Electronic supplementary information

Single-pot synthesis of ordered nanoporous amorphous H-Zn-Aluminosilicate for bulky molecular catalysis †

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1.0 Experimental

1.1 Catalyst preparation

In a typical synthesis method, the nanoporous aluminosilicate (HAlSi) was synthesized by using 1.8 g aluminum iso–propoxide (AIP, SD Fine Chem-Limited) mixed with 24 g tetra-propyl ammonium hydroxide (TPAOH, Merck India Limited) in a beaker to get solution A. Similarly, solution B was prepared by mixing 24 g of tetramethyl ammonium hydroxide (TMAOH, ACROS) with 28.8 g tert-ethyl ortho-silicates (TEOS, Merck India Limited). The resultant solution B was mixed slowly with solution A by drop-wise addition and continuous stirring at room temperature. After the completion of 30 minutes of mixing, the solution gets transformed into wet gel, which was then transferred to a Teflon-bottle for hydrothermal treatment in an autoclave for 48 h at 140^{o}C. The solid product hence obtained after the hydrothermal treatment was thoroughly washed with ample amount of distilled water and then filtered. The solid cake thus obtained was allowed to dry at room temperature and then calcined at 500 ^{o}C for 5 h. The resultant material was denoted by HAlSi. Similar method is used for the synthesis of HZnAlSi, where additional use of 2.6 g zincnitrate hexahydrate (ZNH, Merck India Limited) has been done in the solution B so as to introduce Zn into the structure and the final material obtained was denoted by HZnAlSi.

1.2 Catalyst characterization

Scanning Electron Microscope (SEM)

SEM images were recorded for obtaining particle morphology on Quanta 200f instrument, Netherlands.

Transmission Electron Microscopy (TEM)

TEM images were recorded on JEOL, JSM-2100F instrument, Japan.

X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) patterns were measured on D8 advance, Bruker, Germany has instruments like rotating anode and CuKα radiations. The measurements were carried out in continuous θ/2θ scan refraction mode. The operating conditions at anode are at 30 KV and 15 mA the 2θ angles were measured between 5°-70° at the rate of 2°/min. Low angle XRD patterns also measures at low angle (0.2-1.4°θ).

Fourier transform infrared spectroscopy (FTIR)

The Fourier transform infrared spectroscopy (FTIR) spectra of the zeolite samples were recorded with KBr pellet method on Perkin Elmer-spectrum two, USA.

Surface area measurement

The BET surface area, pore size and pore volume measurements of all the zeolite based catalysts were carried out using a standard adsorption equipment (ASAP 2010, Micromeritics Instruments Inc., Norcross, GA, USA) using N_2 gas (99.995% pure). For measuring above characteristics, 0.2g of the sample is taken in a specially designed sample tube and degassed at 573 K under vacuum of 1.3 $\times 10^{-6}$ bar for 4h A frit is attached to the mouth of the sample tube, so that when the sample tube is removed from the preparation mode, it does not allow the sample to expose in atmosphere. The sample is cooled to room temperature under vacuum and the sample tube is removed from the preparation port and attached to the analysis port of the instrument. For all the samples.

Pore size distribution

N_2 adsorption desorption isotherms were obtained at 77K and the temperature was maintained constant by using liquid nitrogen, whereas helium gas was used for measuring the dead space. The surface area, pore volume and pore size distribution were obtained by measuring the volume adsorbed at different P/P_0 values and by applying different methods. Total pore volume was estimated by measuring the volume of gas adsorbed at P/P_0 of 0.99 whereas, t-plot method was used to calculate the micro pore surface area (0-20Å) using the Harkins-Jura equation. The total micro pore volume (0-20 Å) and the micro pore size distribution were obtained by applying the Horvath-Kawazoe method (H-K).

Temperature program desorption (TPD)

The acidity of the catalyst was measured by temperature programmed desorption of NH_3 (NH_3-TPD) using a Micromeritics chemisorbs 2750 pulse chemisorption system. 0.1g sample was used for each TPD experiment. It was carried out after of the catalyst sample was dehydrated at 500°C in helium gas (30cm^3 min^{-1}) for 1h. The temperature was decreased to 100°C and NH_3 was adsorbed by exposing sample treated in this manner to a stream containing 10% NH_3 in helium for 1h at 100°C. It was then flushed with helium for another 1h to remove physically adsorbed NH_3. The desorption of NH_3 was carried out in helium gas flow (30 cm^3 min^{-1}) by increasing the temperature up to 800°C at 10°C min^{-1} heating rate, measuring NH_3 desorption using TCD detector.

Thermo gravimetric analyses (TGA)

TGA of the catalysts were carried out in a Pyris Diamond, Perkin Elmer TGA 4000, USA instrument by heating 2.15 mg samples at 5°C min^{-1} in flowing air atmosphere.

Raman spectra

Raman spectra were collected by using a confocal Raman microscope (XploRA ONE from Horiba) with 25 mW 532 nm laser (laser spot size: 2 lm) line from a diode-pumped solid-state laser for excitation.

