Supplemental information

for

Two-way Desorption Coupling to Enhance Syngas to Aromatics by MnO/H-ZSM-5

*Syed Zulfiqar Ali Gilani, le lu, Muhammad Tahir Arslan, Babar Ali, Wang Qi, Fei Wei**

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084

Experimental Procedures

Preparation of metal oxide

Manganese oxide (Mn_2O_3) was prepared by a method of co-precipitation. Aqueous solution of Manganese nitrate $Mn(NO_3)_2$ 50% in water and ammonium carbonate $(NH_4)_2CO_3$ solutions 0.5 M were co-precipitated simultaneously slowly in distilled water at 70 ^oC temperature. The pH of the main solution was maintained at 7 by controlling the flow rate. After precipitation, the liquid was aged for 3 hours at a same temperature. The precipitate was thoroughly washed with distilled water and dried in an oven at 100 ^oC overnight. Calcination was performed at 500 ^oC for 5 hours in air.

Preparation of nano-size short b-axis H-ZSM-5

Zeolite H-ZSM-5 was prepared according to the method reported elsewhere.[1] In summary 0.1 g NaOH (Sodium hydroxide), 0.3 g $Al(NO_3)_3$. $9H_2O$ (Aluminum nitrate), 0.1 g IPA (Iso-propyl alcohol), 13.1 g TPAOH (Tetrapropylammonium hydroxide, 25% in water), 11.2 g TEOS (Tetraethyl orthosilicate), 2.0 g CH_4N_2O (Urea), 18.4 g H_2O (water) were mixed together and stirred for 2 hours at room temperature. The solution was then transferred to stainless steel teflon lined autoclave for crystallization at 180 ^oC for 48 hours. After crystallization, the sample was washed thoroughly with deionized water and kept in an oven at 100 ^oC for drying overnight. Calcination was done at 550 ^oC for 5 hours in air. The sample was ammonia exchanged 3 times with 1 M NH_4NO_3 solution. To obtain H-ZSM-5 form the sample was again calcinited at 550 ^oC for 5 hours in air.

Catalyst Characterization

Crystal phases for samples were determined by X-ray diffractions (XRD) on a Rigaku D/Max-RB diffractometer with Cu Kα Radiation at 40 kV and 120 mA. SEM (Scanning electron microscope) images were acquired by JEOL, JSM-7401 at 3.0 kV. TEM (Transmission electron microscopy) was carried out at an accelerating voltage of 300 kV in a Titan Cubed Themis G2 300 (FEI) electron microscope. H_2-TPR (Hydrogen-Temperature programmed reduction) was performed in a Quanta-chrome automated chemisorption analyser in a 100 ml min^{-1} H_2/N_2 (H_2/N_2=10/90) gas mixture from 30 ºC to 800 ºC with a ramping temperature of 10 ºC /min. NH_3-TPD (Ammonia-Temperature programmed desorption) was also tested in a Quanta-chrome automated chemisorption analyzer. NH_3 adsorption was performed by flowing 100 ml min^{-1} NH_3/He gas mixture (NH_3/He=5/95) for 1 h, afterwards desorption was performed by flowing He and subsequently raising the temperature to 800 ºC with 10 ºC /min ramping temperature. BET (Brunauer-Emmett-Teller) surface area was obtained in a Quanta-chrome automated surface area and porosity analyser with nitrogen used as the adsorption gas. XPS (X-ray photoelectron spectroscopy) was performed on (Thermo-Fischer ESCALAB 250XL) to acquire a surface elemental analysis.

In situ FTIR

In situ FTIR was performed on Thermo Fisher Nicolet 6700 at atmospheric pressure. Prior to experiment the sample was prepared by making a thin wafer out of it and then placed it in transmission cell. At first Catalyst was reduced in H_2 (H_2 = 6%, N_2 = 94) environment at 350 ^oC for 1 hr at 20 ml/min, followed by sweeping with N_2 for 20 min at 20 ml/min and IR spectra was recorded. At the same temperature of 350 ^oC, CO (CO = 6%, N_2 = 94) was flowed from the catalyst for 30 min at 10 ml/min, followed by sweeping with N_2 for 20 min at 20 ml/min and IR spectra was recorded. After that H_2 was again flowed through sample at the same 350 ^{o}C temperature for 45 min at 20 ml/min and IR spectra was recorded at 5 min interval, to see surface species evolution with H_2. Same experiment was repeated with syngas (H_2 = 6%, CO = 3%, N_2 = 91%), except FTIR bands were collected after flowing syngas. In Situ FTIR spectra was recorded by collecting 64 scans at 4 cm^{-1} resolutions.

