Supporting Information

Toward a comparative description between transition metal and zeolite catalysts for methanol conversion

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1. Additional Computational Details

For atomistic models, we employed 8-ring cage zeolites (including SAPO-34, SSZ-13, SAPO-18, RUB-50, DNL-6) and some zeolites with tunnel structure, such as ZSM-5, the mordenite and ZSM-22 with 10mr window in one-dimensional structure. The SAPO-34 (a=b=c=9.416 Å, $\alpha=\beta=\gamma=94.28^{\circ}$) and DNL-6 (a=b=c= 15.031 Å, $\alpha = \beta = \gamma = 90^{\circ}$) model were respectively derived from CHA (1×1×1) and RHO $(1 \times 1 \times 1)$ unit cell[1], in which all Si atoms were substituted by P and Al atoms alternatively and one P atom was replaced by Si atom. For comparison to SAPO-34, the SSZ-13 (a=18.842 Å, b=c=9.421 Å, $\alpha = \beta = \gamma = 94.2^{\circ}$) model with the same topology was built by a (2×1×1) supercell, where one Si atom was substituted by Al atom. A $(1 \times 2 \times 1)$ AEI cell[1] with one P atom substituted by Si atom constructed to study a SAPO-18 (a=13.711 Å, b=25.463 Å, c=18.571 Å, $\alpha=\beta=\gamma=90^{\circ}$) zeolite. The unit cell of RUB-50 $(a=b=13.338 \text{ Å}, c=23.014 \text{ Å}, \alpha=\beta=90^{\circ}, \gamma=120^{\circ})$ and ZSM-5 (a=20.090 Å, b=19.738 Å, c=13.142 Å, c=13.142 Å) $\alpha = \beta = \gamma = 90^{\circ}$ zeolites were derived from LEV and MFI structures[1], respectively. A (1×1×1) cell was used for both RUB-50 and ZSM-5. ZSM-22 (a=14.105 Å, b=17.842 Å, c=10.512 Å, $\alpha = \beta = \gamma = 90^{\circ}$) and MOR (a=18.256 Å, b=20.534 Å, c=15.084 Å, $\alpha = \beta = \gamma = 90^{\circ}$) zeolites, with TON and MOR topology[1], respectively, were modeled by a $(1 \times 1 \times 2)$ supercell. For RUB-50, ZSM-5, ZSM-22 and MOR, one Si atom was substituted by Al per supercell. Here, the straight and sinusoidal 10mr channels of ZSM-5 and the 12mr channel, 8mr side pocket, 12&8 intersection of the mordenite were considered and named as ZSM-5_{straight}, ZSM-5_{sinusoidal}, MOR12, MOR8 and MOR12&8, respectively. In our simulation for zeolites, all atoms were allowed to relax with the lattice constant fixed. In addition, the (211) surface of metals (Ni, Pd, Cu and Ag) consisting of four-layer 3×3 slabs were built. The upmost two layers of slab were relaxed with the adsorbates, while the other two layers fixed. For avoiding interactions between images, a vacuum region of about 15 Å was introduced along the z-direction.

The convergence force was set to be 0.05 eV/Å in convergence criterion. The cut-off energies for zeolites and metals were specified to 400 eV and 450 eV, respectively. The cut-off energy of 450 eV specified in zeolite system was tested and the difference in adsorption energies is less than 0.05 eV. Thus, the calculations with an energy cut-off at 400 eV in zeolite system are sufficient, which is expected to decrease the cost. Besides, the $(3\times3\times3)$, $(1\times3\times3)$, $(2\times1\times1)$, $(2\times2\times1)$ and $(2\times2\times2)$ *k*-point grids with the Gamma-centered scheme were used for SAPO-34, SSZ-13, SAPO-18, RUB-50 and DNL-6, respectively.

For ZSM-5, MOR and ZSM-22 zeolites, a $(1 \times 1 \times 1)$ *k*-point sampling was used for the Brillouin zone integration, and $(4 \times 4 \times 1)$ *k*-points was applied for metal surfaces. The *k*-point samplings have been examined for adsorption energies convergence. Moreover, the smearing width was set to 0.2 eV with the Methfessel-Paxton (MP) method (N=1). As the adsorption energies are not affected significantly for these materials, spin polarization was not explicitly treated.