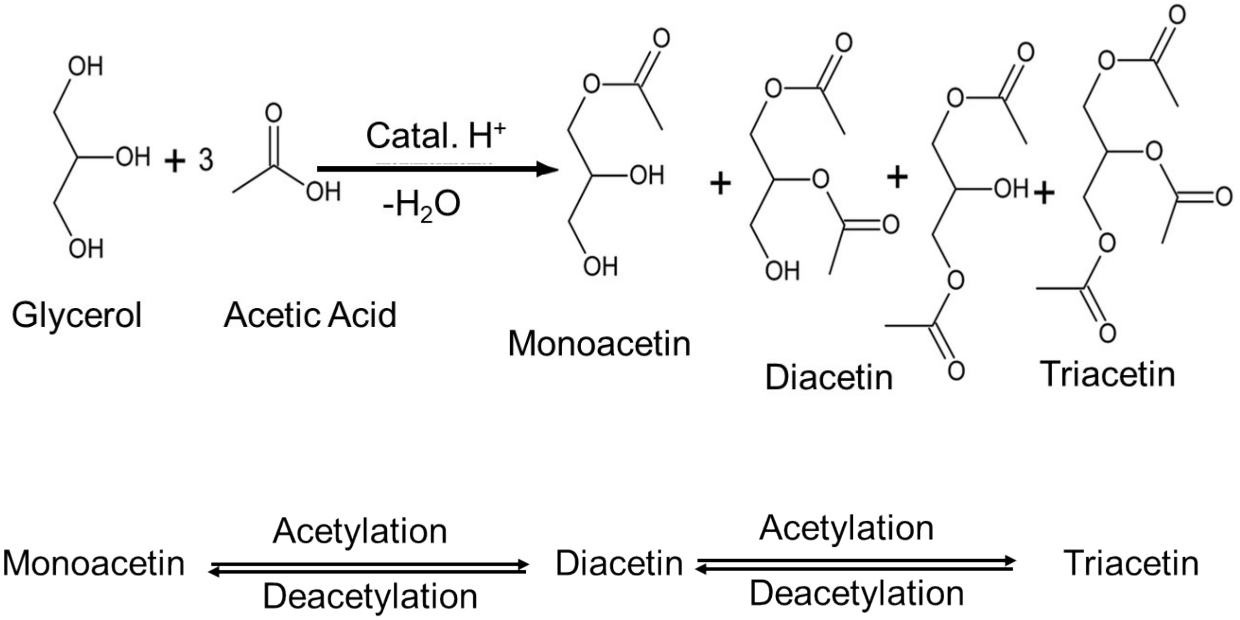
X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed with a Kratos AXIS Ultra DLD apparatus, United Kingdom equipped with monochromated Al Kα radiation X-ray source, a charge neutralizer and a hemispherical electron energy analyzer. During data acquisition, the chamber pressure was kept below 10^{-9} mbar. The spectra were analysed using the CasaXPS software pack and corrected for charging using C1s binding energy (BE) as the reference at 284.8 eV. The Si/Al wt% ratio of the catalysts was carried out by ICP-MS (DRE, PS-3000UV, LEEMAN LABS, INC, USA).

2.0 Catalyst testing

2.1 Glycerol acetalization

In a typical glycerol acetylation reaction 1:6/1:3 (glycerol : acetic acid) mole ratio of the reactant has been taken and 4.7 wt% of catalyst is used to catalyse the reaction. For this, 0.64 g of catalyst was added to a mixture of 2.7 g of glycerol (MERCK) and 10.8 g of acetic acid (MERCK) taken in a 50 ml of round bottom flask equipped with water condenser. Temperature of the reaction mixture was taken to 110/120 ^{o}C by using IKA (C-MAG HS7) hotplate and the reaction was perfomed at this temperature for 5 hrs by continues starring of mixture at 500 RPM for 5 hour. At the end of the reaction, the mixture was cooled up to room temperature (25^{o}C). The reaction product and catalyst was separated by filtration and the catalyst was washed with distilled water and calcined at 500^{o}C for regeneration of catalyst for further uses. The reaction product was analysed by using Agilant GC (7890B) equipped with the HP-1 column (30m X 0.25mm) and Agilant MS (5977A) detector.



SchemeS1. Reaction scheme for glycerol acetylation with acetic acid

3.0 Supporting Tables

Table: S1 Performance comparison of the present catalyst with those reported for glycerol acylation

