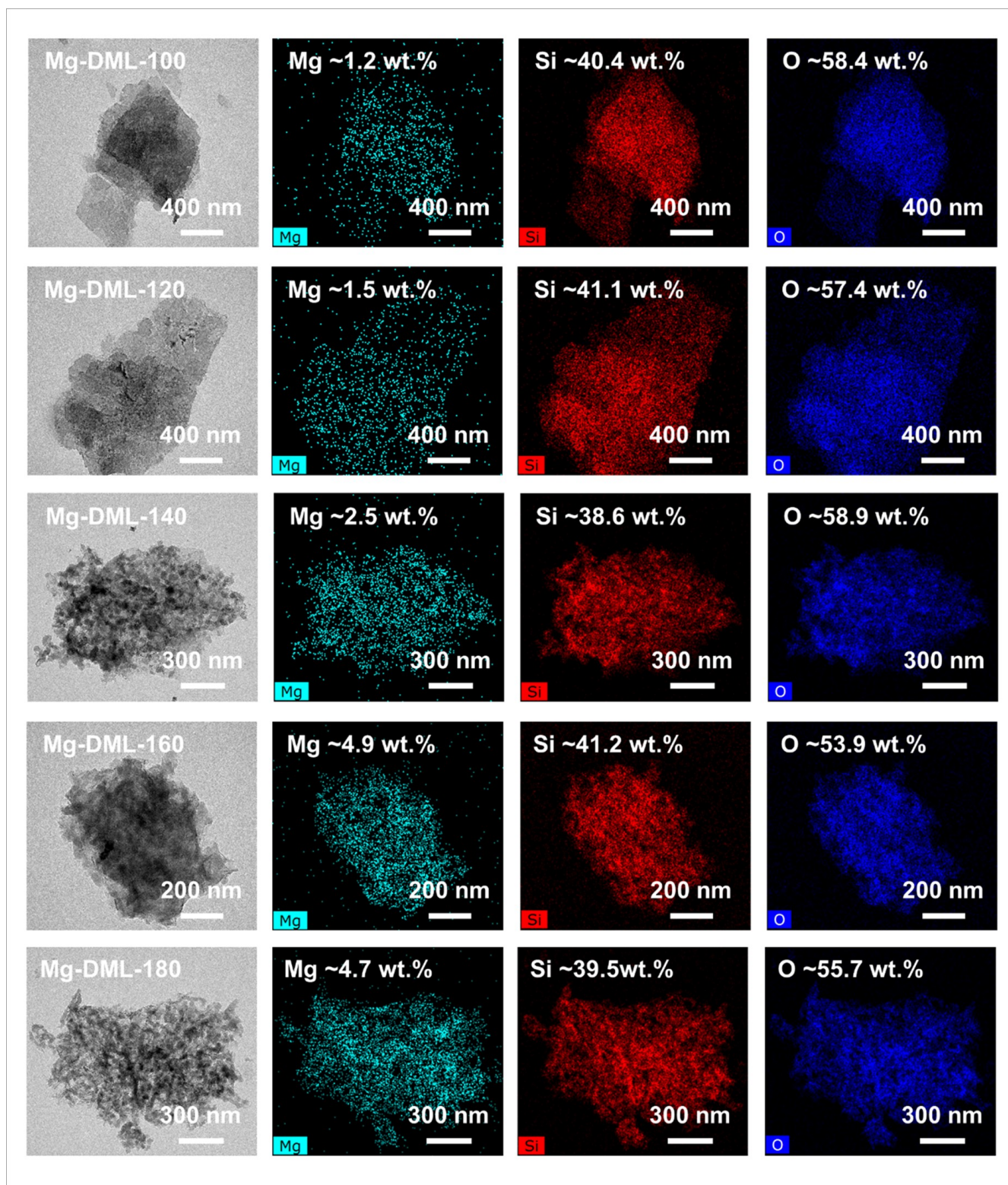


Figure 4

TEM and STEM-EDS elemental mapping images of Mg-DML- x ($x = 100-180$) catalysts

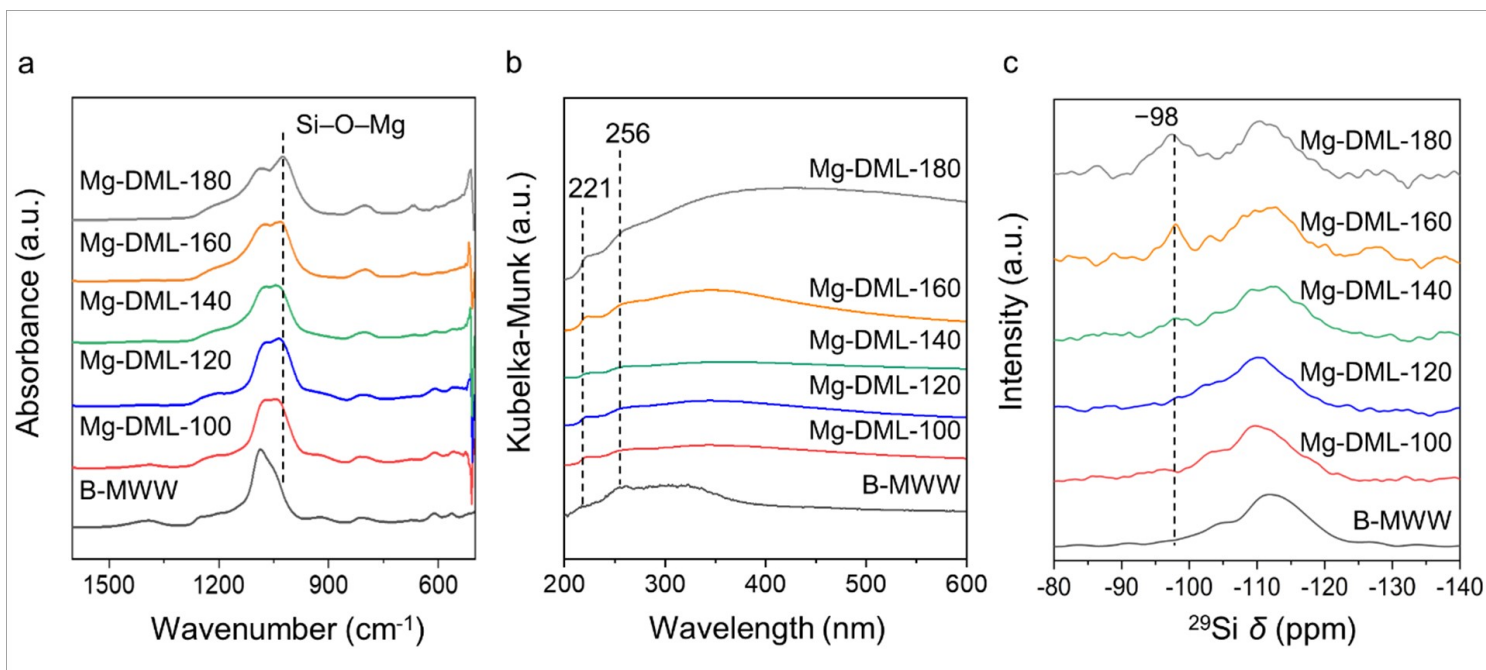


Figure 5

(a) FT-IR, (b) UV-vis, and (c) ²⁹Si MAS NMR spectra of B-MWW and Mg-DML-*x* (*x* = 100–180) catalysts

