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Correlation of acid sites with morphology of layered silicates

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ABSTRACT

Acid sites of clay minerals are active to catalyze numerous organic reactions. Previous studies had focused on the types and strength of these sites by correlating them with acid, pillaring or heat treatments, but the relation of acid sites with clay mineral morphology is not well understood. In this study, the synthesis of samples having similar chemical composition and structure, but different morphology characteristics was realized. The surface of samples was characterized by low-pressure argon adsorption at 77 K. The acid sites were probed by thermal desorption of 2-phenylethylamine. Three sites of different acid strength were identified. Whereas the assignment of these sites to basal and edge surfaces remains debatable, the method of thermal desorption of 2-phenylethylamine could clearly distinguish different sites related to homogenous and heterogeneous surfaces.

1. Introduction

Catalysts increase the rate of a reaction without modifying the overall standard Gibbs energy (McNaught and Wilkinson, 1997). In chemical engineering, heterogeneous catalysis, in which the reaction occurs at or near an interface between the active phase and the reactants (solid-gas or solid-liquid), is recognized as a more sustainable pathway compared to homogenous catalysis (liquid-liquid), in which only one phase is involved (Corma and García, 2003). Different solid catalysts are used in heterogeneous acid-catalyzed reactions. Zeolites are probably the most widely used solid catalysts due to their high thermal resistance, presence of strong acid sites and possibility to tune pore size and chemical composition (Yilmaz and Müller, 2009; Zeolite catalysts come into focus, 2020). Before the discovery and massive use of zeolites, clay minerals were also used (Chitnis and Mohan Sharma, 1997). These layered silicates present poorer characteristics compared to zeolites due to their lower thermal stability and weaker acid sites (Barrer, 1984; Busca and Gervasini, 2020). However, despite these drawbacks, clay minerals may catalyze numerous organic reactions (Laszlo, 1987; Vogels et al., 2005; Theng, 2018). In particular, their role in the emergence of life on Earth by serving as a catalyst for amino-acid formation reactions is still vividly debated (Bernal, 1949; Schumann et al., 2012; PedreiraSegade et al., 2018; He et al., 2023). The catalytic activity of clay minerals is sometimes referred to as "enzyme-like" due to the presence of weak and medium-strength acid sites, which can be more advantageous for some catalytic reactions compared to the sole presence of strong acid sites (Laszlo, 1990; Vogels et al., 2005; Tkachenko et al., 2017). In addition, their layered morphology allows the expansion of interlayer space upon the adsorption of other chemical entities, and thus the adsorption of large molecular edifices, owing to this expandable pore size (Schoonheydt, 2016). This is not the case for zeolites, which have fixed pore sizes. Moreover, their large natural abundance makes them easily available and relatively cheap.

Despite the ability of clay minerals to catalyze numerous organic reactions (Theng, 2018), the nature and strength of sites implied in these catalytic processes have not been explicitly elucidated so far, possibly owing to the complex structure of clay minerals. This complexity arises from the presence of three different surfaces: interlayer, basal and edge surfaces, and from variable chemical compositions, where aluminum can be found in both tetrahedral and octahedral configurations and in various amounts and proportions. For this reason, previous studies have mostly been empirical, i.e., the types and strength of the sites have been correlated with the behavior of clay minerals upon/after acid, pillaring or heat treatment (Polverejan et al., 2002; Varma, 2002; Adams and

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McCabe, 2006; Bisio et al., 2008; Bian and Kawi, 2020), but systematic understanding is lacking. The correlation of catalytical activity with particle morphology has been previously described for oxides and layer double hydroxides. Bailly et al. (2005) prepared MgO with different morphology and particle size, and thus different proportions of several types of O^{2-} . They showed that the strength of the sites was related to the coordination of O^{2-} (located on faces, edges or terrace) and that OH had a peculiar reactivity. The different reactivity of sites located on faces or edges of hexagonal crystals of layered double hydroxides has been also previously investigated by Roeffaers et al. (2006) by monitoring the chemical transformation of individual organic molecules by fluorescence microscopy.

