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Supporting Information

Insights into the catalytic activity of Ru/NaY catalysts for efficient H_2 production through aqueous phase reforming

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1. Chemicals

All chemicals used for these studies are reagent grade. NaY zeolite (CBV-100, Si/Al ratio = 2.5) were obtained from Zeolyst International, USA. Whereas, Glycerol, ethylene glycol, $RuCl_3.3H_2O$, 1,2-propanediol were purchased from Sigma Aldrich and KNO_3, $Ca(NO_3)_2$ $Cs(NO_3)_2$,$Sr(NO_3)_2$, $Ba(NO_3)_2$, isopropyl alcohol were purchased from Merck and Alfa Aesar. Sodium borohydride ($NaBH_4$) was purchased from sd. fine chemicals.

2. Characterization techniques:

All the above prepared catalysts were thoroughly characterized by various physicochemical and spectroscopic techniques such as powder X-ray diffraction (XRD), transmission electron microscopy (TEM), N_2-sorption, inductively coupled plasma-optical emission spectrometry (ICP-OES), H_2-Chemisorption, temperature programmed reduction (H_2-TPR), temperature programmed desorption (CO_2-TPD/NH_3-TPD), solid state Nuclear Magnetic Resonance spectroscopy (NMR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS) and insitu CO-FTIR (DRIFT). The powder XRD pattern of the different catalysts were recorded on Rigakuminiflex 600 using Cu K_α radiation operated at 40 kV and 15 mA. The XRD data were recorded at scanning rate of 4° min-1 in the 2θ range of 10-90°. The BET surface area of all the catalysts were examined by N_2 adsorption-desorption isotherms at -196 °C using Brunauer-Emmett-Teller (BET) equation in Quanta chrome Autosorb IQ instrument. Prior to the sorption, all the samples were degassed at 300 °C for 3h to a residual pressure of 2 x10-3 torr. The Ru metal dispersion and active Ru metal surface area of the catalysts were calculated by using H_2 chemisorption study. Prior to the chemisorption at 40 °C, the catalysts were subjected to insitu reduction under H_2 flow at 250 °C.

The X-ray photoelectron spectroscopy were carried out on VG Micro Tech ESCA 3000 model instrument operated at ~ 1× 10-9 toor pressure (pass energy of 50 eV, electron take-off angle of 60° with overall resolution of ~0.1 eV), equipped with a concentric hemi spherical electron analyzer and Al $K_\alpha$monochromator source (1486 eV). The XPS peak at 284.5 eV corresponding to C 1s was taken as reference peak to estimate the binding energy of various elements present on the surface of the catalysts.

Scanning electron micrograph (SEM) images of the catalysts were recorded on JEOL-JSM-5200 instrument to study the morphology of the catalysts. Transmission electron microscopic (TEM) image of the catalysts were obtained by using a FEI Technai TF-30 instrument operating at 300 k V. All the samples were prepared by dispersing them in isopropyl alcohol under ultra-sonication followed by placing a droplet of highly diluted suspension of the sample on carbon coated copper grid (200 mesh) and allowing it to dry at room temperature. The carbon (C), nitrogen (N) and hydrogen (H) content of the catalysts were calculated by elemental analysis method using thermal conductivity detector. Thermogravimetric analysis of the catalysts was studied in presence of air (50 mL min^{-1}) using mettle toledo instrument (TGA/SDTA851e). ^{29}Si and ^{27}Al MAS NMR spectra were obtained by using a BRUKAR DSX300 spectrometer at 7.05T (resonance frequencies 59.595 MHz, rotor speed 10000 Hz; and 75.43 MHz rotor speed 10000Hz).

