

Role of water on the activity of magnesium silicate for transesterification reaction

Longfei Lin, Damien Cornu[#], Maya Mounir Daou, Cyril Domingos, Virginie Herledan, Jean-Marc Krafft, Guillaume Laugel, Yannick Millot, and Hélène Lauron-Pernot^{*[a]}

Abstract: This study aims to reveal how water adsorbed on a solid influences its catalytic properties for transesterification reaction in liquid phase. The reactivity of a commercial magnesium silicate was studied after various thermal pretreatments for the reaction of transesterification of ethyl acetate with methanol. It was observed that the conversion decreases with the increase of the pretreatment temperature, therefore with the release of the water content of the magnesium silicate. Thermogravimetric analysis, DRIFT and ¹H NMR spectroscopies show that physically adsorbed water has little influence on the reactivity, while water incorporated within the catalysts thus desorbing at higher temperatures plays a key role on the conversion. Calorimetry, in situ DRIFT spectroscopy and ¹H NMR indicate that two kinds of active sites exist, that are created from the water coordinated to magnesium located on the edge of the clay-like particles or in the defects present in the silicate layer, respectively. Their role could be to stabilise methanol deprotonated by basic Mg-OH groups, activate ester or help the departure of the alkoxyl moiety.

Introduction

the field of biomass derivatives valorisation. In transesterification reactions are used in a wide range of applications, for instance in liquid phase for the production of biodiesel^[1] and lubricant^[2–4] and in gas phase for the generation of monomers for polymerization^[5]. Because of global warming issues and depletion of the fossil fuels, the production of biodiesel, used as an alternative to fossil sources has attracted a great deal of interest^[6-11]. Homogeneous catalysts, such as sodium and potassium hydroxides, could achieve a high yield for the conversion of triglycerides^[12]. However, the high cost for the purification of products make heterogeneous catalysts more attractive^[13,14]. Basic solids have gained more attention than acidic materials due to their higher activity^[7]. Catalysts with strong basic properties, such as calcium and magnesium oxides^[15-20] or zeolites^[21-25] were reported to catalyse transesterification reactions. In addition, some other solids with weaker surface basicity are also able to catalyse these reactions, i.e. hydrotalcites $^{\left[26-29\right] },$ potassium carbonate or phosphate $^{\left[30\right] },$ barium hydroxide^[31], or zinc based materials^[32,33]. In a previous

publication^[34], we worked on a model transesterification reaction, the conversion of ethyl acetate with methanol in order to compare the activities of a series of magnesium based catalysts in both liquid and gas phases. We found that magnesium silicate shows a very good activity, in agreement with the results obtained by Narasimharao et al.^[35]. We also found that they are more active than the strongly basic material MgO in the transesterification in liquid phase and exhibit Magnesium Silicate Hydrates (MSH) surface species that we proposed to play a key role in the reactivity^[34].

Magnesium silicate can be synthesized by different as mechano-chemical dehydration^[36-40], methods such hydrothermal synthesis^[35] and precipitation^[41]. Sol-gel method was also proposed by some authors^[42]. Magnesium silicate exists under different phases, such as chondrodite, clinohumite, forsterite, phase B, superhydrous B^[43]. The very hydroxylated magnesium silicate (MSH) structure has been described by Roosz et al.^[40] based on results from X-ray diffraction, modelling XRD patterns and ²⁹Si MAS NMR spectroscopy. XRD patterns of MSH showed some broad peaks at $2\theta = 20$, 35, 60 and 72°. Very recently it has been modelled by DFT calculations and showed to be very similar to defective talc^[44]. This kind of phase thus consists in magnesium surrounded by an octahedron formed by oxygen, sandwiched between defective silicate layers^[40].

It is well-known that water inhibits base-catalysed transesterification reactions since it competes with the alcohol (reactant), thus lowering the conversion as observed for MgO in gas phase^[15] or transforming the required transesterification reaction into ester hydrolysis, leading to the formation of free fatty acids^[45,46]. This latter effect is however less pronounced in heterogeneous catalysis than in the homogeneous one^[45]. Nevertheless, water has also been shown to play a positive role in different heterogeneous catalytic reactions^[47]. For example, in the case of biodiesel production, Zabeti et al.^[8] noted that the presence of little amounts of water in the reaction medium can enhance the catalytic activity of calcium oxide (CaO). Their conclusion is that water is necessary to form hydroxide ions, which will be an homogeneous catalyst in the reaction. However, all these publications study the influence of water in the reaction mixture, as biomass products often contain water. Few works have studied specifically the influence of adsorbed water on the catalyst.

In previous work^[34], we reported that magnesium silicate is a bifunctional catalyst and offers on the same surface acidic and basic active sites. This bifunctional character may be a key parameter to explain the high activity but it is well known that water and other adsorbates may modify the reactivity of a surface^[48]. Such a phenomenon has been evidenced, in the case of hydrotalcites, in transesterification reactions^[28,49].

The aim of this work is to study the role of adsorbed water on the catalytic behaviour of a commercial magnesium silicate

 [[]a] L, Lin, Dr. D. Cornu, M. M. Daou, C. Domingos, Dr. V. Herledan, Dr. J. Krafft, Dr. G. Laugel, Dr. Y. Millot, Prof. H. Lauron-Pernot Sorbonne Universités, UPMC Univ Paris 06, UMR CNRS 7197, Laboratoire de Réactivité de Surface Tour 43-33, 3^{éme} étage, Case 178, 4 Place Jussieu, F-75252, Paris, France
 *E-mail: helene.pernot@upmc.fr
 # Present address: Foundation ICIQ Avda. Països Catalans, 16 43007 Tarragona, Spain

(labelled MS) in the model reaction of transesterification of ethyl acetate by methanol. In order to link the yield obtained in catalysis to surface properties, the characterization of the catalysts is achieved by infrared and ¹H Nuclear Magnetic Resonance spectroscopies.

