Supplementary Information

DFT Approach to Predict ¹³C NMR Chemical Shifts of Hydrocarbon Species Adsorbed on Zn-modified Zeolite

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Figure S1. Location of the T sites in BEA zeolite. The figure was reproduced from Ref. 1 with permission from the PCCP Owner Societies.



Figure S2. Representative geometries of the molecular clusters: T6T6 (a), T8T8 (b), T3T8 (c), T4T7 (d).

Table S1. Experimentally detected ${}^{13}C$ chemical shifts $\delta({}^{13}C)$ for the calibration set of hydrocarbon

species.

Molecule	Formula	Molecular	δ(¹³ C) /	Reference
	<u> </u>	naginent	ppm	1
letramethylsilane	S1(CH ₃) ₄	-CH ₃	0	1
Propane		-CH ₂ -	16.6	-
		-CH ₃	16.4	1
Propene		=CH	133.9	1
		$=CH_2$	115.7	-
		-CH ₃	19.5	
trans-But-2-ene		-CH=	126	1
		-CH ₃	17.6	
cis-But-2-ene	\backslash	-CH=	124.6	1
		-CH ₃	12.1	
Zn(allyl) ₂ (in THF)		Zn-CH ₂ -	20	2
		-CH=	145.4	
	$ 2n\rangle$ \langle $/_2$	=CH ₂	99.8	-
$Zn(2-methylallyl)_2$ (in THF)		Zn-CH ₂ -	24.3	2
		>C=	153.0	
	Znt /	-CH ₃	26.7	
	1 12	$=CH_2$	98.1	
		0112	,	
Cp [*] ZnEt (in benzene- <i>d6</i>)		Cp ring	107.8	3
		Cp–CH ₃	9.8	
		Zn-CH ₂ -	-8.2	
	Zn Zn Zn Zn	-CH ₃	12.9	
(3,3-dimethyallyl)ZnCl (in		Zn-CH ₂ -	14.6	2
THF)		-CH=	129.1	-
		>C=	117.1	_
	CI-Zn	-CH ₃	17.3,	
			26.0	-
(2-methyallyl)ZnCl (in THF)		Zn-CH ₂ -	21.2	2
	CI-Zn Y	>C=	152.5	
		$=CH_2$	100.1	
		-CH ₃	26.6	

