Electronic Supplementary Information

Towards molecular control of elementary reactions in zeolite catalysis by advanced molecular simulations mimicking operating conditions

Kristof De Wispelaere, Simon Bailleul and Veronique Van Speybroeck*

Center for Molecular Modeling (CMM), Ghent University, Technologiepark 903, B-9052 Zwijnaarde, Belgium

^{*}Corresponding author: veronique.vanspeybroeck@ugent.be

Contents

1.	Catalyst models S3
2.	Time-averaged cell parameters S4
3.	Details on the metadynamics simulations S5
4.	Calculated adsorption energies for benzene and propene in AFI S8
5.	Temperature influence on histograms of hydrocarbon orientation in H-SAPO-5
6.	Histograms of hydrocarbon orientation with extra protic molecules
7.	Bridging hydroxyl group bond distance
8.	Influence of temperature on the reactivity indices S12
9.	Convergence of reactivity indices
10.	Influence of acid strength on methoxide formation S14
11.	FES and snapshots metadynamics simulations with 1 MeOH molecule
12.	Orientation of guest molecules during methylation reactions with 1 MeOH molecule S20
13.	FES and snapshots metadynamics simulations with 2 MeOH molecules
14.	Videos from the MTD simulations
Refe	erences

1. Catalyst models



Figure S1 (a) 1x1x2 super cell representing the AFI topology. (b) 1x1x3 super cell representing the TON topology. Each super cell contains one Brønsted acid site. (c) Comparison of the ring size of the AFI and TON zeolites.

2. Time-averaged cell parameters

For each combination of a catalyst material, guest molecules and temperature an NPT MD simulation has been performed around ambient pressure. From these NPT runs, the time-averaged super cell volume and corresponding cell parameters have been calculated.

Material	Loading	т (°С)	V (ų)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
H-SSZ-24	1 MeOH, 1 BZ	350	2804.02	13.88	13.88	16.81	90	90	120
		250	2797.53	13.86	13.89	16.78	90	90	120
	1 MeOH, 1 C ₃	350	2803.27	13.87	13.89	16.81	90	90	120
		250	2792.04	13.86	13.87	16.78	90	90	120
	2 MeOH, 1 BZ	350	2804.28	13.93	13.931	16.69	90	90	120
	2 MeOH, 1 C $_3$	350	2800.94	13.86342	13.87	16.82	90	90	120
H-SAPO-5	1 MeOH, 1 BZ	350	2894.70	14.00	14.08	16.96	90	90	120
		250	2878.60	13.98	14.06	16.92	90	90	120
	1 MeOH, 1 C ₃	350	2888.67	13.99	14.07	16.95	90	90	120
		250	2884.20	13.98	14.06	16.94	90	90	120
	2 MeOH, 1 BZ	350	2892.30	14.00	14.07	16.96	90	90	120
	2 MeOH, 1 C ₃	350	2890.51	13.99	14.07	16.95	90	90	120
H-ZSM-22	1 MeOH, 1 BZ	350	3818.28	14.15	17.65	15.29	90	90	90
	1 MeOH, 1 C ₃	350	3813.07	14.17	17.61	15.28	90	90	90

Table S1 Time-averaged cell volume (v) and cell parameters (a, b, c, α , β , γ)

3. Details on the metadynamics simulations

We performed metadynamics (MTD) simulations to assess the reactivity of the co-adsorbed complexes and calculate free energy barriers. From an earlier kinetic MD study on benzene methylation in H-ZSM-5 we know that typical intrinsic rate coefficients are in the range of 10° - 10° s⁻¹ for this reaction. This means that very long time scales would be required to sample such reaction with regular MD. For this reason, chemical reactions are also referred to as 'rare events'. Accelerated MD schemes have been developed to alleviate the sampling of rare events with MD. In this study we opted to use the metadynamics scheme, originally developed by Laio and Parrinnello.^{1, 2} By adding Gaussian hills to the free energy surface along a certain number of collective variables the system is forced to cross the free energy barrier that separates reactants and products. As such, time in a MTD simulation no longer has a physical meaning as the bias potential that is being constructed on the fly accelerates the dynamics. A recent study of Tiwari and Parrinello has been devoted to a scheme to translate metadynamics results back to regular dynamics with physical time to extract rate coefficients.³ In general, the metadynamics approach is able to efficiently sample all degrees of freedom that are perpendicular to the reaction coordinate.^{1, 2, 4-8} Furthermore, as stated in the Materials and Methods section of the manuscript, the reported free energies were calculated as the mean free energy over the part of the simulation where the barrier height starts to fluctuate around a mean value and the dynamics along the reaction coordinate become diffusive. In our MTD approach we gradually lowered the height of the Gaussian hills to ensure convergence of the free energy profile. The statistical errors as reported in Table 1 of the manuscript were computed as the standard deviation of the mean after removal of correlated data values. The MTD simulations were continued until a statistical error lower than 5 kJ/mol on the barrier height was obtained. This resulted in total simulation times varying between 50 and 140 ps. Note however that these simulation times do not reflect physical time scales as described above.

