Supplementary Materials

In situ synthesis of nanosized ZSM-12 zeolite isomorphously substituted by gallium for the *n*-hexadecane hydroisomerization

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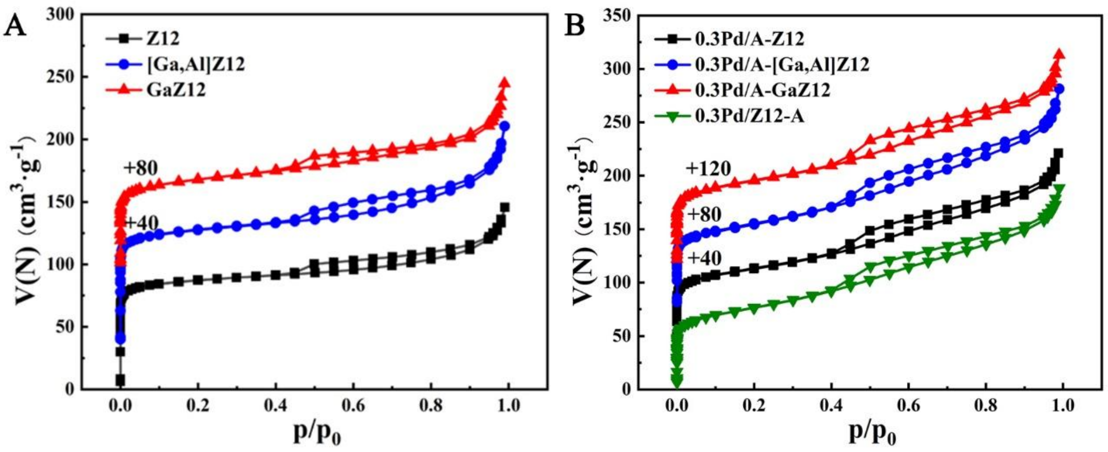
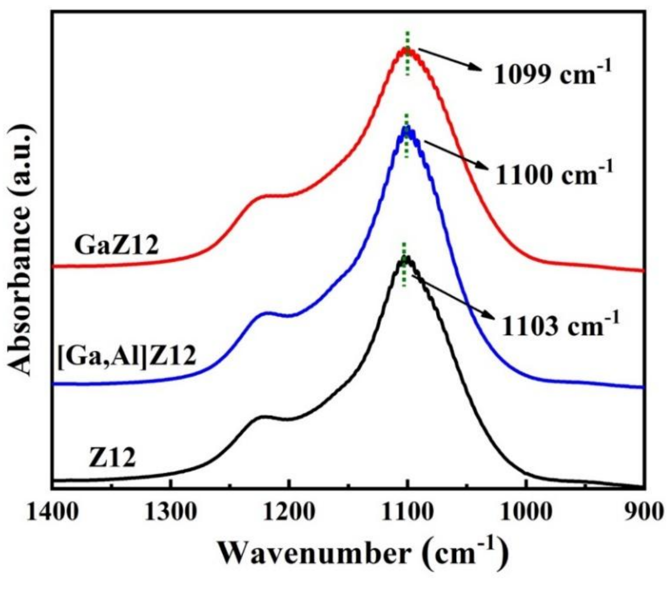
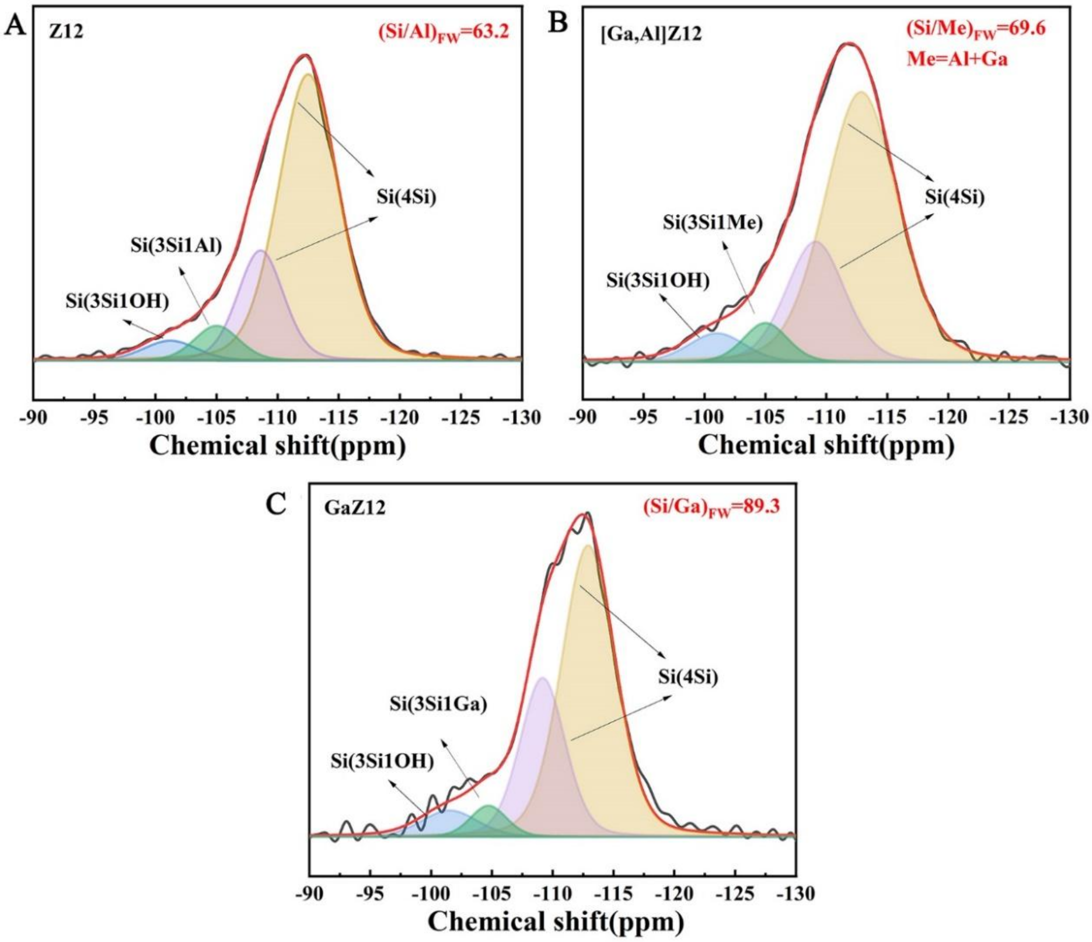