Molecule	Molecul	¹³ C chemical shielding constants ^a / ppm								
	ar fragmen t	PBE0/aug- cc-pVDZ	PBE0/cc- pVTZ	PBE0/pcsS eg-2	TPSS0/cc- pVTZ	TPSS0/pcs Seg-2	ωB97X	TPSS/cc- pVTZ	TPSS/pcsS eg-2	M062X- pcSseg2
TMS	-CH ₃	196.6	189.1	186.0	189.5	190.2	192.2	185.7	187.4	188.3
Bronono	CH2	176.1	169.0	165.0	168.8	168.2	173.0	163.5	163.6	170.8
Propane	-CH3	178.9	171.1	167.1	170.6	170.6	174.4	166.3	167.1	171.6
	=CH	60.4	46.9	37.8	52.3	46.3	51.0	51.7	45.3	27.7
Propene	=CH ₂	81.9	68.5	61.1	73.6	69.1	72.1	73.0	68.6	50.3
	-CH3	174.9	166.8	162.8	166.6	166.6	171.0	161.6	162.8	167.9
trans-But-2-	-CH=	69.1	55.8	47.3	60.4	54.9	59.7	59.3	53.9	38.3
ene	-CH ₃	176.7	168.3	164.3	167.7	167.9	172.5	162.8	164.1	169.6
	-CH=	70.9	57.7	49.3	62.2	56.8	61.6	61.1	55.8	40.3
cis-But-2-ene	-CH ₃	183.1	174.9	171.2	173.9	174.4	178.7	169.4	170.9	176.6
	Zn– CH ₂ –	176.4	168.0	164.2	170.0	169.7	175.4	162.4	162.7	167.4
Zn(allyl)2 ^b	-CH=	53.8	39.6	29.7	44.5	37.7	41.6	45.6	38.7	18.9
	=CH ₂	96.5	83.9	77.0	88.7	84.9	88.0	87.1	83.6	68.4
	Zn– CH ₂ –	172.0	163.5	159.6	165.5	165.3	170.7	158.0	158.5	162.6
Zn(2-	-C=	43.2	29.8	19.4	34.8	26.9	31.7	35.5	27.4	7.9
b b	-CH ₃	170.7	161.2	157.0	160.9	161.3	165.3	155.9	157.5	161.8
	=CH ₂	99.2	86.7	79.8	90.9	87.1	91.0	89.1	85.4	71.7
	Cp ring	88.8	77.4	69.9	79.4	75.7	81.3	76.4	73.3	72.4
°C≈*7nEt	Cp–CH ₃	185.0	178.0	174.5	176.8	177.4	181.6	172.0	173.8	179.5
Ср~2пы	Zn– CH ₂ –	203.9	197.6	195.0	197.8	198.1	203.7	190.2	190.9	202.0
	-CH3	182.5	174.6	171.0	173.5	173.8	178.4	168.5	169.7	176.2
	Zn– CH ₂ –	183.7	175.9	172.7	177.3	177.7	183.7	168.9	169.8	177.4
(2.2	-CH=	74.2	60.4	52.3	63.6	58.5	63.1	63.5	58.4	44.2
(5,5- dimethyallyl)	>C=	70.0	58.0	49.7	62.9	57.1	62.7	59.8	53.8	43.2
LICI	-CH3	180.7	171.8	167.8	170.8	171.3	175.4	166.2	168.0	173.3
	-CH ₃	171.0	162.2	158.1	161.7	162.0	166.4	156.7	158.2	163.4
<i>(</i> 2	Zn– CH ₂ –	174.1	165.3	161.5	167.1	167.2	172.9	159.3	159.9	165.5
(2- methyallyl)Z	>C=	44.6	31.5	21.3	36.5	28.8	34.0	36.8	28.8	10.1
IICI*	=CH ₂	95.7	82.8	75.8	87.3	83.3	87.4	85.3	81.5	67.6
	-CH3	170.5	161.3	157.1	161.0	161.4	165.5	156.0	157.5	161.9

Table S2. Calculated isotropic chemical shieldings $\sigma(^{13}C)$ for the calibration set of hydrocarbon

species.

^aShieldings for chemically equivalent groups (e.g. methyl groups in TMS) were averaged.

^bCalculated using CPCM solvation model to emulate the THF solution.

^cCalculated using CPCM solvation model to emulate the benzene-*d*₆ solution.



Figure S3. Constructed linear regressions for different calculation methods.

Method	¹³ C NMR chemical shielding constant σ ⁽¹³ C), ppm						
	Methylzinc	Propene π-co	Propene π -complex with Zn ²⁺				
	-Zn-CH3	=CH ₂	CH=	-CH ₃			
PBE0/aug-cc-pVDZ*	208.7	84.9	28.1	172.9			
PBE0/cc-pVTZ	203.1	73.8	15.1	164.9			
PBE0/psSeg2-	200.8	66.1	4.7	160.8			
TPSS0/cc-pVTZ	203.4	78.6	22.0	165.0			
TPSS0/pcSseg-2	204.4	74.7	14.9	165.3			
ωB97X/cc-pVTZ	207.2	78.1	19.4	169.6			
TPSS/cc-pVTZ	197.5	77.1	22.3	159.7			
TPSS/pcsSeg-2	199.1	73.8	15.2	161.2			
M062X/cc-pVTZ	204.9	54.8	-8.6	166.0			

Table S3. Calculated chemical shielding constants for methylzinc and propene π -complex.

Double hybrid calculations were performed using the double-hybrid DSD-PBEP-86⁴ functional with domain-based local pair natural pair (DLPNO) approximation for MP2 part.⁵ Because of the high calculation cost, we performed such calculations using the smaller cluster, constructed from the PBE0-optimized ones. We calculated chemical shifts for the smaller cluster with TPSS/cc-pVTZ method to ensure that size of the cluster does not significantly influence the results. The structure of the smaller cluster is presented in Figure 3. The linear regression equation for this method is $\delta = 193.04 - 0.993 \times \sigma$.

