Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Hydroisomerization of *n*-hexadecane over the Pd-Ni_2P/SAPO-31 bifunctional catalyst: synergistic effect of bimetallic active sites

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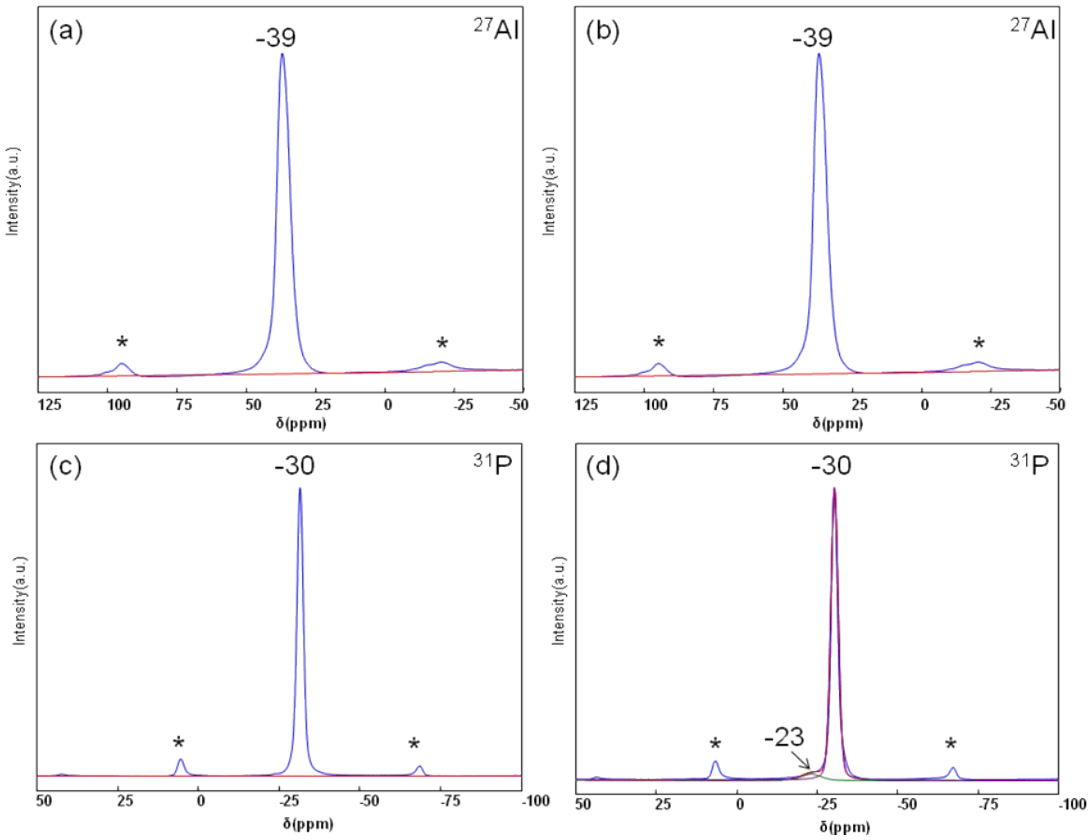

Fig.S1 ^{27}Al MAS NMR spectra of (a) SAPO-31 support and (b) 0.05Pd-4Ni_2P/S31;

^{31}P MAS NMR spectra of (c) SAPO-31 support and (d) 0.05Pd-4Ni_2P/S31.

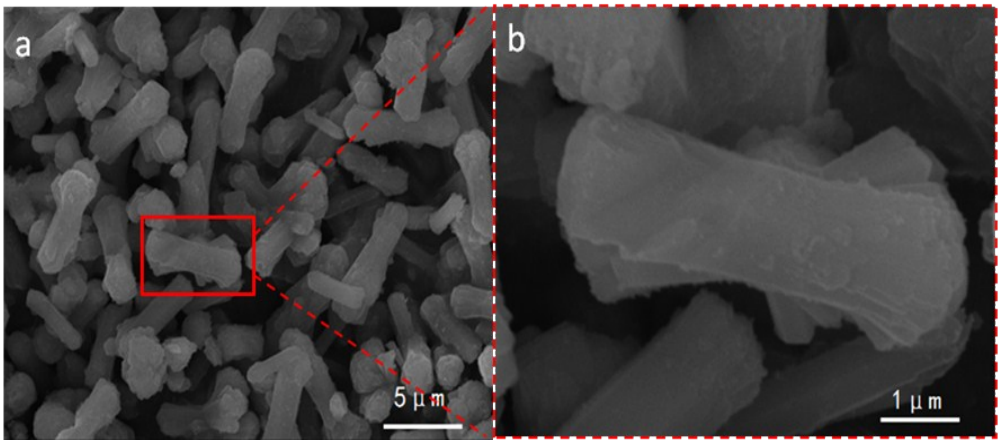

Fig. S2. SEM images of SAPO-31 molecular sieves.