Calculation for desorption activation energy

Kissinger method was used to calculate activation energies. P-Xylene was adsorbed on H-ZSM-5 catalysts with and without Mn_2O_3 and ultra-sonicated for 20 mins. Then the samples were heated in TGA/DSC 1 LF/1100 at different ramping/heating rates (β) of 5, 10, 15, 20 k/min and simultaneously, p-xylene desorption peak was recorded on Thermo^{star} PFEIFFER VZCCM Gas Analysis System. The desorption peak temperature denoted as "Tmax" was observed for each ramping rate and was taken as constant conversion point. A fitted straight line was drawn by plotting x = ln(β/Tmax) against y = 1/Tmax. Considering 1st reaction order, desorption activation energy was calculated using the formula below,

$$\ln\left\{\frac{\beta}{{T_{max}}^{2}}\right\} = \ln\left\{\frac{ZR}{E}\right\} - \frac{E}{RT_{max}}$$

Where,

E = Activation energy.

Z = Arrhenius pre-exponential factor

R = Universal gas constant (8.314 J/mol K)

Slope = $-\frac{E}{RT_{max}}$

Intercep**t =** $\ln\left\{\frac{ZR}{E}\right\}$

Performing Cold-trap experiment

Cold-trap experiment was performed on the same fixed bed, continuous flow, titanium reactor used for reaction tests. The products were collected in cold-traps set to temperature -20 ^{o}C and -193 ^{o}C, and gas bag connected at the end. The detailed schematic diagram was presented in Fig S1.

Identification of hydrocarbon-pool species

Hydrocarbon pool (HP) Species were identified by using the Guisnet's method.[2] After the reaction reached our desired time, the catalysts were immediately quenched by liquid nitrogen. After that, required amount of HF (hydrofluoric dissolution) (20%) was poured dropwise onto 0.9g of composite catalyst (MnO/HZSM-5) to destroy zeolite structure. Afterwards, methylene chloride (CH_2Cl_2) was added in a small quantity to dissolve Hydrocarbons. The solution was centrifuged to get clearly divided layers of aqua solution and oil. The oil was then carefully separated and collected from the mother solution to be analyzed on a GC-MS. The same procedure was repeated for different samples.

Catalytic Reaction test

Catalytic reaction experiments were performed in a fixed bed, continuous flow, titanium reactor. Typically, 0.9g composite catalyst containing Mn_2O_3:H-ZSM-5 = 2:1 (mass ratio) with mesh size of 80–100 was used. The catalyst was reduced in-situ in H_2 environment for 2 hr at 350 ºC prior to reaction. Then a premixed feed gas (H_2/CO=2) containing 4% N_2 as internal standard was introduced in the reactor. The reaction condition like pressure, temperature and space velocity were maintained at 2 MPa, 350 ºC and 333 mL/h·gcat, respectively, unless otherwise stated.

Reaction products were determined by online GC (Agilent 7890B) equipped with two flame ionization detector (FID) and one thermal conductivity detector (TCD). FID was used to analyze Hydrocarbons by using HP-INNOWAX and HP-AL/S capillary columns whereas, uni-beads and 5Å molecular sieves packed columns with TCD were used to determine H_2, CO, CO_2 in the products. The CO conversion and Hydrocarbon based selectivity were calculated with following equations,

$$CO\ conversion = \frac{(CO\ in - CO\ out)}{CO\ in} \times 100$$

$$CO2\ Selectivity = \frac{CO2}{(CO\ in - CO\ out)} \times 100$$

$$Hydrocarbon\ selectivity\ (CnHm) = \frac{NCnHm\ (carbon\ number\ of\ Hydrocarbon)}{Total\ carbon\ atoms\ detected\ by\ FID} \times 100$$

