# A novel route to improve methane aromatization by using a simple composite catalyst

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## Experimental methods

### (1) Catalyst preparation

The 6 wt% Mo loading HZSM-5 catalyst was prepared by impregnation of HZSM-5 (Si/Al = 25, Nankai University Catalyst Co.) with an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) from an incipient wetness technique. The resulting material was dried at 120 °C overnight and calcined at 500 °C for 4 h to obtain the final Mo/HZSM-5 catalyst. Gadolinium doped ceria ($Ce_{0.9}Gd_{0.1}O_2$, denoted as CGO) was prepared by co-precipitation method. This technique consists of the dissolution of 11.724 g $Ce(NO_3)_3\cdot 6H_2O$ and 1.354 g $GdN_3O_9\cdot 6H_2O$ with the molar ratio 0.9:0.1 in 150 ml deionized water at 50 °C. 225 ml of $(NH_4)_2CO_3$ solution as the precipitant in a 1:1.5 molar ratio was dropped under stirring into the nitrates solution to achieve the total precipitation. The resulting precursor was dried at 120 °C overnight after centrifugation and rinsing, and was calcined at 800 °C for 5 h to decompose the residual nitrates and carbonates and to favor the formation of the fluorite phase. The composite catalyst was prepared by mechanically mixing 0.3 g Mo/HZSM-5 (20-40 mesh) and 0.5 g CGO (20-40 mesh).

### (2) Catalyst characterizations

Powder X-ray diffraction (XRD) pattern was recorded in a 2θ angle range of 20 °–80 ° with a Bruker D8 ADVANCE diffractometer using Cu Kα radiation (40 kV, 40 mA).

The oxygen release property of CGO was measured by a flow microbalance (Perkinelmer Rubotherm-DynTHERM Pyris 1 TGA). For a typical experimental measurement, ~60 mg of a powder sample was placed in an alumina holder. The sample was pretreated at 110 °C in a flow of $N_2$ to remove the water until a stable weight value was achieved. The sample was then heated to the desired temperature (e.g., 900 $^{o}$C, heating rate = 10 $^{o}$C min$^{-1}$) in a 10 % $H_2/N_2$ (100 ml min$^{-1}$) atmosphere and kept isothermally for 120 min. The weight change of the sample was observed from the thermogravimetric analysis (TGA) kinetic curves. The dynamic reduction-oxidation cycles were measure in the same system. For this experiment, the sample was first heated in a flow of $N_2$ up to 700 $^{o}$C, where the constant weight was attained within 30 min. The gas fed to the sample was then switched at a certain interval between 10 % $H_2/N_2$ and 10 % $O_2/N_2$ (100 ml min$^{-1}$) with recording the sample weight at this temperature.

The amount of coke deposited on spent catalysts (Mo/HZSM-5 treated under feed gas for 35 min and 100 min, and the composite catalyst treated under feed gas for 35 min and 100 min, respectively) was determined by a thermogravimetric analyzer Perkinelmer Rubotherm-DynTHERM Pyris 1 TGA. Prior to combustion of the deposited material, the catalyst (~50 mg) was pretreated with flowing $N_2$ (100 ml min$^{-1}$) at 200 $^{o}$C for 1 h, and cooled to the room temperature. The sample was then exposed to a mixture of 20 % $O_2/N_2$ flowing (100 ml min$^{-1}$) and oxidized from room temperature to 900 $^{o}$C at a heating rate of 10 $^{o}$C min$^{-1}$. The amount of coke deposition could be calculated from the weight loss of the samples.

Temperature-programmed reduction (TPR) of $H_2$-$CH_4$-Ar was performed on a Micromeritics AutoChem 2920 II instrument to evaluate the selectivity of CGO towards hydrogen combustion. Typically, about 0.3 g of the sample loaded in a quartz reactor was first pretreated with Ar at 200 $^{o}$C for 1 h. After the sample was cooled to 100 $^{o}$C, the sample was heated at 10 $^{o}$C min$^{-1}$ in flowing 5 %$H_2$/10 %$CH_4$/Ar. The effluent of $H_2$, $CH_4$, $H_2O$, $CO_2$, and CO with the signal of $m/e$ = 2, 16, 18, 44, and 28 were detected by ThermoStar GSD 301 T2 mass spectrometer as the temperature was ramped up to 750 $^{o}$C.