Results and Discussion

Catalysis performances and TGA results

Table 1 indicates the conversion of ethyl acetate (AcOEt) for magnesium silicate with (MS-X, X being the temperature of the pretreatment in °C) and without (MS) pretreatment. Conversions of ethyl acetate decreases for increasing pretreatment temperatures, especially for pretreatment temperatures higher than 70°C. Figure 1 shows the results from thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA) of MS and MS-X. DTA curves (Figure 1B) show a main weight loss feature, occurring below 200 °C that can be attributed to the removal of water^[38]. Water adsorbed on catalysts is released step by step (Figure 1A) and the maximum for DTA curve shifts towards higher temperatures (Figure 1B) for increasing pretreatment temperatures. The data are listed in Table 1 to compare with catalytic performance. The quite significant decrease of conversion does not occur for the important loss weight under 70°C, attributed to water weakly bonded to the surface, but when more strongly adsorbed water molecules are desorbed. Similar results were also found by Xi et al.^[28,29] for the activity of rehydrated hydrotalcites in the transesterification reaction of tributyrin with methanol. This effect was ascribed to the loss of OH⁻ base sites that were produced by dissociating interlayer water^[28,29,50].

Table 1. Conversion and TGA/DTG measurements for magnesium silicate without (MS) and with (MS-X) pretreatment (X being the pretreatment temperature in $^{\circ}$ C).

Sample AcO Conv (%) ^a	AcOEt	t Conv./Mass	TGA/DTA Measurement			
	(%) ^a	(⁷ g)	Weight loss (%) ^c	Temp. maximum desorp. (°C)		
MS	22.8	1.52	16.5	71		
MS-70	22.0	1.45	5.4	128		
MS-90	15.2	1.03	4.5	136		
MS-110	14.5	1.00	3.4	145		
MS-140	13.8	0.88	1.8	148		

[a] The mass of catalysts added in schlenk flask is around 15 -18 mg, and thus pure mass of catalyst (excluding water) is around 15 mg.

[b] Conversion of ethyl acetate divided by pure mass of catalyst (excluding water).

[c] Weight lost below 200 °C.



WILEY-VCH

Figure 1. (A)	Thermog	ravimetr	ic	analys	sis (TGA),	(B)	differentia
hermogravimetric	analysis	(DTA)	for	MS	depending	on	pretreatment
emperature. Little	rehydratio	n in the	over	n is re	sponsible fo	r the	slight weight
ncrease at low tem	perature.						

Rehydration experiments were performed in water saturated atmosphere on the sample MS-140. As shown in Table 2 and Figure 2, 0.4 h exposure is enough to fully recover the global water content of the sample MS, with similar desorption pattern. Longer exposure times increase slowly the water content of the sample, reaching 51.8% after 425 h. Catalytic tests of rehydrated samples show that the activity can be fully recovered after 0.4 h rehydration period (Table 2). It indicates that the catalyst is not irreversibly modified upon drying and that the decrease of the reactivity cannot be explained by a structure modification. However, excessive rehydration is harmful to the reactivity, leading to some decrease of the conversion (Table 2). The effect of this excessive water in the catalyst is similar to the one observed with direct introduction in the reactant mixture of liquid water: when 0.1 mL of water is added into the schlenk together with the reactants, the conversion decreases to 4.7%, compared to 22.8% initially. This may be due to the deactivation caused by the hydrolysis of the ester molecules over the catalyst as mentioned by Xi et al. on hydrotalcites catalyst ^[29].

WILEY-VCH

Table 2. Results of catalytic tests and	TGA/DTG measurement as a function
of rehydration time for MS-140.	

-					
Sample	AcOEt	Conv./Mass	TGA/DTA Measurement		
	Conv. (%)	(%g)	Weight loss (%) [°]	Temp. maximum desorp. (°C)	
MS	22.8	1.52	16.5	69	
MS-140	13.8	0.88	1.8	148	
MS-140-R0.4	22.0	1.47	17.1	69	
MS-140-R2.5	16.1	1.21	26.2	64	
MS-140-R24	16.1	1.26	29.0	61	
MS-140-R425	11.2	1.29	51.8	70	

[a] The mass of catalysts added in schlenk flask is 18 mg (except for MS-140 that is 16 mg).

[b] Conversion of ethyl acetate divided by pure mass of catalyst (excluding water).

[c] Weight lost below 200 °C.



DRIFTS analysis

Figure 3 gathers DRIFT spectra of MS and MS-X. Only wavenumbers from 4000 to 1500 cm⁻¹ are shown because they provide information on hydroxyl groups and water stretching and bending. In each spectrum four bands can be observed, at 3740 - 3720, 3672, 3620 - 3200, and 1636 $\mbox{cm}^{-1}.$ The $\nu_{\mbox{OH}}$ band is located at 3737 cm⁻¹ for the stretching of silanols over silica^[51] and at 3720 cm⁻¹ on sepiolite, a magnesium silicate clay^[52,53]. The band observed here at 3740 to 3720 cm⁻¹ is thus assigned to OH stretching of silanols species. The band located at 3672 cm⁻¹ has been ascribed to hydroxyls coordinated to the magnesium (Mg-OH stretching)^[38], as what is observed in sepiolite, antigorites and $talc^{[52,54]}$. The broad band from 3620 to 3200 cm⁻¹ was attributed to OH stretching of adsorbed water^[35,51] either coordinated to magnesium or adsorbed on silanols^[55]. The contribution at 1636 cm⁻¹ was assigned to H-O-H bending vibrations of molecular bound water^[35,38,39,51]. The suggested assignments found in the literature are listed in Table 3.