Table S4. Calculated ¹³C chemical shifts (in ppm) for the methylzinc on different levels of theory.

TPSS/cc-pVTZ	TPSS/cc-pVTZ	DLPNO-DSD-PBEB86/cc-pVTZ
(Large cluster)	(Small cluster)	(Small cluster)
-17	-17	-16



Figure S4. The structure of the smaller cluster for double-hybrid DFT calculation.

Table S5. Calculated TPSS/cc-pVTZ chemical shielding constants for methylzinc and propene π complex with difference geometry convergence criteria.

Geometry convergence	¹³ C NMR chemical shielding constant $\sigma(13C)$, ppm					
criteria	Methylzinc	nc π -Complex of propene with Zn ²⁺				
	–Zn–CH3	=CH ₂	=CH	-CH3		
RMS gradient = 10^{-6} a.u Max gradient = $3 \cdot 10^{-6}$ a.u.	197.512	77.080	22.351	159.716		
RMS gradient =1 10^{-8} a.u Max gradient = $5 \cdot 10^{-8}$ a.u.	197.514	77.135	22.295	159.718		

The difference between the calculated values is no more than 0.056 ppm, which is insignificant considering the accuracy of the experimental chemical shift determination (± 0.5 ppm). Therefore, we reasonably conclude that initially applied geometry convergence criteria are tight enough to obtain accurate and reproducible results.

Table S6. TPSS/cc-pVTZ calculated chemical isotropic chemical shielding constants $\sigma(^{13}C)$ of the considered species.

Species		Calculated $\sigma(^{13}C)$, ppm				
-I		Т6Т6	T8T8	T3T8	T4T7	
Propene	=CH ₂	77.1	80.3	79.5	77.8	
complex with $7n^{2+}$	=CH-	22.3	16.8	20.1	23.6	
2.11	-CH3	159.7	157.6	157.5	157.6	
Isobutene	=CH ₂	91.1	94.7	85.5	89	
complex with $7n^{2+}$	=C<	-6.3	-18.3	1.8	-6.3	
	-CH3	154.5;152.0	153.6;150.9	152.9;149.6	150.4;153.6	
<i>trans</i> -But-2-ene	-CH3	161.6;161.4	161.3;161.3	159.2;158.6	160.0;160.1	
Zn ²⁺	=CH-	45.6;46.7	43.1;43.5	50.0;42.7	46.8;47.5	
<i>cis</i> -But-2-ene	-CH3	167.0;165.9	166.0;165.7	42.9;50.9	50.3;43.4	
complex with Zn ²⁺	=CH-	49.4;46.4	43.5;45.7	166.0;164.1	163.3;166.2	
	Zn-CH2-	162	161.2	159.5	160.1	
σ-allylzinc	=CH-	48.4	48.9	50.8	50.9	
	=CH ₂	78	79.4	74.8	76.1	
σ-allylzinc with	Zn-CH ₂ -	159	155.5	161	160.8	
π -BAS	=CH-	18.5	17.9	24.2	19.7	
Interaction	=CH ₂	90.2	91.6	86.5	89.4	
	ZnCH2	155.1	157.3	158.5	155.4	
2-methyl-σ-	=C<	41.7	43.8	42.5	40.8	
allylzinc	=CH ₂	77.5	77.5	79.4	77	
	-CH3	152.4	152.1	153.6	153.2	
2-methyl-σ-	ZnCH2-			156.9	155.5	
allylzinc(with π -BAS	=C<			10.7	2.2	
interaction)	=CH ₂			87.2	95.3	

	-CH ₃			150.4	154.4
Methylzinc	Zn–CH3	195	195.9	195.5	197.5
Ethylzine	Zn-CH2-	175.4	176.4	175.3	178.4
	-CH3	169.6	169.7	168.1	169.3
	Zn-CH ₂ -	167.5	163.7	168.1	167.8
n-Propylzinc	-CH2-	157.3	157.7	157.7	157.5
	-CH ₃	158.8	157.3	159.6	158.9

Table S7. TPSS/cc-pVTZ calculated components of isotropic chemical shielding (σ_{xx} , σ_{yy} , and of σ_{zz}) the considered species.