Laser Raman spectroscopic measurements were carried out at room temperature on a DXR microscope with a 532 nm excitation source and 2 $cm^{-1}$ resolution of the apparatus, to investigate the coke deposition over the spent catalysts and also the catalyst species after regeneration.

### (3) Catalytic reaction

The methane dehydroaromatization was performed on a fixed-bed flow reactor (inner diameter, 6 mm) operated at atmospheric pressure in a continuous flow system. The composite catalyst (20-40 mesh) was held between two quartz wool plugs in the isothermal zone of the tubular quartz reactor. The catalyst was heated up in a 15 ml $min^{-1}$ flow of air at a rate of 3 $^{o}C$ $min^{-1}$, and purged with He (20 ml $min^{-1}$) at 700 $^{o}C$ for 20 min. The GC analysis started (time-on-stream = 0) once the feed gas mixture of 50 % $CH_4$ and 40 % He as the balance gas and 10 % $N_2$ as the internal standard gas for analysis was introduced into the reactor at 15 ml $min^{-1}$ at 700 $^{o}C$. The flow rates were controlled by mass flow controllers (Bronkhorst), the outlet pipe line from the reactor was kept at higher than 180 $^{o}C$ to prevent the condensation or adsorption of higher hydrocarbon products. The tail gas was sampled and analyzed by gas chromatography (GC) (Agilent 7890B), equipped with a flame ionization detector (FID) for the analysis of $CH_4$ and higher hydrocarbons (e.g., $C_6H_6$, $C_7H_8$, $C_{10}H_{12}$) and a thermal conductivity detector (TCD) for the analysis of $H_2$, $N_2$, CO, $CH_4$, and $CO_2$, etc.