H_2-TPR studies were recorded on a micrometrics Autochem 2920 instrument, equipped with thermal conductivity detector (TCD). Prior to the analysis, the catalysts were pretreated at 300 °C for 1h under 5% O_2 in He flow at a ramp of 10 °C min^{-1}. After cooling the samples to 50 °C under Ar atmosphere, the samples were subjected to H_2-TPR analysis in the temperature range of 50-500 °C (5 °C min^{-1}) using a gas mixture of 5%H_2 in He at a flow rate of 30 mL/min. The changed in the H_2 concentration in the outlet was estimated by thermal conductivity detector (TCD), which was calibrated before TPR analysis.

Basicity of the catalysts was measured by CO_2-TPD using Autochem 2920 instrument (micrometrics) equipped with TCD detector. In each experiment, 50 mg of the catalyst was pretreated at 300 °C under He flow (30mL/min) for 1h followed by subsequent cooling to 50 °C and saturated with 10% CO_2 in He mixture for 30 min. Further, the sample was flushed with He for 1h by at a temperature 100 °C in order to remove the physisorbed CO_2 on the catalysts surface. Subsequently the sample was heated to 800 °C under He flow (30mL/min), and the desorbed CO_2 was monitored by pre-calibrated TCD.

Insitu CO-FTIR was carried out in diffuse reflectance mode (DRIFT) using NICOLET iS50FT-IR (Thermo Scientific) spectrometer, equipped with a high temperature chamber fitted with KBr window and a MCT detector. Each spectrum was recorded at a resolution of 4 cm^{-1} and 200 scans. Before the analysis, the sample was flushed with N_2 (30 ml/min) to drive out the unwanted gas inside the reaction chamber. Subsequently the sample was reduced at 300 °C (heating rate 5 °C min^{-1}) under 5 vol% H_2/N_2 flow for 1h. The reduced sample was then flushed with N_2 and subsequently cools down to room temperature under N_2 flow. After cooling the sample to room temperature, a background spectrum was recorded under N_2 flow. Finally, the CO gas mixture (1 vol % CO/N_2) was introduced into the reaction chamber and the FTIR spectra was recorded at every 50 °C interval while the temperature was stepwise (5 °C min^{-1}) increased up to 300 °C.