S. No.	Catalyst	Conversion of glycerol (%)	Product Yield (wt %)			
			Monoacetin	Diacetin	Triacetin	Other
1*	**HZnAlSi**	**99.9**	**16.5**	**--**	**83.4**	**--**
2*	**HAlSi**	**96.4**	**76.4**	**7.9**	**12.0**	**--**
3	[1]Amberlyst-15	97	30.0	52.4	12.6	1.9
4	[1]K-10	96	42.2	47.0	4.8	1.9
5	[1]Niobic Acid	30	24.9	--	--	5.1
6	[1]HZSM-5	30	24.9	3.0	--	2.1
7	[1]HUSY	14	11.0	1.9	--	0.9
8	[2]Pr-SBA-15	76	25.8	33.4	16.7	--
9	[3]A15	100	--	12.3	83.9	3.8
10	[3]STA/S11	100	1.0	55.5	35.8	7.7
11	[3]TPA/S11	100	4.9	71.3	21.8	2.0
12	[4]H_2SO_4	96.3	58.3	24.8	13.2	--
13	[5]H_2SO_4	96.3	60.5	25.8	13.7	--
14	[5]H_2SO_4	98.51	41.7	49.3	8.9	--
15	[6]Al-clay	60	41	10	9	--
16	[6]PDSA-clay	96	14	26	56	--
17	[6]p-TSA	94	30	35	29	--
18	[7]Ar-SBA-15	96	15	47	38	--
19	[8]Silica-alumina	71	88.5	11.2	0.3	--

* Present studies

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[3] S. Kale, U. Armbruster, S. Umbarkar, M. Dongare, A. Martin, 10th Green Chem. Conf. (2013) 70–71.
[4] Z. Mufrodi, Rochmadi, Sutijan, A. Budiman, Eng. J. 18 (2014) 29–39.
[5] Z. Mufrodi, S. Rochmadi, A. Budiman, Int. J. Chem. 4 (2012) 101–107. doi:10.5539/ijc.v4n2p101.
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[8] Kim I, Kim J, Lee D. Appl. Catal. B Environ. 148–149 (2014) 295–303.

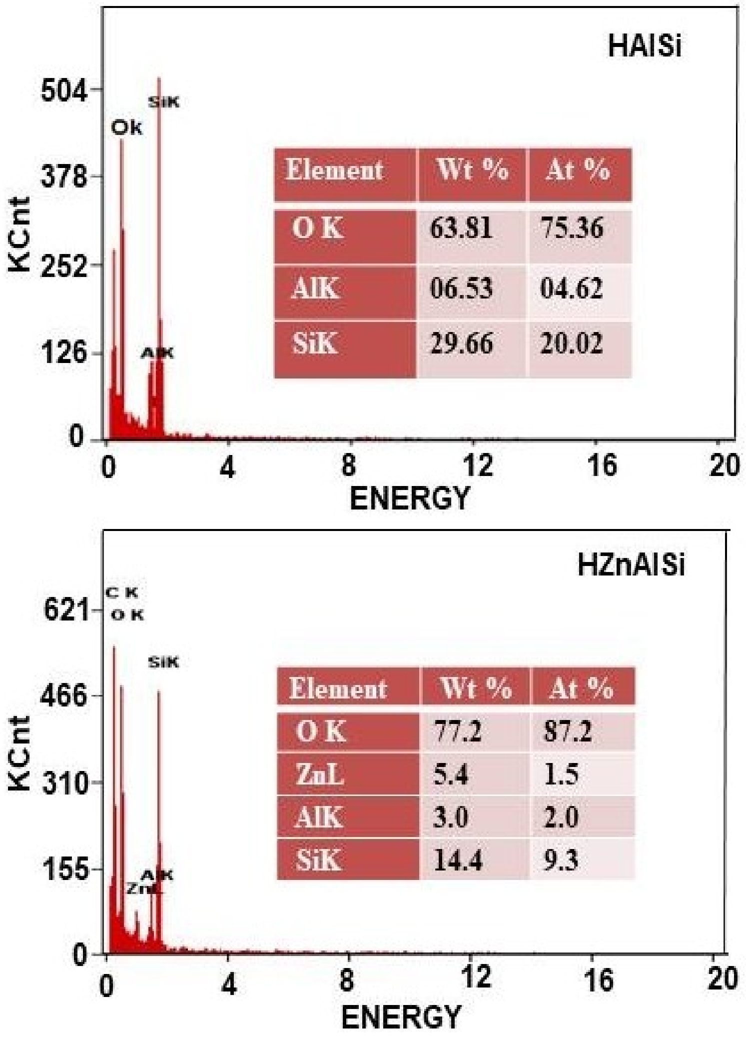
Table: S2 Chemical composition and acidic properties of the catalysts system

Catalyst	ICP analysis			Si/Al (ICP)	Si/Al (SEM-EDX)	Acidity (m.mol g^{-1})		
	Si (wt%)	Al (wt%)	Zn (wt%)			Total	Strong	Weak
HAlSi	28.7	5.4	--	5.3	4.5	7.16	1.66	5.5
HZnAlSi	28.3	4.2	4.6	6.7	4.8	6.8	0.7	6.14

Table: S3 Physiochemical properties of the catalysts system

Sample	S_{BET} (m^2/g)	t-plot S_{Micro}(m^2/g)	t-plot S_{Exter}(m^2/g)	V_{Total}(cm^2/g)	t-plot V_{Micro}(cm^2/g)	V_{Meso} (cm^2/g)
HAlSi	265.5	17.5	247.8	0.37	0.0098	0.36
HZnAlSi	213.0	17.0	195.8	0.70	0.0091	0.69

