



Research article

A systematic study of CO methylation by surface methoxy species in different zeolites

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ABSTRACT

Ketene chemistry is a topic of continuous investigation in zeolite catalysis, as it is key to carbon valorization processes towards high value hydrocarbons. Ketene formation typically occurs through CO methylation by a surface methoxy species (SMS) formed at Brønsted acid sites of zeolites. Here, we present a systematic study of SMS carbonylation reactions on all the possible active sites of six of the most commonly used zeolite frameworks: MOR, FER, CHA, MFI, Beta polymorph A (BEA), and FAU. Density Functional Theory (DFT) calculations were performed using the PBE-D3 functional with single point calculations with the ωB97M-D4 functional. The lowest Gibbs free energy barrier obtained for CO methylation by an SMS is 143 kJ mol⁻¹ at the most favorable site of both MFI and MOR zeolites. For MOR, this is the well-known position in the side pocket, which allows for a favorable positioning of the transition state with a high dispersion contribution from the surrounding framework. On FER and BEA zeolites, comparable sites do not exist, and thus higher free energy barriers were obtained. The CHA and FAU zeolites, which present large cavities, showed the highest barriers, indicating their lower activity for this reaction, compared to other reactions with larger molecules. The results were compared to those obtained experimentally, with an overall good agreement in terms of carbonylation rates.

1. Introduction

Ketenes have been suggested to play pivotal roles in reaction mechanisms in many zeolite-catalyzed processes, such as the conversion of syngas and/or methanol to hydrocarbons [1–5] and the formation of acetates through carbonylation of dimethyl ether [6–8]. Since ketenes are highly reactive, identifying them as reaction intermediates is inherently difficult [9,10], and the formation of them often constitutes the rate determining step of the process of carbonylation as schematically depicted in Fig. 1. Here, a surface methoxy species (SMS) is first formed through the reaction of a Brønsted acid site (BAS) with methanol or dimethyl ether (DME) [11–13]. This SMS is subsequently reacting with CO via a Koch-type carbonylation to form a surface bound acetate species (basically physisorbed protonated ketene) that is in equilibrium with ketene within the zeolite pores [9,10,14–16]. While this reaction mechanism and the existence of ketene have been the subject of several studies recently, there are still various aspects that are vividly debated to date. These comprise the influence of the framework type of the zeolite and in particular the existence of special locations within the zeolite,

such as cages or side pockets (e.g. in mordenite) and their influence on the transition state energies [17,18]. Similarly, it has been suggested that 8 member rings (8-MR) play a special role for this reaction providing a unique microporous environment [19–22].

While mordenite (MOR) has been reported to exhibit the highest activity for DME carbonylation [6,7], several other zeolites have also been studied for this reaction, including CHA, FER, FAU, MFI, and Beta polymorph A (BEA), the characteristics of which are given in Table 1. These zeolites thus comprise various channel topologies and range from 8-MR (MOR, CHA, FER), 10-MR (FER, MFI) to 12-MR (MOR, FAU, BEA) (see Fig. 2). Based on the experimentally observed rate, the presence of 8-MR has been identified as the main structural descriptor for catalytic activity in carbonylation.

MOR consists of 12-MR channels of 6.5 × 7.0 Å and 8-MR channels of 2.6 × 5.7 Å, with 6-MR channels in between, like the FER zeolite. Despite having 4 distinguishable T-sites [23], several studies have demonstrated the higher activity of the T3 site [9,17,24,25], which is located in the 8-MR. Boronat et al. [26] investigated the carbonylation of SMS theoretically at several positions in MOR using the ONIOM

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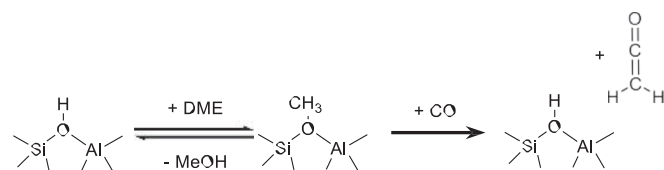


Fig. 1. Overview of the methanol- and dimethyl ether (DME) mediated ketene formation mechanism.

Table 1

Characteristic features of the most used frameworks for carbonylation reactions. Pore sizes and cavity sizes (in Å) correspond to crystallographic [28] and diffusional sizes [29], respectively. Number of T-sites and distinct sites are obtained for the references indicated for each zeolite.

Framework	channels	pore size	cavity	T-sites	n° sites
MOR [23]	12-MR	6.5 × 7.0	—	4	14
	8-MR	2.6 × 5.7			
FER [30]	10-MR	4.2 × 5.4	—	4	11
	8-MR	3.5 × 4.8			
CHA [31]	8-MR	3.8 × 3.8	7.4	1	4
MFI [32]	10-MR	5.3 × 5.6	—	12	48
		5.1 × 5.5			
BEA [33]	12-MR	5.6 × 5.6	6.6	9	32
		6.6 × 6.7			
FAU [34]	12-MR	7.4	11.2	1	4
	SOD*	2.2–2.5	6.3		

*SOD: Sodalite.

scheme for cluster models using B3PW91 functional and semiempirical MNDO.

They found carbonylation to be most favorable at the T3 site for the O33 oxygen (O4 using Meier's notation [23]). This was attributed to a special orientation of the TS in the T3-O33, which is parallel to the 8-MR cylinder axis reaching inside the side pocket of MOR. The T3-O31 site, which is also in the 8-MR channel without an axial orientation to the side pocket, is less selective. Gešvandtnerová et al. [27] used molecular dynamics and came to the same conclusion. They observed that carbonylation of the SMS by CO is more favorable on the 8-MR ring than on the 12-MR by ca. 16 kJ mol⁻¹, which they attributed to long-range dispersion interactions. Chen et al. [8] studied the conversion of DME to MA with *in situ* FTIR, NMR, and MD simulations in MOR. Computed free energy barriers at 165 °C supported that the SMS carbonylation takes place in the 8-MR.

Cheung et al. [6] studied the conversion of DME to methyl acetate proceeding via carbonylation of an SMS over different zeolites, and observed the highest reaction rate for H-MOR (Si/Al = 10:1) (compared to FER or MFI). They also determined that the rates depend on CO pressure, while there is no influence of the DME pressure.