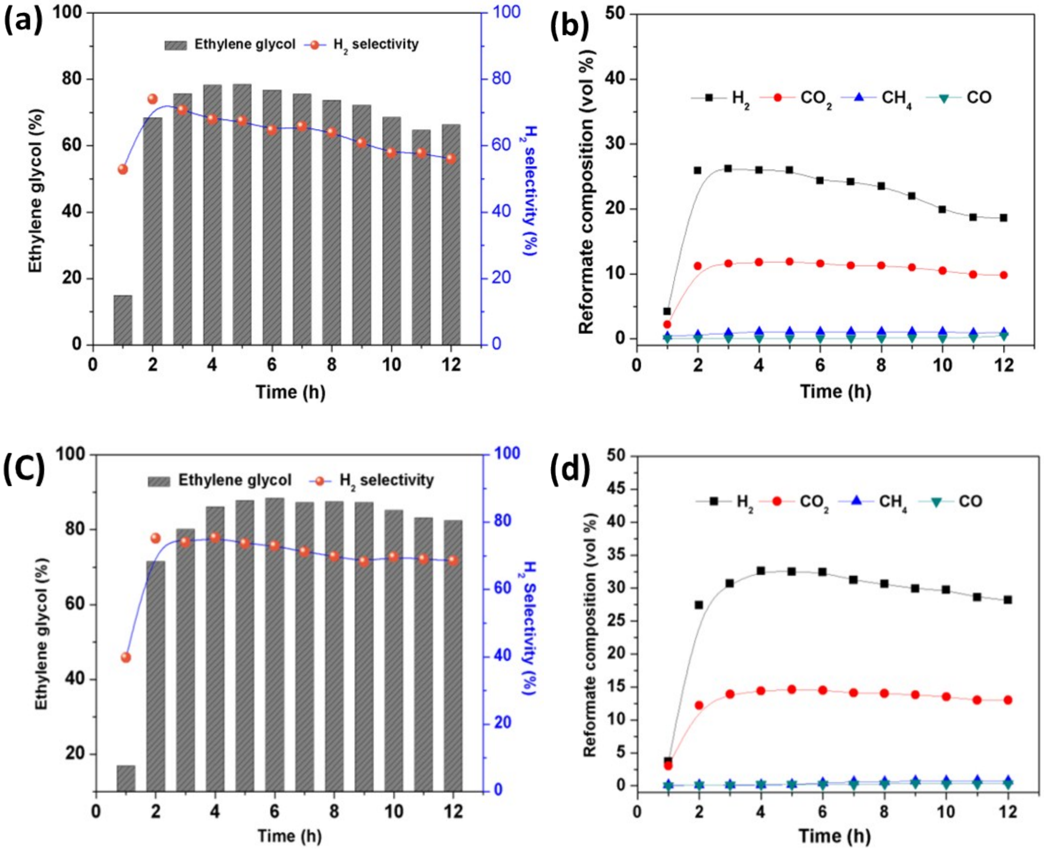
3. Evaluation of catalysts

APR reactions were performed in stainless steel 300 mL semi batch reactor equipped with back pressure regulator (**Tescom**) under continuous N_2 flow (30mL/min). In a typical experiment, a 0.3g of freshly reduced catalyst was charged into the autoclave containing 100 mL of deionized water. The excess water in the vessel is attributed to efficient WGS reaction. Prior to the APR reaction, the mixture was thoroughly purged with N_2 to drive out unwanted gases trapped inside the vessel. The reactor was then heated up 250 °C (controlled within ±1 °C) and simultaneously pressurized the system up to 600 Psi (40bar) pressure. On achieving desired temperature and pressure, 10 wt% glycerol or ethylene glycol (5ml/hr.) was charged in to the catalytic reactor chamber using high precision syringe (Isco 500D) pump. The gaseous products were analyzed every hour by using an online gas chromatograph (**Thermo scientific Trace-1110**) while the liquid products were analyzed by HPLC. **H_2, CO, CO_2** and **CH_4** were observed as the main gaseous products during APR reaction, which were analyzed by TCD equipped with carbosieve S II packed column (1/8 OD" 2 mm ID and 6 feet length). On the other hand hydrocarbons higher than C1 were analyzed by flame ionization detector equipped with porapak-Q column. However in our case we hardly observed hydrocarbons higher than C1. Liquid products also withdrawn periodically and analyzed with the help of HPLC equipped with RID detector using C18 column (4.6 × 100 mm, 3.5 micron). The conversion and H_2 selectivity were calculated using following equations:

$$Glycerol\ Conversion\ (\%) = \frac{Carbon\ products\ (mol)}{Total\ carbon\ product\ in\ feedstock\ (mol)} \times 100$$

$$H_2\ selectivity\ (\%) = \frac{H_2\ in\ product\ (mol)}{C\ produced\ in\ products\ (mol)} \times \frac{1}{R} \times 100$$

Where R is 2/5 and 2/7 is the reciprocal H_2/CO_2 reforming ratio of ethylene glycol and glycerol respectively.