4.0 Supporting Figures



Element	Wt %	At %
O K	63.81	75.36
AlK	06.53	04.62
SiK	29.66	20.02

Element	Wt %	At %
O K	77.2	87.2
ZnL	5.4	1.5
AlK	3.0	2.0
SiK	14.4	9.3

Fig. S1 SEM-EDX analysis of fresh sample

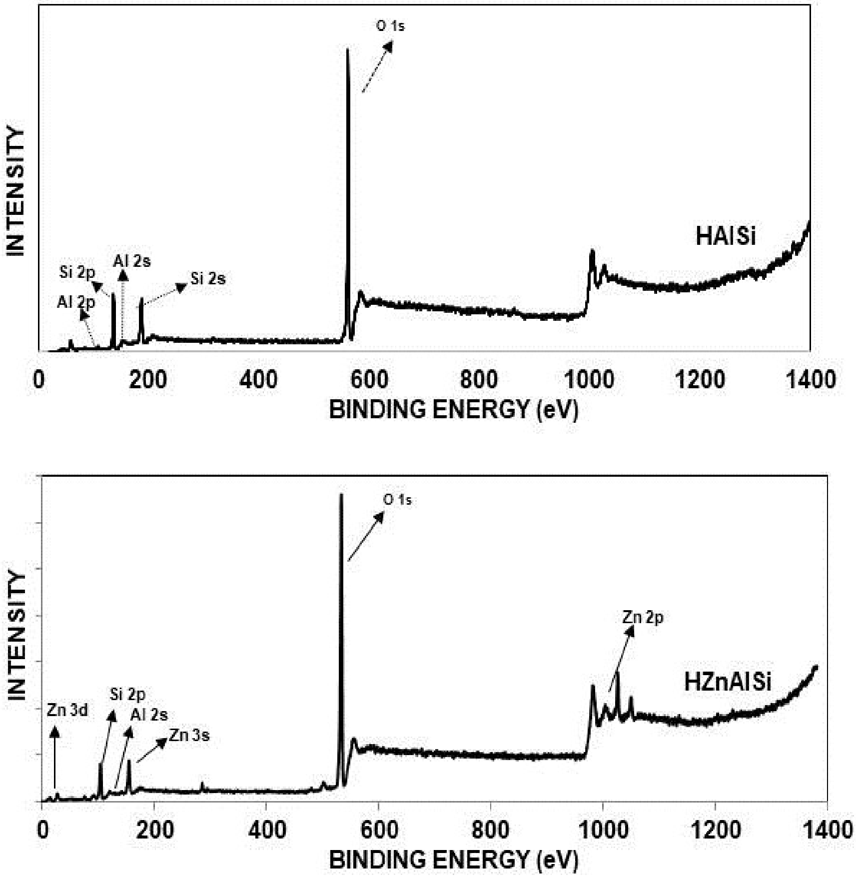


Fig. S2 XPS analysis of materials

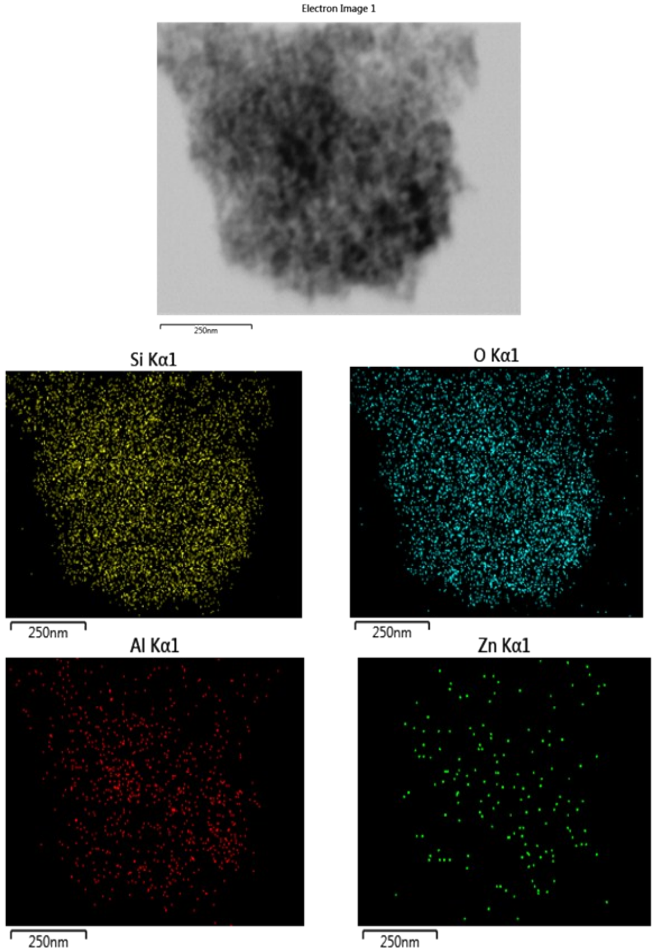