FER has 8-, and 10-MR channels of 3.5 × 4.8 Å and 4.2 × 5.4 Å, respectively, with 6-MR of 2.2–2.6 Å that are inaccessible connecting the 8- and 10-MR channels. Four possible T-site positions can be distinguished: T1 and T2 at the intersection of the 8- and 10-MR, and T3 and T4 sites at the 8- and 10-MR, respectively [30]. In total, 11 possible active sites are identified, reduced by symmetry from a total of 16. The 8-MR can be accessed by structures no larger than n-hexane, with n-pentane being accessible at high pressures, and lower alkanes having a preference for this channel over the 10-MR one [35,36]. Mechanistic studies by Feng et al. [37] applied the ONIOM method to their cluster models, using DFT (Density functional Theory) with the B3LYP/6-31G (d,p) functional for the inner part and molecular dynamics (MD) with AM1 for the outer part to calculate carbonylation barriers. They observed that, while SMS formation from MeOH or DME occurs preferentially on the T-sites located within the 8-MR and 10-MR channels, the reaction of CO with the SMS presented the lowest energy barriers (but higher than SMS formation) at the active sites of the 8-MR located

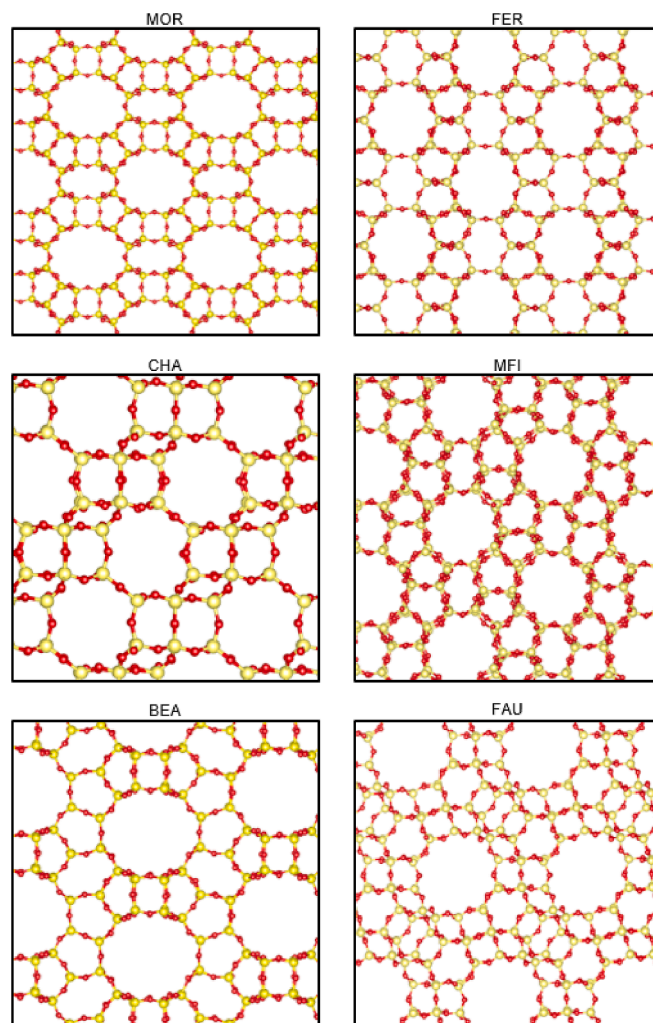


Fig. 2. Investigated frameworks. Color code: Si – yellow, O – red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

in the intersection with the 6-MR channels. The higher activity of 8-MR channels was also proven by Román-Leshkov et al. [38], who observed that an increase of acid site density in the 8-MR channels lead to higher carbonylation rates during DME carbonylation compared to 10-MR channels.

The structure of the CHA framework (H-SSZ-13) consists of an 8-MR with a small-pore entrance of 3.8 × 3.8 Å and interior cavities of 7.4 Å in the channel interceptions. It has a single unique T-site [31] and a small unit cell size, which is why it is widely used for mechanistic studies. Lusardi et al. [39] studied the conversion of DME to methyl acetate at 165 °C over H-SSZ-13. DFT calculations showed that the carbonylation of a SMS occurred with a lower barrier on O1 and O2 oxygen positions (O1 and O3 according to Calligaris numbering [31]), which are the sites located within the 8-MR, rather than in the 6-MR space. This preferential position was also verified in the latter work of Zhang et al. [40].

MFI consists of cage-less interconnected ellipsoidal and sinusoidal 10-MR channels of 5.3 × 5.6 Å and 5.1 × 5.5 Å, respectively, with 12 distinguishable T-sites [32]. The T12 site is typically used in computational studies, as it is thermodynamically stable and accessible, followed by T1, T2 and T7-9, which are located in the intersection of the channels [41–43]. Nevertheless, the preference for a specific site may vary depending on the reaction studied, with differences up to 35 kJ mol⁻¹ between different T-sites [41,44]. While a general preference can not be identified, the T4, T5, T6, T9, and T12 site all have relative low barriers.

Sheik et al. [45] studied the carbonylation of DMM to MMA over MFI zeolite. They reported DMM conversions of between 4.5 and 13 %, increasing with zeolite acidity, and MMA concentrations of up to 36 %. Both, the conversion and product concentration were higher than those observed for FAU type zeolites at comparable conditions (1.5 and 14 %, respectively), contrary to what has been reported by Celik et al. [21,22].

BEA has 12-MR rings of different pore entrance sizes of $5.6 \times 5.6 \text{ \AA}$, and $6.6 \times 6.7 \text{ \AA}$ that intersect without any cage formation. It has 9 different T-sites arranged in a corner sharing system [33], which are located in the 12-MR channels (66 T model [46]) or in the channel intersections (59 T model [47]). The BEA zeolite is mostly used for the methanol-to-hydrocarbons (MTH) process, as its medium pore size with no cavities leads to high selectivity towards gasoline range hydrocarbons, especially those in a favorable range of aviation fuels [48,49]. Regarding carbonylation reactions, dimethoxy methane (DMM) carbonylation was reported to be slower on BEA, MFI and MOR zeolites compared to FAU [21,22]. This reaction occurs by adsorption of the DMM species on a BAS, yielding an adsorbed methoxymethyl species, which has been experimentally detected, as well as MeOH. Subsequently, CO insertion occurs at the adsorbed methoxymethyl to form methyl methoxy-acetate (MMA). Xu et al. [20] studied isobutylene formation via *tert*-butanol carbonylation on MFI, BEA and MOR zeolites. They reported faster conversion of *tert*-butanol with BEA, which they attributed to the dehydration and posterior conversion to oligomers, rather than to faster 2,2-dimethylpropanoic acid formation by carbonylation.