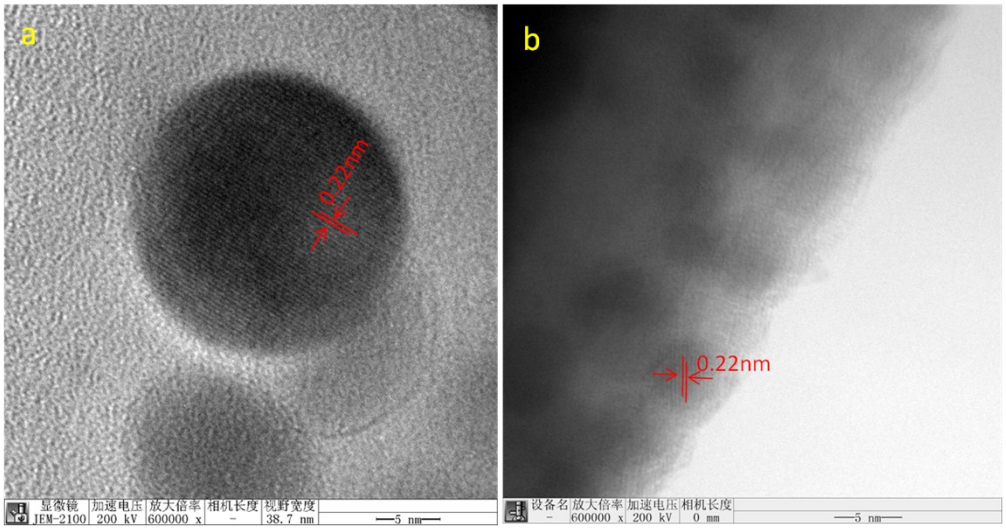

Fig. S3. HR-TEM images of Me/S31 bifunctional catalysts: (a) $4Ni_2P$/S31 and (b) 0.05Pd-$4Ni_2P$/S31.

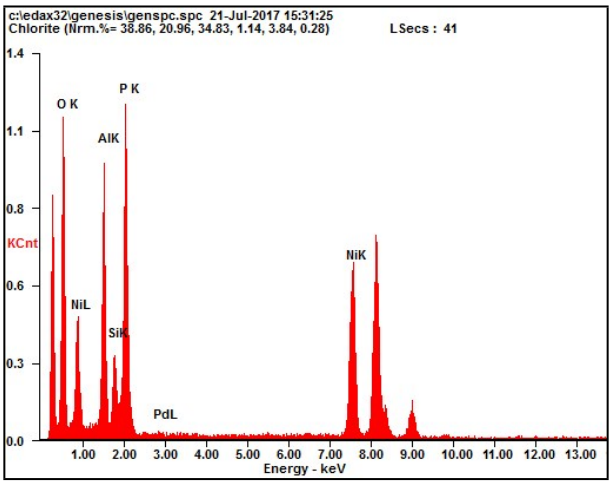

Fig. S4. The EDS spectrum of 0.05Pd-4Ni_2P/S31 bifunctional catalysts from TEM results.

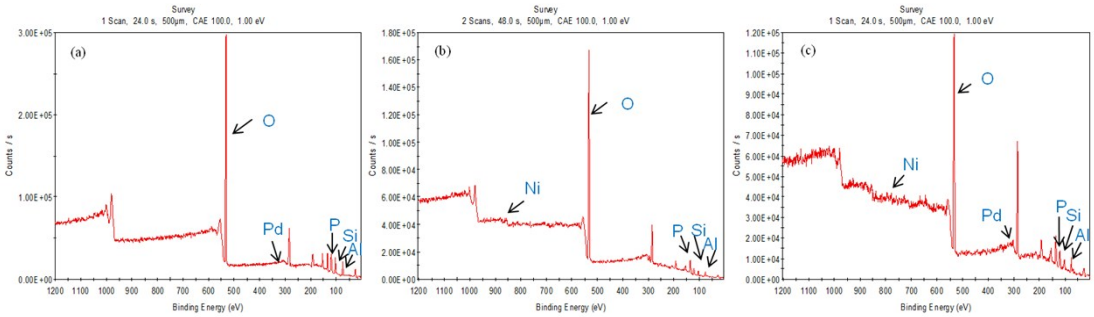

Fig. S5. XPS spectra of bifunctional catalysts Me/S31: (a) 0.05Pd/S31, (b) $4Ni_2P$/S31 and (c) 0.05Pd-$4Ni_2P$/S31.