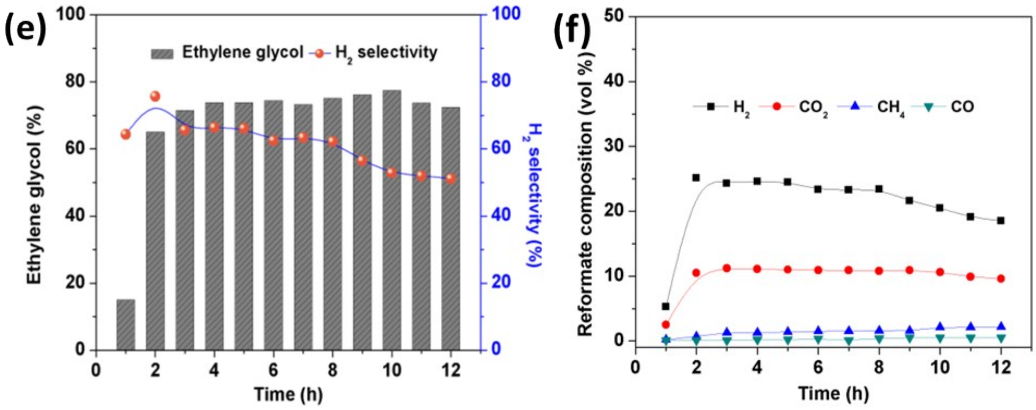


Fig.S1. (a), (c), (e) Ethylene glycol conversion and hydrogen selectivity with time and **(b), (d), (f)** reformate composition (vol %) with time over 2wt%Ru-NaY, 3wt%Ru-NaY, 5wt%Ru-NaY catalyst respectively. **Reaction conditions:** 10wt% Ethylene glycol (5mL/hr), 250 °C, 600 psi (N_2) and 300 mg catalyst.

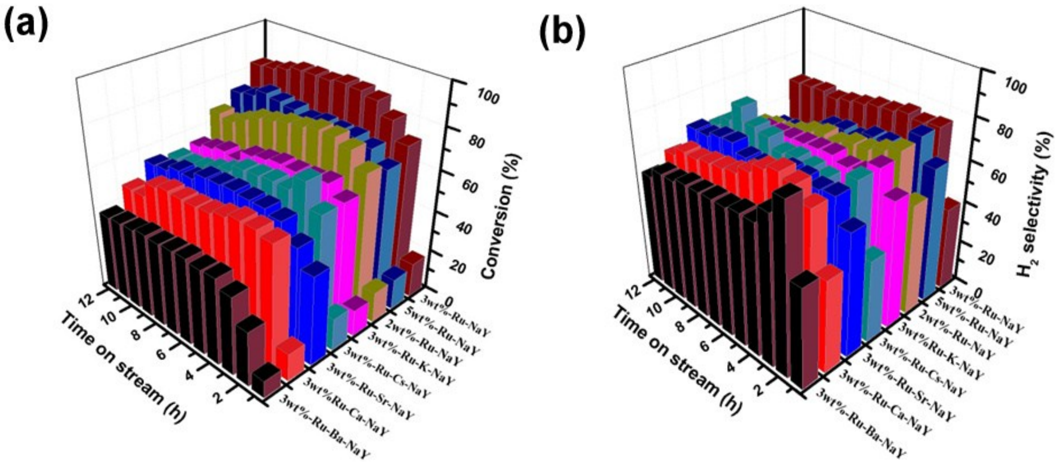


Fig.S2. Comparison of catalytic performance of alkali and alkaline earth metal exchanged Ru/NaY catalysts for APR of EG.

Reaction conditions: 10wt% Ethylene glycol (5mL/hr), 250 °C, 600 psi (N_2) and 300 mg catalyst.

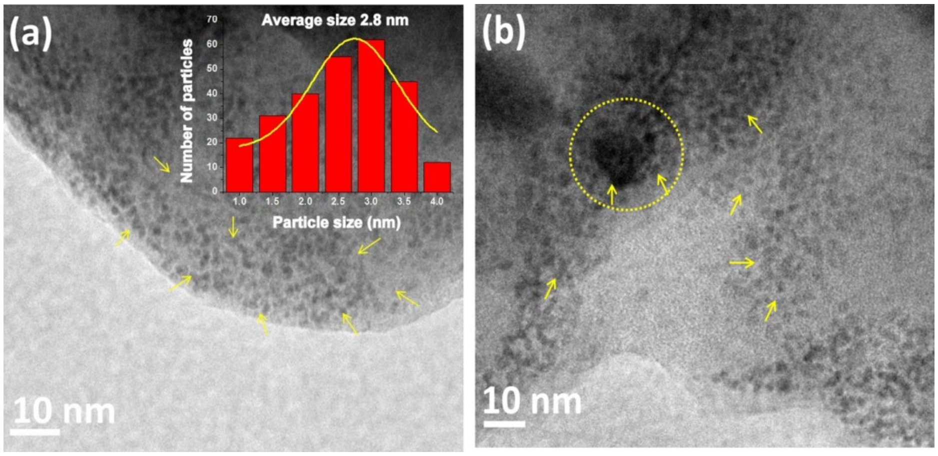


Fig.S3. TEM images of fresh (a) 2wt% Ru-NaY and spent (b) 2wt% Ru-NaY catalyst.