Supplementary Figure 1. N_2 adsorption-desorption isotherms of (A) Z12, [Ga,Al]Z12 and GaZ12 samples and (B) 0.3Pd/A-Z12, 0.3Pd/A-[Ga,Al]Z12, 0.3Pd/A-GaZ12 and 0.3Pd/Z12-A catalysts.



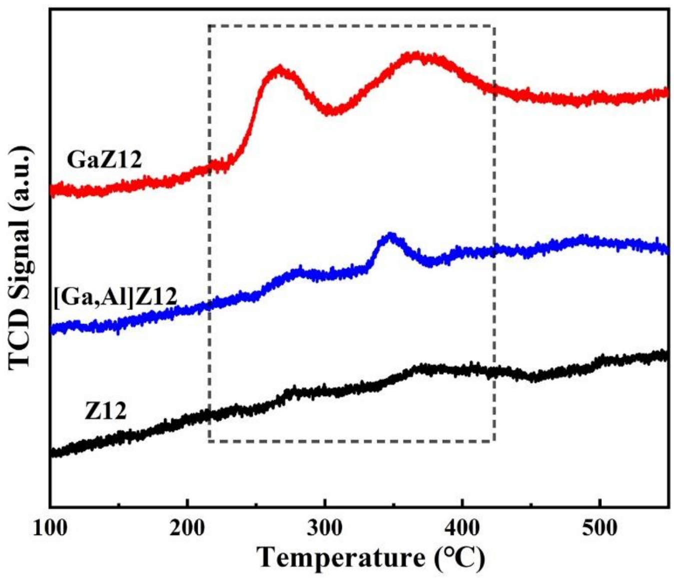
Supplementary Figure 2. FT-IR spectra of Z12, [Ga,Al]Z12 and GaZ12 samples.



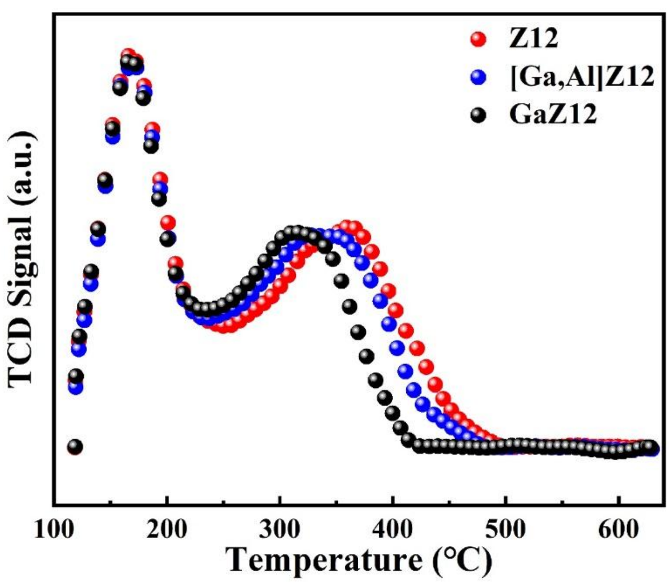
Supplementary Figure 3. ^{29}Si MAS NMR spectra of (A) Z12, (B) [Ga,Al]Z12 and (C) GaZ12 samples.