FAU features 12-MR with large pore diameters of $7.4 \text{ \AA}$ that form supercavities of $11.2 \text{ \AA}$ surrounded by SOD (sodalite) cages of $2.2\text{--}2.5 \text{ \AA}$ entrance and $6.3 \text{ \AA}$ diameter. It has one T-site only, which is located at the intersection of the two SOD cages and the 12-MR channel [34]. FAU is often modified with transition metals such as Cu, Ag or Au [50,51] in order to promote carbonylation activity. Celik et al. also studied DMM carbonylation on pure FAU zeolite [21,22] and observed higher MMA formation with FAU zeolite compared to MOR, MFI, FER, or BEA

zeolites, which they attributed to lower available space in the cage-less MOR, MFI and BEA zeolites that instead lead mainly to the formation of DME and methyl formate (MF).

In summary, it is generally accepted that 8-MR containing zeolites are much more active for methanol/DME or DMM carbonylation [17,52]. For example, IR experiments showed higher DME carbonylation rates over MOR and FER zeolites than over BEA, FAU, and MFI zeolites. Moreover, Bhan et al. [17] performed Na^+ exchange on the H-MOR zeolite, which predominantly exchanges sites in the 8-MR over those in the 12-MR. They observed that the higher the Na^+ exchange, the lower the DME carbonylation rate, thus elucidating that the BAS of the 8-MR contribute most to the overall carbonylation rate.

In this work, we theoretically investigate the carbonylation of a SMS with carbon monoxide to ketene for several zeolite frameworks to elucidate their reactivity. We systematically study this reaction at all possible positions (all T-sites and oxygen positions) for the MOR, FER, CHA, MFI, BEA, and FAU zeotypes using periodic DFT calculations. We computed the carbonylation barriers using DFT at the PBE-D3 level for geometry optimization, and higher level $\omega\text{B97M-D4}$ calculations for single point energy calculations.

2. Computational details

DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP), in version 5.4.1 [53,54]. The projector augmented wave (PAW) method [53,55] with standard PAW potentials [56] and k-point sampling only at the Γ -point only was employed. All structures were optimized using the PBE functional [57] with Grimmes D3 dispersion correction (BJ damping) [58] (PBE-D3). A plane wave basis set with an energy cutoff of 400 eV, a Gaussian smearing width of 0.1 eV and a convergence criterion of 0.001 eV/ $\text{\AA}$ were used. Transition states were calculated using the automated relaxed potential surface scans (ARPESS) method [59], whose nature have been verified through the existence of a single imaginary frequency. Vibrational analysis was performed by calculating a partial Hessian that included the adsorbate and the acid site, consisting of the aluminum atom and all adjacent oxygen and silicon atoms (four oxygen and silicon atoms for each active site), with atomic displacements of 0.01 $\text{\AA}$. Since low harmonic frequencies lead to large errors in free energy calculations, we raised the vibrations below 12 cm^{-1} to this value [60]. In previous work using molecular dynamics (MD) simulations, we obtained differences of less than 2.5 kJ mol^{-1} for apparent CO methylation barriers compared to the harmonic approximation [61], thus proving the reliability of the harmonic approximation for this work. For gas-phase species, the rigid rotor and free translator model based on the structures and frequencies obtained with PBE-D3 were used.

DFT calculations were performed employing periodic unit cells of the MOR, FER, CHA, MFI, BEA, and FAU frameworks. The computational models of CHA [12], FER [62], MFI [41], BEA [62], and MOR [62] have been taken from previous works. The FAU unit cell was optimized based on the initial structure extracted from the IZA Database of Zeolite Structures [63] using an energy cutoff of 800 eV and a convergence criterion of 0.001 eV/ $\text{\AA}$, with SCF convergence of 10^{-8} eV. All models contain a $1 \times 1 \times 1$ supercell with one silicon being replaced by aluminum and thus a Si/Al ratios of 35 (CHA), 71 (FER), 47 (FAU), 96, (MFI), 63 (BEA) and 95 (MOR). Brønsted acidity has been introduced through a proton next to the aluminum substitution compensating the charge, hence always one proton per unit cell. The protons can easily shift between the different oxygen atoms [34,64,65], hence all oxygen positions have been studied to correctly identify the preferential active site that yields the lowest reaction energy barrier for a given reaction mechanism. As indicated in Table 1, the following number of sites are considered (after neglecting those that are analogous due to symmetry): CHA and FAU 4 sites in 1 T-site; FER 11 sites in 4 T-sites; MFI 48 sites in 12 T-sites; BEA 32 sites in 9 T-sites; and MOR 14 sites in 4 T-sites. The numbering of atoms in the zeolite structures was adapted from Meier