Experimental and theoretical studies have elucidated the difference in reactivity with respect to inorganic cations between the three different surfaces of clay minerals: basal, edge and interlayer (Liu et al., 2022). It can be then deduced, and expected, that the relative proportions of sites with different strengths are related to the morphology of clay mineral particles. Indeed, the study of Cornélis et al. (1993), which investigated a Friedel-Krafts acylation reaction, found a good correlation between the number of edge sites of clay platelets and the amount of inhibitor used. The hypothesis of the present study is that basal and edge surfaces have distinct reactivity and different strengths of acid sites.

To test this hypothesis, two synthetic saponite-like samples, aspidolite, were prepared from the same gel precursor at two synthesis temperatures: 400 and 200 °C. Such an approach allowed to produce two samples with similar crystal chemistry, one well crystalline mainly with basal surfaces, in which the edge surface could be neglected, and a second with an increased fraction of edge sites resulting from a smaller particle size. Saponite is a tri-octahedral, 2:1 type swelling clay mineral containing Na, Si, Mg, Al, O and H in its structure. In addition, these compounds exhibit the highest thermal stability among this class of materials (Földvári, 2011; Zhou et al., 2019), and aluminum is mainly present in tetrahedral configuration. The crystal chemistry corresponding to the highest possible Al content in the tetrahedral sheet, *i.e.*, with Al/Si = 0.33, was chosen. The strength of acid sites was probed with temperature controlled desorption method, using 2-phenylethylamine as a basic probe (Busca and Gervasini, 2020).

The knowledge of strength and types of acid sites present on different clay minerals could allow gaining a better understanding of sites implied in the catalytic reactions of organic molecules, and assist in smart design of novel catalysts.

2. Material and methods

2.1. Synthesis of aspidolite

Two samples of saponite-like mineral samples, aspidolite, were synthesized using hydrothermal treatment at 200 and 400 °C, and labeled "Aspi-200" and "Aspi-400", respectively. The precursor gel was the same for the two syntheses and was prepared by mixing 0.2 M Mg (NO₃)₂, 0.2 M Al(NO₃)₃ and 0.2 M Na₄SiO₄ solutions in such a way that the molar ratio corresponded to the theoretical structure of Na1.00Mg3.00(Si3.00Al1.00)O10(OH)2. After the precipitation, the suspension was homogenized for 3 h by stirring at room conditions, then calcined at 450 °C for 1 h prior to the hydrothermal treatment. The heating rate was 5 °C/min and the cooling rate of <10 °C/min for the calcination step. For the 200 °C synthesis, the calcined precursor was transferred to the mineralization bomb with Teflon liner. 70 mL of 0.01 M NaOH solution was added, and the mineralization bomb was tightly sealed and put for 5 days at 200 °C. High-temperature synthesis was performed for 6 days at 400 $^\circ C$ and a water pressure of ${\sim}230$ bars in an externally heated Morey-type pressure vessel with an internal silver tubing, starting from ${\approx}2.0$ g of gel and ${\approx}33.5$ mL H_2O to reach the required pressure.

After the hydrothermal treatment, samples were recovered, washed three times with deionized water by centrifugation at 8000 rpm (9946 \times g) for 10 min, and then saturated with 1 M CaCl₂, following common saturation protocol (Carrado et al., 2006).

The chemicals used to prepare solutions were: magnesium nitrate 99 wt% (Mg(NO₃)₂·6H₂O) from Sigma Aldrich (India), aluminum nitrate 98-102 wt% (Al(NO₃)₃•9H₂O) from Carlo Erba (Val de Reuil, France), sodium orthosilicate (Na₄SiO₄) from Alfa Aesar (Karlsruhe, Germany), sodium hydroxide 97 wt% (NaOH) from Sigma Aldrich (St Louis, Missouri, USA), calcium chloride 99 wt% (CaCl₂·2H₂O) from Sigma Aldrich (Japan) and deionized water (18.2 MΩ·cm).

2.2. Characterization of synthesized solid

The prepared solids were characterized by powder X-ray diffraction (XRD), ²⁷Al solid nuclear magnetic resonance (NMR) spectroscopy, energy dispersive X-ray analysis (EDX) and nitrogen and argon adsorption. The methods, except nitrogen and argon adsorption, have been previously described in Meyer et al. (2020) and are given in Supplementary information.

2.3. Nitrogen adsorption-desorption and low-pressure argon adsorption at 77 ${\rm K}$

Nitrogen adsorption-desorption isotherms were collected at 77 K on a Belsorp max II (MicrotracBEL Corp.) adsorbometer. The step-by-step method was used for evaluating specific surface areas by BET method (Brunauer et al., 1938).