The adsorption energy (E_{ad}) of relevant intermediates refers to the gas-phase energies of H₂, H₂O and CH₃OH, which is denoted according to the following equation:

$$E_{ad} = E_{tot} - E_{cat} - (\alpha E_C + \beta E_H + \gamma E_O)$$

where E_{tot} is the total energy of the catalysts with adsorbates, E_{cat} is the energy of bare catalysts, $E_H = \frac{1}{2}E_{H_2}E_0 = E_{H_20} - E_{H_2}E_c = E_{CH_3OH} - E_{H_20} - E_{H_2}$, and α, β, γ represents the number of carbon, hydrogen and oxygen atoms in intermediates. Furthermore, the standard free energies (finite differences) were calculated under 723 K, which follows the equation:

$$\Delta G = E_{ad} + \Delta E_{ZPE} - T\Delta S$$

where ΔE_{ZPE} and ΔS represents the zero-point energy (ZPE) and entropy correction for the adsorption, respectively. ΔE_{ZPE} and ΔS were obtained from the vibrational frequency calculations. The E_{ZPE} and TScan be calculated by the equations, respectively:

$$E_{ZPE} = \frac{1}{2} \sum_{i} hv_i$$
$$TS = K_B T \sum_{i} \ln\left(1 - e^{-\frac{hv_i}{K_B T}}\right) - \sum_{i} hv_i \left(\frac{1}{\frac{hv_i}{\frac{hv_i}{K_B T}}}\right)$$

where h, v and K_B are Planck constant, vibrational frequencies and Boltzmann constant, respectively.

Element	Н	С	Ο	Al	Si
Pseudopotential type	PAW_PB E 15Jun2001	PAW_PBE 08Apr2002	PAW_PBE 08Apr2002	PAW_PBE 04Jan2001	PAW_PBE 05Jan2001
Element	Р	Ni	Pd	Cu	Ag

The relevant pseudopotential types are listed in the following table:

2. Adsorption Energies

E _{ad} (eV)	CH ₂ *	CH ₃ OH*			* 011*	CU 011*	CU 0*
		CH ₃ OH_HZ CH ₃	BOH_Z	I* CH ₃	* OH*	CH ₂ OH*	CH ₃ O*
Ni(211)	-0.56	-0.71	-0.	62 -0.90	-0.7 1	-0.37	-0.79
Pd(211)	-0.26	-0.54		39 -0.7	5 0.16	-0.11	0.01
Cu(211)	0.40	-0.52		27 -0.57	7 -0.44	0.33	-0.46
Ag(211)	1.32	-0.36		21 -0.07	0.25	0.96	0.21
SAPO-34	0.23	-1.03 -	0.73 -2.	37 -2.5	1 1.28		
SSZ-13	0.02	-1.02 -	0.70 -2.	30 -2.43	3 1.35		
SAPO-18	-0.06	-1.27 -	0.68 -2.	41 -2.59	9 1.26		
RUB-50	0.41	-0.88 -	0.63 -2.	37 -2.28	8 1.40		
DNL-6	-1.11	-1.02 -	1.96 -3.	58 -3.70	0.06		
MOR12&8	-0.23	-1.21 -	0.92 -2.	38 -2.64	4 1.15		
MOR12	-0.95	-1.01 -	1.69 -3.	31 -3.47	0.23		
MOR8	-0.73	-1.30 -	1.51 -3.	21 -3.43	3 0.40		
ZSM-5 _{straight}	-0.11	-1.08 -	0.88 -2.	42 -2.63	3 1.31		
$ZSM-5_{sinusoidal}$	0.12	-1.05 -	0.92 -2.	39 -2.4	1 1.35		
ZSM-22	0.29	-0.96	0.79 -2.	32 -2.4	1 1.56		

Table S1. The adsorption energies of all the relevant intermediates calculated via GGA-rPBE-vdW.