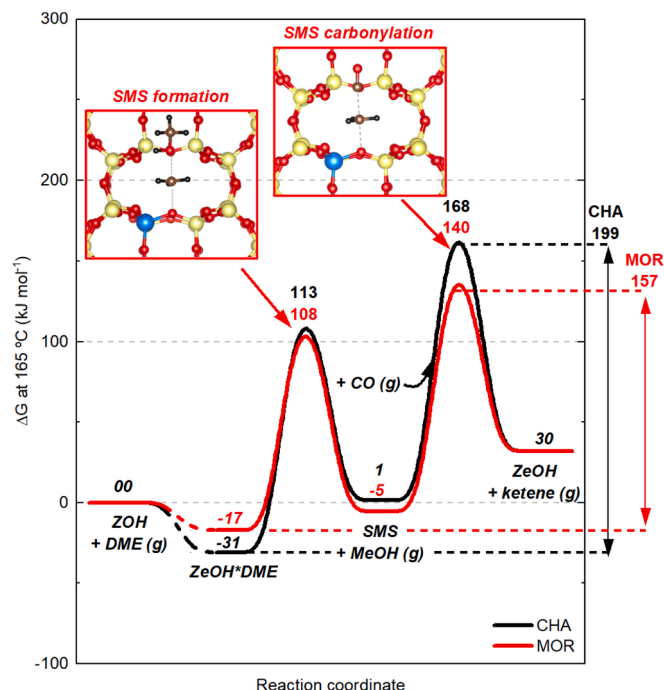


Fig. 3. Gibbs free energy diagram of the SMS carbonylation mechanism over CHA and MOR zeolites at 165 °C and 1 bar with the $\omega\text{B97M-D4}$ functional. Color code: Al – blue, Si – yellow, O – red, H – black, C – brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

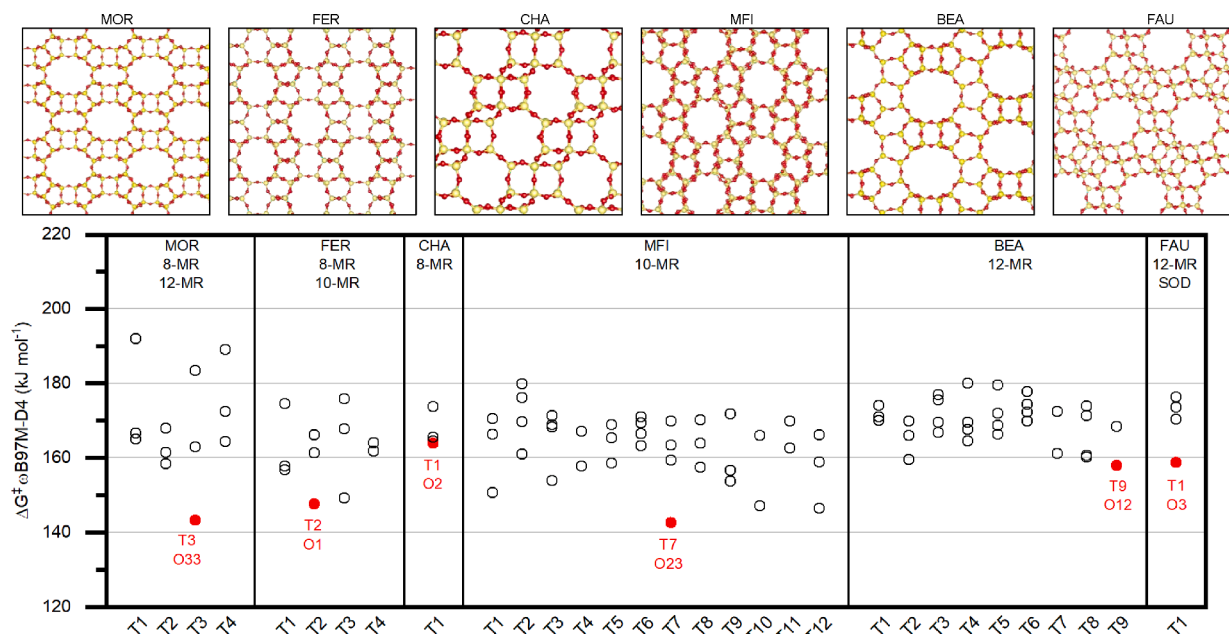


Fig. 4. Gibbs free energy barriers for the SMS carbonylation in MOR, FER, CHA, MFI, BEA, and FAU at 165 °C referenced to SMS with ω B97M-D4//PBE-D3. The best sites are highlighted in red and are labeled. Barriers higher than 220 kJ mol⁻¹ at 165 °C corresponding to sterically unfavorable transition states are not shown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[23] for MOR, from Vaughan [30] for FER, from Olsen et al. [32] for MFI, from Calligaris et al. [31] for CHA, from Sierka et al. [34] for FAU, and from Bare et al. [33] (only T-sites) for BEA. The numbering of oxygen atoms for BEA is defined in this work.

Since DFT calculations employing the PBE-D3 functional underestimate reaction barriers related to the MTH process in zeotypes by an

average of 50 kJ mol⁻¹ [66,67], all energies were corrected by single point calculations employing the ω B97M functional [68] with D4-corrections [69,70] (ω B97M-D4), as implemented in a local VASP version, as this functional has been shown to perform best in a recent benchmarking study, with mean absolute errors well below 8 kJ mol⁻¹ [71].

