

Supporting Information

Ni/H-ZSM-5 as a stable and promising catalyst for CO_x free H₂ production by CH₄ decomposition

Chatla Anjaneyulu^a, Gutta Naresh^{a,c}, Velisoju Vijay Kumar^{a,c}, Aytam Hari Padmasri^b, James Tardio^c, Suresh Kumar Bhargava^c and Akula Venugopal^{*,a}

^a Catalysis Laboratory, Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Tarnaka - 500007, Hyderabad, Telangana, India. *Corresponding author; E-mail: akula@iiict.res.in Tel: +91-40-27191720/3510; Fax: +91-40-27160921

^b Department of Chemistry, University College for Women Osmania University, Koti, Hyderabad - 500 095, Telangana, India.

^c Centre for Advanced Materials & Industrial Chemistry (CAMIC), School of Applied Sciences, RMIT University, GPO BOX-2476, Melbourne 3001, Australia.

| Contents | Page no. |
|--|----------|
| A. Preparation of H-ZSM 5 (Si/Al = 500) catalyst | S2 |
| B. CO formation vs catalyst reduction time (min) | S2 |
| C. FT-IR analysis | S2 |
| D. XRD analysis | S4 |
| E. SEM images of fresh and used catalysts | S5 |

A). Preparation method of H-ZSM 5 (Si/Al = 485)

The TPABr (0.29 gms) and TEOS (49.19 ml) were mixed with distilled water (5ml), and after 1 h stirring, diethelene triamine (0.05 ml) was added to make a solution (mixture (I)). NaOH (0.09 g) was also added with distilled water (5ml). Aluminum isopropoxide (AIP) (0.09 g) was added to distilled water (5ml) and stirred for 1 h. The resulting mixture (II) was added drop wise to mixture (I) with stirring, and the resulting gel was stirred for 120 min. Then the gel was transferred to a stainless-steel autoclave with 100 ml PTFE (polytetrafluoroethylene). The sealed autoclave was placed in air oven at 175 °C, for 3 days. The autoclave was quenched with water, and the solid product was filtered, washed with distilled water and dried at 110 °C overnight. To remove organic template (TPABr) the sample was calcined at 550 °C for 8 h. Ion exchange was then performed to replace Na^+ with the NH_4^+ by dissolving ZSM-5 powder in 1.0 M NH_4NO_3 solution (1 g of ZSM-5 sample per 10 mL of solution) at 50 °C for 24 h, and the procedure was repeated twice to ensure the complete ion exchange. The product after ion exchange was again calcined at 550 °C for 5 h.

B). Formation of CO_x vs catalyst reduction (min)

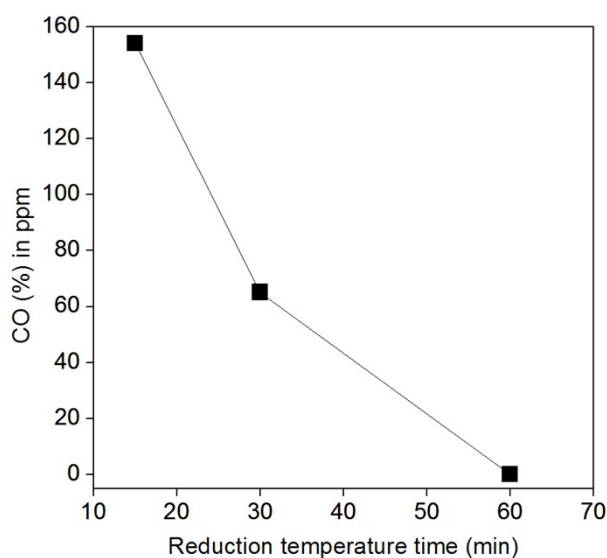


Figure S1:

Formation of CO with reduction temperature time over 30wt%Ni/H-ZSM-5 (Si/Al = 150) sample is shown in Figure S1. It shows that about 156 ppm of CO is observed when the sample reduced at 550 °C for 15 min. Upon increasing the reduction time to 30 min the CO levels

drastically decreased to 62 ppm. The CO formation is absent when the sample reduced for 1 h. Therefore it is suggested that partially unreduced Ni species may be contributing to form CO_x species during the initial activity of the catalysts.