In addition, high-resolution adsorption isotherms were recorded using a lab-built automatic quasi-equilibrium volumetric setup, described elsewhere (Michot et al., 1990; Villiéras et al., 1997; Bardot, 1998). The quasi-equilibrium technique is based on the low-pressure argon adsorption at 77 K with a slow, constant, and continuous flow rate of the adsorbate through a micro leak. High-resolution adsorption isotherms were recorded at least up to the BET domain, corresponding to the formation of the first adsorbed monolayer on the adsorbent with more than 3000 data points. The experimental adsorption isotherms were then analyzed by the derivative isotherm summary (DIS) procedures introduced by Villieras et al. (1992). Due to a large number of experimental data points, the experimental derivative adsorption isotherms can be calculated as a function of the logarithm of relative pressure, $\ln(P/P_0)$, which corresponds to the free energy of adsorption expressed in kT or RT units. This procedure allows for the study of energetic surface heterogeneity in highly heterogeneous materials such as clay particles. DIS method is performed by fitting the experimental derivative isotherm to local theoretical isotherms that are assigned to different adsorption energy domains (basal and lateral surfaces). Each local derivative isotherm is defined by three parameters (Bardot, 1998): the interaction energy between the solid and the adsorbed molecule, which is deduced from the $(\ln P/P_0)$ peak position, the lateral interaction between two adjacent gas molecules (ω), and the monolayer capacity $(V_{\rm m})$ of the domain, which can be used to calculate the surface area by taking into account argon cross-sectional area (13.8 $Å^2$).

All sorption measurements were performed with high purity nitrogen and argon (99.9995 %) supplied by Alphagaz (France).

2.4. Thermal desorption of 2-phenylethylamine

Preliminary tests were carried out to establish a method taking into account the stability of the studied material and the time needed to reach constant mass. The experiment consisted of three steps: (1) heating an empty crucible, (2) heating the sample alone, and (3) heating the sample after the addition of 15 μ L of 2-phenylethylamine (PEA). In each step, the heating was performed from 50 to 330 °C at different rates (5, 10, 15 and 20 °C/min) under N₂ flow at 100 mL/min. For the first step (heating of crucible), the hold time was 30 min at 50 °C before starting to increase the temperature. For the second step (heating of the sample), the hold time was 60 min at 50 °C, and for the third step (heating after

the addition of PEA), the hold time was 6 h at 50 °C. This time was chosen after performing a preliminary experiment by evaporating PEA alone (Fig. S1 in Supplementary information). It showed that 6 h were sufficient to remove the excess PEA from the surface. After reaching 330 °C, the temperature was held constant for 30 min to ensure that a stable mass had been reached. In the second step, after 30 min of holding time at 330 °C, the sample was cooled in the furnace under N₂ at the rate 20 °C/min to ensure that the sample was not exposed to atmosphere humidity prior to the addition of PEA. The scheme of a typical experiment is given in Fig. S2 in Supplementary Information.

3. Results and discussion

3.1. Solid sample characterization

Several characterization techniques, powder XRD, EDX, 27 Al MAS NMR, and gas (N₂ and Ar) adsorption, were employed to determine the crystal chemistry and microstructure of the prepared samples.

3.1.1. Powder XRD

Powder XRD showed that the diffracted peak intensities were situated at the same positions °20 for both samples (Fig. 1), consistent with a unique crystal structure. The d₀₀₁ value was 14.7 Å corresponding to 2:1 swelling type clay mineral (Brindley and Brown, 1980). Aspi-400 had much sharper peaks compared to Aspi-200 suggesting larger coherent scattering domains. In addition, XRD pattern of Aspi-400 exhibited distinct *hkl* reflections, typical for highly ordered structures (Kalo et al., 2012), whereas the pattern of Aspi-200 was typical for smectite with the sole presence of *hk* bands, owing to sample turbostratism.

