Electronic Supplementary Information

A strategy to convert propane to aromatics (BTX) using $TiNp_4$ grafted on ZSM-5 by surface organometallic chemistry.

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General Procedures.

All experiments have been carried out using the SOMC tools developed by us since 1980. [1-10]

In particular, the experiments were all carried out under inert atmosphere by using high vacuum lines and glove boxes. The amount of silanols were measured by reaction of MeLi and titration of the evolved methane. This determination was beneficial to react to half of the silanols with a calculated amount of $TiNp_4$.

- Preparation of [ZSM-5_{300}].

[H-ZSM-5] was obtained after calcination of commercial [NH_3-ZSM-5] purchased from Alpha-Aesar at 550 °C under air for 6 hours. The dehydration of [H-ZSM-5] at 300 °C under vacuum afford the [H-ZSM-5_{300}]. The concentration of isolated silanols (≡Si-OH) after dehydration at 300 °C of [H-ZSM-5_{300}] was calculated by the quantity of MeLi reacting with ≡Si-OH. 0.4 ± 0.1 mmol of Si-OH per gram of [H-ZSM-5_{300}] are found.

- Synthesis of [Ti/ZSM-5].(**Catalyst 1**):

A mixture of (150 mg, 0.80 mmol) of $TiNp_4$ and [H-ZSM-5_{300}] (1 g) in pentane (15 mL) was stirred at room temperature for 8 h. After filtration, the solid was washed 3 times with pentane. The resulting powder was dried under vacuum (10^{-5} bar) at 80 °C. Elemental analysis: Ti ~ 0.8 wt. %, C= 3.9 wt. %.

- Synthesis of [Ti-H/ZSM-5].(**Catalyst 2**):

The catalyst 2 [Ti-H/ZSM-5] was prepared after heat treatment under H_2 of catalyst 1 freshly prepared at 550 °C for 2h. Elemental analysis: Ti~ 0.8 wt. %, C~ 0.2 wt. %.

- Catalytic test

Reactivity toward propane was studied in a stainless steel continuous flow reactor unit (PID® unit) =1 bar, T = 550 °C, total flow rate = 20 mL min^{-1} (100 vol % propane), with (2 ml) of N_2 as standard and catalyst =(150 mg). The gases were purified by passing through a filter (Cu_2O/Al_2O_3), with flow rates controlled by Brooks mass flow controllers. Catalysts were loaded into the reactor inside the glovebox. The lines were purged before starting the reaction. The produced gases were analyzed by Gas Chromatography in a Varian CG-450 with three channels: 1 TCD and 2 FID as described below:

- 1 TCD connected to Molsieve 13X column for N_2 detection

- 1 FID connected to Alumina column for alkanes and olefins from C1 to C4.
- 1 FID connected to Rxi-624 Sil MS column (10 m x 0.53 mm x 3 µm) for aromatics.

The conversion was calculated concerning the carbon numbers from FID.