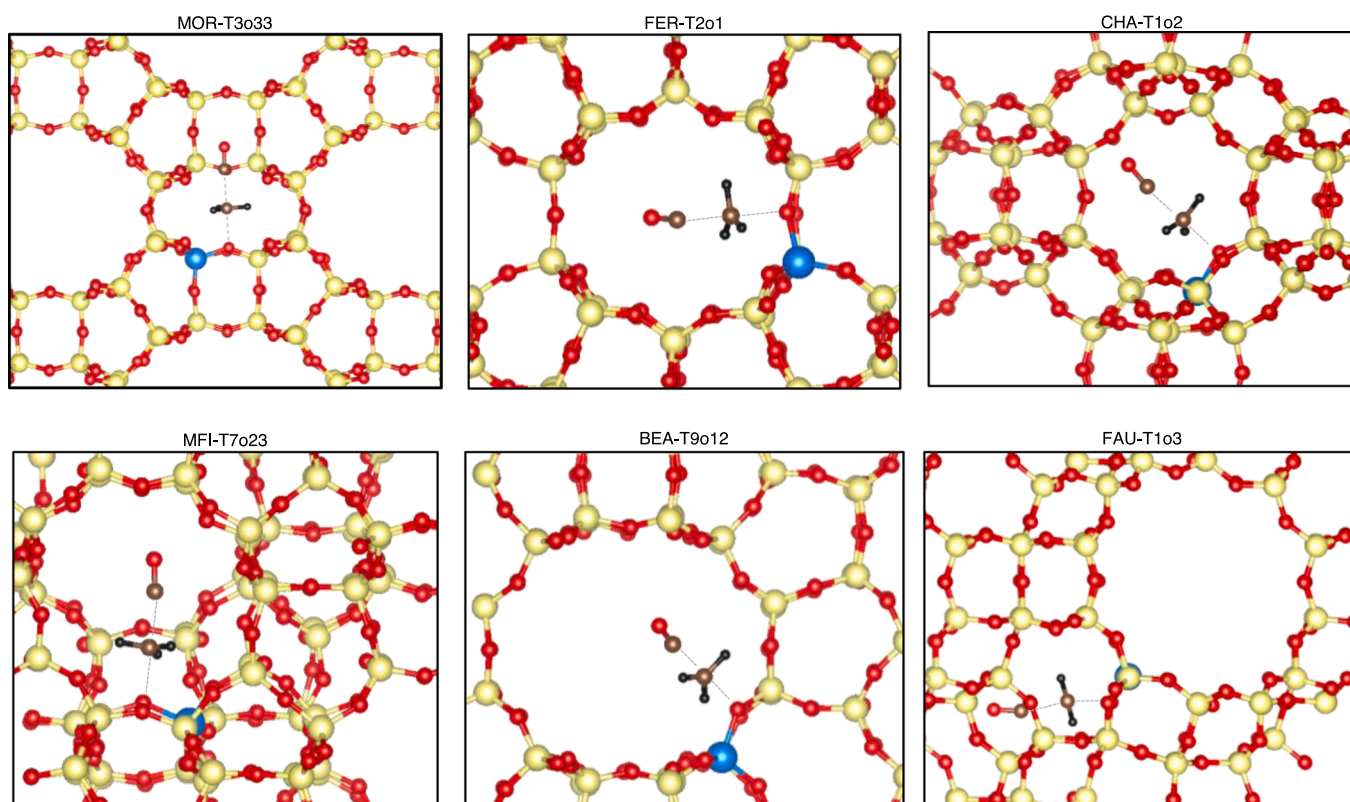


Fig. 5. Most stable transition states at 165 °C. Color code: Al – blue, Si – yellow, O – red, H – black, C – brown. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Gibbs free energies were obtained at 1 bar reference pressure a temperature of 165 °C as:

$$\Delta G_{\omega B97M-D4} = E_{\omega B97M-D4//PBE-D3} + G_{\text{vib-rot-trans}} \quad (1)$$

where $\Delta G_{\omega B97M-D4}$ is the Gibbs free energy using the $\omega B97M-D4$ functional, $E_{\omega B97M-D4//PBE-D3}$ is the potential energy using single point $\omega B97M-D4$ calculation over the optimized structure with the PBE-D3 functional, and $G_{\text{vib-rot-trans}}$ is the term for the vibrational, rotational and translational contributions to the Gibbs free energy.

3. Results

Carbonylation by DME proceeds as introduced in Fig. 2: DME first adsorbs on a clean acid site, is then protonated and transfers its methyl group to create an SMS, while MeOH is formed as a byproduct and is desorbed. The entire reaction pathway is illustrated in a Gibbs free energy diagram in Fig. 3, which compares the two most active sites for CHA and MOR. It can be seen that adsorption of DME is much stronger on CHA, being downhill in free energy by -31 kJ mol⁻¹. For MOR, adsorption of DME is slightly weaker, which we attribute, at least partially, to the confined position in the special side pocket. The formed SMS then methylates CO, to form an intermediate acylium cation, which is quickly deprotonated to give ketene. Ketene easily reacts with methanol or DME to form methyl acetate, which we did not study and include in Fig. 3. It can be seen that the barrier for methylation is the highest for both CHA and MOR and the SMS formation is lower for MOR. Furthermore, the energetic span [72] is shown on the right hand site of the figure, which is even lower for MOR by about 40 kJ mol⁻¹. We studied DME adsorption in other oxygen positions of the T3 site of MOR zeolite, and obtained slightly lower adsorption free energies, but the differences (4–8 kJ mol⁻¹) do not lead to any meaningful change of the conclusions extracted from Fig. 3. When compared with the MFI zeolite, which is shown in Fig. S1 in the Supplementary Information, the adsorption of DME in the most favorable site is similar to that of the CHA, due to the considerable space available in the MFI channels' intersection. Then, the CO methylation proceeds with a slightly lower barrier than for CHA, but still higher than the SMS formation barrier. In the following, we will thus focus on the highest barrier, which is the transition state for methylation of CO.

3.1. Calculating SMS carbonylation barriers

To analyze the results, we will first discuss the impact of the different T-sites and oxygen positions on the SMS carbonylation barrier for each of the zeolites studied. The free energy barriers of the SMS carbonylation for each zeolite are given relative to the zeolite structure with the SMS, and CO in the gas phase and are shown at 165 °C in Fig. 4, with the lowest barrier for each zeolite marked and labeled in red. The temperature of 165 °C is chosen, as it is typically used when studying carbonylation reactions [6,21,22,38,39]. Note that barriers that are higher in free energy than 220 kJ mol⁻¹ at 165 °C correspond to sterically unfavorable TS and are thus omitted in Fig. 4 (a collection of all calculated barriers is given in Table S1 of the SI). We will now discuss the results of the individual zeolites, before an in depth comparison across the frameworks and acid sites.

3.1.1. MOR

The barriers for the carbonylation in the MOR zeolite range from 143 kJ mol⁻¹ to 197 kJ mol⁻¹, with the lowest barrier corresponding to T3o33 as shown in Fig. 4. The particularly low barrier in this site is because the TS is optimally located in the small 8-MR, for which it has a strong dispersion contribution. Moreover, the reaction coordinate is centered across the side pocket, with the SMS in the 8-MR and the CO molecule through the ring wall (see Fig. 5), allowing for an optimal geometry and thus the lowest potential energy and strong dispersion

forces. Precisely because of this special configuration, MOR zeolite is the zeolite of choice for methanol carbonylation [17,24–27], with all studies reporting lower barriers on the sites located in the 8-MR compared to those within the 12-MR. The transition state at the T1o10 site is unfavorable with a barrier over 240 kJ mol⁻¹. The SMS at the T2o12 site is very unstable (see Fig. S2) because the corresponding oxygen atoms are sterically hindered and it is thus not further investigated.