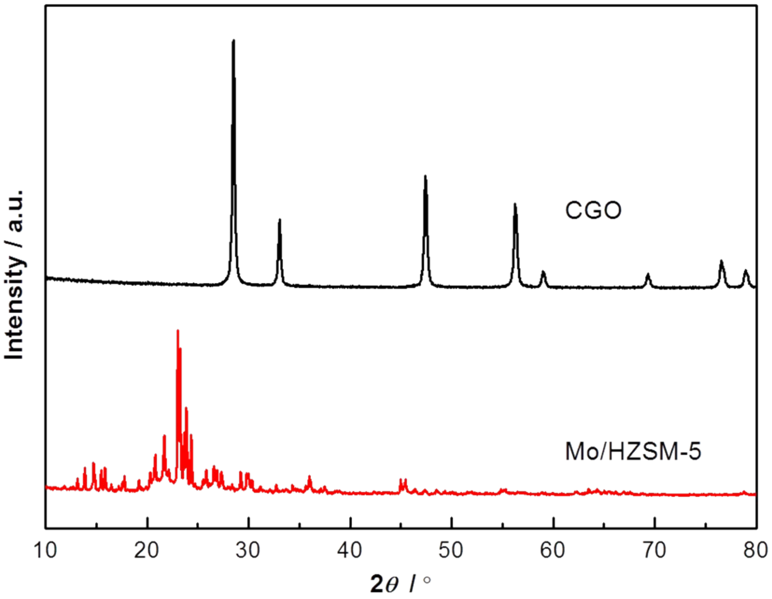

**Fig. S1** Powder X-ray diffraction pattern for CGO oxygen reservoir and Mo/HZSM-5.

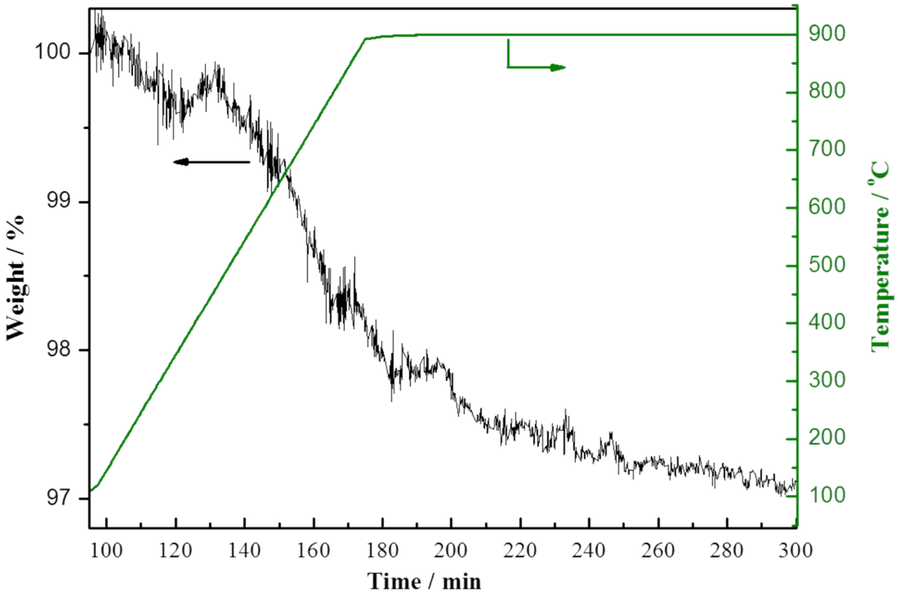

**Fig. S2** Thermogravimetric analysis by programmed heating (10 °C min$^{-1}$) from 100 °C to 900 °C in a flow of 10 % $H_2/N_2$ (100 ml min$^{-1}$) and holding at 900 °C for 120 min.

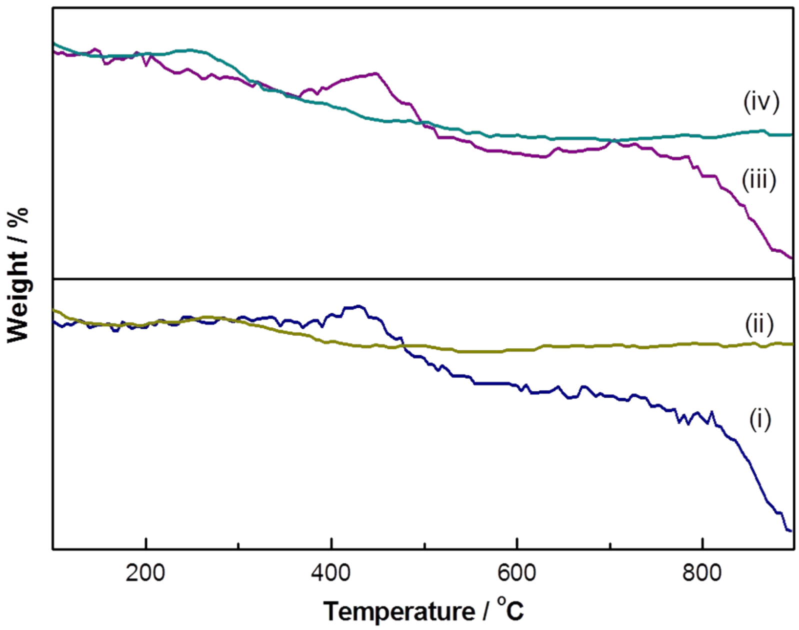

**Fig. S3** Thermogravimetry profiles for the used catalysts, (i) Mo/HZSM-5 treated under feed gas for 35 min, (ii) the composite catalyst treated under feed gas for 35 min, (iii) Mo/HZSM-5 treated under feed gas for 100 min, (iv) the composite catalyst treated under feed gas for 100 min.