Supporting Section 1: Nitrogen adsorption/desorption measurements

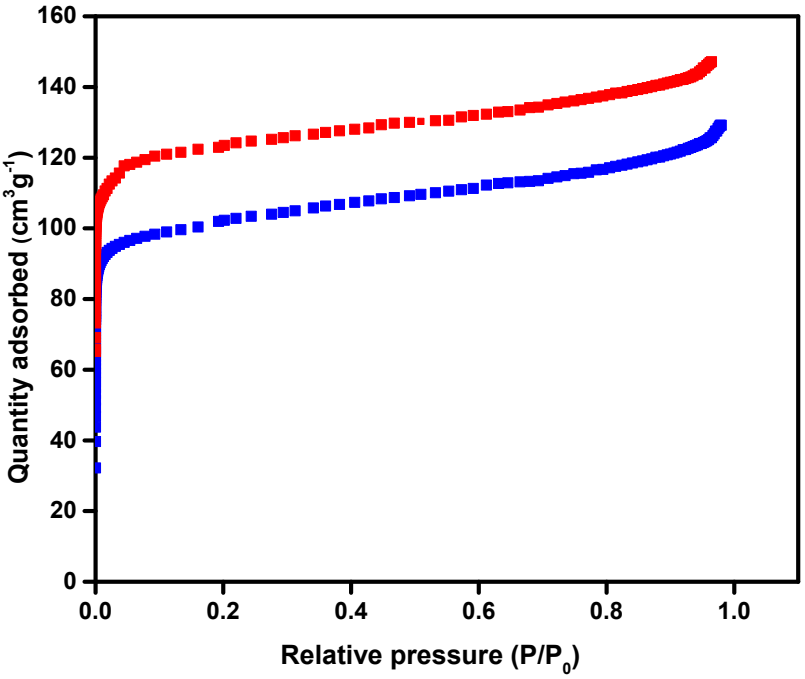

Fig. 1-ESI: N_2-Physisorption for [H-ZSM-5_{300}] (blue), and [Ti-H/ZSM-5] (Red) (after treatment under H_2 at 550 ^oC for 2 h).

Supporting Section 2: XRD analysis

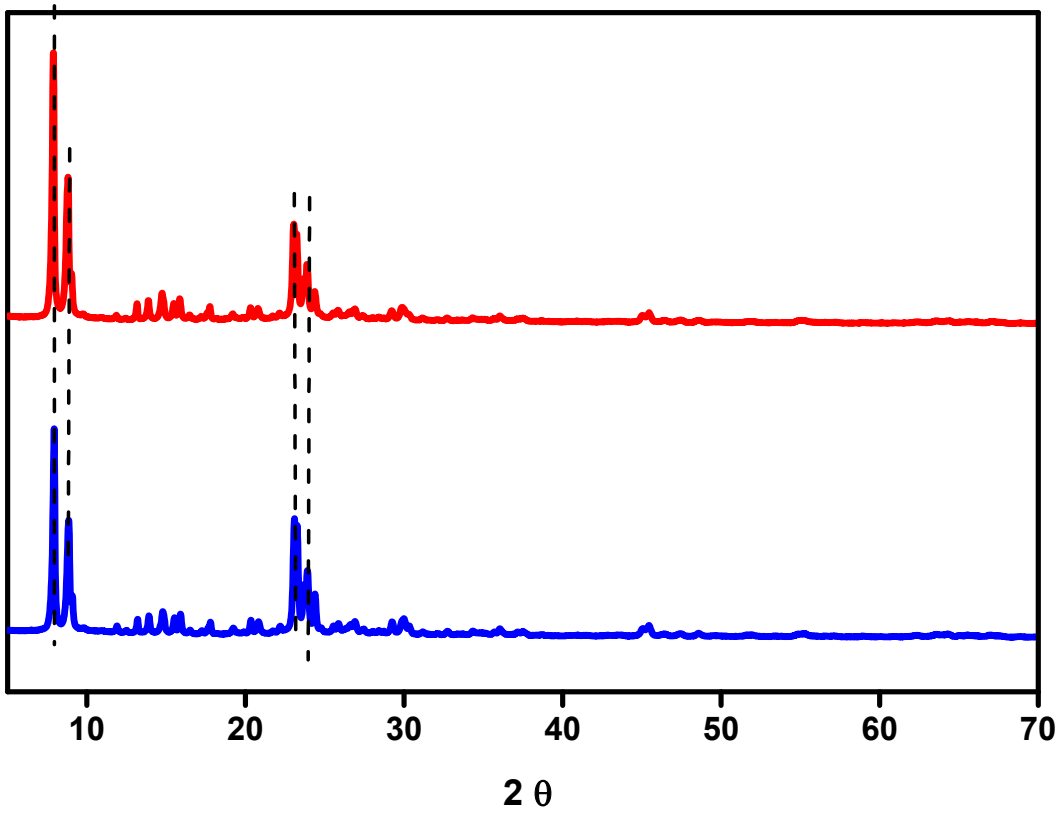

Fig. 2-ESI: Powder X-ray diffraction patterns of the parent zeolite [H-ZSM-5_{300}] (blue), [Ti-H/ZSM-5] (Red) after treatment under H_2 at 550 ^oC for 2 h.