E _{ad} (eV)	CH ₂ *	CH ₃ OH*		11*	CII *	011*	CU OU*	CU 0*
		CH ₃ OH_HZ	CH ₃ OH_Z	H*	CH ₃ *	OH*	CH ₂ OH*	CH ₃ O*
Ni(211)	-0.27	-0.26		-0.51	-0.62	-0.48	0.09	-0.43
Pd(211)	-0.06	-0.14		-0.32	-0.50	0.37	0.32	0.40
Cu(211)	0.69	-0.13		-0.17	-0.25	-0.21	0.78	-0.13
Ag(211)	1.50	-0.06		0.27	0.11	0.43	1.32	0.53
SAPO-34	0.44	-0.51	-0.39	-2.33	-2.27	1.46		
SSZ-13	0.57	-0.56	-0.36	-2.23	-2.15	1.56		
SAPO-18	0.20	-0.80	-0.39	-0.36	-2.50	1.48		
RUB-50	0.79	-0.43	-0.22	-2.19	-1.83	1.67		
DNL-6	-1.01	-0.56	-1.68	-3.64	-3.53	0.12		
MOR12&8	0.28	-0.72	-0.30	-2.31	-2.35	1.48		
MOR12	-0.47	-0.64	-1.18	-3.09	-2.97	0.65		
MOR8	-0.23	-0.67	-0.88	-2.98	-2.79	1.42		
ZSM-5 _{straight}	0.17	-0.88	-0.52	-2.33	-2.31	1.55		
$ZSM-5_{sinusoidal}$	0.51	-0.52	-0.38	-2.32	-2.08	1.58		
ZSM-22	0.72	-0.50	-0.36	-2.28	-2.06	1.81		

Table S2. The adsorption energies of all the relevant intermediates calculated via GGA-rPBE functional without van der Waals correction.

3. Comparison between GGA-rPBE and HSE06



Figure S1. Adsorption energies of CH₃OH calculated by GGA-rPBE-vdW and HSE06-vdW on some critical zeolites.

4. Scaling Relations and Projected Density of States

The scaling relations for adsorption energies of CH_2^* and CH_3OH^* are shown in Figure S2 and S3, respectively, with the analysis of electronic structure through projected density of states.



Figure S2. (a) The adsorption energies of CH_2^* over zeolites (red) and metals (black). From left to right, the zeolites are DNL-6, MOR12, MOR8, MOR12&8, ZSM-5_{straight}, SAPO-18, SSZ-13, ZSM-5_{sinusoidal}, SAPO-34, ZSM-22, RUB-50 and the metals are Ni(211), Pd(211), Cu(211), Ag(211). (b) The C-2p states of adsorbed CH_2^* (red) and the O-2p states of zeolite RUB-50 (black). (c) The C-2p states of adsorbed CH_2^* (red) and the Cu d-band on metallic Cu(211) surfaces with adsorbates (black).



Figure S3. (a) The comparison between zeolites (red) and metals (black) in the adsorption energies of CH₃OH*. (b) Projected DOS of metals and zeolites are shown in black and adsorbates in red.

5. Electronic Localization Functions



Figure S4. The ELFs and the line profiles of O_{methanol}-H-O_{zeolites} for CH₃OH adsorption at the Brønsted acid sites.

6. Optimized Configurations of Intermediates

The optimized configurations of relevant species in methanol activation on serious metals are shown in Figure S5.



Figure S5. Calculated adsorption configurations of several intermediates on stepped transition metal surfaces (M(211), M=Pd, Ni, Cu, Ag).

The optimized adsorption structures of various intermediates over the zeolite MOR8 as an example are presented in Figure S6.



Figure S6. The adsorption configurations of various intermediates over zeolite MOR8 as an example. The zeolite frameworks are shown in thin stick and the local geometries are bold for highlight.

The similar adsorption configurations of methanol over various zeolites are shown in Figure S7.



Figure S7. The adsorption structures of CH₃OH at the Brønsted acid site of all studied zeolites (except MOR8).

Reference

[1] Database of Zeolite Structures. International Zeolite Association.