Fig. S3 Elemental mapping HZnAlSi

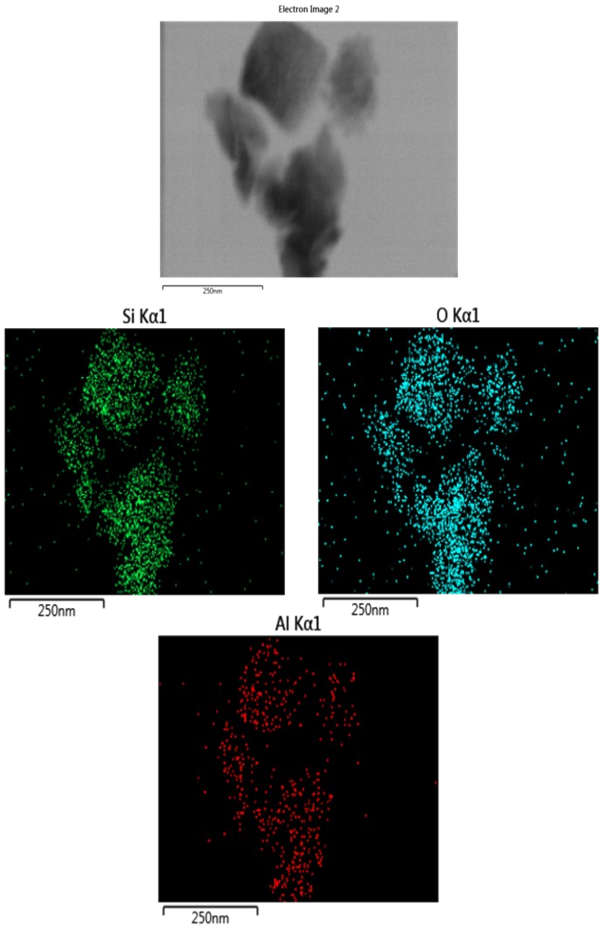


Fig. S4 Elemental mapping HAlSi

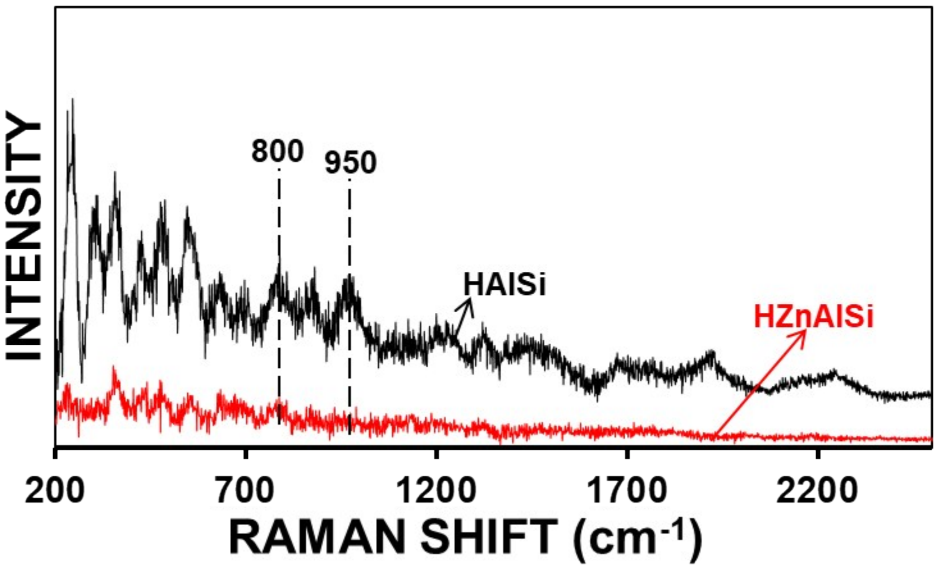


Fig. S5 Raman spectrum of the materials

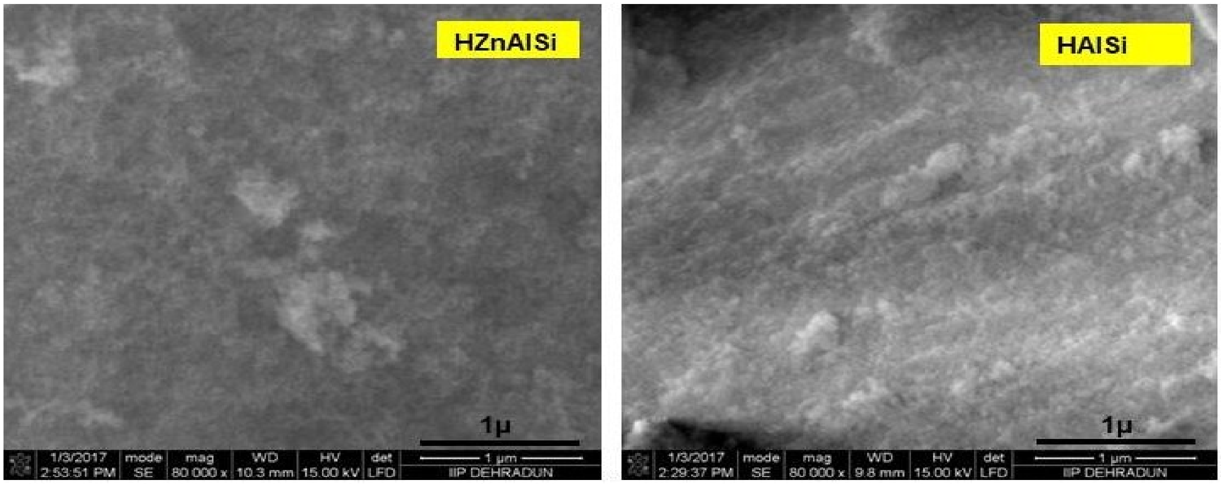


Fig. S6 SEM images of the materials

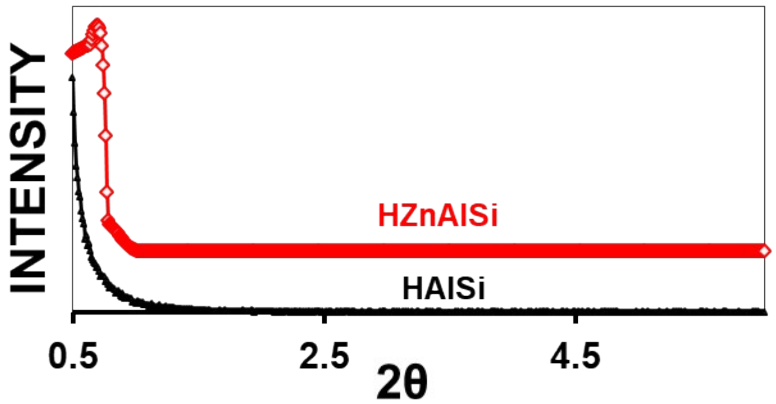