It can be seen in **Figure 3** that, when increasing the pretreatment temperature, the intensity of the band at 1636 cm⁻¹ and that of the broad band at 3620 to 3200 cm⁻¹ decrease significantly, which is well consistent with the water loss observed with TGA results. As the catalytic performances (Table 1), show a significant decrease in conversion by pretreating the sample from 70 to 140 °C, the spectrum of MS-140 is compared to the one of MS-70, with the curve log(MS-140/MS-70) (**Figure 4**). A sharp band appears at 3732 cm⁻¹, which means that the intensity of this band increases for MS-140 compared to MS-70. However, the band at 3672 cm⁻¹ is quasi not altered.

Thus, accompanying the release of adsorbed water, the intensity of silanol bands (3740 to 3720 cm⁻¹) arises, whereas the intensity of Mg-OH stretching band is not changed, although the bands are revealed and become more apparent.

Table 3. Assignments of Infrared absorption bands of MS comparing with that of sepiolite given in the literature (wavelength in cm⁻¹).

MS	Sepiolite ^[52,53,55,56]	Suggested assignments
3740 - 3720	3720	Si-OH hydroxyl stretch
3672	3680	Internal Mg-OH stretch
3620 - 3200	3620	Mg-OH stretch
	3565	OH-stretch of water coordinated to Mg
	3430	Water OH-stretch
	3230	Water OH-stretch
1717	1710	Eventually a bending mode of water with strong hydrogen bonding
1684	1660 - 1670	Bending of water coordinated to Mg
1651	1656	Bending of zeolite-like water (2 H-bonded)
1632	1630	Bending of zeolite-like water

WILEY-VCH



Figure 3. DRIFT spectra of MS after each pretreatment step. They are taken at the pretreatment temperature.



Figure 4. DRIFT spectra of MS-70 and MS-140, and their subtraction curve.

A more precise assignment can be obtained from comparison with the IR spectra of crystalline magnesium silicates: chysolite, talc, sepiolite. Chrysotile is a 1:1 layered silicate, in which an octahedral brucite-like sheet is covered up by a SiO₄ tetrahedral sheet^[57]. Hence, there are two kinds of Mg-OH, one is at the top of the brucite-like sheet (external Mg-OH) with a stretching frequency of 3695 cm⁻¹, and the other one is at the bottom of the brucite-like sheet next to the silicate one (internal Mg-OH) with a frequency of 3649 cm^{-1[58]}. Only external Mg-OH is accessible to water. On the opposite, talc, is a 2:1

layered silicate. The brucite-like sheet is thus sandwiched between two silicate sheets. The talc is therefore centrosymmetric and exhibits only internal OH with a stretching mode at 3677 cm^{-1[59]}. For our MS sample, the intensity of the band at 3672 cm⁻¹ is not altered while releasing water, this band should therefore be ascribed to internal Mg-OH.



Figure 5. Two dominant modes of adsorption of water on magnesium: (a) adsorption of water on magnesium located at the edge of layer, (b) adsorption of water on magnesium located in defects.

Sepiolite is another kind of layered silicate, with ordered cavities filled with water molecules. For this solid, the bands at 3620 - 3200 cm⁻¹ in mid-IR spectrum were deconvoluted into four bands at 3620, 3565, 3430 and 3230 cm^{-1[52]}. By comparing near-infrared with mid-IR spectroscopy, the authors assigned the band at 3620 cm⁻¹ to OH stretching for hydroxyl group adsorbed on Mg, the one at 3565 cm⁻¹ to the OH stretching of water also coordinated to Mg cation, and bands at 3430 and 3230 cm⁻¹ were assigned to water OH-stretching weakly coordinated to the surface. For the same magnesium silicate, Cannings et al.^[55] ascribed the bands at 3599 and 3532 cm⁻¹ to antisymmetric and symmetric stretching modes of molecular water coordinated to Mg cation at the edges of the channels. Water molecule could be adsorbed and dissociated on Mg²⁺-O²⁻ pairs to form two OH groups associated by H-bonding^[60,61], and these OH groups contribute in a stretching band around 3583 and 3515 cm^{-1[62,63]}. As MSH is a defective structure (Figure 5) in silicate groups, Mg located at the edge or close to the defects of the silicate layer are probably able to adsorb water or exhibit OH groups. The broad bands at 3620 - 3200 cm⁻¹ may result from different contributions such as the stretching of Mg-OH at edge or defects of layer, water OH-stretch linked to magnesium, water OH-stretch adsorbed on Mg-OH or silanols.



Figure 6. Deconvoluted DRIFT spectra of MS and MS-X at the region of 1800 – 1500 cm⁻¹.



Figure 7. The areas of deconvoluted DRIFT spectra at the region of $1800 - 1500 \text{ cm}^{-1}$ evolved with pretreatment temperature.