Supporting Section 3: Solid stat S NMR analysis

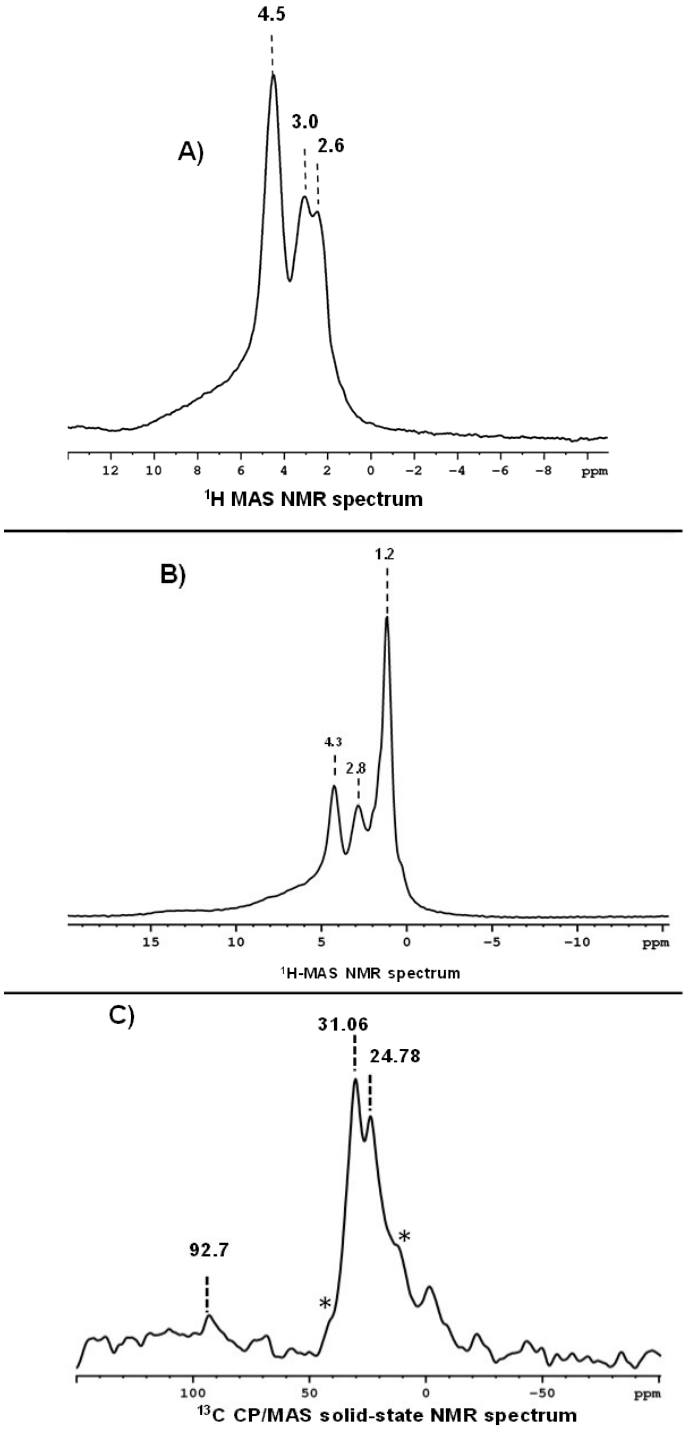

Fig. 3-ESI: (A) ^{1}H NMR spectrum of H-ZSM-5_{300}, **(B)** ^{1}H NMR spectrum of [Ti/ZSM-5] fresh catalyst, (C) ^{13}C CP-MAS NMR spectrum of [Ti/ZSM-5] fresh catalyst. * Carbon peaks of pentane.