Fig. S7 Low-angle X-Ray Diffraction pattern of the materials

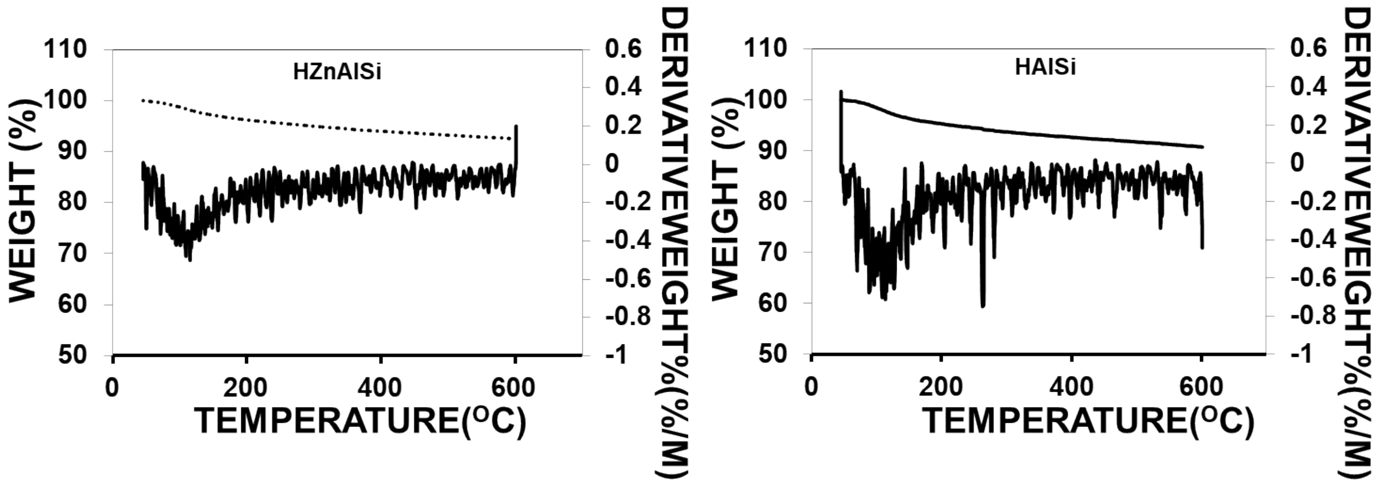


Fig. S8 TG/DT Analysis of the materials

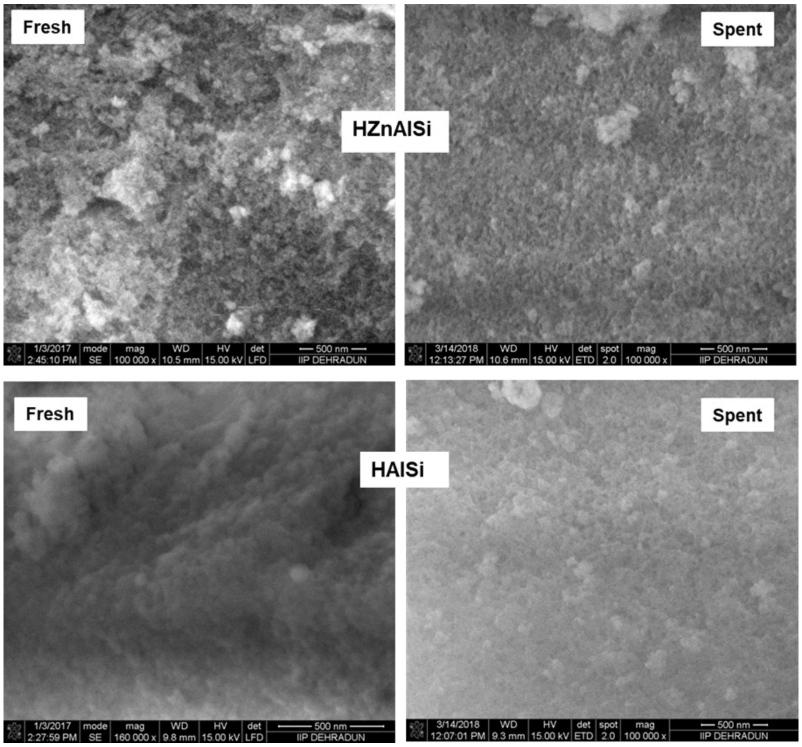


Fig. S9 SEM images of the spent catalysts

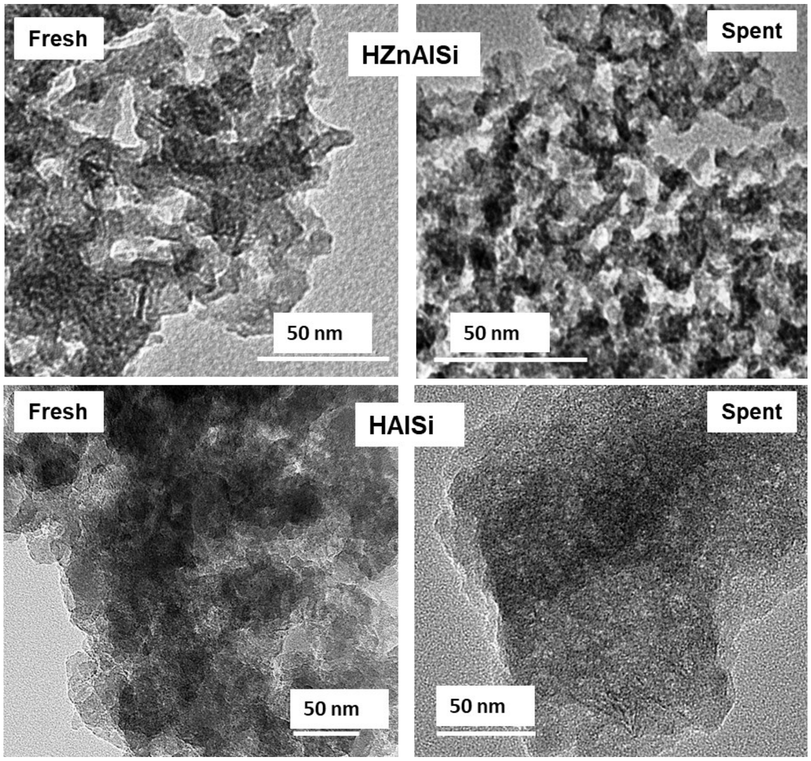


Fig. S10 TEM images of the spent materials