C). FT-IR analysis

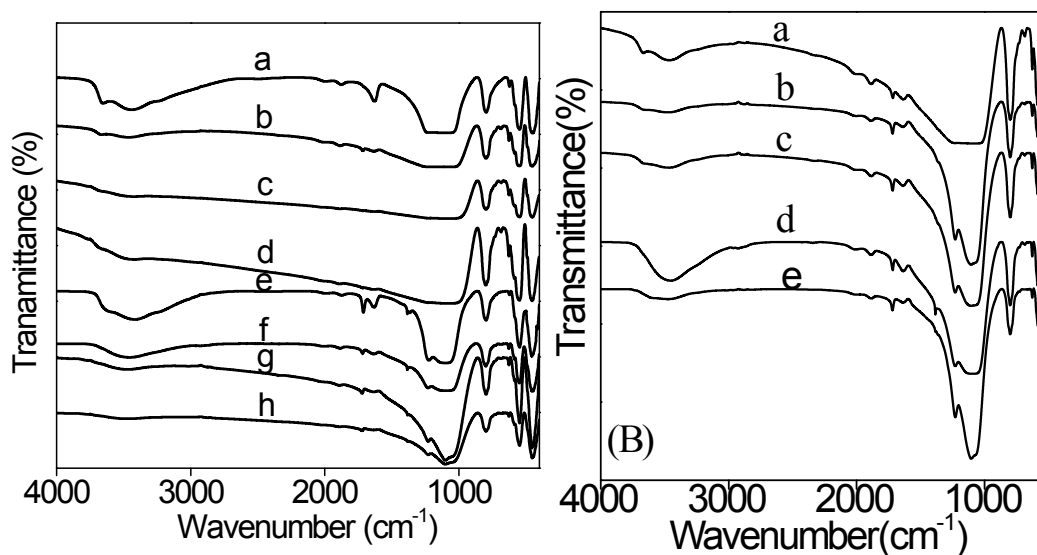


Figure S2: FT-IR spectra of parent and fresh calcined **(A)** H-ZSM-5 with various Si/Al ratio (a) parent(Si/Al=40), (b) parent H-ZSM-5 (Si/A/=150), (c) parent H-ZSM-5 (Si/Al=300), (d) parent H-ZSM-5 (Si/Al=485) (e) 30wt% Ni/H-ZSM-5 (Si/Al=40), (f) 30wt% Ni/H-ZSM-5 (Si/Al=150) and (g) 30wt% Ni/H-ZSM-5 (Si/Al=300) and (h) 30wt% Ni/H-ZSM-5 (Si/Al=485) catalysts. **(B)** Different Ni loaded on H-ZSM-5 (Si/Al=150); (a) parent H-ZSM-5 (Si/Al=150), (b) 10wt%, (c) 20wt% (d) 30wt% and (e) 50wt% catalysts.