Species		Calculated σ_{xx} , σ_{yy} , and σ_{zz} values, ppm				
species		T6T6	T8T8	T3T8	T4T7	
		-14.4	-9.4	-12.6	-12.9	
	=CH ₂	83.4	90.2	89.8	86.1	
		162.2	160.1	161.3	160.0	
Propene		-3.3	-10.8	-4.4	2.34	
complex with $7r^{2+}$	=CH-	-97.0	-106.4	-100.7	-98.1	
Zn		167.3	167.7	165.4	166.5	
		142.0	140.3	141.7	138.0	
	-CH3	160.7	159.0	158.1	159.1	
		176.5	173.6	172.7	175.7	
		15.6	21.0	9.0	13.1	
	=CH ₂	111.3	113.6	101.8	108.2	
		146.4	149.5	145.8	145.6	
		-58.1	-78.6	-48.1	-59.8	
	=C<	-125.5	-140.4	-110.9	-123.4	
Isobutene complex with		164.5	164.1	164.3	164.5	
Zn ²⁺		136.5	133.8	135.9	130.0	
	-CH3	150.2	151.8	147.1	142.8	
		176.7	175.2	175.9	178.4	
		131.6	129.0	129.1	134.2	
	-CH3	145.9	146.0	139.9	148.5	
		178.5	177.6	179.6	178.1	
trans-But-2-ene		146.8	145.3	142.3	146.1	
complex with $7n^{2+}$	-CH3	161.1	162.3	158.0	157.4	
Z.II		176.9	176.5	177.2	176.8	

		146.6	145.2	142.1	142.9
	-CH3	160.9	162.3	154.4	159.2
		176.7	176.4	179.2	177.8
		40.2	32.2	23.80	38.5
	=CH-	-52.6	-56.9	-25.6	-51.2
		152.6	154.0	151.7	152.9
		38.4	32.6	34.4	40.9
	=CH-	-54.5	-56.2	-55.2	-50.4
		152.8	154.2	148.9	152.0
		144.5	146.5	34.5	44.0
	-CH2	175.6	173.6	64.0	-52.1
		177.4	178.1	158.3	159.0
		147.8	144.3	42.5	36.4
	-CH ₂	174.5	175.4	-47.8	-66.0
<i>cis</i> -But-2-ene		178.6	177.3	158.1	159.7
Zn ²⁺		42.8	30.6	145.8	141.2
	=СН-	-54.6	-60.1	175.1	174.0
		159.9	159.9	177.0	174.7
		35.2	36.2	139.7	148.0
	=CH-	-55.5	-59.3	175.3	173.0
		159.5	160.4	177.3	177.8
		135.8	134.7	134.6	137.0
	Zn-CH2-	155.8	153.9	155.7	152.0
		194.3	195.164	188.216	191.2
		47.4-	47.6	38.1	3.9
	=CH-	59.6	-60.3	-42.6	-4.3
		157.4	159.4	156.8	153.0
	-CII	-20.3	-18.6	-24.9	-22.8
	=CH2	101.2	101.3	96.1	103.8

		153.1	155.6	153.2	147.3
		127.2	124.1	134.2	128.2
	Zn-CH2-	166.6	163.3	164.0	165.3
		183.3	179.0	185.0	188.7
σ -allylzinc with		0.9	7.7	10.0	7.2
π -BAS	=CH-	-107.5	-112.7	-97.1	-107.5
interaction		162.2	158.7	159.6	159.5
		2.5	2.2	-2.4	4.1
	=CH ₂	106.8	120.0	103.5	104.2
		161.4	152.6	158.4	159.9
		131.2	137.0	134.3	131.0
	Zn–CH2–	145.6	145.3	148.0	141.8
		188.4	189.5	193.1	193.4
		38.8	40.0	35.6	38.5
	=C<	-67.2	-65.5	-66.3	-69.4
2-methyl-σ-		153.6	156.8	158.1	153.5
allylzinc		-8.1	-11.1	-11.2	-10.1
	=CH ₂	108.3	104.3	107.9	112.1
		132.2	139.3	141.5	128.9
		133.9	133.5	135.9	131.5
	-CH3	144.7	142.9	144.6	145.5
		178.7	179.8	180.4	182.4
				129.4	123.1
	Zn–CH2–			154.0	152.6
2-methyl-σ-				187.4	190.9
allylzinc(with π -BAS				-24.3	-37.6
interaction)	=C<			-104.8	-118.7
				161.1	162.7
	=CH ₂			133.2	22.2