3.1.2. Chemical analysis

Chemical analysis of samples by EDX gave Al/Si molar ratios of 0.40 and 0.31 for Aspi-200 and Aspi-400, respectively (Table 1). The later experimentally determined molar ratio was in agreement with the theoretical one of 0.33. For Aspi-200, the experimentally determined molar ratio was slightly higher, suggesting more Al with respect to Si than introduced. A small amount of silica could have been leached due to the basic synthesis pH of about 12 for Aspi-200. The chemical analysis results confirmed that samples were successfully exchanged with Ca^{2+} , and only small amount of Na⁺ was detected. It has to be noted that Aspi-400 was more homogenous in terms of chemical composition compared to Aspi-200.

3.1.3. ²⁷Al MAS NMR

In clay mineral structure, Al can be present in both octahedral and/or



Table 1

The chemical composition of Aspi-200 and Aspi-400 determined by EDX spectroscopy.

Element	Aspi-200 (at.%)	Aspi-400 (at.%)		
0	60.6 ± 0.8	58.0 ± 0.2		
Na	0.4 ± 0.1	$\textbf{0.42} \pm \textbf{0.05}$		
Mg	16 ± 1	15.76 ± 0.09		
Al	5.7 ± 0.4	5.55 ± 0.07		
Si	14.4 ± 0.9	18.0 ± 0.1		
Са	2.5 ± 1.4	$\textbf{2.34} \pm \textbf{0.08}$		

tetrahedral configurations. In our synthesis we aimed to obtain a structure with Al mainly in a tetrahedral configuration. To assess the actual configuration of Al in synthesized samples, ²⁷Al MAS NMR was performed. Two signals with chemical shifts at 8 and 62 ppm were present (Fig. 2) corresponding to ^{VI}Al and ^{IV}Al configurations, respectively (Goodman and Stucki, 1984). The relative quantification obtained from the fit of spectra, gave 87 ± 5 % and 81 ± 5 % of ^{IV}Al for Aspi-200 and Aspi-400, respectively. For Aspi-400 slightly more Al was found in an octahedral configuration compared to Aspi-200. However, most of Al was found to be in a tetrahedral configuration for both samples.

Considering the chemical analysis and NMR spectroscopy results an average chemical formula could be then calculated. For Aspi-200 the





Fig. 1. Powder XRD traces of aspidolite synthesized at 200 °C (left) and 400 °C (right). The diffracted intensity scale was increased x5 after 10°20.

average chemical formula was $(Mg_{0.34}Ca_{0.49}Na_{0.08})Mg_{2.85}Al_{0.15}(-Si_{2.80}Al_{0.97})O_{10}(OH)_2$ and for Aspi-400 it was $(Ca_{0.41}Na_{0.07})Mg_{2.77}Al_{0.19}(Si_{3.16}Al_{0.79})O_{10}(OH)_2$. It has to be noted that for Aspi-200 the distribution of elements within the analyzed range was more heterogeneous compared to Aspi-400, and the given formula represents the average result. The results suggest that for Aspi-200 a small quantity of Si was leached from the synthesis solution due to the basic pH synthesis conditions. Indeed, above pH 11 silica becomes soluble (Dzene et al., 2024). This in turn, resulted in the higher amount of Mg^{2+} for Aspi-200, which then had to be considered in the interlayer to ensure electroneutrality.

3.1.4. N_2 adsorption/desorption experiments

Differences in sample microstructure suggested by powder XRD were confirmed by N₂ adsorption/desorption experiments. Aspi-200 presented an isotherm of type IV(a) and a hysteresis loop of type H5, whereas Aspi-400 presented an isotherm of type II and no hysteresis loop (Fig. 3) according to IUPAC classification (Thommes et al., 2015). Type II isotherm is characteristic of nonporous or macroporous adsorbents, suggesting a large crystallite size for Aspi-400, in agreement with powder XRD results. Type IVa isotherm is characteristic of mesoporous adsorbents with cylindrical mesopores, and the hysteresis loop of type H5 suggests the presence of both, open and partially blocked mesopores. As N₂ does not allow probing interlayer porosity, and the observed difference is essentially due to microstructure. Aspi-200 and Aspi-400 possessed specific surface area (SSA) of $140 \pm 6 \text{ m}^2 \text{ g}^{-1}$ and $21 \pm 3 \text{ m}^2 \text{ g}^{-1}$, respectively, the former (Aspi-200) being typical for synthetic 2:1 type clay minerals (Michot and Villieras, 2002; Dogan et al., 2006).