The experimental bands of water bending modes around 1636 cm⁻¹ are decomposed and fitted with five bands at 1717, 1684, 1651, 1632, and 1613 cm⁻¹ using Gaussian line shape functions (**Figure 6**). The areas for each band evolved with pretreatment temperature (in **Figure 7**). Sepiolite is a structure with several water molecules incorporated in the channel. For this structure, the band at 1710 cm⁻¹ is difficult to attribute, as Frost et al, states that it is not sure that this absorption is done

by water molecule. The band at 1660 - 1670 cm⁻¹ is assigned to water strongly bonded to magnesium cation in sepiolite. Famer et al.^[64] assigned the bands at 1656 and 1630 cm⁻¹ to two distinct water molecules in sepiolite: the former has two OH groups involved in hydrogen bonding, the later only one^[56]. Prost et al.^[56] reported that when sepiolite was dehydrated, a band at 1616 cm⁻¹ appeared. They attributed this band to water molecules connected with weak hydrogen bonds in agreement with physical considerations showing that the wavenumber of water bending vibration should decrease with a decrease in the strength of hydrogen bonding^[65]. Nevertheless an inverse relationship was observed by Kolesov et al. and a low wavenumber of around 1590 cm⁻¹ was ascribed to the bending of water adsorbed on cation and strongly H-bond to structural oxide^[66].

As can be shown from Figure 7, up to 90°C, the bands at 1684, 1651, 1632 and 1613 cm⁻¹ decrease substantially in the same way. Then, beyond 90°C, the band located at 1684 cm⁻¹ does not seem to evolve. The band at 1613 cm⁻¹ is not modified for pretreatment temperatures higher than 110°C. It is possible that the bands at 1651, 1632 and 1613 cm⁻¹ characterize the water interacting with other water molecules or silanols and that the band at 1684 cm⁻¹ characterizes the water molecules interacting with magnesium, therefore more rigid than the one in the H bond network. The evolution of the intensities of this band with pretreatment temperature (Figure 7) can be understood considering two kinds of magnesium presented on Figure 5: the one located on the edge of the clay-like particles and the other one in the defects of the silicate layer, respectively a and b on the scheme proposed Figure 5. Please note that in each site, water molecule can also interact through H-bond with Mg-OH or Si-OH groups but for sake of clarity, these H-bonds are not shown on Figure 5. One of these species may be released up to 90°C while the other one, more strongly bounded is stable up to 140°C.

The evolution of the band located at 1613 cm⁻¹ is more difficult to comment due to controversial assignment in literature. Again two different species must be involved in this contribution, both adsorbed on the H-bond network formed on sites a or b **Figure 5** (not represented). The first one is weakly bonded in agreement with the assignment of Prost et al.^[56] and desorbed at low temperature. The second one is stable above 110 °C and must be linked to water more strongly bonded.

Further work is necessary to confirm these hypotheses and to determine water adsorption energy on both sites.¹H NMR analysis

¹H NMR spectra are obtained for MS and MS-X and shown in **Figure 8**. For sake of comparison, the spectrum of fully dehydrated sample, thus pretreated at 350°C, is also given. Three resonance regions are observed. The broad resonance at 5 ppm can be assigned to adsorbed water^[38,43,51]. The resonance at 1.8 ppm can be attributed to silanol^[51]. And the resonance in the range 0 - 1 ppm can be assigned to Mg-OH^[38].

When increasing pretreatment temperature, the peak at 5 ppm decreases dramatically and the maximum shifts to lower value. Yesinowski et al. found that, for water in mineral, ¹H isotropic chemical shifts of oxygen-bound hydrogen depend

linearly on the O-H··O distance. For instance, two structurally distinct water molecules were observed in nepheline (which is natural aluminosilicate), located at 4.6 and 3.4 ppm, corresponding to O-H O distances of 2.92 and 2.97 Å, respectively. Furthermore, the peak at 5 ppm is assigned to highly mobile water molecules found in fluid inclusions and the broad peak at around 4 ppm is ascribed to a structurally isolated water group^[67]. In our experiments, the highly mobile water molecules are released at low pretreatment temperatures. This desorption leads to higher O-H·O distances, thus the peak is shifted to lower values. Confronting these results to catalytic performances, we can note that the activity of catalyst is not affected by removal of the highly mobile water below 70°C, but the activity decreases significantly for pretreatment temperatures higher than 90 °C when the structurally isolated water molecules at 4 ppm are released.

The silanol resonance at 1.8 ppm appears after the pretreatment at 70 °C and does not shift upon further dehydratation.

On the reverse, the Mg-OH contribution at 0-1 ppm is shifted upon the pretreatements. In the fully hydrated sample, the centre of Mg-OH resonance is located at 0.4 ppm. A moderate thermal treatment releases the highly mobile water and reveals the structurally isolated water molecules that are adsorbed on Mg-OH, shifting the resonance to 0.6 ppm. Then further thermal treatment at 350 °C removes the isolated water molecules and leaves bare Mg-OH, causing a further shift to 0.8 ppm. This is also observed by Nied et al. for the position of the Mg-OH peak which shifts from 0.57 to 0.74 ppm as the amount of water in MSH decreases^[38]. In addition, on MS-350, a new contribution appears at 3.6 ppm that can be related to bridging OH groups formed upon dehydroxylation, as the case of Si-(OH)-Al in zeolite^[68,69].

The appearance of the silanol resonance at 1.8 ppm upon drying at 70 °C is in agreement with DRIFTS experiments showing that the silanol contribution at 3732 cm⁻¹ grows for higher pretreatment temperatures. Concerning the Mg-OH contribution, DRIFT spectroscopy shows clearly that internal Mg-OH (3672 cm⁻¹) are not affected by water adsorption but cannot conclude about the interaction between external Mg-OH and water as the contribution is located in the 3620 – 3200 cm⁻¹ large band. By ¹H NMR, the shift of the Mg-OH band upon dehydration clearly evidences that water desorbs from sites implying Mg-OH groups. Two successive shifts are evidenced at moderated temperature and at 350 °C, that can be related to the successive desorption of water from sites a and b (Figure 5) in which it may interact with Mg-OH groups by H-bonding. This hypothesis is in line with the evolution of water adsorbed IR bands located 1684 and 1613 cm⁻¹ that is discussed above.