Supporting Section 4: Survey spectra of XPS analysis

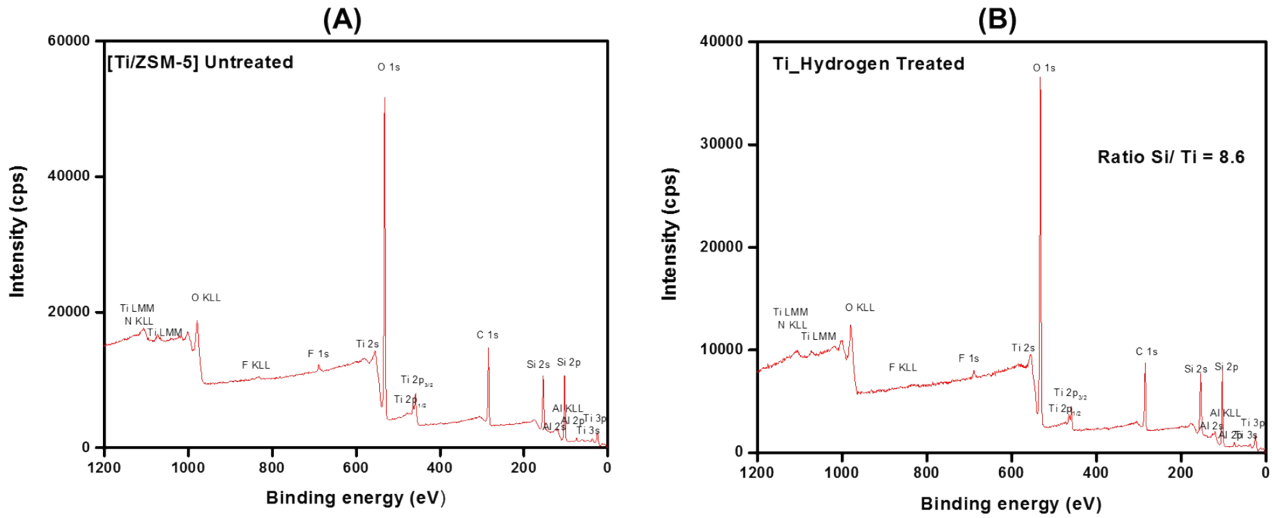

Fig. 4-ESI: (A) The survey spectra for the fresh catalysts **1** [Ti/ZSM-5], **(B)** The survey spectra for the catalysts **2** after treatment under H_2 for 2h at 550 ^{o}C.

Supporting Section 5: HR-TEM analysis (HAADF-STEM)

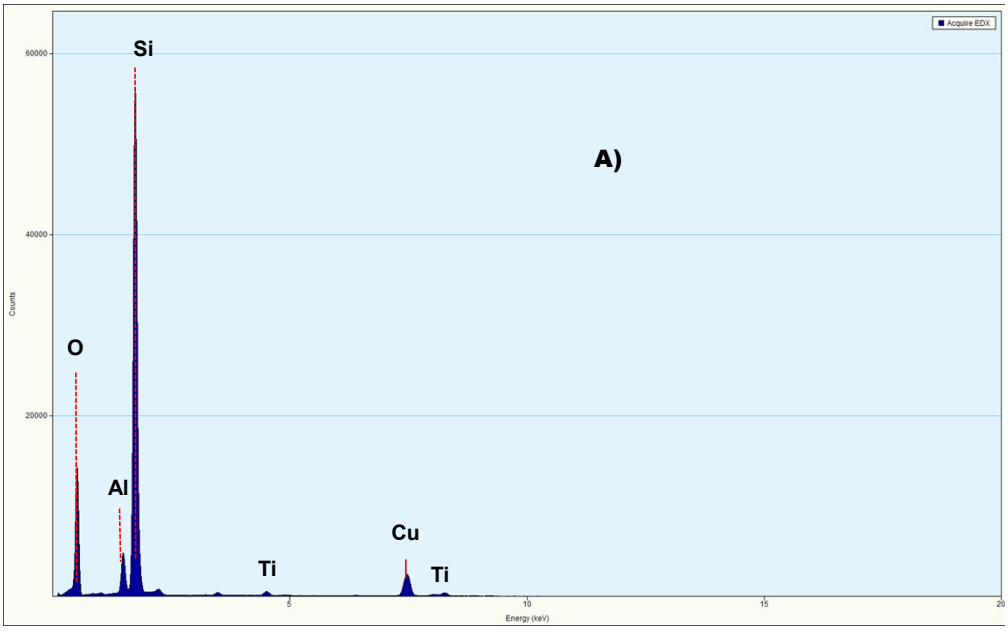

Fig. 5-ESI: (A) EDX spectrum of [Ti-H/ZSM-5] after treatment under H_2 at 550 ^oC for 2h.