3.1.5. Low-pressure argon adsorption

Low-pressure argon adsorption isotherms were recorded to assess the lateral and basal surface areas of both samples (Fig. 4), DIS modeling parameters being listed in Table 2. The total SSA from Ar adsorption, corresponding to the sum of the lateral and basal contribution, were estimated to be equal to 19.7 and 117.5 $\text{m}^2 \cdot \text{g}^{-1}$ for Aspi-400 and Aspi-200, respectively, consistent with N₂ adsorption results. For Aspi-400, the derivative isotherm was similar to clay minerals (illite, vermiculite, talc and montmorillonite) previously studied by this method (Michot et al., 1994; Bardot et al., 1998; Tournassat et al., 2003; Reinholdt et al., 2013; Zhang et al., 2020). The isotherm was decomposed into five contributions (Fig. 4 right, Table 2). Based on previous studies (Bardot et al., 1998), two highly energetic domains were attributed to high-energy adsorption sites (HEAS) (lnP/P₀ = -12.66 and lnP/P₀ = -10.84), one contribution would correspond to adsorption on lateral surfaces (lnP/P₀ = -7.23), and two contributions were attributed to Ar

adsorption on basal surfaces $(\ln P/P_0 = -4.95 \text{ and } \ln P/P_0 = -2.40)$. It can be noticed that the basal peak at -4.95 seems high in adsorption energy for basal surfaces although similar values were reported for illite, with K⁺ on the surface, micas and high-charge Na⁺-saturated saponite (Bardot et al., 1998; Michot and Villiéras, 2002). The assignment of the highest energy peak $(\ln P/P_0 = -12.66)$ was not obvious. According to previous results, it could correspond to particular sites of the basal surface (case of talc in Michot et al., 1994), high energy sites on the lateral surface or micropores. In case of Ca²⁺-saturated clay minerals these HEAS were also tentatively attributed to the strong interaction of Ar with modified surface oxygen electronegativity in the vicinity of Ca²⁺ of basal surfaces (Bardot, 1998).

The derivative isotherm of Aspi-200 presented a shape typical for small particles with Ca²⁺ as exchangeable cations (Bardot et al., 1998), and was decomposed into six contributions. Four contributions were similar to those of Aspi-400. A highly energetic domain at $\ln P/P_0 = -13.60$ was attributed to adsorption on HEAS related to the presence of Ca²⁺ on basal surfaces, the contribution with $\ln P/P_0 = -11.07$ was also attributed to HEAS, and two contributions were attributed to basal surfaces ($\ln P/P_0 = -4.86$ and $\ln P/P_0 = -2.73$). Two sites corresponding to high-to-medium energy sites and attributed to lateral surface ($\ln P/P_0 = -8.67$ and $\ln P/P_0 = -6.45$) were different from those of Aspi-400. For Aspi-400 only one site was present in this range at $\ln P/P_0 = -7.23$. The data from this experiment showed that Aspi-200 had more surface of higher energy sites than Aspi-400.

The results of different characterization techniques for both samples are summarized in Table 3. The contributions of $\ln P/P_0 = -11.07$ for Aspi-400 and $\ln P/P_0 = -10.84$ for Aspi-200 were not taken into account for the lateral surface as their assignment was uncertain. It can be concluded that both samples had the same structure and a similar chemical composition, but different crystallite sizes and ratios between basal and lateral surfaces. Aspi-400 had a low surface area, a smaller proportion of lateral surface and sharp diffraction peaks typical for large phyllosilicate crystals. For this sample, the contribution of basal surface was mainly expected in PEA adsorption experiments. Aspi-200 had an average surface area, a significant contribution of lateral surfaces, and broader diffraction peaks typical for fine-grained phyllosilicates. For this sample, thus the contribution of both basal and edge (lateral) surfaces was expected in adsorption experiments.

3.2. Identification of three types of sites by thermal desorption of 2phenylethylamine

The quantity of PEA retained by each material after the desorption of excess is shown in Table 4. The amount of PEA left after the hold was



Fig. 3. N₂ adsorption (**a**) -desorption(**a**) isotherms of aspidolite synthesized at 200 °C (left) and 400 °C (right).



Fig. 4. Experimental low-pressure Ar derivative isotherms obtained at 77 K (open red circles) and the decomposition of the derivative isotherm summation (DIS) (broken lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

 Table 2

 Parameters of the DIS method for low-pressure Ar adsorption isotherms.