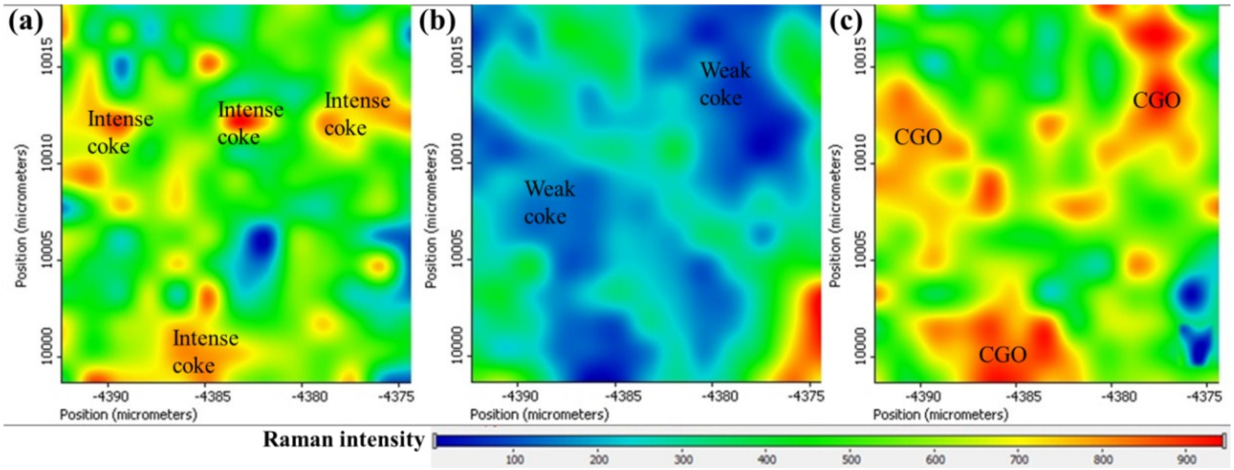

**Fig. S4** Raman mapping images of the spent catalysts after 100 min on stream. (a) Distribution of coke deposit over the spent Mo/HZSM-5. (b) Distribution of coke deposit over the spent composite catalyst. (c) Distribution of CGO components over the spent composite catalyst.

Figure S4 depicts the coke distribution over the spent catalysts after 100 min on feed gas stream at 700 °C by employing Raman mapping technology. Different colors in the images, changing from blue to red as given in the intensity bar, are based on the intensity of corresponding Raman bands. Coke distribution measurements for the spent catalysts concluded that the Raman band corresponding to the carbonate species was less intense for the composite catalyst (Figure S4(b)) than the bare Mo/HZSM-5 which displayed higher intensity color signals ranging from green to red (Figure S4(a)). It is noteworthy that the distribution of coke deposit corresponding to lower intensity in Figure S4(b) is to some extent consistent with the mapping of CGO species shown in Figure S4(c). This direct correspondence demonstrates that the CGO oxygen reservoir minimizes coke formation on the catalyst during reactions, which accounts for the experimental observation that the composite catalyst was much more stable than that of the Mo/HZSM-5 catalyst.

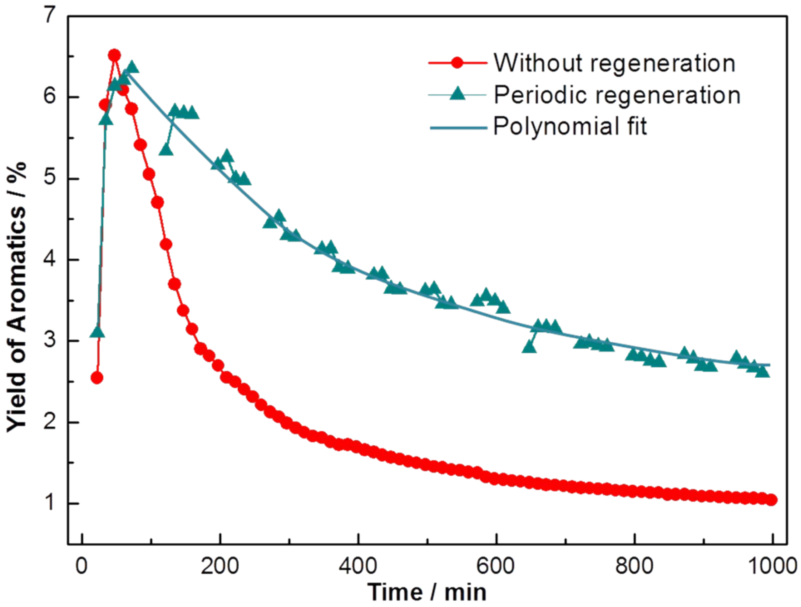

**Fig. S5** Aromatics yield for the composite catalyst as a function of time with or without periodic regeneration. Full dark cyan line represents average yield of aromatics. Regeneration conditions: 7 % $O_2/N_2$, total flow rate = 15 ml min$^{-1}$, T = 700 $^{o}$C, regeneration time = 10 min.