			137.5	116.0
			180.6	147.7
			133.2	140.8
-CH3			137.5	143.7
			180.6	178.7
	188.7	190.8	192.2	192.1
Zn–CH3	196.8	195.1	194.3	197.4
	199.5	201.8	200.0	203.0
	164.3	168.3	161.7	168.7
Zn-CH2-	177.5	174.8	171.5	175.0
	184.4	186.0	192.6	191.6
	162.0	159.0	158.8	157.8
-CH ₃	167.1	166.6	161.0	166.2
	179.9	183.5	184.6	184.0
	144.7	138.1	147.6	151.4
Zn-CH2-	164.7	155.5	164.0	159.1
	192.9	197.4	192.8	193.0
	146.1	143.2	145.1	146.0
CH2	155.0	156.1	155.9	153.9
	170.9	173.7	172.2	172.7
	141.1	137.3	139.8	141.0
-CH ₃	151.1	151.0	153.2	150.3
	184.3	183.7	185.9	185.5
	CH3 ZnCH2- CH3 ZnCH2- CH2-	CH3 -CH3 -CH3 -CH3 -CH3 -CH3 -CH3 -CH3	-CH3Ian-CH3Image: strain st	-CH3 137.5 -CH3 133.2 137.5 180.6 -CH3 133.2 137.5 137.5 188.7 190.8 199.5 201.8 20.0 164.3 199.5 201.8 20.0 164.3 164.3 168.3 164.4 186.0 188.7 171.5 184.4 186.0 162.0 159.0 164.3 161.7 20.0 158.8 -CH2- 162.0 159.0 162.0 159.0 158.8 -CH3 167.1 166.6 161.0 179.9 183.5 184.6 Zn-CH2- 164.7 155.5 164.0 192.9 197.4 192.8 -CH2- 155.0 156.1 155.9 170.9 173.7 172.2 -CH3 151.1 151.0 153.2 184.3 183.7

Tables S8. TPSS0/cc-pvTZ calculated chemical shifts.

Species		Calculated o	Calculated $\sigma(^{13}C)$, ppm				
species		T6T6	T8T8	T3T8	T4T7		
Pronvlene	=CH ₂	109	106	107	109		
complex with $7n^{2+}$	=СН-	166	171	168	165		
ZII	-CH3	23	25	25	25		
Isobutene	=CH ₂	94	90	100	97		
complex with $7n^{2+}$	=C<	195	207	187	195		
ZII	-CH ₃	28;30	31;29	32;30	33;29		
<i>trans</i> -but-2-ene	-CH3	21;21	21;21	23;24	23;23		
Zn ²⁺	=СН-	141;139	143;143	136;144	141;140		
<i>cis</i> -but-2-ene	-CH3	16;17	16;17	16;18	19;16		
Zn ²⁺	=СН-	137;140	143;140	144;135	137;144		
	Zn-CH2-	18	19	19	20		
σ-allylzinc	=СН-	139	138	136	136		
	=CH ₂	108	107	112	110		
σ-allylzinc with	Zn-CH2-	21	25	19	20		
π -BAS	=CH-	171	172	164	170		
Interaction	=CH ₂	95	94	99	96		
	Zn–CH2–	24	22	21	24		
2-methyl-σ-	=C<	145	143	145	146		
allylzinc	=CH ₂	109	109	106	109		
	-CH3	30	30	29	30		
	Zn-CH2-			23	25		
2-methyl- σ - allylzinc(with π -	=C<			177	188		
BAS interaction)	=CH ₂			98	89		
	-CH ₃			32	28		