3.1.2. FER

The FER zeolite has four possible T-sites with a different number of oxygen positions for each of them (some of these are similar because of symmetry). For the T1o5 site, the TS takes place in the narrow side pockets of the zeolite, which leads to extremely unfavorable activation free energy (barrier above 300 kJ mol⁻¹), and it is thus discarded from the analysis and not presented in Fig. 4, but is included in Table S1. The T2o1 and T3o2 sites show the lowest barriers, with values of 147.6 and 149.3 kJ mol⁻¹, respectively. The T3o2 site is located in the intersection of the 10- and 8-MR, with the TS oriented towards the side pocket of the 8-MR with the 6-MR. This is in agreement with the existing literature [37,38] in which higher reaction rates were observed by increasing the number of sites in the 8-MR close to the 6-MR intersection, which can be attributed to the strong dispersion forces in the more constrained region of the 6-MR channel.

Nevertheless, the TS in the T2o1 site presents a lower barrier, despite being located in the interchannel of the 10-MR and 8-MR. In this position, as shown in Fig. 5, the TS is oriented parallel to the direction of the 8-MR, which results in a minimum potential energy, with a relatively high contribution from dispersion forces by its proximity to the 8-MR channel wall. The reaction barriers in the other sites are overall 10 kJ mol⁻¹ or more higher, mostly due to higher potential energies caused by the proximity of the cavity walls to the O atom of the CO molecule.

3.1.3. CHA

CHA zeolite is the simplest zeolite of the ones studied here and possesses only one T-site. As shown in Fig. 4, the lowest barrier with a value of 163.8 kJ mol⁻¹ corresponds to the O2 site (see Fig. 5), although barriers in O1 and O3 positions are quite close to this value. For O4, the calculated barrier is around 8–10 kJ mol⁻¹ higher. Over the O4 site, the reaction takes place close to the 6-MR entrance of the cavity, which leads to a less favorable TS, positioned further away from the O atom of the zeolite to avoid the small 6-MR. On the other oxygen positions, the reaction takes place towards the large supercavity of the CHA framework, and thus there is no significant steric hindrance and the barriers are correspondingly lower. These findings align well with previous works [39,40], which reported higher carbonylation barriers close to the 6-MR.

3.1.4. MFI

The MFI zeolite has the highest number of possible active site positions, with 12 T-sites. Eight of these sites present unfavorable barriers above 220 kJ mol⁻¹, and are thus not considered in and Fig. 4. Additionally, there are three sites in which the SMS intermediate is extremely unstable because the corresponding oxygen atoms are sterically hindered, similarly to the case in MOR. The corresponding sites T5o14, T10o10, and T11o10 were hence also not considered for further analysis.

Apart from this, several sites in MFI have relatively low barriers. The T7o23 site has the lowest barrier of 142.3 kJ mol⁻¹. In this active site the potential energy is low, as the CO is allocated centered inside the straight 10-MR channel, as it is shown in Fig. 5, and dispersion forces are strong, with the methyl group being partially stabilized within the 6-MR walls of the straight channel.

The T10o26 and T12o24 sites have also low barriers of 147.1 and 146.5 kJ mol⁻¹, respectively. Similarly to T7o23, the Al atom is part of the straight 10-MR channel, but in this case the reaction takes place within the same channel. Because of this, the surrounding atoms of the

Table 2

Most active sites, leading to lowest barriers, and carbonylation barrier values (with separated contributions) for MOR, FER, CHA, MFI, BEA, and FAU at 165 °C with ω B97M-D4//PBE-D3. Values are given in kJ mol⁻¹.

Framework	MOR	FER	CHA	MFI	BEA	FAU
Site	T3o33	T2o1	T1o2	T7o23	T9o12	T1o3
$\Delta G_{\omega B97M-D4}^\ddagger$	143.3	147.6	163.8	142.6	158.0	158.7
$\Delta E_{\omega B97M-D4}^\ddagger$	86.3	92.1	108.2	90.0	106.7	106.9
$\Delta E_{D4}^\ddagger$	-35.7	-26.4	-23.0	-24.1	-14.4	-29.5
$-T\Delta S^\ddagger$	57.0	55.5	55.6	52.6	51.3	51.8
k_{TST} (10 ⁻³ h)	267.6	82.2	1.0	324.3	4.7	3.9

$\Delta G_{\omega B97M-D4}^\ddagger$: Apparent Gibbs free energy barrier.

$\Delta E_{\omega B97M-D4}^\ddagger$: Apparent energy barrier.

$\Delta E_{D4}^\ddagger$: D4 dispersion contribution to barrier.

$-T\Delta S^\ddagger$: Thermal contributions to barrier at 165 °C.

k_{TST} : rate constant at 165 °C.

channel wall repel the methyl group, which is hence positioned slightly further from the Al atom, eventually increasing the energy barrier. The T1o22 site is in the sinusoidal channel, with the TS oriented perpendicular to the channel. Due to the length of the TS, the CO molecule is slightly tilted in order to fit into the channel, and the potential energy is thus higher compared to the aforementioned sites.

3.1.5. BEA

The BEA zeolite presents five sites with comparable energy barriers. On the T2o6, T7o13, T8o10, T8o17 and T9o12 sites, SMS carbonylation takes place with energy barrier values of around 160 kJ mol⁻¹. The reaction in these sites takes place in the 12-MR channel, which is the largest possible space in the BEA zeolite, and at O atoms pointing towards the channel center. Therefore, the potential energies are lower compared to other sites, that allocate in more constrained spaces within the channel walls (e.g. T3O8 or T6o13 with energies around 17 kJ mol⁻¹ higher). In addition, the reaction coordinate for T7o13, T8o10, T8o17, and T9o12, the latter being the most favorable one with a barrier of 158 kJ mol⁻¹, is positioned in parallel to the channel direction, which allows for a more favorable positioning of the TS (see Fig. 5). For the T2o6 site the TS occurs towards the channel center, leading to a higher potential energy compared to the other two sites.