Table S1. Element atom percent content from the surface of the Me/S31catalysts

Element names	Content of the surface for 0.05Pd/S31(At.%)	Content of the surface for $4Ni_2P$/S31(At.%)	Content of the surface for 0.05Pd-$4Ni_2P$/S31 (At.%)
Al_{2p}	16.17	14.92	16.70
Si_{2p}	9.41	7.81	8.02
P_{2p}	12.12	15.84	13.95
O_{1s}	62.30	60.05	59.33
Ni_{2p}	--	1.37	2.01
Pd_{3d}	--	--	--

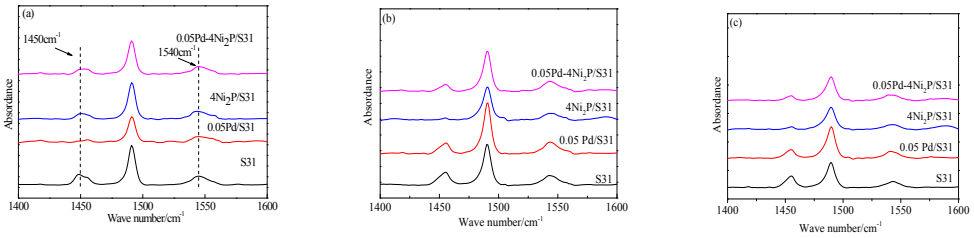

Fig. S6. Py-IR spectra of SAPO-31 molecular sieves and Me/S31 catalysts: (a) 150 ℃, (b) 250 ℃ and (c) 350 ℃.

Table S2. Summary of relevant work done for the performance of *n*-alkanes hydroisomerization over bifunctional catalysts.

Catalyst	*n*-alkanes	Reaction conditions		Conversion of *n*-alkanes(%)	Yeild for *iso*-paraffin(%)	Reference
		T(℃)	Pressure			
0.05%Pt30%Ni_2P/Hβ	*n*-C_7	320	20bar	48.7	37.2	[44]
0.4%Pt-Pd/H-beta	*n*-C_{16}	200	1bar	71.6	63.9	[41]
0.05%Pd/SAPO-11	*n*-C_{10}	350	20bar	82.3	70.1	[28]
0.1%Pd/SAPO-41	*n*-C_{16}	350	20bar	95.1	69.0	[13]
0.18%Pd/Siral[a] 40	*n*-C_{16}	310	30bar	47.1	43.9	[27]
3%Ni_2P/ SAPO-11	*n*-C_{12}	350	20bar	90.0	65.0	[38]
0.05%Pd-4%Ni_2P/SAPO-31	*n*-C_{16}	380	20bar	83.1	72.7	This work

[a] A commercial silica–alumina (Siral 40, Sasol Germany GmbH) was used as the support material and consists of 40wt% of $SiO_2$and 60wt% of Al_2O_3.

Table S3. Estimation of n_{as}, the average number of acid steps involved in the transformation of one molecule of *n*-C_{16} and the branched/linear ratios (i/n).

Catalysts	M	B	C	n_{as}[d]	i/n
0.05Pd/S31	0.48[a]	0.24[a]x2.5[b]=0.60	0.28[a]x4.19[c]=1.17	2.25	0.67
4Ni_2P/S31	0.58[a]	0.22[a]x2.5[b]=0.55	0.20[a]x4.05[c]=0.81	1.94	1.12
0.05Pd-4Ni_2P/S31	0.68[a]	0.13[a]x2.5[b]=0.33	0.19[a]x4.02[c]=0.76	1.77	1.55

[a] Wt fractions of monobranched (M), multibranched (B) isomers and cracking products (C).

[b] Number of acid steps involved in the apparent transformation of one molecule of *n*-C_{16} into B product.

[c] Number of acid steps involved in the apparent transformation of one molecule of *n*-C_{16} into C product.

[d] n_{as}=Mono× 1+Multi × 2.5+ Cracked× [4+ (N_C-2)/ 2].

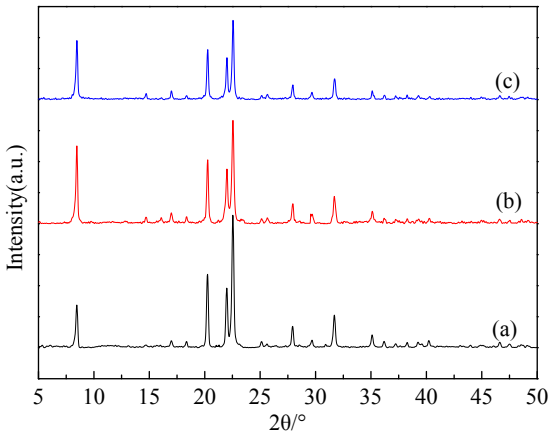

Figure S7. X-ray diffraction pattern for the (a) used 0.05Pd/S31, (b) used $4Ni_2P$/S31 and (c) used 0.05Pd-$4Ni_2P$/S31.