During the two-dimensional metadynamics simulations some walls have been applied on the collective variables to constrain the simulation to the region of interest. An overview is given in Figure S2.



Figure S2 Walls applied to constrain the MTD simulations to an area of interest.

For the **concerted** methylation the following quadratic walls have been applied (with K the force constant):

• $0.04 \le CN1$ with K = 50 a.u. to prevent the formed water molecule to diffuse to far from the methyl group. This is done to enhance barrier recrossings.

- $0.03 \le CN2 \le 0.72$ with K = 200 a.u. and K = 15 a.u. The first wall prevents the hydrocarbon and methanol molecule to diffuse too far away from each other. The second wall prevents the full sampling of the methylated product. Upon methylation, not the most stable carbocation is formed. At high temperature, rapid H-shifts enable the spontaneous isomerization to more stable carbocations, which has to be prevented to enhance barrier recrossings in view of obtaining good statistics.
- $CN3 \le 0.3$ with K = 15 a.u. to prevent the formation of methoxides.
- Methanol was forced to stay close enough to the proton of the BAS by requiring that the corresponding coordination number CN(Om-Hz) always exceeds the value 0.03 with K = 100 a.u.

For the **first step of the stepwise methylation** – i.e. methoxide formation – the following quadratic walls have been applied (with K the force constant):

- 0.04 ≤ CN1 with K = 50 a.u. to prevent the formed water molecule to diffuse to far from the methyl group. This is done to enhance barrier recrossings.
- 0.03 ≤ CN3 with K = 200 a.u. to prevent that the methanol molecule diffuses too far away from the BAS.
- Methanol was forced to stay close enough to the proton of the BAS by requiring that the corresponding coordination number CN(Om-Hz) always exceeds the value 0.03 with K = 100 a.u.

For the **second step of the stepwise methylation** – i.e. methylation from a methoxide – the following quadratic walls have been applied (with K the force constant):

CN2 ≤ 0.72 with K = 15 a.u. to prevent the full sampling of the methylated product. Upon methylation, not the most stable carbocation is formed. At high temperature, rapid H-shifts enable the spontaneous isomerization to more stable carbocations, which has to be prevented to enhance barrier recrossings in view of obtaining good statistics.

4. Calculated adsorption energies for benzene and propene in AFI

A rough estimation of the interaction energy between the AFI framework and benzene or propene was made by performing static optimizations at 0 K with a similar level of theory as adopted during the MD simulations. As we are mainly interested in the interactions with the channel walls and not in π -H interactions, benzene and propene were placed in the two AFI super cells such that there is no interaction with the acid site. In we report the resulting potential energies of adsorption calculated as $\Delta E = E_{complex} - E_{framework} - E_{hydrocarbon}$

Table S2 Electronic adsorption energy (kJ/mol) for benzene (BZ) and propene (C3⁼) not adsorbed on the acid site in H-SSZ-24 and H-SAPO-5 (Level of theory: revPBE-D3).

	H-SSZ-24	H-SAPO-5
	ΔE [kJ/mol]	ΔE [kJ/mol]
BZ	-72.6	-63.5
C ₃ ⁼	-39.2	-27.3

The interaction strength between the framework and the hydrocarbon molecules is roughly 10 kJ/mol stronger in the more acidic H-SSZ-24 material.

5. Temperature influence on histograms of hydrocarbon orientation in H-



SAPO-5

Figure S3 Two-dimensional normalized histograms displaying the orientation of co-adsorbed benzene and propene in H-SAPO-5 at 350 °C (a,b) and 250 °C (c,d) with 1 methanol molecule during a 50 ps MD simulation around ambient pressure.