3.1.6. FAU

Despite having a single possible T-site, the FAU zeolite shows significant differences between its possible oxygen positions. O3 shows the lowest barrier, with a value of 158.7 kJ mol⁻¹, with the other barriers being more than 12 kJ mol⁻¹ higher in free energy compared to O3. At O3, the reaction takes place on the SOD cages surrounding the 12-MR supercavity, as it can be seen in Fig. 5. Because of this, the space is more limited than for the other oxygen positions, which leads to strong dispersion energies of -29 kJ mol⁻¹. This is around 20 kJ mol⁻¹ stronger than for the other O positions, as the reaction in these sites takes place pointing towards the large cavity of the FAU structure. It is also worth mentioning that the TS in T1o2 presents the lowest potential energy of this particular reaction, but could be unfavorable for other reactions, as the O atom is allocated towards the small 6-MR wall of the FAU cavity, and could cause significant steric hindrances.

3.2. Zeolite comparison

We will now compare the reactivity of the different zeolites starting with a comparison of the most active site in each framework. In Table 2 the most active site for each zeolite is displayed, with the corresponding carbonylation barrier, and the different contributions. The optimized transition states are displayed in Fig. 5. The order is as follows: CHA (163.8) > FAU (158.7) > BEA (158.0) > FER (147.6) > MOR (143.3) >

MFI (142.6). With the exception of the MOR framework, the trend is also close to the averaged free energy barriers for every framework. This trend overall agrees with the available literature, with carbonylation reactions taking place more favorably in zeolites with 8-MR, such as MOR, or FER zeolites, on which the CO molecule can allocate with enough space and stabilization with the surrounding framework [17,52].

The differences between barriers are, overall, defined by the potential energy and D4 dispersion contribution, with values ranging from 114 to 136.4 kJ mol⁻¹ for the $\Delta E_{\omega B97M-D4}^\ddagger$, and -14.4 to -35.7 kJ mol⁻¹ for $\Delta E_{D4}^\ddagger$. Although there is no clear trend between the different contributions and the structural features (from Table 1) it can be observed that the MFI and MOR zeolites, which present the two lowest barriers, show the lowest $\Delta E_{\omega B97M-D4}^\ddagger$ and $\Delta E_{D4}^\ddagger$ values, respectively.

The contribution from translation, rotation, and vibration of atoms has low impact on the selection of the T-site with lowest barrier, with values ranging from 51.3 to 57.0 kJ mol⁻¹. Moreover, temperature has no significant effect on the ordering of the sites in terms of their activity as the entropic contributions are very similar across all investigated systems. Fig. S3 shows that the variation in ZPVE is much smaller than that of the thermal corrections at 165 °C. For the two temperatures of interest, 165 °C and 400 °C, Fig. S4 shows that the thermal contributions to the free energy do not change in order so that the assignment of the most active site is temperature-independent in this temperature range. We also investigated the ordering of the activity of the active sites, when evaluated using Gibbs free energies based on PBE-D3 energies. The plot in Fig. S5 shows that only MFI and BEA frameworks show a change in the most active T-site, when switching the functional. The change corresponds to a difference in the resulting total energy values of the transition state, which is in every case below the 5.1 kJ mol⁻¹ mean absolute error reported in our benchmarking work [71] for the ω B97M-D4 functional. The plots in Figs. S6, S7, and S8, show the correlation between the free energy barriers, energy values and dispersion contributions calculated with PBE-D3 and ω B97M-D4, with good agreement of the different points, all being within the ± 10 % lines.

The CHA and FAU zeolites have a single T-site that is located in the large cavity of the structure. In the case of the CHA, the TS in the four O atoms position towards a large 7.4 Å cavity, which leads to little steric hindrance, but also to weak dispersion interactions. For the FAU, three O atoms (O1, O2 and O4) orient towards the even bigger 11.2 Å cavity, while O3 points to a 6.3 Å SOD cage. Due to its larger cavity, FAU is reported to be more active than MOR, MFI, FER, or BEA for carbonylation of bigger molecules like DMM [21,22], on which the smaller space of the cage-less zeolites prevents the favorable positioning of the reactants. But in this case, the small space provided by the SOD cage is enough for carbonylation of the SMS species, and the strong dispersion interaction on O3 leads to a smaller reaction barrier compared to the other possible O positions (see Fig. 4).

BEA also presents a high barrier in its most favorable active site, with a value of 158 kJ mol⁻¹. This zeolite presents no cavities, but instead two different large intersecting channels, which provide several positions with sufficient space to obtain low potential energies. Moreover, the sites exhibiting the lowest barriers for this zeolite have the O atom oriented towards the channel direction, which leads to low potential energies, but also stronger dispersion contributions, as the TS atoms stabilize due to their proximity with the atoms in the channel wall. The FER zeolite does not exhibit this orientation in parallel with the channel direction for any of its sites. Nevertheless, the site with the lowest barrier (147.6 kJ mol⁻¹) orients towards the 10-MR channel, and thus steric hindrance is low. Because this channel is smaller compared to BEA framework channels or the supercavities of the CHA and FAU frameworks, the dispersion forces are strong and thus the barrier is relatively low.

The MFI and MOR zeolites show the sites with the lowest barriers, which are also quite similar in energy, with values of 142.6 and 143.3 kJ