Supplementary Table 1. The ICP data of the Z12, [Ga,Al]Z12 and GaZ12 samples

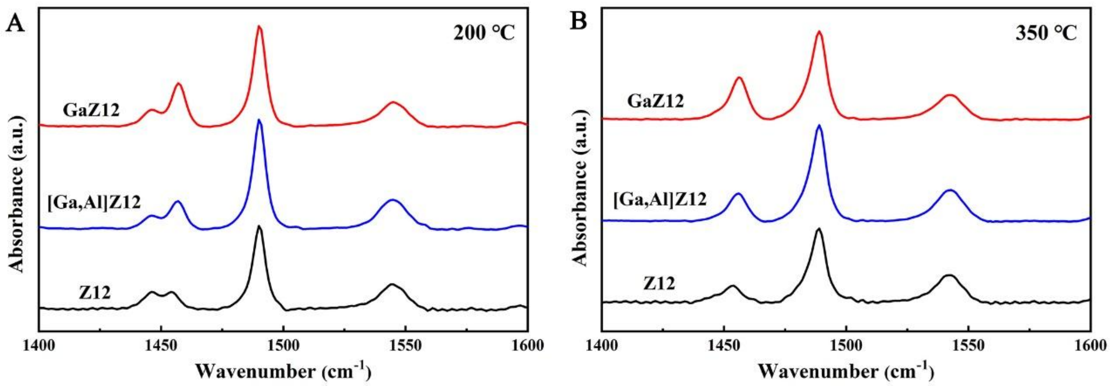
Samples	**ICP results (wt.%)**		
	Si	**Al**	**Ga**
Z12	98.47	1.53	-
[Ga,Al]Z12	98.40	1.30	0.30
GaZ12	97.17	-	2.83



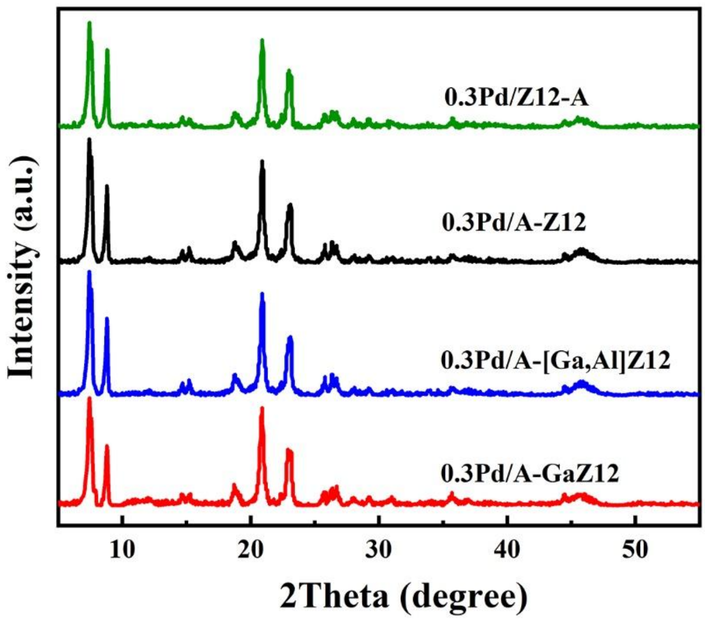
Supplementary Figure 4. H_2-TPR profiles of Z12, [Ga,Al]Z12 and GaZ12 samples.



Supplementary Figure 5. NH_3-TPD profiles of Z12, [Ga,Al]Z12 and GaZ12 samples.



Supplementary Figure 6. Py-IR spectra of Z12, [Ga,Al]Z12 and GaZ12 samples at (A) 200 ºC and (B) 350 ºC.



Supplementary Figure 7. The XRD patterns of 0.3Pd/Z12-A, 0.3Pd/A-Z12, 0.3Pd/A-[Ga,Al]Z12 and 0.3Pd/A-GaZ12 catalysts.

Supplementary Table 2. The textural property of 0.3Pd/Z12-A, 0.3Pd/A-Z12, 0.3Pd/A-[Ga,Al]Z12 and 0.3Pd/A-GaZ12 catalysts

Catalysts	Surface area (m^2/g)			Pore volume (cm^3/g)		
	BET	Micropore[a]	External	Total[b]	Micropore[a]	Mesopore
0.3Pd/Z12-A	275	77	198	0.291	0.030	0.261
0.3Pd/A-Z12	264	82	182	0.280	0.031	0.249
0.3Pd/A-[Ga,Al]Z12	272	69	203	0.312	0.027	0.285
0.3Pd/A-GaZ12	270	59	211	0.307	0.023	0.284

Obtained by [a] t-plot method, [b] Volume adsorbed at p/p_0 = 0.99.