Supporting Section 6: Fourier transform infrared (FTIR) spectroscopy of adsorbed pyridine

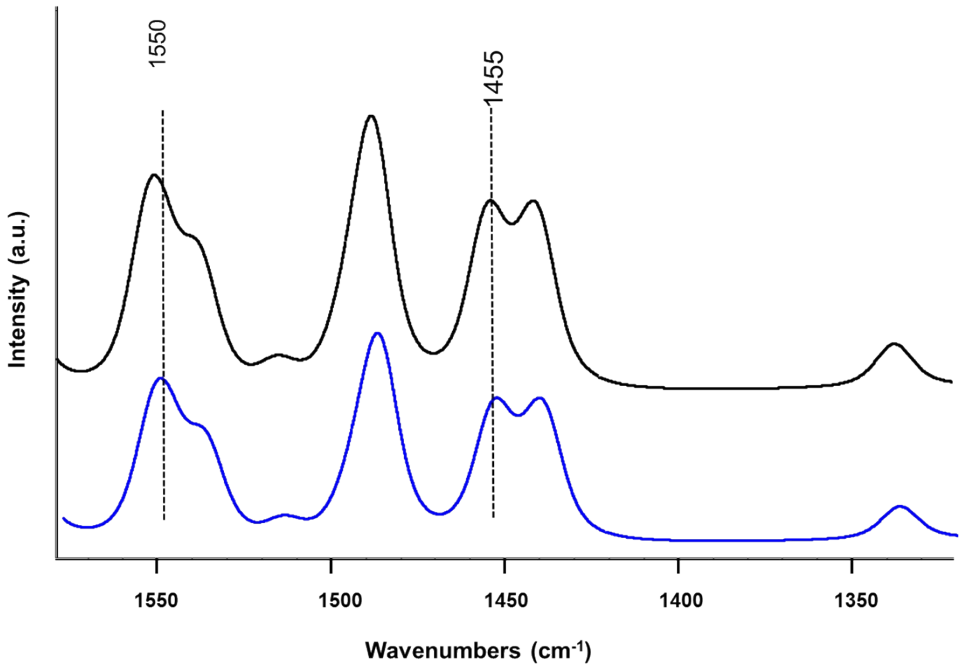

Fig. 6-ESI: FT-IR spectra of the pyridine adsorption of the catalysts, [H-ZSM-5_{300}] (blue), and [Ti/ZSM-5] (black) catalyst **1**.