Sample	Position ln P/P ₀	V_{ads} (cm ³ ·g ⁻¹)	ω∕kT	Specific surface of adsorption (m ² ·g ⁻¹)	Type of surface
Aspi-	-13.60	0.59	0	2.18	HEAS*
200	-11.07	2.49	-0.1	9.25	HEAS or
					lateral
	-8.67	2.29	0	8.48	lateral
	-6.45	4.75	-0.2	17.63	lateral
	-4.86	10.36	1.1	38.45	basal
	-2.73	11.19	0	41.50	basal
Aspi-	-12.66	0.29	0	1.07	HEAS
400	-10.84	0.14	0.5	0.53	HEAS or
					lateral
	-7.23	0.43	-1.7	1.61	lateral
	-4.95	2.65	1.6	9.83	basal
	-2.40	1.78	0	6.62	basal

HEAS: high energy adsorption sites.

Table 3

Summary of characteristics of prepared material.

	Aspi-200	Aspi-400
Average chemical formula	$\begin{array}{l} (Mg_{0.34}Ca_{0.49}Na_{0.08}) \\ Mg_{2.85}Al_{0.15}(Si_{2.80}Al_{0.97})O_{10}(OH)_2 \end{array}$	$\begin{array}{l}(\text{Ca}_{0.41}\text{Na}_{0.07})\text{Mg}_{2.77}\text{Al}_{0.19}\\(\text{Si}_{3.16}\text{Al}_{0.79})\text{O}_{10}(\text{OH})_2\end{array}$
Molar Al/Si ^{IV} Al (%) $a_{s} N_{2} (m^{2} \cdot g^{-1})$ $a_{s} Ar (m^{2} \cdot g^{-1})$ Lateral surface	0.40 87 140 117.5 26.1	0.31 81 21 19.7 1.6
$(m^2 \cdot g^{-1})$ Basal surface $(m^2 \cdot g^{-1})$	80.0	16.5

Table 4

The quantity of PEA desorbed during experiment. The variation of the amount of PEA desorbed (\pm) was estimated from the experiments at four different heating rates.

	PEA left after hold	PEA left after hold	PEA desorbed
Sample	$(10^{-3} \text{ mol} \cdot \text{g}^{-1})$	$(10^{-5} \text{ mol} \cdot \text{m}^{-2})$	(%)
Aspi-200	1.49 ± 0.04	1.27 ± 0.03	90 ± 2
Aspi-400	0.46 ± 0.06	2.4 ± 0.3	98 ± 6

consistent with those reported in previous studies involving saponite (Prieto et al., 1999; Polverejan et al., 2002), where 0.90 mmol H⁺/g material and 0.63 mmol of cyclohexylamine/g material were reported, respectively. After heating to 330 °C, all PEA was desorbed from Aspi-400, whereas Aspi-200 retained ~10 % of the initially adsorbed PEA, consistent with the larger amount of strong acid sites.

The choice to heat the samples only to 330 °C, and thus to probe only partially the acid sites of different strengths, was imposed by the particularity of clay-like material structure. Until 330 °C the structure of clay-like materials was not altered, and only adsorbed water from the surface and the interlayer was removed (Fig. S3 in Supplementary Information). Above 330 °C, changes of clay mineral structure, such as dehydroxylation (Guggenheim and van Groos, 2001), could occur and it became impossible to distinguish between different phenomena (*i.e.*,



Fig. 5. Temperature programmed desorption (TPD) of 2-phenylethylamine (PEA) in a form of derivative $(mg \cdot min^{-1})$ at heating rate 5 °C·min⁻¹.

structural changes vs. PEA desorption).

Fig. 5 represents the results of temperature-programmed desorption (TPD) of PEA in the form of derivative (mg·min⁻¹) at a heating rate of 5 °C·min⁻¹. The results with other heating rates (10, 15 and 20 °C·min⁻¹) are provided in Fig. S4 (Supplementary Information).