6. Histograms of hydrocarbon orientation with extra protic molecules

Figure S4 Two-dimensional normalized histograms displaying the orientation of co-adsorbed benzene and propene in H-SSZ-24 (a,b) and H-SAPO-5 (c,d) with 2 methanol molecules at 350 °C during a 50 ps MD simulation around ambient pressure.

7. Bridging hydroxyl group bond distance

During the performed MD simulations, the bond length of the Brønsted acidic hydroxyl group has been measured and the resulting non-normalized probability distribution is displayed in Figure S5. The curved for the two zeolites, namely H-ZSM-22 and H-SSZ-24 almost completely overlap, indicating that they exhibit a similar acid strength. For H-SAPO-5, the distribution of the bond length is shifted towards smaller values, confirming the lower acid strength of H-SAPO-5.







8. Influence of temperature on the reactivity indices

Figure S6 Two-dimensional normalized histograms of the α and γ angles, defining the orientation of co-adsorbed benzene with respect to the channel axis and the orientation of methanol and benzene with respect to each other in H-SSZ-24 (a,b) and H-SAPO-5 (c,d) with 1 methanol molecule at 250 °C (a,c) and 350 °C (b,d) during a 50 ps MD simulation around ambient pressure. The green areas indicate where pre-reactive complexes can be formed (α > 30° and γ > 30°), including the corresponding probability that α > 30° and γ > 30°.

9. Convergence of reactivity indices

We performed 50 ps regular MD simulations in the NPT ensemble. The aim of these MD simulations was to assess the behavior of methanol with benzene or propene in different materials at different temperatures. A measure that indicates whether the simulated time scale gives sufficient data for good statistics is the convergence of the quantities of interest. To illustrate this we show the evolution of the calculated probabilities for methanol protonation and the probability that a pre-reactive complex for methylation is formed during the last 5 ps of a 50 ps MD simulation of methanol and benzene in H-SSZ-24 at 350 °C (Figure S7). From S7 is becomes clear that the two quantities are relatively good sampled as no large variations of the calculated probabilities can be observed. Consequently, it is fair to assume that the applied time scales for the simulation are sufficient for our purposes. Moreover, when sufficient convergence of the quantities and properties of interest are achieved, longer ab initio molecular dynamics simulations would signify an unnecessary additional computational cost. To study phenomena that occur on longer time scales like chemical reactions and diffusion much longer time scales are required as these can be classified as rare events (*vide infra*).^{9,10}



Figure S7. Convergence of the probability of methanol protonation and pre-reactive complex formation for methanol and benzene co-adsorbed in H-SSZ-24 at 350 °C.

10.Influence of acid strength on methoxide formation

As mentioned in the discussion of the results in Table 1 for methoxide formation in the two AFI materials, we cannot observe a significant influence of acid strength on the free energy barrier for methoxide formation. This conclusion can be further strengthened by comparison with earlier reported values obtained with the same methodology. In H-ZSM-5 at 350 °C, a free energy barrier for methoxide formation from a single methanol molecule of 160 ± 5 kJ/mol was reported ¹¹ and in H-SAPO-34 at 330 °C this barrier was found to be 167 ± 4 kJ/mol.¹² It appears that the free energy barriers for methoxide formation in both AFI materials at 350 °C as tabulated in Table 1 (160 ± 3 for H-SSZ-24 and 162 ± 3 for H-SAPO-5) are very similar to these earlier reported values. In H-ZSM-22, a lower free energy barrier has been found (148 ± 3 kJ/mol), indicating that the 10-ring sized pores offer a slightly better stabilization for this reaction.

11.FES and snapshots metadynamics simulations with **1** MeOH molecule



Figure S8 Legend for the interpretation of the free energy surfaces of benzene and propene

methylation shown in the following figures.



Figure S9 Free energy surfaces for the concerted and stepwise benzene and propene methylations in

H-SSZ-24 at 250 °C and 350 °C.



Figure S10 Free energy surfaces for the concerted and stepwise benzene and propene methylations

in H-SAPO-5 at 250 $^{\circ}\mathrm{C}$ and 350 $^{\circ}\mathrm{C}.$



Figure S11 Free energy surfaces for the concerted and stepwise benzene and propene methylations

in H-ZSM-22 at 350 °C.



