Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supplementary Information for

Synthesis and catalytic application of alumina@SAPO-11 composite *via* the *in situ* assembly of silicoaluminophosphate nanoclusters at an alumina substrate

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Table of contents

1. Supplementary Figures and Tables

Fig. S1 Photographs of the products synthesized following the procedure of alumina@SAPO-11 without adding CTAB.

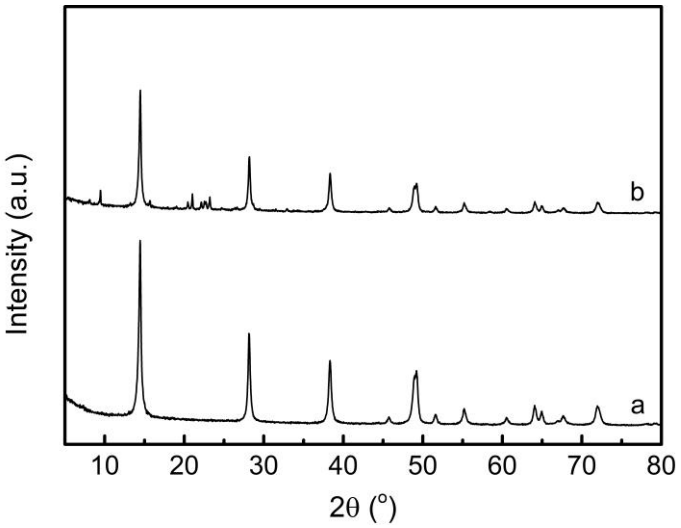

Fig. S2 XRD patterns of the alumina substrate modified without H_3PO_4 (a) and the product synthesized from alumina without H_3PO_4 modification (b).

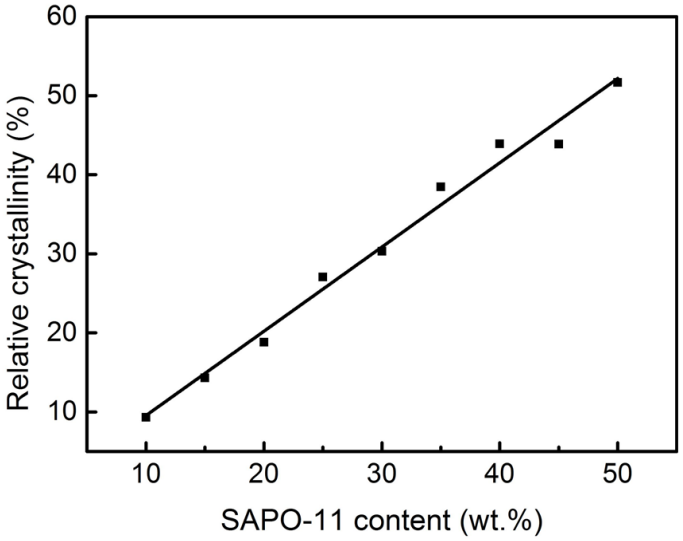

Fig. S3 The relationship between the SAPO-11 content and the relative crystallinity. This curve was obtained by plotting the relative crystallinity of SAPO-11 versus the mass fraction of SAPO-11 in a series of mechanical mixtures of pure SAPO-11 and H_3PO_4 modified alumina.