Figure 8. ¹H NMR spectra of MS and MS-X.

Calorimetry analysis

Figure 9 shows the adsorption of ethyl acetate on MS and MS-X by calorimetry measurement. The experiments were conducted in solid-liquid phase at 30 °C, measuring the heat released by contacting 3.8 mmol of ethyl acetate with 0.15 g of the sample. The overall heat of adsorption is thus obtained by integration after reaching equilibrium (8 h). Heats of adsorption increase with the pretreatment temperature up to 90 °C. A further increase of pretreatment temperature no longer improves it. There are two dominant modes of adsorption of ester on the surface of MSH, either via its electronegative oxygen in carbonyl group to surface cation^[70] or through a hydrogen bond to OH group^[49]. Similarly, water can also adsorb on surface cation through its nucleophilic properties[70] or on OH group via hydrogen bonding^[71]. Clausen et al. studied the adsorption of ethyl acetate and water on the dry surface of a smectite clay through density functional theory and they showed that adsorption energy of ethyl acetate on sodium cation is close to the one of water^[70]. Even if our system is different, a competition between the adsorption of ethyl acetate and water exists. This

may explain the increase of heat of adsorption of ethyl acetate when releasing water.

The fact that the mean heat of ester adsorption is constant for pretreatment temperature over 90 °C can be understood considering the two sites proposed from IR results for water coordination on Mg cations (a and b on **Figure 5**). At room temperature, both sites are hydrated leading to a low value of heat of adsorption. Up to 90 °C, water is desorbed from one of the sites leading to the decrease of the IR band located at 1684 cm⁻¹ and to a more efficient adsorption of the ester. Over 90 °C no more water is released from these sites as seen by DRIFTS, in agreement with a constant value of the mean heat adsorption measured by calorimetry.



Figure 9. Adsorption heats of ethyl acetate on MS and MS-X. The unit J g^{-1} is Joule per gramme of pure mass of catalyst (excluding water).

Discussion of the structural characterizations and role of water

Combining the analyses of DRIFTS, ¹H NMR and calorimetry, various types of adsorption of water molecules over MSH surface are evidenced.

- Water molecules adsorbed on silanol groups via hydrogen bonding can easily be desorbed, and the uncovered silanol groups are evidenced both by DRIFTS (band at 3732 cm⁻¹) and ¹H NMR (peak at 1.8 ppm).
- Although internal Mg-OH cannot be accessed directly and are therefore not perturbed during dehydratation, water molecules can interact with Mg-OH and/or Mg cations located on the edge of the clay-like particles or in the defects present in the silicate layer. Specifically, the two modes of the water molecules linked to Mg cations (Figure 5 a and b) can be released at different temperatures. The band at 1684 cm⁻¹ in DRIFTS show that one species can be released up to 90°C while the other one, is stable up to 140°C. This observation is consistent with the evolution of the peak at 4 ppm in ¹H NMR (ascribed to isolated water) that decreases up to 90°C and is stable up to 140°C. The adsorption of these two kinds of water molecules competes with that of ethyl acetate on the surface of MSH. The evolution of the mean heat adsorption of ethyl acetate

measured by calorimetry as a function of pretreatment temperature exhibit a comparable shape: it increases up to 90 °C and is stable up to 140°C, in agreement with a two steps water releasing.

Water is known to inhibit the activity of basic catalysts^[15,45,46]. Nevertheless, the above results show that water molecules are beneficial to this reaction. From literature analysis we can formulated three hypothesis to explain the specific role of water in our systems.

- It was reported that in amorphous silica-alumina, water molecules adsorbed on aluminium atoms and interacting with neighbouring silanols can easily be deprotonated and therefore are Brønsted acidic sites^[72,73]. Thus in MSH, magnesium may polarize adsorbed water and form Brønsted acidic sites Figure 5 a and b), which could stabilise the methoxide molecule, or activate ester, directly by bonding to the carbonyl group, or indirectly, favouring the departure of the alkoxyl group as reported by Greenwell et al. for adsorbed water on MgAl-layered double hydroxides^[49].
- Besides, water may also act as an inhibitor of too strong acidic sites that retain too strongly the reactants, especially the ester as shown by calorimetry.
- Moreover, water contained in catalyst can facilitate the migration of methanol due to the high miscibility between water and methanol, as mentioned by several researchers^[28,35]. The removal of this positive water may also affect the conversion of ethyl acetate.

The precise role of this water molecule on the mechanism needs further studies to be elucidated.

Conclusions

Magnesium silicate was thermally treated to remove water adsorbed, and the catalytic performance of this solid before and after pretreatments was tested in the transesterification of ethyl acetate with methanol. Based on DRIFT spectra and ¹H NMR results, the effect of water adsorbed on MS on the conversion in transesterification reaction is the following: highly mobile water molecules released for pretreatment temperature lower than 70 °C have no effect on the reactivity. Then, for pretreatment temperatures between 70 to 90 °C, water molecules that are believed to be bonded to magnesium from their DRIFT spectra and ¹H NMR characteristics are lost, and the conversion for the transesterification reaction decreases markedly. Further increase of the pretreatment temperature only led to a small decrease of the conversion as the number of water molecules bonded to magnesium is maintained. Two kinds of active sites are proposed to be water molecules bonded to magnesium located on the edge or in the defects of the clay-like particles. They role may be to stabilise methanol deprotonated by basic Mg-OH groups, activate ester or help the departure of the alkoxyl moiety. Upon their removal, the adsorption energy of ethyl acetate over the catalyst increases, which mean that the ester can directly be connected to the magnesium ion. Too

strong adsorption energy of the ester is therefore detrimental for its reactivity.