Figure S12 Snapshots of barrier crossings during MTD simulations of the concerted benzene methylation and first step of the stepwise pathway (methoxide formation) in H-SSZ-24, H-SAPO-5 and H-ZSM-22 at 350 °C by a single methanol molecule.

12. Orientation of guest molecules during methylation reactions with 1 MeOH molecule



Figure S13 Variation of the geometrical parameters α , β , γ and Δ during the methylation of benzene and propene by a single methanol molecule (concerted) or a methoxide (stepwise) in H-SSZ-24, H-SAPO-5 and H-ZSM-22 at 350 °C.

Figure S13 displays the orientation of the guest molecules in the AFI and TON channels during a short timeframe of the 2D metadynamics simulations of the concerted benzene methylation with 1 methanol molecule at 350 °C in H-SSZ-24, H-SAPO-5 and H-ZSM-22. The timeframe starts and ends 50 fs before and after the first barrier crossing. It can be seen from the changes in angles α and β that benzene needs to adopt a favorable orientation with respect to the channel walls during the course of the reaction. Also the angle γ and distance Δ change, as the methyl group has to approach the benzene ring. From this analysis, we can further rationalize the choice of the applied criterion for pre-reactive complex formation, i.e. $\Delta > 0.5$ Å, $\alpha > 30^{\circ}$ and $\gamma > 30^{\circ}$. Prior to the barrier crossings, all of these criteria have to be met for all simulated reactions. Note that the curves in Figure S13 do not start from the co-adsorption hotspots – i.e. the most stable configurations in the reactant valley – but are just taken 100 fs prior to the TS.



Figure S14 shows the regions in which α and β are situated during the course of the reactions.

Figure S14 Range of the angles α and β adopted along the reaction paths sampled with metadynamics for benzene and propene methylation by 1 methanol molecule in H-SSZ-24, H-SAPO-5 and H-ZSM-22 at 350 °C. The location of the co-adsorption hotspots from MD are indicated with arrows.

13.FES and snapshots metadynamics simulations with 2 MeOH molecules



Figure S15 Free energy surfaces for the concerted benzene methylation and methoxide formation in H-SSZ-24 and H-SAPO-5 at 350 °C with 2 methanol molecules.



Figure S16 Snapshots of barrier crossings during MTD simulations of the concerted benzene methylation and first step of the stepwise pathway (methoxide formation) in H-SSZ-24 at 350 °C in the presence of an additional methanol molecule. Snapshots in which the additional protic molecule is not playing an active role and snapshots in which it does are displayed.



Figure S17 Snapshots of barrier crossings during MTD simulations of the concerted benzene methylation and first step of the stepwise pathway (methoxide formation) in H-SAPO-5 at 350 °C in the presence of an additional methanol molecule. Only snapshots in which the additional protic molecule is playing an active role are displayed.

14.Videos from the MTD simulations

Attached to this ESI a selection of videos is provided showing fragments of the metadynamics simulations.

- Benzene methylation in H-SSZ-24 at 350 °C by 1 methanol molecule (file: SSZ24_1MeOH_BZ_350C_concerted.mpg)
- Benzene methylation in H-SSZ-24 at 350 °C by a methoxide (file: SSZ24_1MeOH_BZ_350C_step2.mpg)
- Benzene methylation in H-ZSM-22 at 350 °C by 1 methanol molecule (file: ZSM22_1MeOH_BZ_350C_concerted.mpg)
- Benzene methylation in H-ZSM-22 at 350 °C by by a methoxide (file: ZSM22_1MeOH_BZ_350C_step2.mpg)
- Methoxide formation in H-SSZ-24 at 350 °C from 1 methanol molecule (file: SSZ24_1MeOH_BZ_350C_step1.mpg)

These videos visualize the trajectories around the transition points displayed in Figure 5 of the manuscript and show how the guest molecules reorient prior to and during reaction. Because the mobility is quite similar in H-SAPO-5 and H-SSZ-24, only videos of H-SSZ-24 are shown. Moreover, only benzene methylation is shown because for this molecule the most important differences could be identified. It becomes clear that the mobility is indeed much higher in AFI materials compared to TON materials.

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