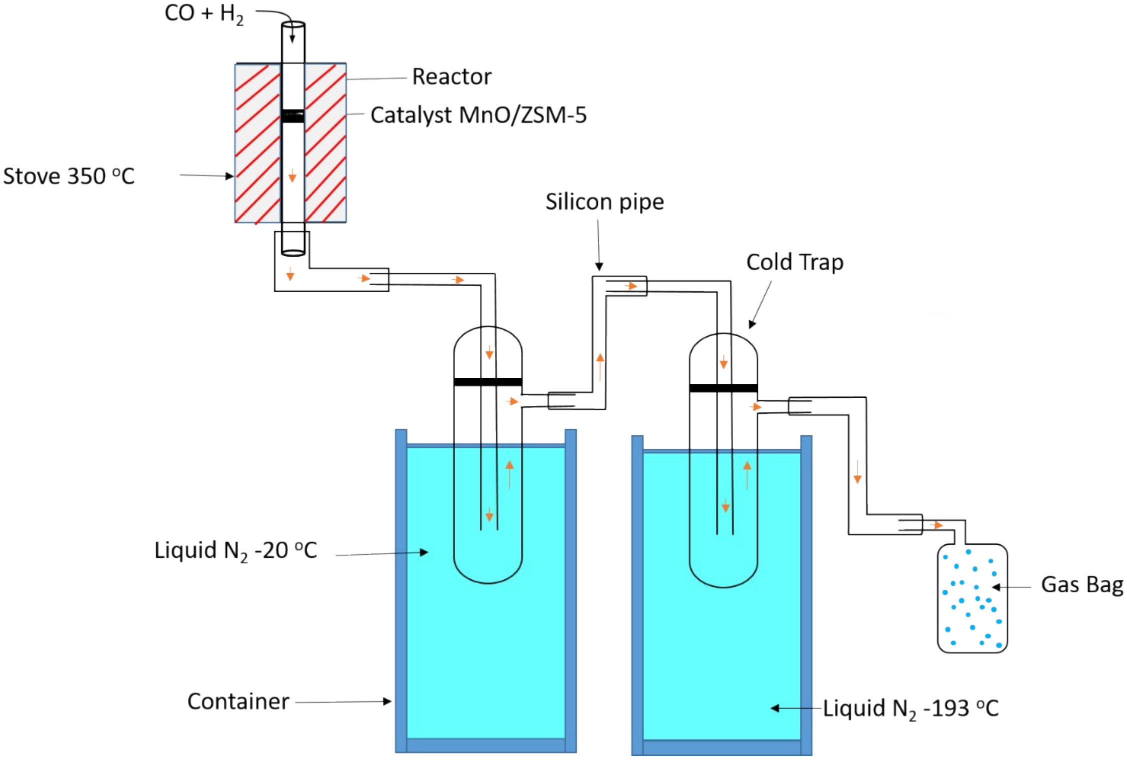


Fig. S1 Schematic design of cold-trap experiment

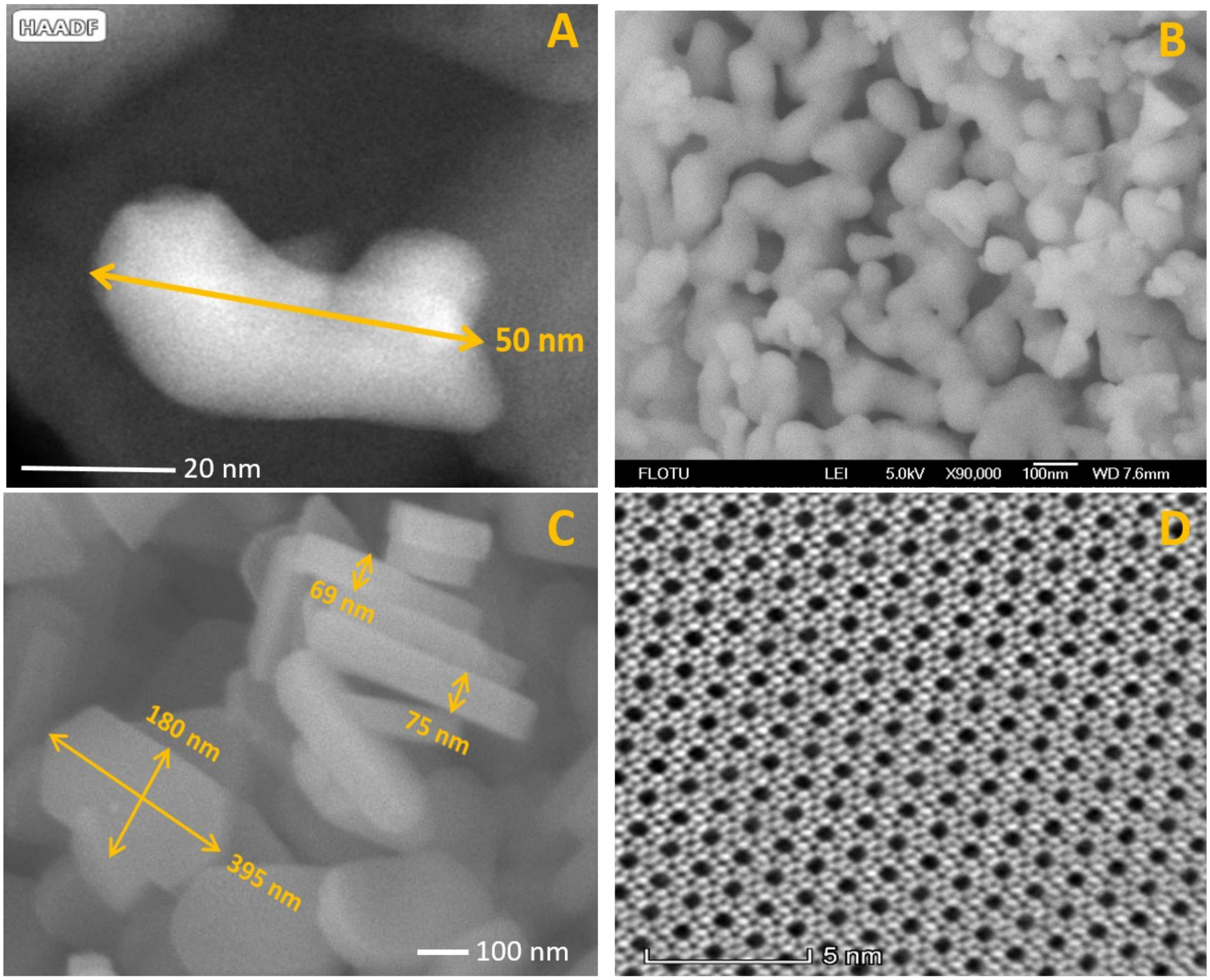


Fig S2 (A) STEM images of manganese oxide showing the single crystal size (B) Magnified SEM image of manganese oxide (C) Magnified SEM images of nano-size H-ZSM-5 showing the single crystal size (D) iDPC image of fresh nano-size H-ZSM-5 along [010] surface, showing empty accessible holes