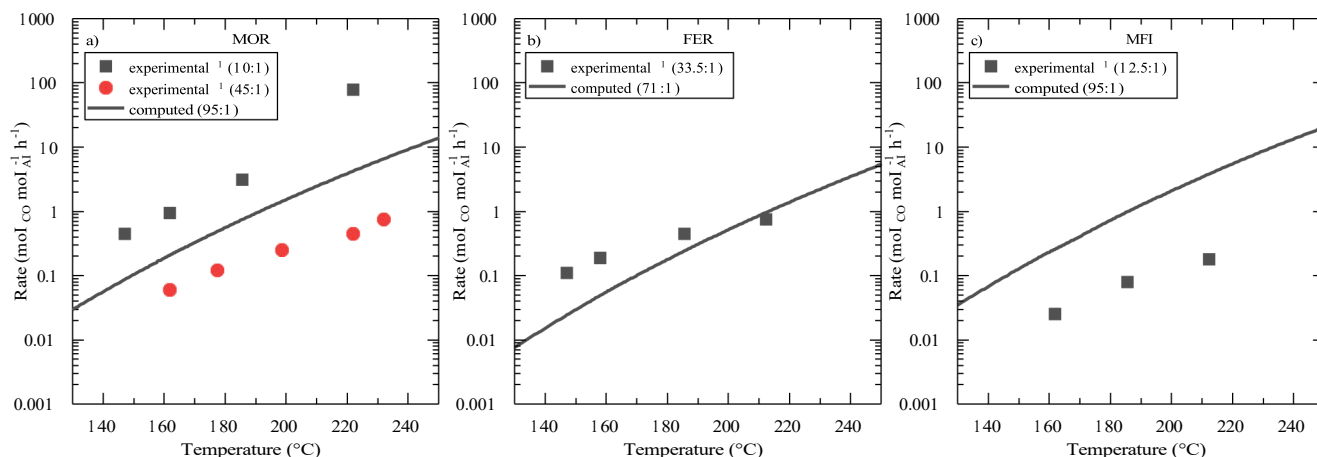


Fig. 6. Comparison of the experimental reaction rates for DME carbonylation and the computed reaction rates for MeOH carbonylation for a) MOR, b) FER, and c) MFI zeolites with ω B97M-D4//PBE-D3. Experimental values are obtained from [6].

mol^{-1} , respectively. In both cases, the reaction occurs in a special position, which is particularly evident in the case of the MOR zeolite, for which the barriers in the rest of sites are more than 10 kJ mol^{-1} higher. In this position part of the reaction takes place through a ring of a side pocket of the main channels (see Fig. 5). The MOR zeolite is extensively used and studied because of this special T3o33 site that permits these particular geometry which leads to low energy barriers especially during carbonylation reaction [6,8,26,27]. Over this site, the SMS is stabilized within the small 8-MR, and the carbon atom of CO allocates in the middle of the side pocket. For MFI, the methyl group of the SMS is stabilized by the side pocket ring and the CO is almost centered in the 8-MR channel. For MOR, the dispersion contribution is greater than for the MFI, ($-35.7 \text{ kJ mol}^{-1}$ and $-24.1 \text{ kJ mol}^{-1}$) as the SMS and CO are perfectly centered across the side pocket. This special geometry is likely particular to the reaction with a small and linear molecule such as CO and the trends in reactivity can thus not be transferred to larger substrates.

Additionally, we compared our values to the experimental values reported by [6] for DME carbonylation over different zeolites. The reaction rates predicted using ω B97M-D4//PBE-D3 results are shown in Fig. 6 and are in the same order of magnitude as the rates observed experimentally and the temperature-dependence also agrees very well. Note, that the Al/Si ratio employed in our study are somewhat different than those employed experimentally, all being rather high, owing to the use of periodic computational models with one Al substitution per unit cell. The corresponding results based on PBE-D3 are shown in Fig. S9 and are three to four orders of magnitude higher, which demonstrates the better accuracy of the ω B97M-D4//PBE-D3 correction.

4. Summary and conclusion

This work provides a unified theoretical analysis of the carbonylation activity for several zeolite frameworks, where each active site has been investigated. This allows to compare the activity of different zeolites at the same level of theory. Furthermore, we employ the range-separated hybrid functional ω B97M-D4, which was previously shown to be highly accurate for acidic zeolites in general and for carbonylation in particular for H-SSZ-13 [71]. The difference in barriers between the zeolites is mainly due to the variations in the activation energy, while the contributions from the thermal motion of the nuclei is similar. For MOR, there is a strong contribution from the D4 dispersion correction (-36 kJ mol^{-1}), which is mostly in the range of -25 kJ mol^{-1} for the other zeolites.

Our calculations confirm the well-known high activity for the special site in the side-pocket of MOR, where we find a barrier of 143 kJ mol^{-1} at 165°C . The computed barrier for FER is only slightly higher (148 kJ

mol^{-1}) in agreement with the known high activity for FER. Surprisingly, we also found very active sites in MFI, where the T7o23 site has the same barrier height as that found for MOR, being only 143 kJ mol^{-1} . The 12-MR zeolites BEA and FAU give barriers of 158 and 159 kJ mol^{-1} , which are thus only 15 kJ mol^{-1} higher than in MOR. This difference in barriers would only decrease the rate constant by a factor of about $1/60$, which could be enough to explain the lack of activity observed for FAU and BEA previously [6,24]. We were surprised, however, by the relatively small difference in barriers for the most favorable sites across the different frameworks. Here it is important to recall that it is not always clear to which extent the respective sites are present. Additionally, in experiments, poisoning by oxygenates was found to be important and the extent of this effect may well differ between the different zeolites. Another factor is Si/Al ratio, which was shown to have a pronounced effect on activity for MOR and is not considered here.

Lastly, we want to point out the important role of the electronic structure method. Using PBE-D3 instead of ω B97M-D4//PBE-D3, we obtain barriers which are about 35 kJ mol^{-1} lower, giving rates, that are three to four orders of magnitude higher. Furthermore, the observed trends between the zeolites are smaller and partially reverse. The lowest barrier in MFI (113 kJ mol^{-1}) is then lower than that in MOR (119 kJ mol^{-1}). The barriers for FAU and BEA (122 and 127 kJ mol^{-1}) are also lowered and the difference between MOR and FAU (3 kJ mol^{-1}) is insignificant.

Full, quantitative prediction of the carbonylation activity will require knowledge of the actual Al-siting, both in terms of T-site, but also proximity. Furthermore, poisoning effects by oxygenates and water need to be considered in addition to diffusion limitations of reactants and products.

CRediT authorship contribution statement

Hector Vicente: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Philipp Huber:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Felix Studt:** Writing – original draft, Validation, Supervision, Resources, Project administration, Funding acquisition. **Philipp N. Plessow:** Writing – original draft, Validation, Supervision, Software, Resources, Project administration, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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Appendix A. Supplementary data

Total PBE-D3 and ω B97M-D4 energies, reaction barriers, free energy, and dispersion contributions. Cartesian coordinates and vibrational frequencies. Supplementary data to this article can be found online at <http://doi.org/10.1016/j.jcat.2026.117177>.

Data availability

Data is provided as supporting information.

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