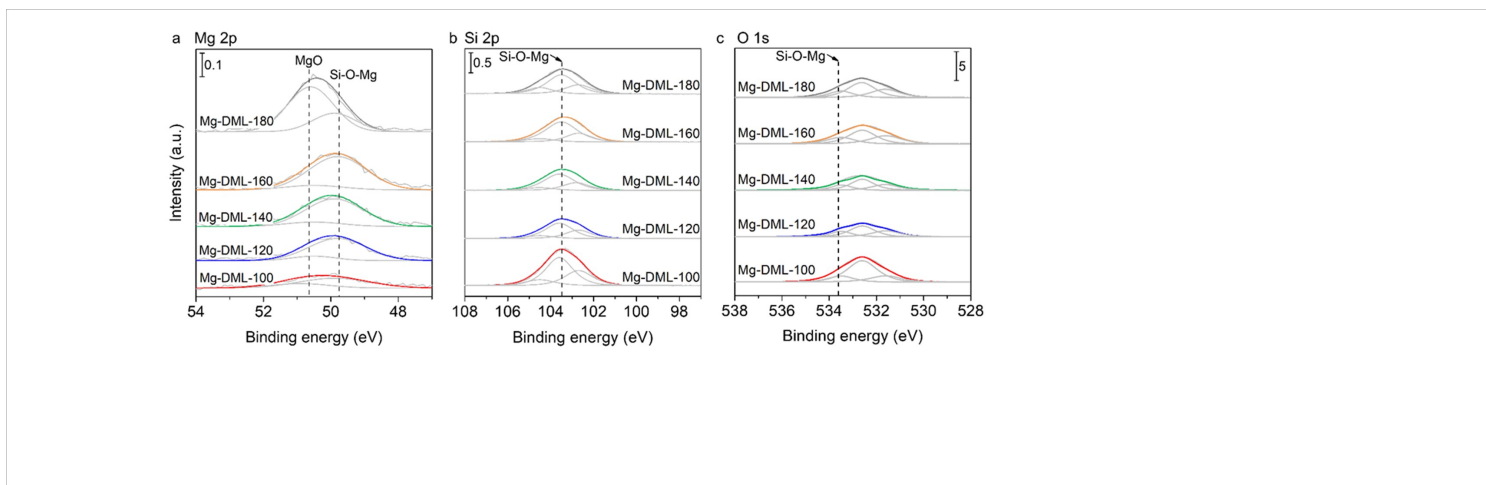


Figure 6

XPS spectra of Mg-DML-*x* (*x* = 100–180) catalysts in (a) Mg 2p, (b) Si 2p, and (c) O 1s regions