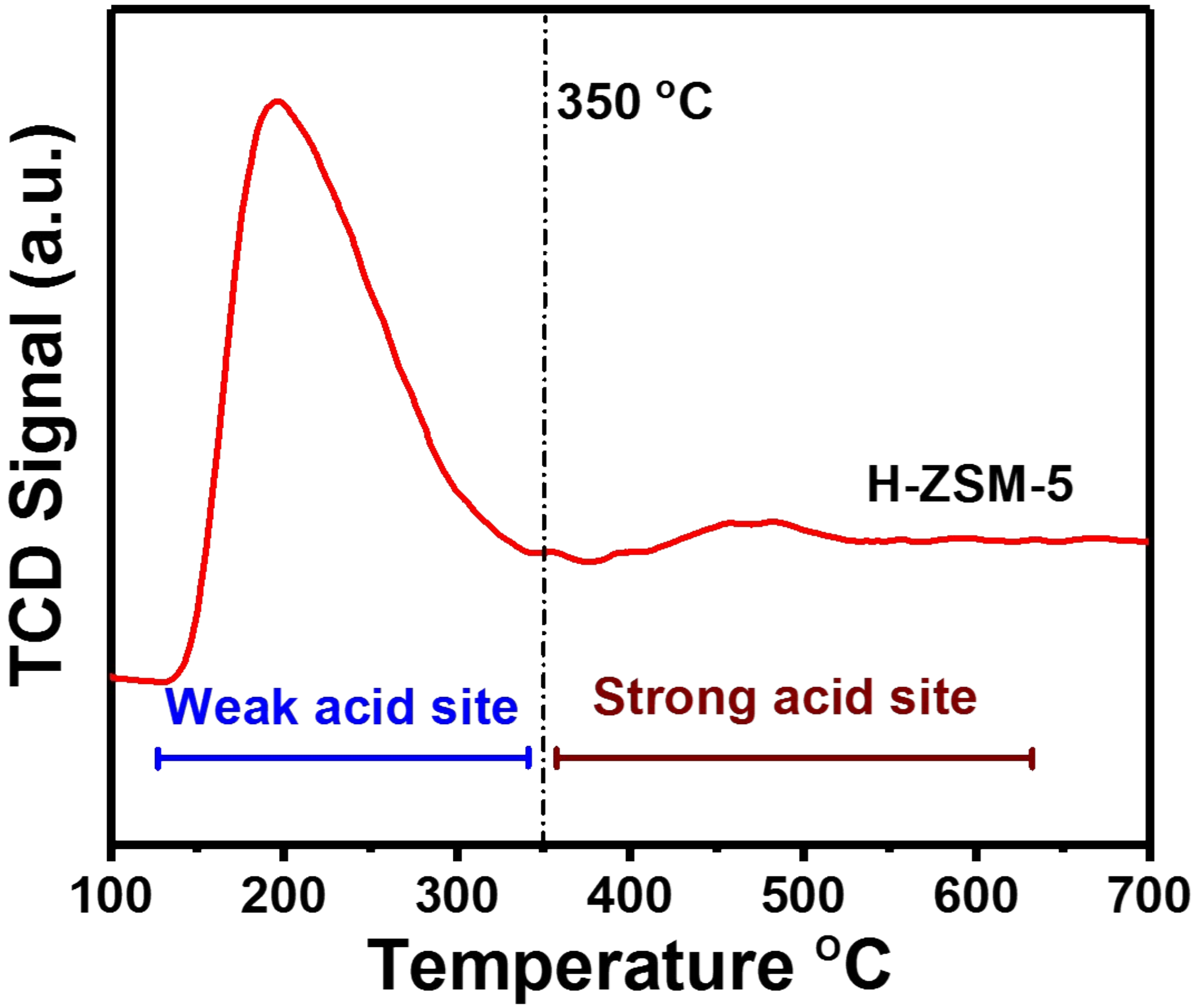


Fig. S3 NH_3-temperature program desorption profiles of nano-size H-ZSM-5

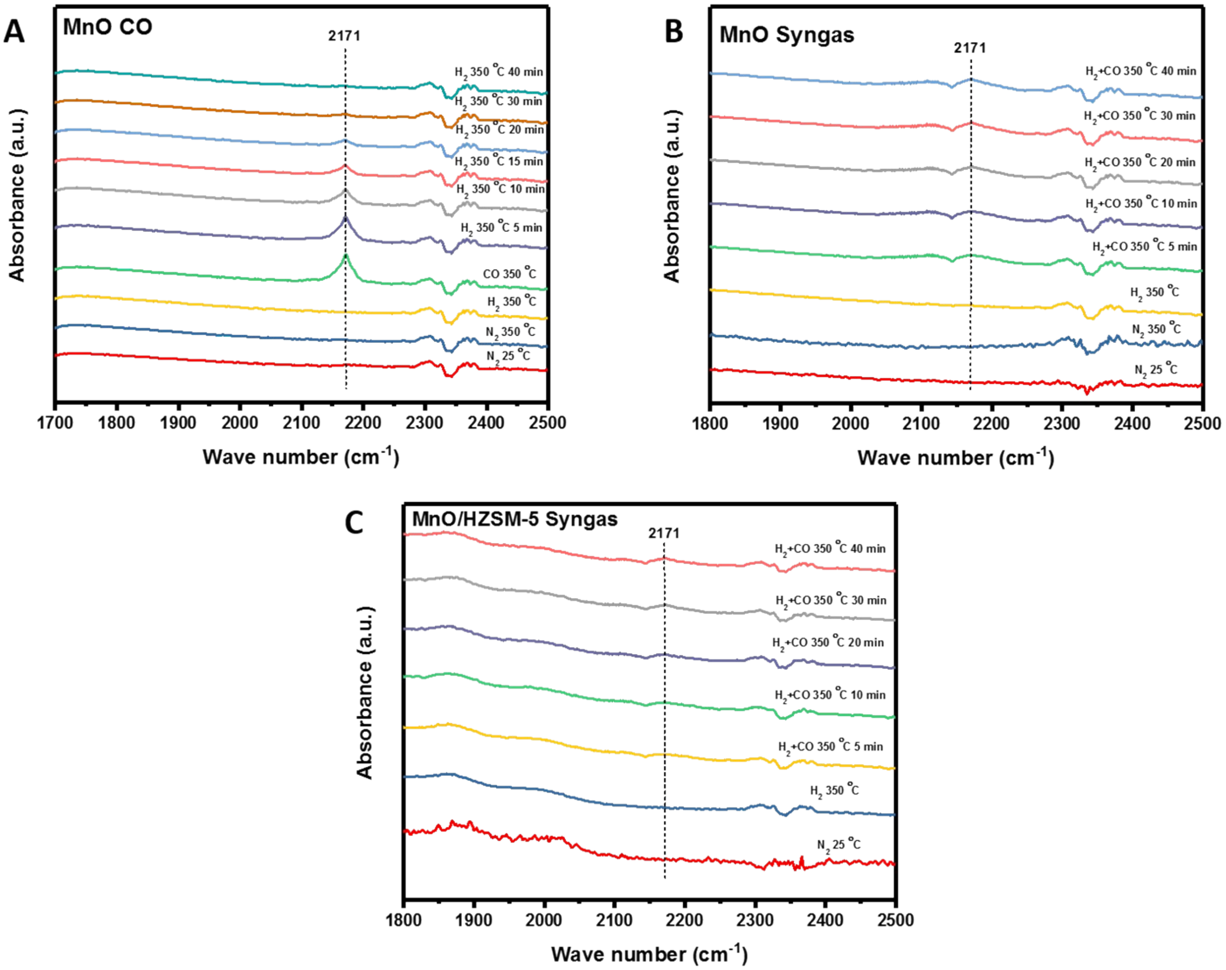


Fig S4 In-situ FTIR spectra obtained after performing experiment under same reaction conditions as were used for catalyst evaluation, except for pressure which was 1 atm for this experiment (A) Manganese oxide with CO and H_2, (B) Manganese oxide with syngas, (C) Manganese oxide with H-ZSM-5 in syngas environment