Experimental Section

Catalysts pretreatment

Magnesol® catasorb was kindly provided by the Dallas group of America®. It contains Cl (<0.5%) and Na (<2%) impurities. Here it is denoted as MS. The MS were thermally treated at 70, 90, 110, 140 °C respectively for 2 h after heating at a rate of 5 °C min⁻¹ in 20 mL min⁻¹ of flowing N2. Then they cooled down to room temperature. These samples are denoted as MS-70, MS-90, MS-110 and MS-140, respectively. MS-140 was put in a desiccator with water at bottom for rehydrating. Then the samples were noted as MS-140-Rt, t is the time of rehydration (hour),

Transesterification reaction

Around 18 mg of the catalyst were introduced in a Schlenk flask. Vacuum was performed in the Schlenk flask through a vacuum manifold (10⁻³ torr). Nitrogen (Air liquide 99.99%) was introduced into the Schlenk (1 bar) and then methanol (10 mL, Sigma Aldrich anhydrous 99.8%) as well as 1,4 dioxane (1 mL, Sigma Aldrich anhydrous 99.8%), as standard reference, were introduced through needles into the Schlenk. The temperature of the liquid phase was maintained at 60 °C. The introduction of ethyl acetate (AcOEt, 1 mL, Sigma Aldrich anhydrous 99.8%) determines the initial time of the reaction (t = 0). The molar ratio between the reactants was kept at 24.25. The ratios AcOEt/dioxane was checked at the beginning (t = 0 h) and after 5 hours of reaction (t = 5h) by gas chromatography (Perichrom PR2100 equipped with a FID detector and a CP WAX 57 CB column). To perform these analyses a few drops of reaction mixture were drawn from the Schlenk and diluted in 2 mL of 1-propanol (Sigma Aldrich, ACS reagent). The only detected products were methyl acetate and ethanol; therefore the conversion was calculated through equation 1:

Conv. = $[(AcOEt/dioxane)_{t=0} - (AcOEt/dioxane)_{t=5}] / (AcOEt/dioxane)_{t=0}]$ Pure mass of catalyst that was used to calculate Conv./Mass in Table 1 and 2, was given by equation 2:

Pure mass = mass of catalyst x (100% - weight loss below 200 °C)

Characterizations of the catalysts

Thermogravimetric analysis were carried out on a STD Q600 apparatus from TA® instruments under 20 mL min⁻¹ of N₂ with a ramp rate of 5 °C min⁻¹ up to 400 °C.

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was performed using a Vertex70 Bruker spectrometer with a DRIFTS cell (collector from Spectratech). The sample compartment of the cell was filled with the as-prepared sample (20 mg), which was first heated in situ under Ar flow (20 cm³.min⁻¹) up to 50 °C (5 °C min⁻¹) for 2 h. A first spectrum was taken at this temperature. The sample was then pretreated to 70 °C (5 °C min⁻¹) for 2 h and then the second spectrum was taken at 70 °C. The spectra of samples pretreatment at 90, 110 and 140 °C respectively, were then taken in the same way. All spectra were recorded in situ and were converted into Kubelka-Munk units after subtraction of the spectrum recorded on the dehydrated KBr sample (Fluka, purity > 99.5%).

All the ¹H MAS NMR spectra were recorded at room temperature using a Bruker Advance spectrometer operating in a static field of 11.7 T. The resonance frequency of ¹H were 500.16 MHz. The ¹H chemical shifts were referenced to external standards of tetra-methylsilane (TMS). ¹H MAS NMR spectra are performed with a 90° pulse duration of 2.8 µs, a recycle delay of 5 s, and a scan number of 32. The MAS equipment for rotation was carefully cleaned with ethanol then dried to avoid spurious proton signals. From two successive experiments performed in the same recording conditions and using the same empty or filled rotor, the probe and rotor signals were subtracted from the total FID.

Heat of adsorption measurements were conducted on SETARAM Calvet Calorimeter C80 at 30 °C. 0.15 g of sample was loaded into the sample cell (Membrane Mixing Cell), then a tube with a telfon membrane at the bottom was set up at the top of sample cell, and then 0.38 mmol. of ethyl acetate was added into the tube. After the temperature of sample and the heat energy are stable, the measurement was started by breaking the telfon membrane with a stirrer bar so the sample and ethyl acetate mixed. The stirring rate was kept at 1500 rpm.

Acknowledgements

The authors acknowledge China Scholarship Council (File No.201406140144) for Longfei Lin PhD grant. The cluster of excellence Matisse is thanked for Maya M. Daou Master's degree grant. The NMR experiments have been performed on IMPC (Institut des Matériaux de Paris Centre, FR2482) platform.