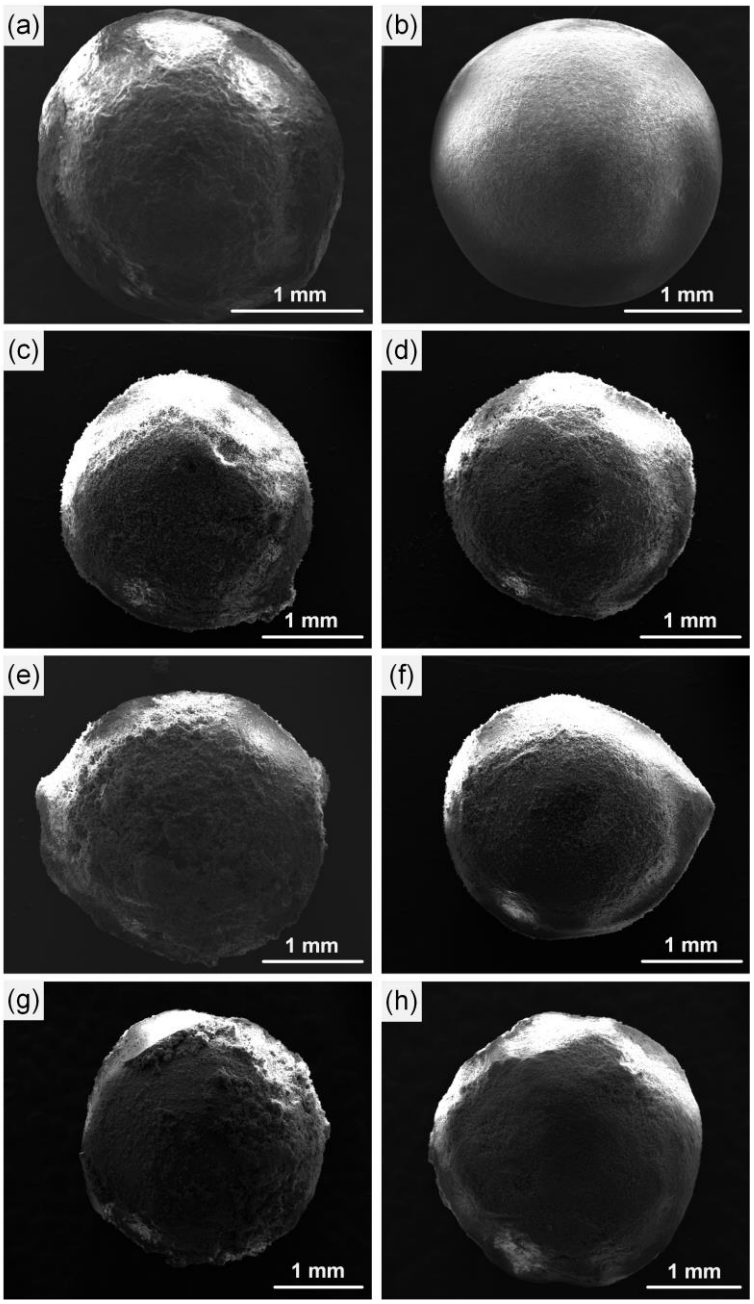

Fig. S4 SEM images of the top-view of the alumina substrate (a), the H_3PO_4 modified alumina substrate (b), and the alumina@SAPO-11 composite (c-h). *Note: In order to check the homogeneity of the alumina@SAPO-11 composite, several particles were randomly selected for taking the SEM images one by one as shown in c-h.*

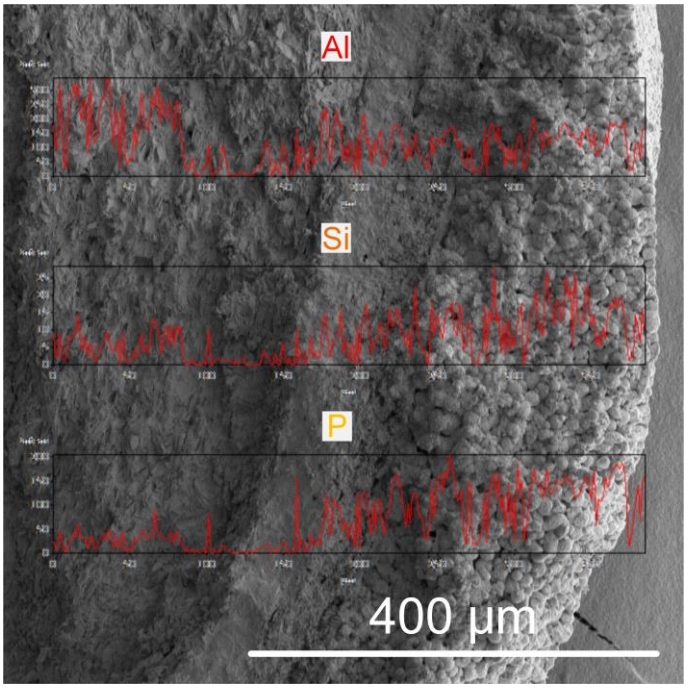

Fig. S5 Line scan analysis for SEM image of the alumina@SAPO-11 composite: Al (red), Si (orange) and P (yellow).

Table S1. Chemical compositions of alumina substrate before/after H_3PO_4 modification.

Sample	Al content[a] %	P content[a] %	Al/P[b] mol/mol
Alumina	52.7	-	∞
H_3PO_4 modified alumina	48.1	3.8	16.6

Notes: [a] Determined by ICP-OES; [b] Determined by XRF.

Table S2. Textural properties of SAPO-11$_{reference}$, alumina@SAPO-11 and alumina-SAPO-11.

Sample	S_{BET}[a] (m^2/g)	S_{micro}[b] (cm^2/g)	S_{ext} (m^2/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)
SAPO-11$_{reference}$	154	112	42	0.05	0.10
alumina@SAPO-11	166	41	125	0.02	0.23
alumina-SAPO-11	120	41	79	0.02	0.22

Notes: [a] BET method; [b] *t*-plot method; [c] BJH method (adsorption branch).