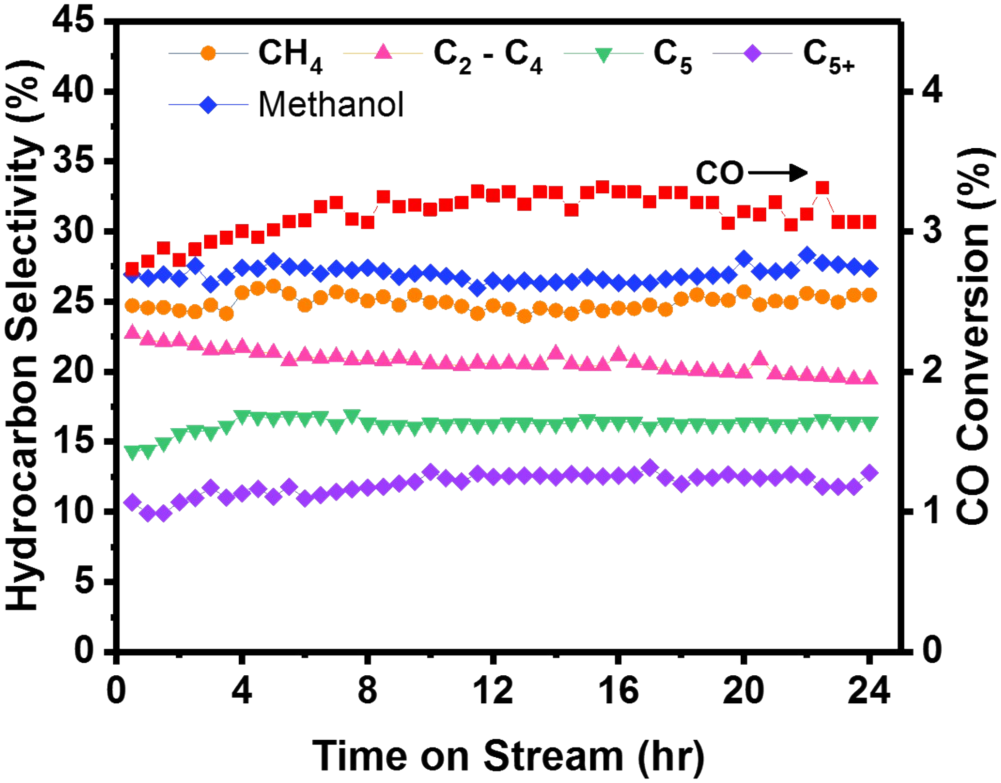


Fig. S5 Catalytic evaluation of, manganese oxide alone under reaction conditions, Temperature = 350 °C, Pressure 2 MPa, Space velocity 333/h·gcat, Syngas ratio $H_2/CO = 2$, for 24 hours

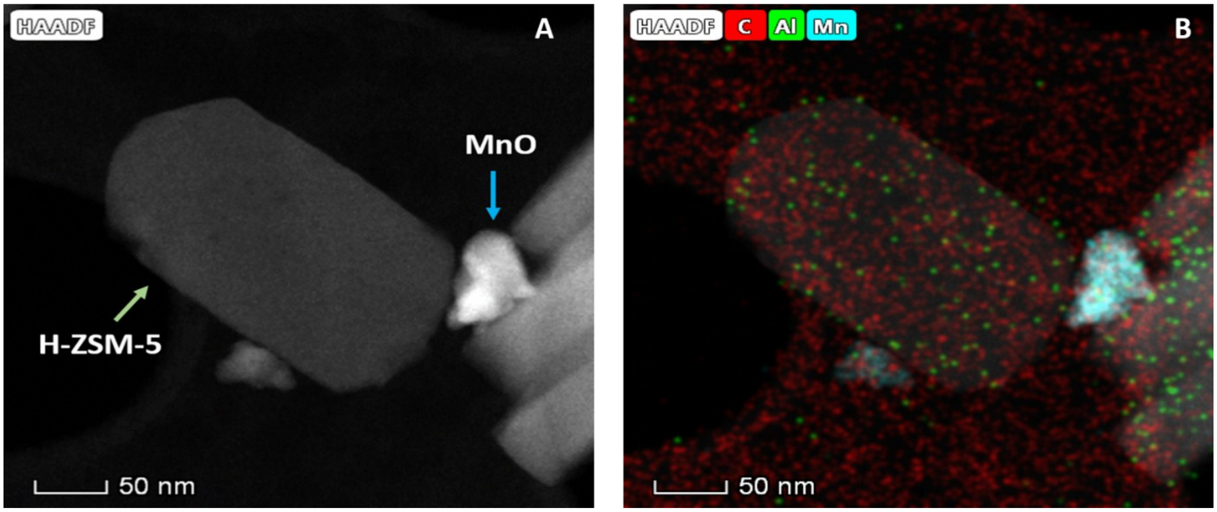
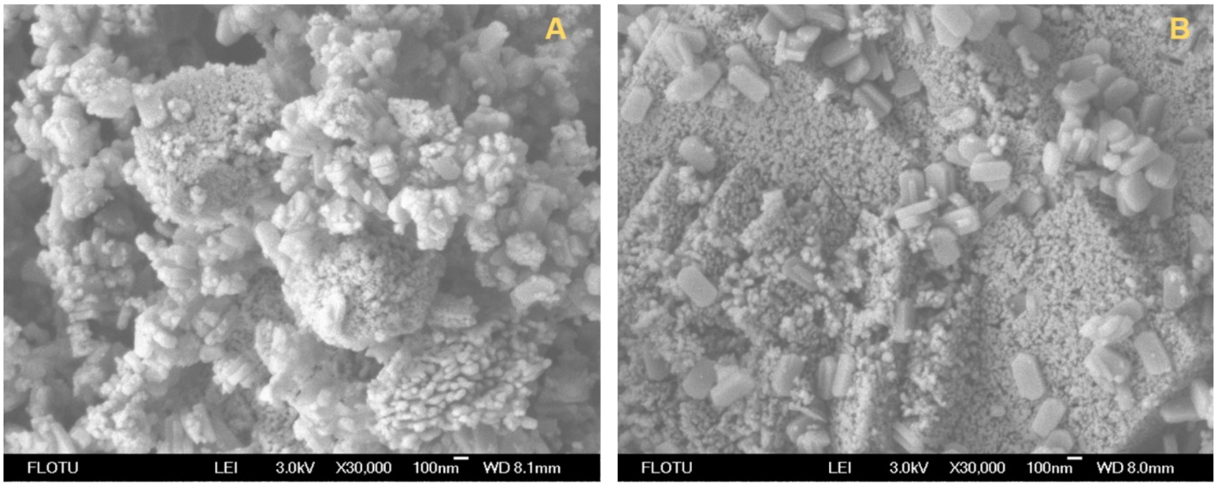