Table S4. The relative crystallinity and textural property of the used Me/S31 catalysts.

Samples	The relative crystallinity (%)	Surface area (m^2/g)			Pore volume (cm^3/g)		
		BET[a]	Micro.[b]	Ext.	Total[c]	Micro.	Meso.
used 0.05Pd/S31	93	183	100	83	0.318	0.038	0.280
used $4Ni_2P$/S31	87	152	98	54	0.305	0.032	0.273
used 0.05Pd-$4Ni_2P$/S31	80	125	85	40	0.270	0.028	0.242

[a] BET method; [b] t-Plot method; [c] Volume absorbed at p/p_0= 0.99.

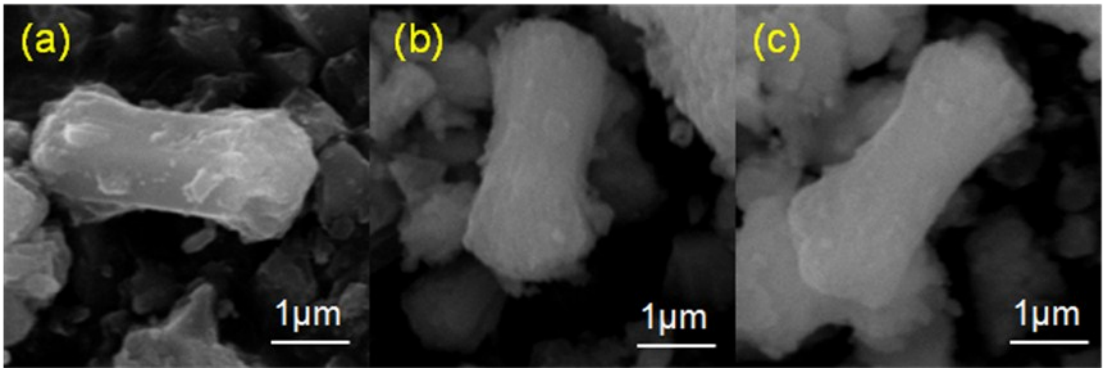

Fig. S8. SEM images of the used Me/S31 catalysts:

(a) used 0.05Pd/S31, (b) used $4Ni_2P$/S31 and (c) used 0.05Pd-$4Ni_2P$/S31.

Table S5. Physicochemical characteristics of the used Me/S31 catalysts.

Sample	Brønsted acid sites (μmol/g)[a]				C_{Me}[b]	Metal content[d]	
	Weak	Medium	Strong	C_{H+}	(μmol/g)	Pd	Ni
used 0.05[c]Pd/S31	11.9	9.6	23.7	45.2	0.834	0.040	-
used 4Ni_2P/S31	9.2	9.0	16.9	35.1	2.087	-	3.5
used 0.05Pd-4Ni_2P/S31	8.4	8.7	16.1	33.2	4.053	0.045	3.8

[a] Measured by Py-IR method.

[b] Calculated from the metal content and metal dispersity measured by H_2 chemisorption method.

[c] The theoretical value of loading metal.

[d]Metal content measured by ICP-OES.

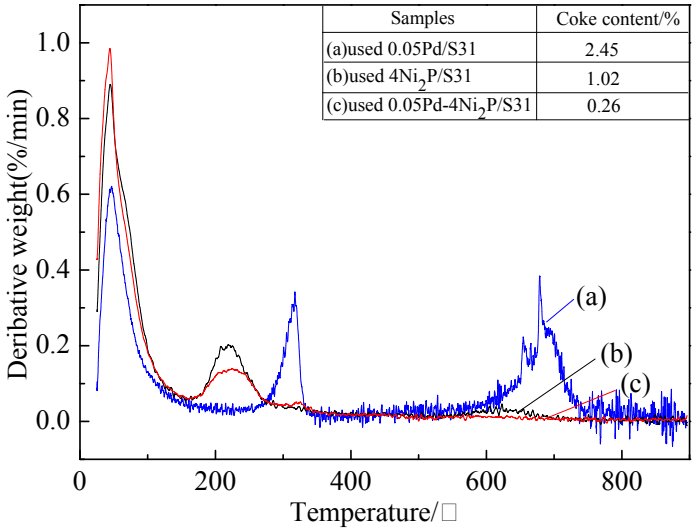

Fig.S9. DTG curves of the used samples:

(a) used 0.05Pd/S31, (b) used $4Ni_2P$/S31 and (c) used 0.05Pd-$4Ni_2P$/S31.