Keywords: Transesterification • magnesium silicate • adsorbed water • infrared spectroscopy • NMR spectroscopy

- [1] L. Bournay, G. Hillion, P. Boucot, J.-A. Chodorge, C. Bronner, A. Forestiere, Process for Producing Alkyl Esters from a Vegetable or Animal Oil and an Aliphatic Monoalcohol, 2005, US 6878837 B2.
- S. Gryglewicz, Appl. Catal. Gen. 2000, 192, 23-28.
- [3] [4]
- J. Barrault, F. Jerome, *Eur. J. Lipid Sci. Technol.* 2008, *110*, 825–830.
 F. Jérôme, Y. Pouilloux, J. Barrault, *ChemSusChem* 2008, *1*, 586–613.
 J.-P. Lange, J. Z. Vestering, R. J. Haan, *Chem. Commun.* 2007, 3488.
 R. Jothiramalingam, M. K. Wang, *Ind. Eng. Chem. Res.* 2009, *48*, 6162– [5] [6]
- 6172.
- [7] D.-W. Lee, Y.-M. Park, K.-Y. Lee, Catal. Surv. Asia 2009, 13, 63-77. [8] M. Zabeti, W. M. A. Wan Daud, M. K. Aroua, Fuel Process. Technol. 2009, 90, 770-777.
- [9] S. Semwal, A. K. Arora, R. P. Badoni, D. K. Tuli, Bioresour. Technol. 2011, 102, 2151-2161
- [10] Y. M. Sani, W. M. A. W. Daud, A. R. Abdul Aziz, Appl. Catal. Gen. 2014, 470, 140-161.
- [11] A. L. de Lima, C. M. Ronconi, C. J. A. Mota, Catal Sci Technol 2016, 6, 2877-2891
- [12] G. Vicente, M. Martínez, J. Aracil, Bioresour. Technol. 2004, 92, 297-305
- [13] M. Di Serio, R. Tesser, L. Pengmei, E. Santacesaria, Energy Fuels 2008, 22 207-217
- Z. Helwani, M. R. Othman, N. Aziz, J. Kim, W. J. N. Fernando, Appl. [14] Catal. Gen. 2009, 363, 1-10.
- D. Cornu, H. Guesmi, G. Laugel, J.-M. Krafft, H. Lauron-Pernot, *Phys Chem Chem Phys* **2015**, *17*, 14168–14176. [15]
- M. Kouzu, T. Kasuno, M. Tajika, Y. Sugimoto, S. Yamanaka, J. Hidaka, [16] Fuel 2008, 87, 2798-2806.
- [17] M. Verziu, B. Cojocaru, J. Hu, R. Richards, C. Ciuculescu, P. Filip, V. I. Parvulescu. Green Chem 2008. 10. 373-381.
- [18] J. M. Montero, P. Gai, K. Wilson, A. F. Lee, Green Chem 2009, 11, 265-268
- [19] H. Jeon, D. J. Kim, S. J. Kim, J. H. Kim, Fuel Process. Technol. 2013, 116, 325-331
- M. Kouzu, J. Hidaka, Fuel 2012, 93, 1-12. [20]
- [21] G. Suppes, Appl. Catal. Gen. 2004, 257, 213-223
- A. Brito, M. E. Borges, N. Otero, *Energy Fuels* **2007**, *21*, 3280–3283. [22]
- W. Xie, X. Huang, H. Li, *Bioresour. Technol.* 2007, *98*, 936–939.
 O. Babajide, N. Musyoka, L. Petrik, F. Ameer, *Catal. Today* 2012, *190*, [23]
- [24] 54 - 60
- H. Wu, J. Zhang, Q. Wei, J. Zheng, J. Zhang, Fuel Process. Technol. [25] 2013, 109, 13-18.
- [26] C. S. Castro, D. Cardoso, P. A. P. Nascente, J. M. Assaf, Catal. Lett. 2011, 141, 1316-1323 [27]
- J. F. P. Gomes, J. F. B. Puna, L. M. Gonçalves, J. C. M. Bordado, Energy 2011, 36, 6770-6778.
- Y. Xi, R. Davis, J. Catal. 2008, 254, 190-197. [28]
- Y. Xi, R. J. Davis, J. Catal. 2009, 268, 307-317 [29]
- [30] S. L. Britton, J. Q. Bond, T. W. Root, Energy Fuels 2010, 24, 4095-4096.

ChemCatChem

- FULL PAPER
- [31] H. Hattori, M. Shima, H. Kabashima, Stud. Surf. Sci. Catal. 2000, 130, 3507-3512
- A. Zięba, A. Pacuła, A. Drelinkiewicz, Energy Fuels 2010, 24, 634-645. [33] D. M. Reinoso, D. E. Damiani, G. M. Tonetto, Appl. Catal. B Environ.
- 2014, 144, 308-316. [34] D. Cornu, L. Lin, M. Daou, M. Jaber, J.-M. Krafft, V. Herledan, G. Laugel,
- Y. Millot, H. Lauron-Pernot, Catal. Sci. Technol. 2017, submitted [35] K. Narasimharao, T. T. Ali, S. Bawaked, S. Basahel, Appl. Catal. Gen. 2014, 488, 208-218
- [36] J. Temuujin, K. Okada, K. J. D. MacKenzie, J. Solid State Chem. 1998, 138, 169-177
- [37] J. Temuujin, K. Okada, K. J. MacKenzie, J. Am. Ceram. Soc. 1998, 81, 754-756
- D. Nied, K. Enemark-Rasmussen, E. L'Hopital, J. Skibsted, B. [38] Lothenbach, Cem. Concr. Res. 2016, 79, 323-332.
- [39]
- F. Jin, A. Al-Tabbaa, *Cem. Concr. Compos.* **2014**, 52, 27–33. C. Roosz, S. Grangeon, P. Blanc, V. Montouillout, B. Lothenbach, P [40] Henocq, E. Giffaut, P. Vieillard, S. Gaboreau, Cem. Concr. Res. 2015, 73, 228-237.
- D. R. M. Brew, F. P. Glasser, Cem. Concr. Res. 2005, 35, 85-98. A. G. Kalampounias, N. Bouropoulos, K. Katerinopoulou, S. N. [42]
- [43]
- Yannopoulos, J. Non-Cryst. Solids 2008, 354, 749–754.
 B. L. Phillips, P. C. Burnley, K. Worminghaus, A. Navrotsky, *Phys. Chem. Miner.* 1997, 24, 179–190.
 A. Pedone, F. Palazzetti, V. Barone, J. *Phys. Chem. C* 2017, DOI [44]
- 10.1021/acs.jpcc.7b00708.
- [45] I. M. Atadashi, M. K. Aroua, A. R. Abdul Aziz, N. M. N. Sulaiman, Renew. Sustain. Energy Rev. 2012, 16, 3456-3470. [46]
- A. F. Lee, J. A. Bennett, J. C. Manayil, K. Wilson, Chem Soc Rev 2014, 43, 7887-7916 [47]
- C.-R. Chang, Z.-Q. Huang, J. Li, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2016**, 6, 679–693. H. Petitjean, H. Guesmi, H. Lauron-Pernot, G. Costentin, D. Loffreda, P. [48]
- Sautet, F. Delbecq, ACS Catal. 2014, 4, 4004-4014. [49] H. C. Greenwell, S. Stackhouse, P. V. Coveney, W. Jones, J. Phys.
- Chem. B 2003, 107, 3476-3485.
- M. J. Kim, S. M. Park, D. R. Chang, G. Seo, Fuel Process. Technol. [50] 2010, 91, 618-624.
- M. Tonelli, F. Martini, L. Calucci, E. Fratini, M. Geppi, F. Ridi, S. [51] Borsacchi, P. Baglioni, Dalton Trans 2016, 45, 3294-3304,