Fig. S6 (A) STEM images of metal oxide (MnO) and zeolite (H-ZSM-5) in a physical mixture showing that both the catalyst were not attached to each other but the distance between them is just few nano-meters (B) Showing the EDS mapping of manganese oxide and H-ZSM-5 in a close proximity.



Ball mined

Co-precipitated

Fig S7 SEM images of samples obtained after (A) ball-mining (B) Co-precipitation on H-ZSM-5.

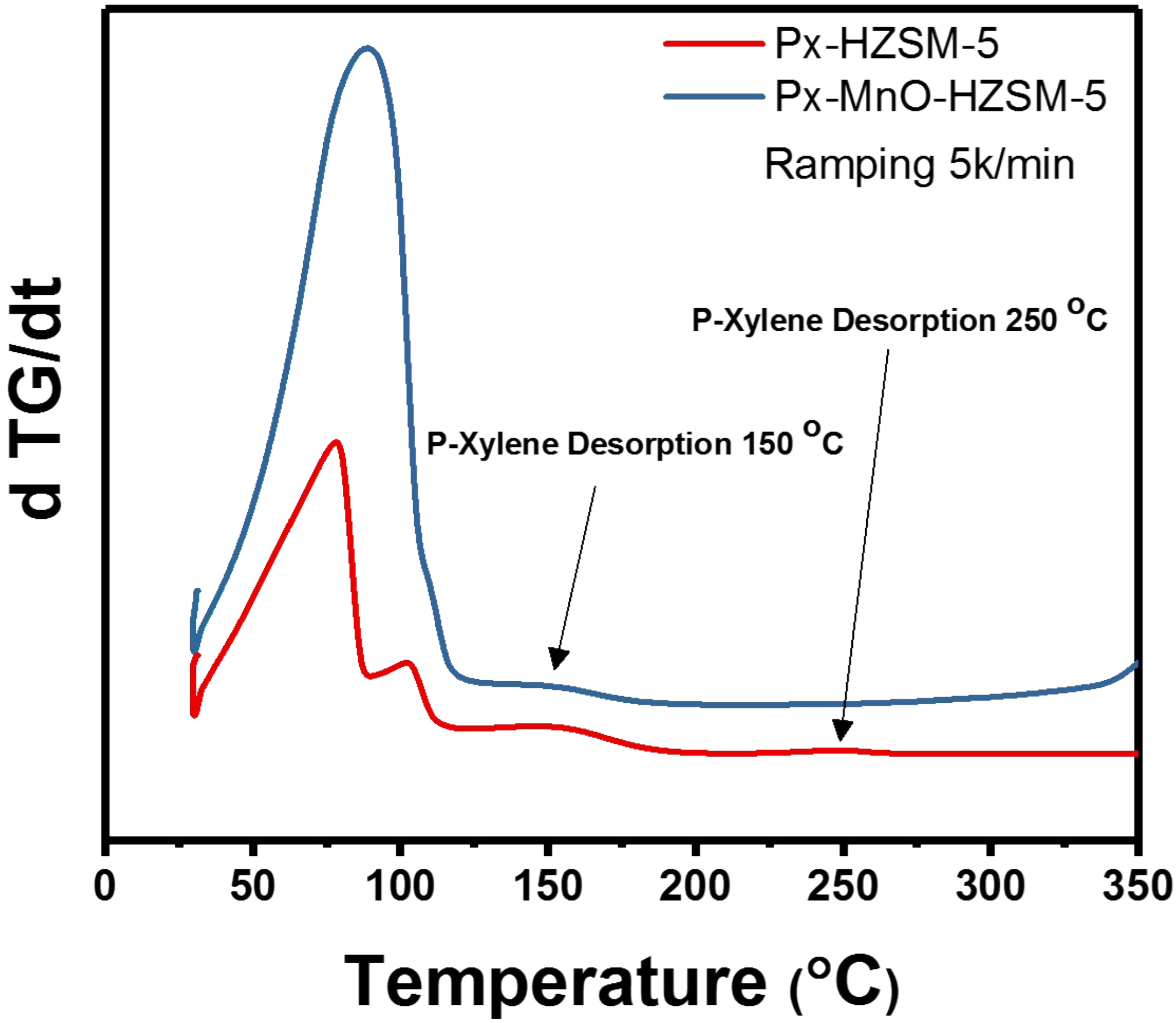


Fig. S8 Desorption of P-xylene from H-ZSM-5 in the presence and absence of manganese oxide