Supporting Section 7: Raman spectroscopy analysis

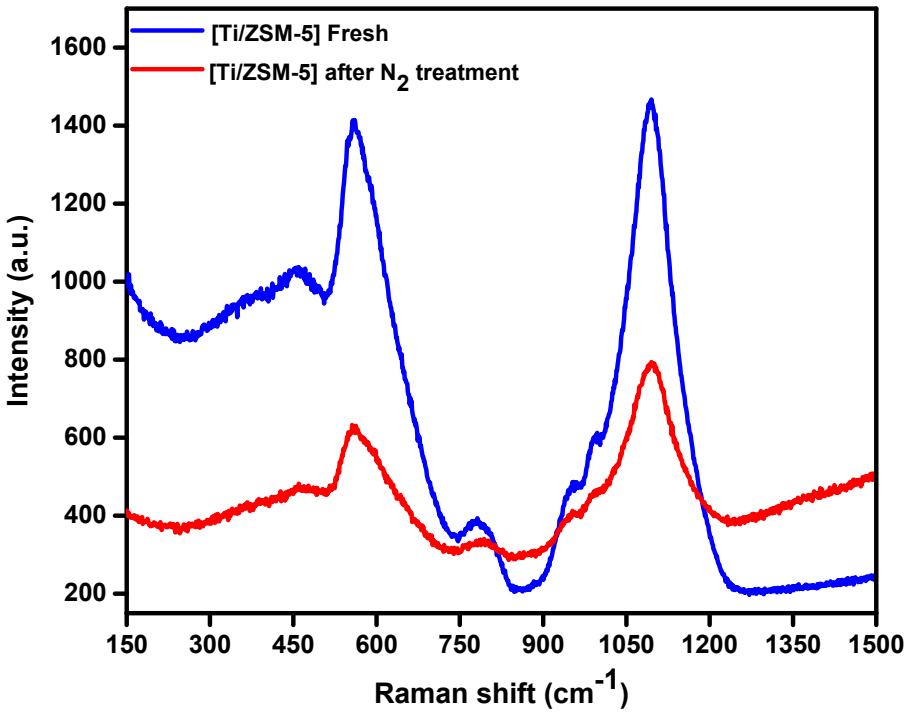

Fig. 7-ESI: Raman spectrum of [Ti/ZSM-5] Fresh sample (blue), and of [Ti-H/ZSM-5] (Red) (after treatment under H_2 at 550 ^oC for 2h).

Supporting Section 8: Catalytic performance

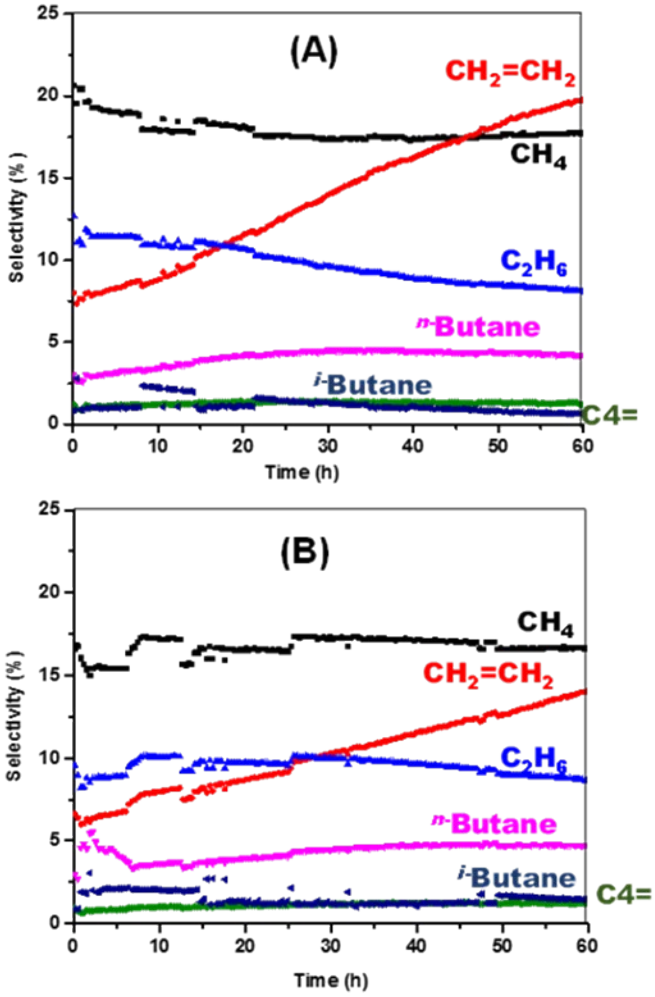

Fig. 8-ESI: Selectivity for CH_4, C_2H_6, C_2H_4, n-butane, *i*-butane and butene(C4=) over [H-ZSM-5_{300}] **(A**) and over [Ti-H/ZSM-5] **(B)**. Reaction conditions: m (catalyst) = 150 mg, P = 1 bar, T = 550 °C, total flow rate (100 % C_3H_8) = 20 mL min^{-1}.