Methylzinc	-14	-14	-14	-15	-14
Ethylzinc	3	3	4	1	3
	13	13	14	13	13
	12	17	11	12	12
n-Propylzinc	24	24	24	24	24
	24	26	24	24	24

Table S9. pPBE-D3(BJ) adsorption energies of the alkenes on different Zn^{2+} sites (in	n kJ mol ⁻¹).
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Zn ²⁺ cation location	Propene	trans-But-2-ene	cis-2-But-2-ene	Isobutene
T6T6	-130	-142	-150	-155
Т6Т8	-160	-180	-180	-186
T3T8	-156	-181	-178	-174
T4T7	-165	-189	-184	-182



Figure S5. Energy profile of the transformation of propene π -complex to σ -allylzinc on the T4T7 site. The zero level is set for a system "free alkene + pure zeolite".

	$\Delta E_{allylzinc}$, kJ mol ⁻¹					
	σ-allylzinc		2-methyl-σ-allylzinc			
	free	π -bonding to BAS	free	π -bonding to BAS		
ТбТб	47	-6	28	a		
Т8Т8	-38	-75	-39	a		
ТЗТ8	-66	-95	-74	-112		
T4T7	-58	-105	-70	-118		

Table S10. pPBE-D3(BJ) electron energies of different allylzinc species on Zn-BEA.

^aNo stable structures for 2-methyl- σ -allylzinc with π -bonding to BAS are found.

Table S11. pPBE-D3(BJ) electron energies of different alkylzinc species on Zn-BEA.

	$\Delta E_{alkylzinc}$, kJ mol ⁻¹				
Zn ²⁺ site	Methylzinc	Ethylzinc	<i>n</i> -Propylzinc		
T6T6	52	58	31		
T8T8	-8	-13	-24		
T3T8	-57	-52	-62		
T4T7	-52	-42	-53		

The energies are defined as follows: $\Delta E_{alkylzinc} = E_{alkylzinc} - E_{alkane} - E_{Zn}$.

Testing different optimization methods. For this test, we considered complex r2SCAN-3c $(mGGA)^6$ and PBEh-3c (hGGA) methods.⁷ We also tested the optimization of the geometry of the extra-framework atoms on the PBE0/def2-qZVP level. Another variant was to use the PBE0/def2-tZVP with triple- ζ basis set applied on all atoms of the zeolite cluster. Linear regressions are presented in Table S12. The resulted chemical shifts are presented in Table S13.

Table S12	. Linear	regression	coefficients.
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Method	Formula	R ²
r ² SCAN-3c//TPSS/cc-pVTZ	$\delta = 180.41 - 0.962 \times \sigma$	0.991
PBEh-3c//TPSS/cc-pVTZ	δ=189.40–1.043×σ	0.998
PBE0/def2-qZVP//TPSS/cc- pVTZ	δ=189.42-1.042×σ	0.998

 Table S13. TPSS/cc-pVTZ calculated chemical shifts for the zeolite clusters optimized with varied

optimization techniques.

Optimization Method	Methylzinc (T4T7)	Ethylzinc (T4T7)		<i>trans</i> -Butene-2 (T6T6)		<i>cis</i> -Butene-2 (T6T6)	
	Zn–CH3	Zn– CH2	-CH3	-CH3	-CH=	–CH3	–CH=
PBE0/def2-tZVP (extraframework only), used in this study	-17	3	13	21;21	142;141	15;16	138;141
r ² SCAN-3c	-10	10	18	26;26	137;137	21;22	133;138
PBEh-3c	-17	6	13	20;20	142;140	15;16	138;142
PBE0/def2-qZVP (extraframework only)	-16	3	13	21;21	142;141	15;17	138;141
PBE0/def2-tZVP (on all atoms)	-17	1	14	21;21	142;141	15;16	137;142
Experimental value	-20	-0.5	9.2	18	140	13	140

Meta-GGA level r²SCAN-3c geometry yields less accurate results, confirming the importance of

proper geometry optimization for the chemical shifts calculations. PBEh-3c produces better results

for 2-butene adsorption complexes. The rest of the methods do not yield significantly improved

results.

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