Supplementary Table 3. Comparison of catalytic performance for *n*-alkane hydroisomerization over bifunctional catalysts in reported works and this work

Catalysts	Metal loading (wt%)	Synthesis method of acid support	n-alkanes	Yield of iso-alkanes (%)	Reference
Pt/ZSM-12	0.5	Hydrothermal synthesis with rigid diquaternary ammonium compounds as template	*n*-hexadecane	72.0	[3]
Pt/Z12-F	0.5	One-pot synthesis with NaF added in the initial gel	*n*-dodecane	77.4	[4]
Pt/ZSM12-at	0.5	Post treatment by 0.2M NaOH aqueous solution	*n*-hexane	≈53	[5]
Pt/Z22-P	0.5	One-pot synthesis with PHMB added in the initial gel	*n*-hexadecane	76.6	[6]
Pt/ZSM-22	0.5	Post treatment by NaOH and HCl aqueous solution	n-octane	≈75.0	[7]
Pt/B-ZSM-22	0.5	One-pot synthesis with boric acid added in the initial gel	n-dodecane	≈73.0	[8]
Pt/ZSM-22	0.5	Hydrothermal synthesis with ethanol as co-solvent	n-dodecane	52.1	[9]
0.3Pd/A-GaZ12	0.3	One-pot synthesis with Ga_2O_3 added in the initial gel	*n*-hexadecane	80.6	This work

Supplementary Table 4. **N_{as} values of 0.3Pd/Z12-A, 0.3Pd/A-Z12, 0.3Pd/A-[Ga,Al]Z12 and 0.3Pd/A-GaZ12 bifunctional catalysts**

Catalysts	**M**	**B**	**C**	**Nc**[d]	**n_{as}**[e]
0.3Pd/Z12-A	0.72[a]	0.08[a]×2.5[b]=0.20	0.20[a]×4.43[c]=0.89	2.85	1.81
0.3Pd/A-Z12	0.76[a]	0.10[a]×2.5[b]=0.25	0.14[a]×4.39[c]=0.61	2.78	1.62
0.3Pd/A-[Ga,Al]Z12	0.80[a]	0.10[a]×2.5[b]=0.25	0.10[a]×4.38[c]=0.44	2.75	1.49
0.3Pd/A-GaZ12	0.84[a]	0.08[a]×2.5[b]=0.20	0.08[a]×4.21[c]=0.34	2.41	1.38

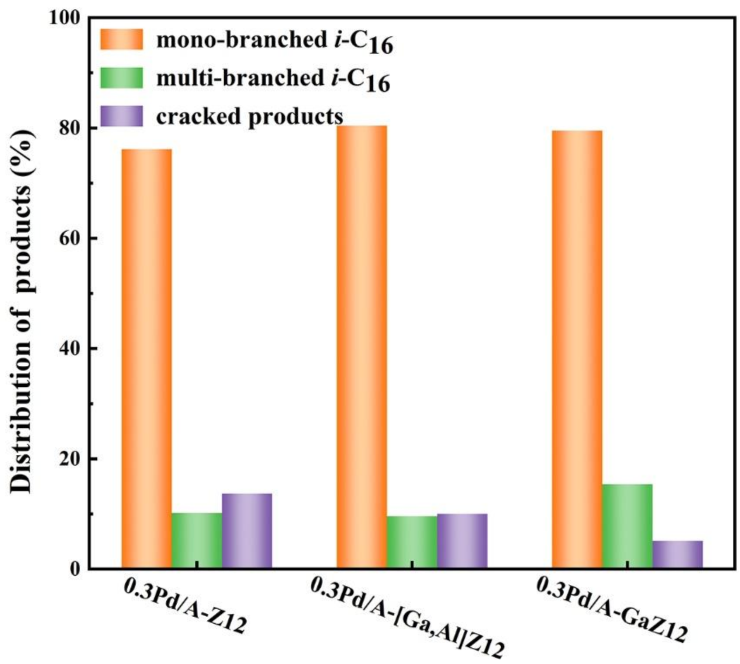
[a] Wt.% of mono-branched (M), multi-branched (B) *iso*-hexadecanes and cracked products (C).

[b] Acid steps number involved in the transformation of one molecule of n-C_{16} into B product.

[c] Acid steps number involved in the transformation of one molecule of n-C_{16} into C product.

[d] Nc: The number of generated molecules per molecule of cracked n-C_{16}.

[e] n_{as}=M×1+B×2.5+C×[4+(Nc-2)/2]



Supplementary Figure 8. Products distribution in the kinetic control region (at n-C_{16} conversion of 9~14%) over 0.3Pd/A-Z12, 0.3Pd/A-[Ga,Al]Z12 and 0.3Pd/A-GaZ12 bifunctional catalysts.

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