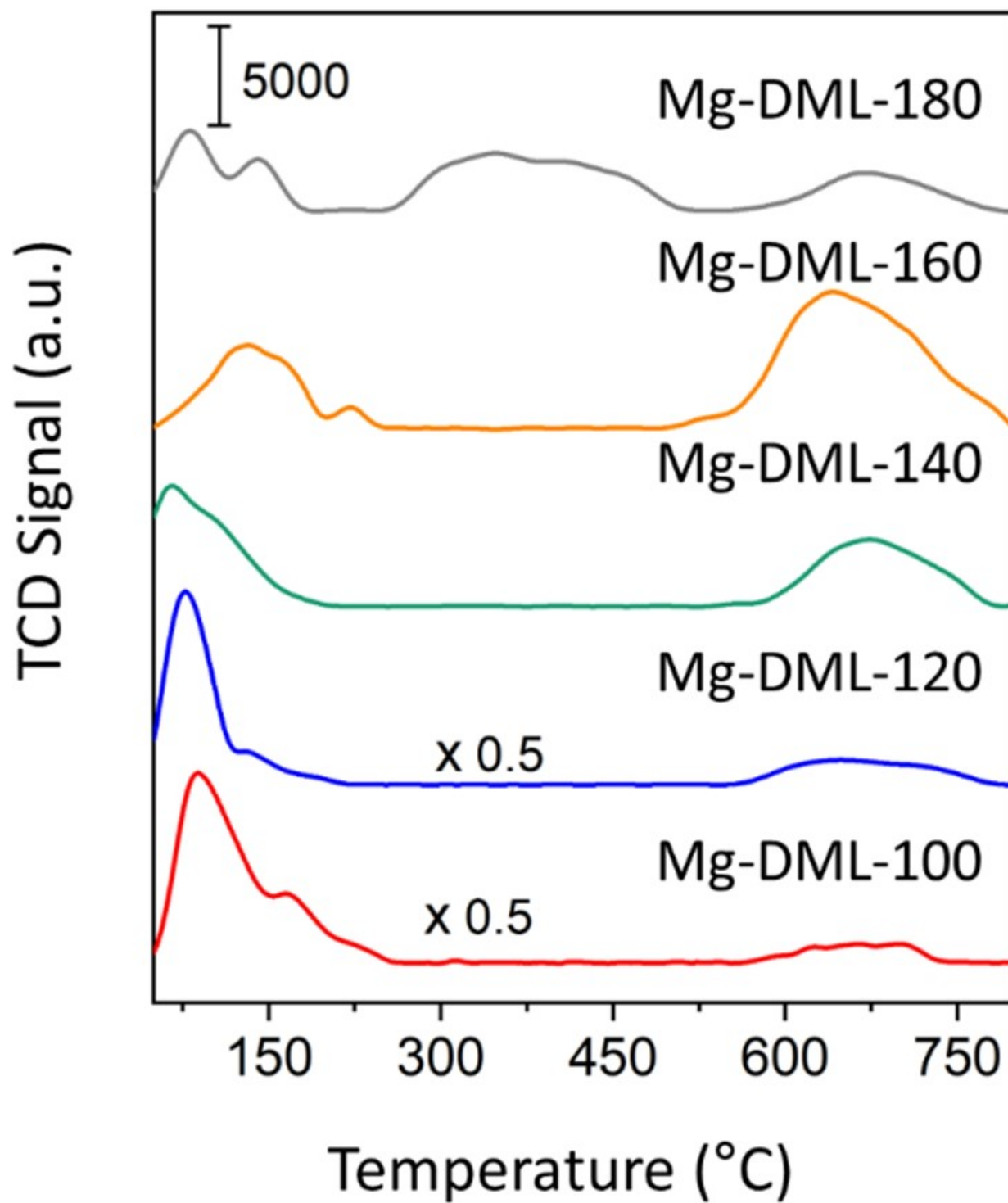


Figure 7

CO₂-TPD profiles of Mg-DML- x ($x = 100-180$) catalysts

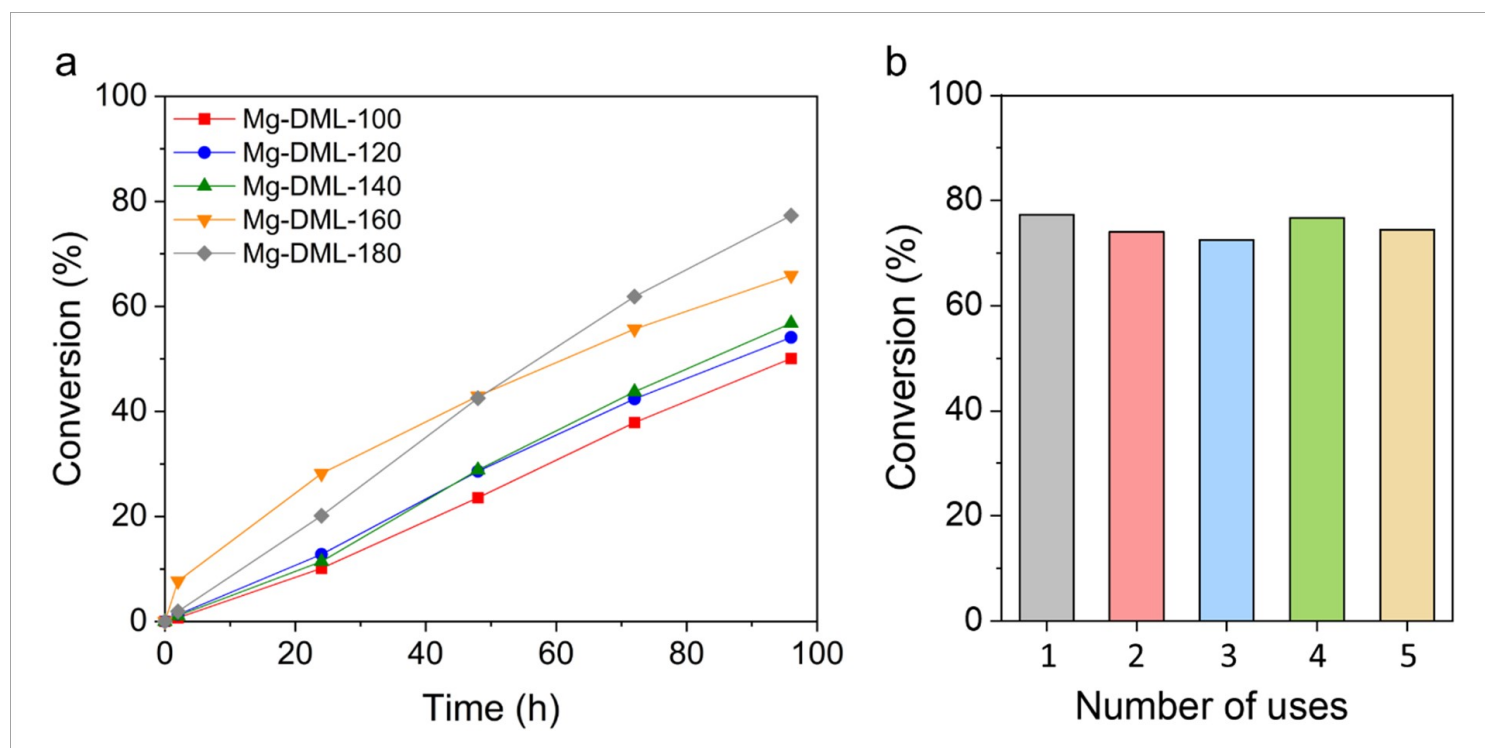


Figure 8

(a) Benzaldehyde conversion over Mg-DML- x ($x = 100-180$) catalysts as a function of reaction time and
 (b) benzaldehyde conversion over Mg-DML-180 with five cycle repeated use

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SIMgDML.docx](#)