D). XRD analysis

(a) XRD analysis of fresh

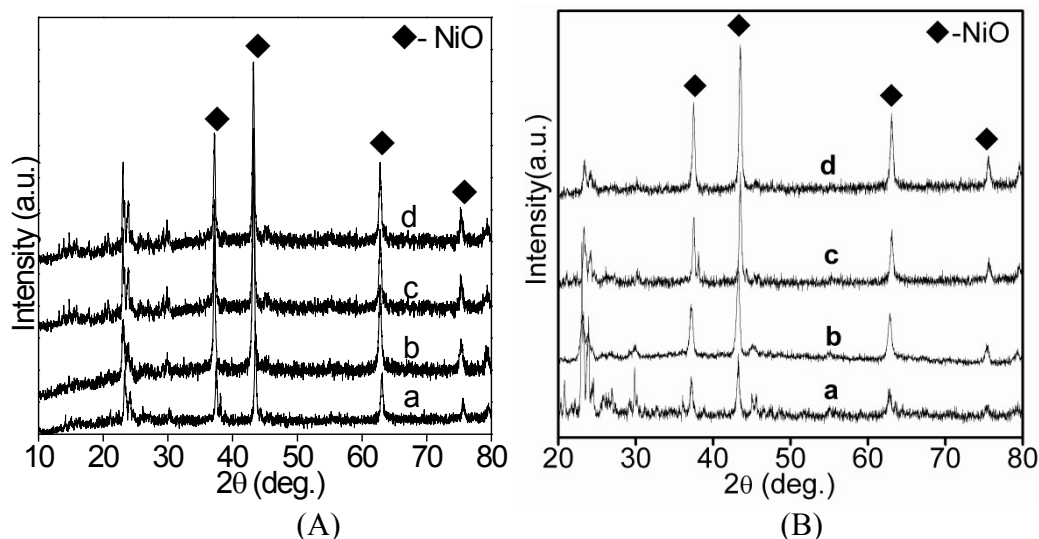


Figure S3 (A).XRD patterns of fresh calcined (a) 30wt%Ni/H-ZSM-5 (Si/Al=40), (b) 30wt%Ni/H-ZSM-5 (Si/Al=150) (c) 30wt%Ni/H-ZSM-5 (Si/Al=300) and (d) 30wt% Ni/H-ZSM-5 (Si/Al = 485) catalysts. (B) Ni loading on H-ZSM-5 (Si/Al=150) (a) 10wt%, (b) 20wt% and (c) 30wt% and (d) 50wt% catalysts.

(b) XRD analysis of reduced catalysts

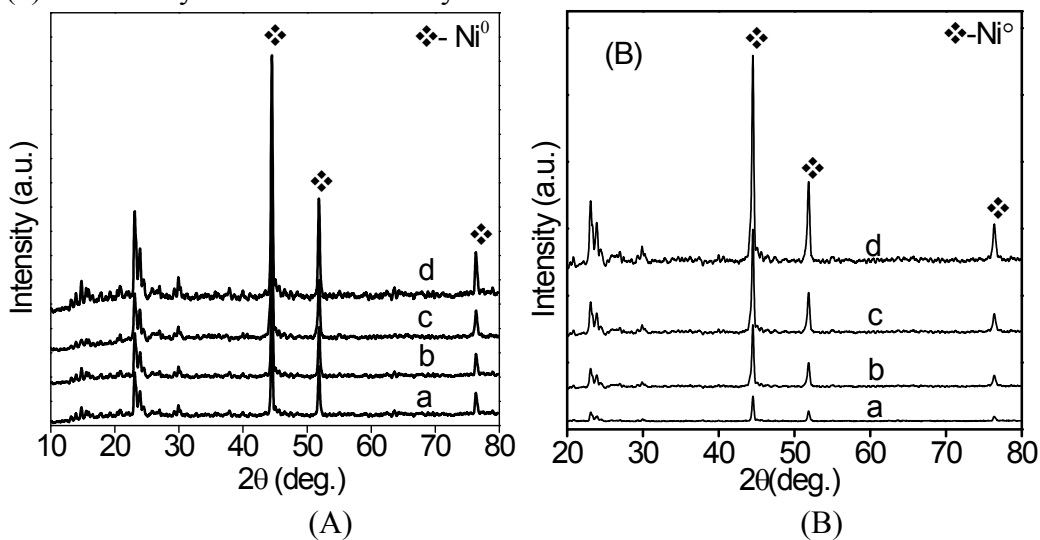


Figure S4 (A); XRD patterns of reduced 30wt% Ni loaded various Si/Al ratios (a) 40, (b) 150 and (c) 300 and (d) 485; **(B)** different Ni loaded H-ZSM-5 (Si/Al=150); (a) 10wt%, (b) 20wt%, (c) 30wt% and (d) 50wt% catalysts.

D). SEM images of fresh and deactivated catalysts

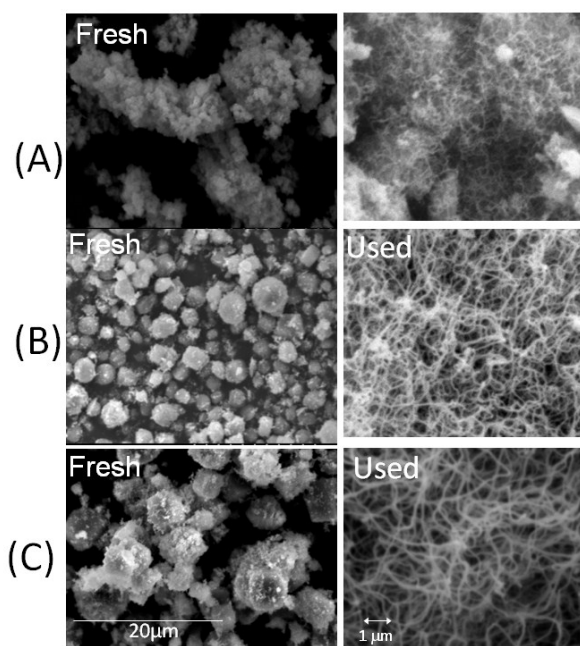


Figure S5: SEM images of deactivated 30wt% Ni loaded with Si/Al ratio; (a) 40, (b) 150 and (c) 300 catalysts.