Table S3. Product distributions of *n*-octane over Pt/alumina@SAPO-11 and Pt/alumina-SAPO-11.[a]

	Pt/alumina@SAPO-11	Pt/alumina-SAPO-11
Conversion (%)	66.9	45.9
Product composition w_i[b]		
2-MC_7	35.4	41.6
3-MC_7	38.8	37.6
4-MC_7	10.2	8.5
2,5-DMC_6	5.0	3.4
2,4-DMC_6	4.1	2.4
2,3-DMC_6	2.4	1.2
2,2-DMC_6	0.9	0.1
i-C_5	1.8	2.6
n-C_5	1.1	1.9
2-MC_5	0.1	0.0
3-MC_5	0.0	0.0
n-C_6	0.0	0.1
2-MC_6	0.1	0.2
3-MC_6	0.1	0.2
n-C_7	0.0	0.2
Total	100.0	100.0

Notes: [a] Reaction conditions: Tests were conducted in a continuous flow tubular fixed-bed micro-reactor, W_{cat} = 5 g, 1.5 MPa, 360 °C, H_2/*n*-octane volumetric ratio 300, weight hourly space velocity 1.5 h^{-1}; [b] w_i is the mass fraction of component *i* in the liquid product.

Table S4. Results of *n*-octane hydroisomerization over Pt/alumina@SAPO-11 and Pt/alumina-SAPO-11 at the same level of conversion of 41%.[a]

	Pt/alumina@SAPO-11	Pt/alumina-SAPO-11
Selectivity (%)		
S_{MB}[b]	85.5	85.7
S_{DB}[b]	8.2	6.1
S_C[b]	6.3	8.2
S_{DB}/S_C	1.3	0.7
MON[c]	34.7	33.3
RON[c]	28.9	27.9

Notes: [a] Reaction conditions: Tests were conducted in a continuous flow tubular fixed-bed micro-reactor, W_{cat} = 5 g, 1.5 MPa, 360 °C, H_2/*n*-octane volumetric ratio 300, weight hourly space velocity 4.0 and 2.0 h^{-1}, respectively; [b] S_{MB}, S_{DB} and S_C correspond to the total selectivity to mono-branched C_8 isomers, total selectivity to di-branched C_8 isomers, and total selectivity to cracking products, respectively, at 41% conversion of *n*-octane; [c] MON (motor octane number) and RON (research octane number) are calculated according to the following formula: octane number = $\sum(a_i\, w_i)$, in which a_i is the octane number of component *i* and w_i is the mass fraction of component *i*;[1] and the RON and MON data for each component in the liquid product are adapted from *Technical Data Book-Petroleum Refining* by API (American Petroleum Institute).

Table S5. Product distributions of *n*-octane over Pt/alumina@SAPO-11 and Pt/alumina-SAPO-11.[a]

	Pt/alumina@SAPO-11	Pt/alumina-SAPO-11
Conversion (%)	41.3	41.6
Product composition w_i[b]		
2-MC_7	38.1	41.7
3-MC_7	39.6	39.1
4-MC_7	11.1	8.0
2,5-DMC_6	2.8	3.0
2,4-DMC_6	2.9	1.8
2,3-DMC_6	1.8	1.1
2,2-DMC_6	1.1	0.1
i-C_5	1.4	1.6
n-C_5	0.9	2.1
2-MC_5	0.1	0.1
3-MC_5	0.1	0.0
n-C_6	0.0	0.1
2-MC_6	0.0	0.9
3-MC_6	0.1	0.2
n-C_7	0.0	0.2
Total	100.0	100.0

Notes: [a] Reaction conditions: Tests were conducted in a continuous flow tubular fixed-bed micro-reactor, W_{cat} = 5 g, 1.5 MPa, 360 °C, H_2/*n*-octane volumetric ratio 300, weight hourly space velocity 4.0 and 2.0 h^{-1}, respectively; [b] w_i is the mass fraction of component *i* in the liquid product.

Table S6. Acidity properties of Pt/alumina@SAPO-11 and Pt/alumina-SAPO-11 determined by Py-IR.

Sample	Amount (μmol/g) and distribution of acid sites					
	Total acid sites (200 °C)			Medium and strong acid sites (350 °C)		
	B	L	B + L	B	L	B + L
Pt/alumina@SAPO-11	18.3	66.0	84.3	10.2	23.2	33.4
Pt/alumina-SAPO-11	11.0	70.4	81.4	5.7	29.3	35.0

2. References

1 R. Sun, S. Shen, D. Zhang, Y. Ren and J. Fan, *Energy Fuels*, 2015, **29**, 7005-7013.