Three temperatures T_{max1} , T_{max2} and T_{max3} corresponding to approximately 100 °C, 160 °C and 260 °C, respectively, could be identified. For Aspi-400 only one peak at T_{max2} was present. The same T_{max2} could be identified for Aspi-200. According to sample characterization, Aspi-400 had large well-crystalized particles with less than 10 % of the lateral surface (Table 3). Assuming that all types of surfaces were randomly exposed to the PEA molecules, the T_{max2} contribution could then be assigned to the main characteristic of Aspi-400, that is to a homogenous basal surface. The contribution of other surface sites identified by argon adsorption experiments might have been too small to be distinguished using PEA desorption. We hypothesize that sites on basal surfaces where PEA was adsorbed could be related to partially dehydrated calcium cations, present on the surface to compensate for the negative surface charge due to the isomorphic substitution of Si^{+IV} by Al^{+III} (Adams and McCabe, 2006; Persson, 2010):

$$\left[\operatorname{Ca}(\mathrm{H}_{2}\mathrm{O})_{8}\right]^{2+} \rightarrow \left[\operatorname{Ca}(\mathrm{H}_{2}\mathrm{O})_{7}\mathrm{OH}\right]^{+} + \mathrm{H}^{+}$$
(1)

Such partial dehydration of calcium cations was related here to the temperature (160 °C), that partially removed water molecules from calcium hydration sphere. Laszlo (1990) proposed that heating to 300 °C resulted in generation of surface radical sites of the O_3SiO silyloxy type referencing the work of Freund et al. (1990). However, if such sites existed, they would be minor compared to Ca^{2+} . The XRD traces of Aspi-200 before and after complete saturation with PEA, did not show any differences in terms of layer-to-layer distance (Fig. S5 in Supplementary Information), suggesting that the interlayer surface could be neglected in this experiment.

For Aspi-200, two additional phenomena could be identified at T_{max1} and T_{max3} (Fig. 5). Such low temperature T_{max1} (~100 °C) indicated the presence of very weak acid sites, or possibly amphoteric sites. Molecular simulation studies of montmorillonite edge sites (another 2:1 swelling clay mineral similar to saponite) showed different chemical sites with various pK_a (Gao et al., 2023). Some similar sites could exist on saponite. The third characteristic peak identified and corresponding to T_{max3} of 260 °C was not observed for Aspi-400. The study of Okada et al. (2006), which used the NH₃ probe TPD method, also reported two sites on clay minerals: at about 200 °C, corresponding to very weak acid sites and at 250-300 °C, corresponding to weak acid sites. Although the used molecular probes presented slightly different basic features (pK_b of 4.75 and 4.20 for NH₃ and PEA, respectively), the desorption temperatures were in the same range as in our study. Polyerejan et al. (2002) also reported the presence of acid sites characterized by a desorption temperature of 230 °C. Aspi-200 was less crystalline with a more heterogeneous surface compared to Aspi-400. Also, Aspi-200 had a larger amount of lateral surface (26 m²·g⁻¹) compared to Aspi-400 (1.6 $m^2 \cdot g^{-1}$), and Aspi-200 had also Mg²⁺ as charge compensating cation in addition to Ca²⁺. Table 5 reports ratios between Aspi-200 and Aspi-400 samples for the amount of PEA adsorbed and different surfaces.

The amount of PEA adsorbed on Aspi-200 sample was three times higher compared to Aspi-400 sample. Sample Aspi-200 presented 16

Table 5

Comparison of different surfaces and adsorbed amount of PEA between both samples.

	Aspi-200 / Aspi-400
PEA left after hold $(10^{-3} \text{ mol} \cdot \text{g}^{-1})$	3.2
$a_{\rm s}$ Ar (m ² ·g ⁻¹)	6.0
Lateral surface $(m^2 \cdot g^{-1})$	16.2
Basal surface $(m^2 \cdot g^{-1})$	4.8
Surface area of the peak at $-\ln(P/P_0) \approx 5$	3.9