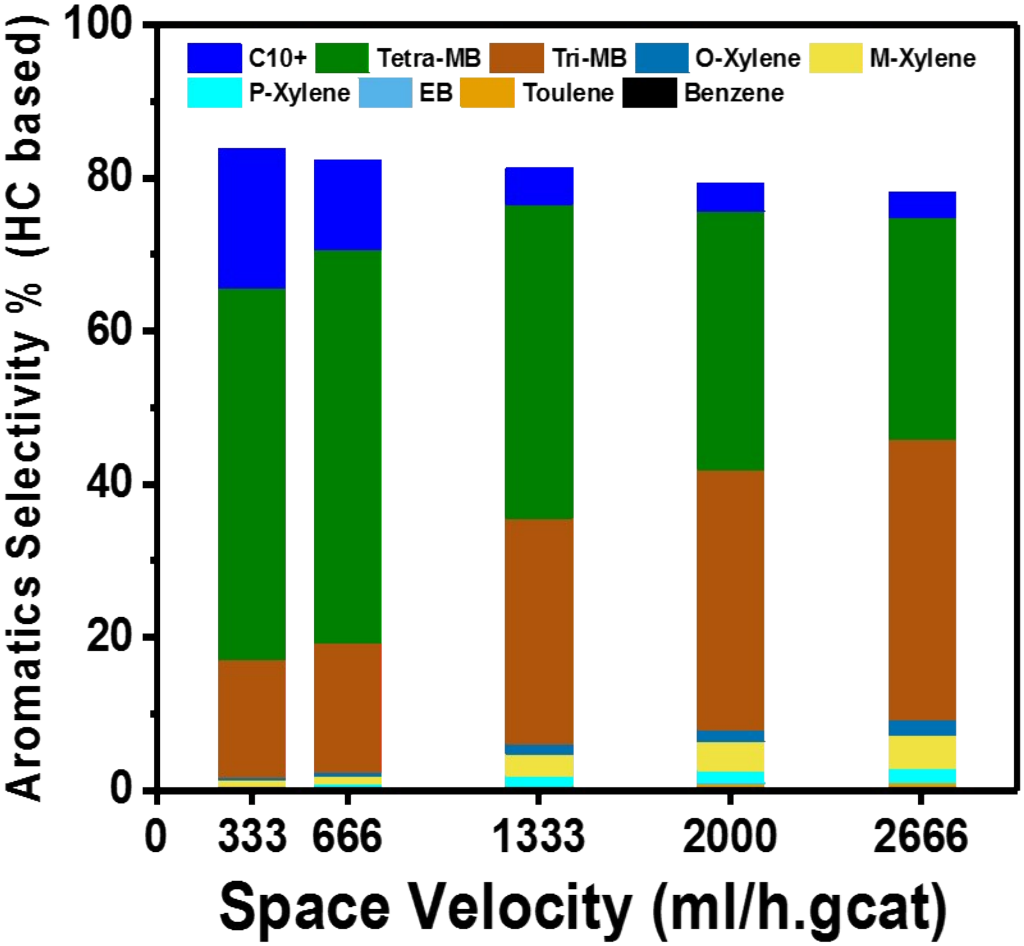


Fig. S9 Effect of space velocity on hydrocarbon-based aromatic selectivity under reaction conditions oxide/zeolite ratio = 2:1, Temperature = 350 °C, Pressure 2 MPa, Syngas ratio $H_2/CO = 2$

Table S1 Effect of weight ratio between oxide and zeolite on catalytic performance

Oxide/Zeolite ratio	CO conversion	CO_2	Hydrocarbon Selectivity				
			CH_4	C_{2-4}^0	$C_{2-4}^=$	$C_{\geq5}$	Aromatics
5:1	11	45	1.53	8.78	1.71	1.49	88
2:1	21	44	1.56	13	0.44	1.18	83.4
1:1	18	46	3.85	18.09	0.55	1.02	79.5
1:2	10	50	0.87	17.15	0.40	1.30	77.5
1:5	7	52	0.24	19.17	0.43	1.53	76

References

1. Y. Ma, D. Cai, Y. Li, N. Wang, U. Muhammad, A. Carlsson, D. Tang, W. Qian, Y. Wang, D. Su and F. Wei, *RSC Adv*, 2016, **6**, 74797-74801.
2. M. Guisnet and P. Magnoux, *Appl. Catal.*, 1989, **54**, 1-27.