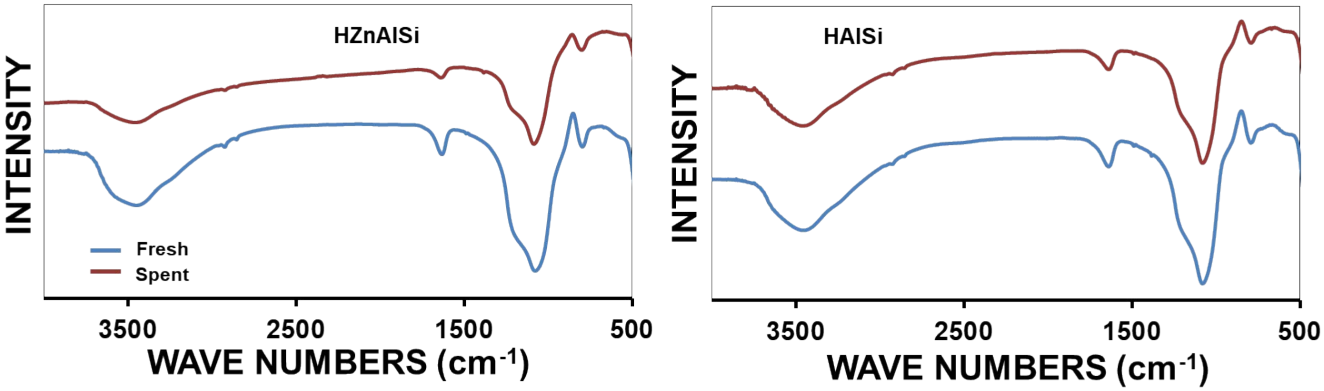


Fig. S11 FTIR analysis of the spent materials

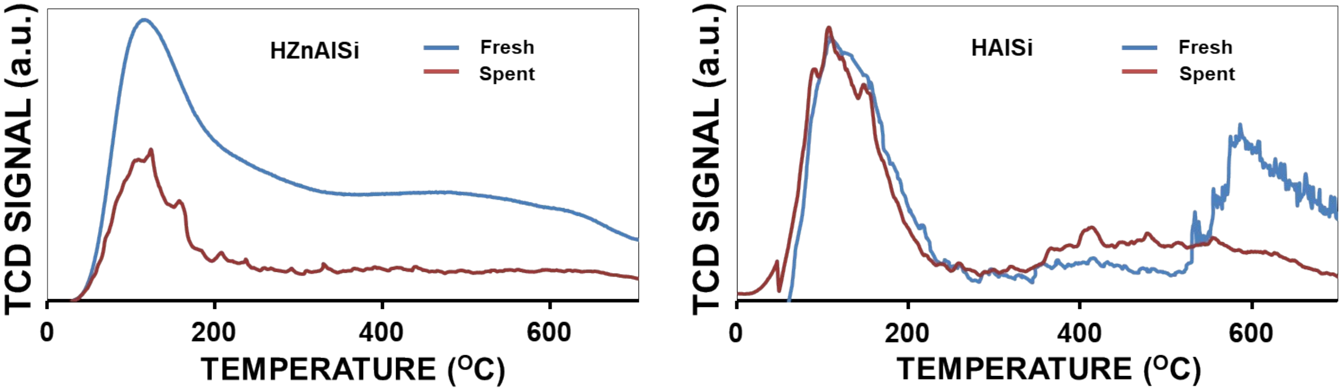
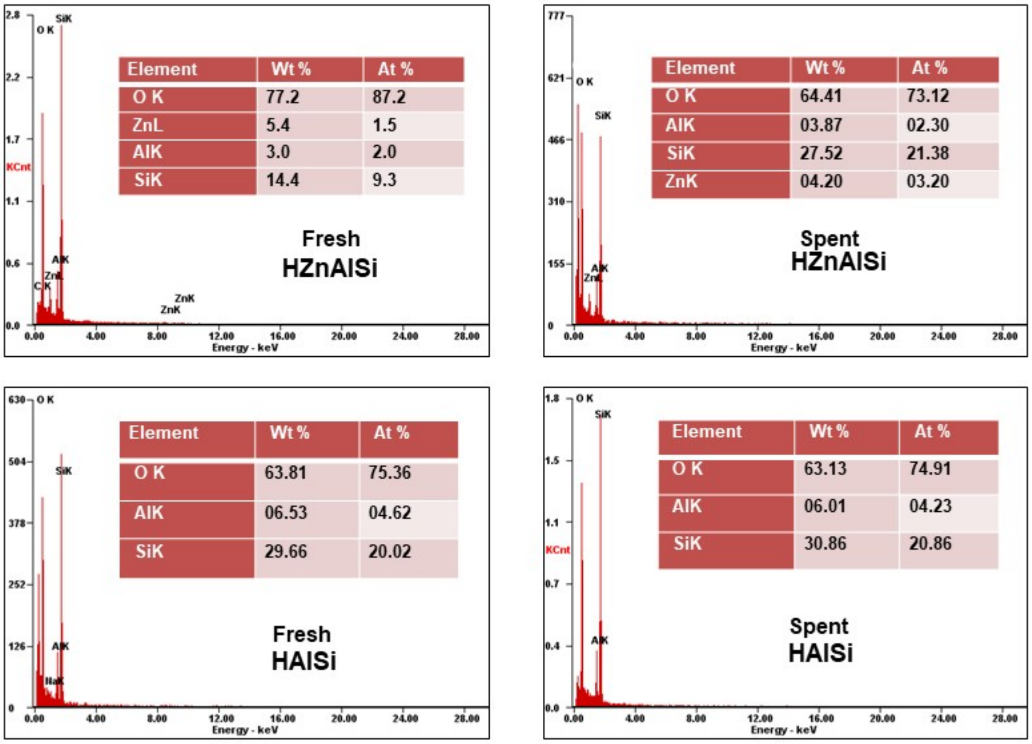


Fig. S12 TPD Analysis of the spent materials



Fresh HZnAlSi

Element	Wt %	At %
O K	77.2	87.2
ZnL	5.4	1.5
AlK	3.0	2.0
SiK	14.4	9.3

Spent HZnAlSi

Element	Wt %	At %
O K	64.41	73.12
AlK	03.87	02.30
SiK	27.52	21.38
ZnK	04.20	03.20

Fresh HAlSi

Element	Wt %	At %
O K	63.81	75.36
AlK	06.53	04.62
SiK	29.66	20.02

Spent HAlSi

Element	Wt %	At %
O K	63.13	74.91
AlK	06.01	04.23
SiK	30.86	20.86

Fig. S13 SEM-EDX Analysis of the spent catalyst systems