- [52] R. L. Frost, O. B. Locos, H. Ruan, J. T. Kloprogge, Vib. Spectrosc. 2001, 27.1-13.
- R. L. Frost, E. Mendelovici, J. Colloid Interface Sci. 2006, 294, 47-52. [53] V. C. (Victor C. Farmer, Infrared Spectra of Minerals, Mineralogical [54]
- Society, 1974.
- F. R. Cannings, J. Phys. Chem. 1968, 72, 1072-1074 [55] [56]
- R. Prost, Spectrochim. Acta Part Mol. Spectrosc. 1975, 31, 1497-1499. [57] J. T. Kloprogge, R. L. Frost, L. Rintoul, Phys. Chem. Chem. Phys. 1999, 1 2559-2564
- M. K. Titulaer, Porous Structure and Particle Size of Silica and [58] Hydrotalcite Catalyst Precursors: A Thermoporometric Study, Faculteit Aardwetenschappen Der Rijksuniversiteit Te Utrecht], [Utrecht, 1993.
- G. J. Rosasco, J. J. Blaha, *Appl. Spectrosc.* **1980**, *34*, 140–144. E. Knözinger, K.-H. Jacob, S. Singh, P. Hofmann, *Surf. Sci.* **1993**, *290*,
- [60] 388-402.
- C. Chizallet, G. Costentin, M. Che, F. Delbecq, P. Sautet, J. Am. Chem. [61] Soc. 2007, 129, 6442-6452. M. Bailly, C. Chizallet, G. Costentin, J. Krafft, H. Lauronpernot, M. Che,
- [62] J. Catal. 2005, 235, 413-422.
- S. Coluccia, L. Marchese, S. Lavagnino, M. Anpo, Spectrochim. Acta [63] Part Mol. Spectrosc. 1987, 43, 1573-1576
- [64] V. C. Farmer, Infrared Spectra of Minerals, Mineralogical Society, London, 1974.
- M. Falk, Spectrochim. Acta Part Mol. Spectrosc. 1984, 40, 43-48. [65]
- B. A. Kolesov, Am. Mineral. 2006, 91, 1039–1048. [66]
- J. P. Yesinowski, H. Eckert, G. R. Rossman, J. Am. Chem. Soc. 1988, [67] 110. 1367-1375.
- J. Jiao, S. Altwasser, W. Wang, J. Weitkamp, M. Hunger, J. Phys. Chem. B 2004, 108, 14305–14310. [68]
- Y. Jiang, J. Huang, W. Dai, M. Hunger, Solid State Nucl. Magn. Reson. [69] 2011. 39. 116-141.
- P. Clausen, W. Andreoni, A. Curioni, E. Hughes, C. J. G. Plummer, J. [70] Phys. Chem. C 2009, 113, 12293-12300.
- [71] A. Krysztafkiewicz, R. Werner, L. K. Lipska, T. Jesionowski, Colloids Surf. Physicochem. Eng. Asp. 2001, 182, 65-81.
- [72] F. Leydier, C. Chizallet, A. Chaumonnot, M. Digne, E. Soyer, A.-A. Quoineaud, D. Costa, P. Raybaud, *J. Catal.* **2011**, *284*, 215–229. J. Blanchard, J.-M. Krafft, C. Dupont, C. Sayag, T. Takahashi, H.
- [73] Yasuda, Catal. Today 2014, 226, 89-96.

This article is protected by copyright. All rights reserved.

WILEY-VCH

Entry for the Table of Contents

FULL PAPER

Two kinds of active sites exist, that are created from the water coordinated to magnesium located on the edge of the clay-like particles or in the defects present in the silicate layer, respectively, which could stabilise methanol deprotonated by basic Mg-OH groups, activate ester or help the departure of the alkoxyl moiety.



Longfei Lin, Damien Cornu[#], Maya Mounir Daou, Cyril Domingos, Virginie Herledan, Jean-Marc Krafft, Guillaume Laugel, Yannick Millot, and Hélène Lauron-Pernot^{*}

Role of water on the activity of magnesium silicate for transesterification reaction

Page No. – Page No.