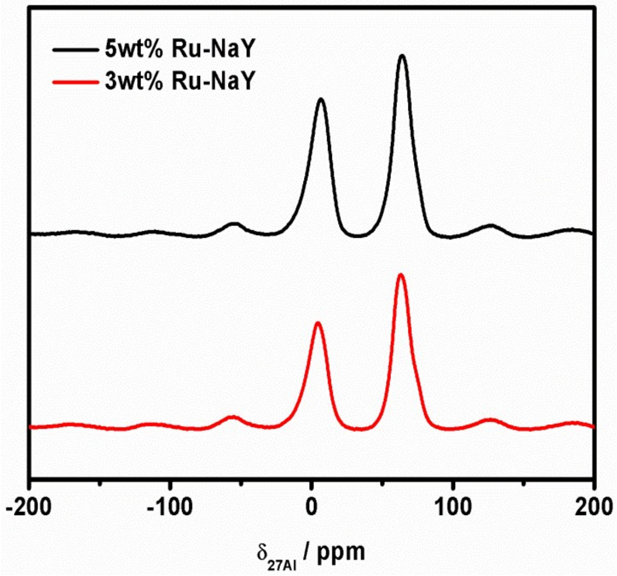


Fig.S4. ^{27}AL solid state MASS NMR spectra of spent catalysts.

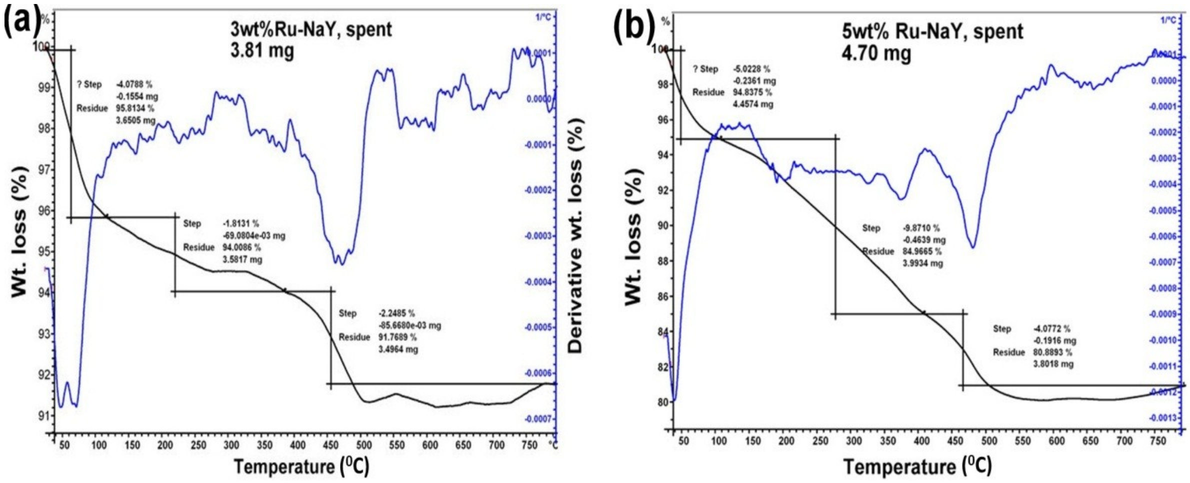


Fig.S5. Thermo-gravimetric analysis of spent catalysts (a) 3wt%Ru-NaY and (b) 5wt%Ru-NaY.