Supporting Section 9: TGA analysis part 1

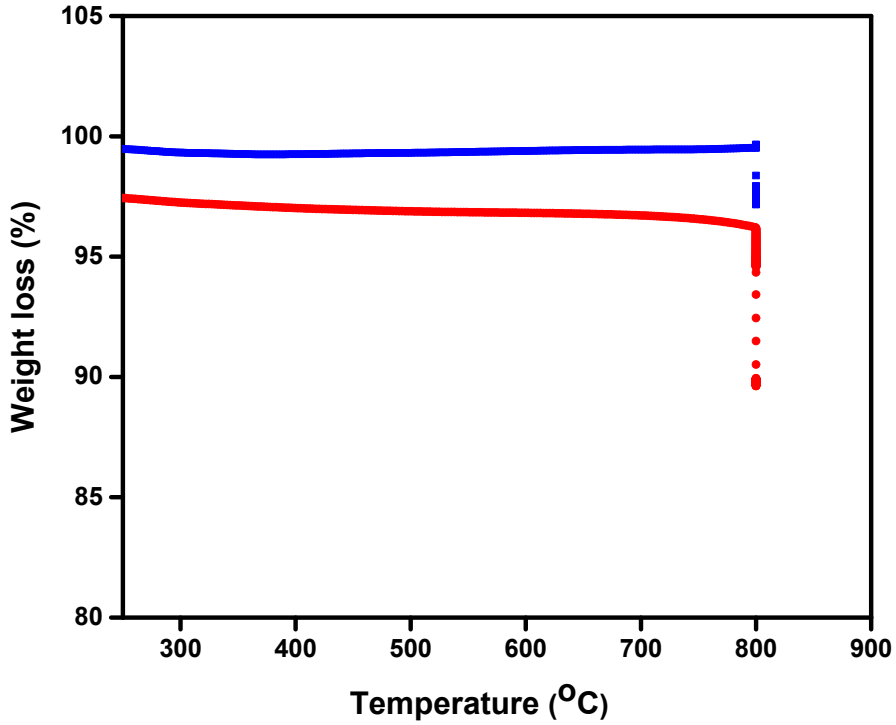

Fig. 9-ESI: TGA analysis of the spent catalysts [ZSM-5_{300}] (blue) and [Ti-H/ZSM-5] (black) after 60 h of conversion of propane.

Supporting Section 10: TGA analysis part 2

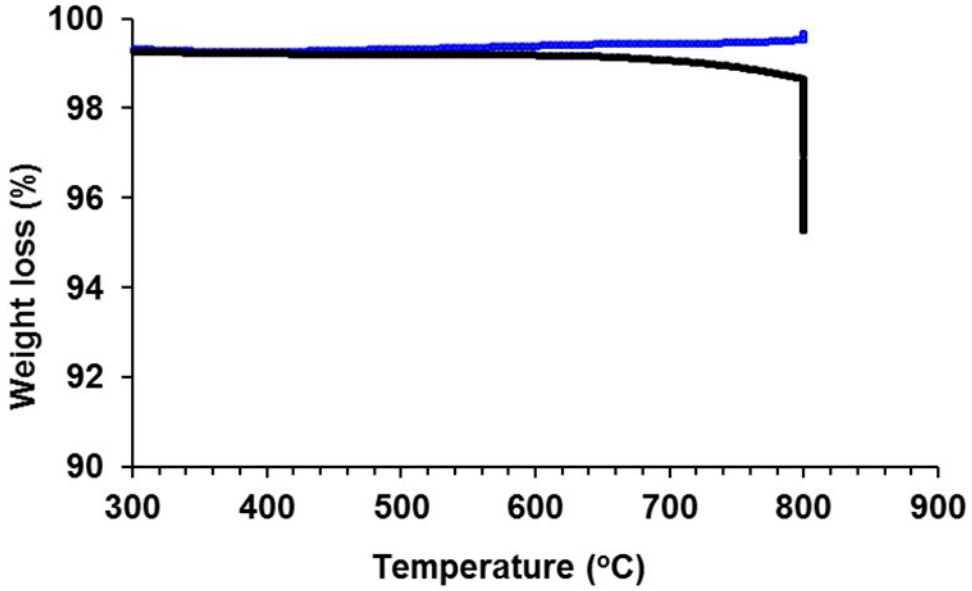

Fig. 10-ESI: TGA analysis of the spent catalysts [Ti-H/ZSM-5] (black), and [H-ZSM-5_{300}] (blue)) after 5 h of conversion of propane.

Reference

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