times higher amount of lateral surfaces compared to Aspi-400 sample. However, the ratio between basal surfaces was lower: 4.8. If the main contribution to basal surfaces (surface with position of $-\ln(P/P_0) \approx 5$) is considered only, this surface is present 4 times more on Aspi-200 sample compared to Aspi-400 sample. Such comparison (Table 5) could suggest that basal surfaces are mainly involved in PEA adsorption phenomenon. If so, then T_{max3} could be attributed to the presence of Mg²⁺ charge compensating cation on Aspi-200 surface. However, a more heterogeneous basal surface could also present some stronger adsorption sites compared to a more homogenous Aspi-400 surface. Alternatively, it is possible that these types of sites of T_{max3} could be correlated possibly to the edge surface. Indeed, Solomon (1968) suggested that sites at crystal edges act as electron acceptors, and the minerals having such sites act then as Lewis acids. The edge sites are expected to be stronger than dehydrated cation sites, and this is in agreement with our data with T_{max3} being higher than T_{max2} . It has to be noted that approximately 10 % of PEA initially adsorbed remained on Aspi-200 (Table 4) after heating to 330 °C suggesting that a small amount of the fourth type of strong acid sites was present. Also, the study of Breen (1991) mentioned Lewis acid centers at 360 °C for the desorption of pyridine (a weaker base than PEA, $pK_{\rm b} = 8.7$) from montmorillonite. Such sites could be then attributed to edge surfaces.

Kissinger's model was applied to estimate the energy of different types of sites identified in the PEA desorption experiment (Kissinger, 1957). It is a relatively simple model, and recently other more sophisticated models have been proposed (Carniti et al., 2005). However, in our experiment three distinct phenomena could be identified, thus allowing to apply the model of Kissinger. The weak acid sites assigned to the homogenous surface of clay minerals and to the acidity arising from partial dehydration of charge-compensating cations, corresponded to the sites with the strength of 14–16 kJ•mol⁻¹ (Table 6). The acid sites attributed to the heterogeneous surface corresponded to the sites with the strength of 50 kJ•mol⁻¹. Both types of site could be considered in absolute (when compared to the literature and to other materials) as very weak and weak acid sites, respectively (Busca and Gervasini, 2020).

4. Conclusion

The synthesis of clay mineral-like materials from the same precursor but at different temperatures allowed to prepare samples with similar structure and chemical composition, but different morphology. The acid sites of different strengths could be detected with the method of thermal desorption of 2-phenylethylamine. The correlation between morphology (lateral and basal surfaces) and the acid sites was not straightforward as low-pressure argon adsorption at 77 K revealed rather complex surface morphology for both samples. Nevertheless, both techniques (lowpressure argon adsorption and thermal desorption of 2-phenylethylamine) showed clear differences between the samples. It could be concluded with certainty that a homogenous surface presented weaker and single adsorption sites compared to a more disorganized surface which had slightly stronger and more numerous adsorption sites. The synthesis approach could then be used to obtain such different samples, but the correlation of the types of sites with morphology would need subsequent treatments (e.g., cation exchange) in addition to the initial characterization.

CRediT authorship contribution statement

Liva Dzene: Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Project administration, Methodology, Investigation, Conceptualization. Martine Lanson: Writing – review & editing, Resources, Methodology, Investigation. Bruno Lanson: Writing – review & editing, Resources, Conceptualization. Sebastian Meyer: Writing – review & editing, Investigation. Angelina Razafitianamaharavo: Writing – review & editing, Writing – original draft, Validation, Resources, Methodology, Investigation, Formal

Table 6

Temperatures and energies of PEA desorption evaluated by thermal analysis and Kissinger's model.

	Heating rate	$T_{\max,1}$	T _{max,2}	$T_{\rm max,3}$	$\ln A_1$	$E_{a,1}$	r_1^2	$\ln A_2$	$E_{a,2}$	r_2^2	$\ln A_3$	$E_{a,3}$	r_{3}^{2}
Sample	$^{\circ}C \cdot min^{-1}$	°C	°C	°C		$kJ \bullet mol^{-1}$			$kJ \bullet mol^{-1}$			$kJ \bullet mol^{-1}$	
	5	103	161	263									
	10	124	168	269									
	15	131	175	275									
Aspi-200	20	137	178	278	-5.6	3	0.91	4.1	16	0.99	15.2	50	0.99
	5		160										
Aspi-400	10		168					2.0	14	0.00			
	15		176				2.8	2.8 14	0.98				
	20		178										

analysis, Data curation, Conceptualization. **Frédéric Villiéras:** Writing – review & editing, Validation, Resources, Methodology, Formal analysis, Conceptualization. **Severinne Rigolet:** Writing – review & editing, Resources, Methodology, Investigation, Formal analysis. **Cyril Vaulot:** Writing – review & editing, Methodology, Investigation. **Simona Bennici:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clay.2025.107714.

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