Ni-phyllosilicate structure derived Ni-SiO₂-MgO catalysts for bireforming applications: acidity, basicity and thermal stability.

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Experimental

The surface area and total pore volume of the freshly calcined, reduced and spent catalysts were measured by N₂ physical adsorption at -196 °C in an ASAP 2020 instrument. Prior to N₂ physical adsorption, all the catalysts were degassed under vacuum at 300°C for 3 h. The specific surface area was calculated by applying the Brunauer-Emmett-Teller (BET) method. HRTEM system JEOL JEM-2100F was used to analyze surface morphology of calcined, reduced and spent catalysts. The catalyst sample was ultrasonically dispersed in ethanol and spread over perforated copper grids. The X-ray diffraction (XRD) patterns of fresh, reduced and spent catalysts were measured on a Shimadzu XRD-6000 diffractometer using Cu K α radiation. The catalyst was scanned for 2 θ range between 10° to 60° at a ramp rate of 2°/min.

Ni and Mg compositions of the catalysts were measured with Thermal Scientific iCAP 6000 ICP-OES Analyser. 15mg powder was dissolved in a mixture of 0.5 ml HF (48%), 2mL HNO₃ (65%) and 40mL DI water aided by ultrasonic treatment. Ni and Mg ICP standard solution diluted to appropriate concentrations was used to prepare the calibration curve.

The H₂ Temperature-programmed reduction (TPR) and CO₂-Temperature-programmed reduction (TPD) experiments was conducted using Thermo Scientific TPDRO 1100 series system (with TCD detector). For H₂-TPR, 0.03 g of catalyst sample was outgassed in N₂ gas for 1 h at 300°C to remove any moisture and then cooled to room temperature. Then, 5% H₂/N₂ gas was introduced to the catalyst while the temperature of the furnace was increased to 950°C (ramp rate of 10°C/min). For CO₂-TPD, about 100 mg of catalyst sample was reduced at 750°C for 1 h under H₂ gas (30 mL/min). After that, the samples were cooled to 50°C where CO₂ adsorption was carried out for 30 min. Then the samples were purged in He gas for 30 min. Desorption of CO₂ took place while heating the sample from 50 to 1000°C (ramp rate of 10°C/min).

The surface Ni metal content and dispersion was calculated by using N₂O titration method. Prior to N₂O titration at 70 °C, the sample (W = 30 mg) was reduced at 750 °C for 1 h under H₂ gas, and then cooled to 70 °C in helium gas flow of 30 mL/min. At this temperature, the N₂O decomposition was carried out by introducing several pulses of N₂O gas using 99.99% N₂O with a loop volume of 344 μ L. This was followed by TPR with temperatures up to 750 °C performed in the TPDRO 1100 series system. The amount of the oxidized Ni surface atoms by N₂O decomposition was estimated by measuring the H₂ consumed during TPR analysis, in accordance to Eq's below.

 $Ni^0 + N_2O \rightarrow NiO + N_2$

 $NiO + H_2 \rightarrow Ni^0 + H_2O$

The reduced and spent catalysts surface analysis was performed using X-ray photoelectron spectroscopy (XPS) from a KRATOS AXIS Hsi 165 equipped with Mg-Kα source (1253.6 eV). Prior to the analysis for reduced catalysts, the catalyst was reduced at 750°C under

 H_2 for 1 h. For spent catalyst, the catalysts were used as collected from reforming reactor. Then the sample was mounted on the standard sample stub using double-sided adhesive tapes. All binding energies were referenced to C 1s hydrocarbon peak at 284.6 eV. Shimadzu DTG-60 thermo gravimetric analyzer was used to analyse total amount and nature of deposited carbon on the spent catalysts. Around 10 mg of spent catalyst was used in each DTA/TGA experiment and heated in air to 1000°C with a heating rate of 10°C/min.

Table S1. The amount of metal precursors taken for synthesizing $Ni-SiO_2-Mg[x]$ catalysts, nominal and actual metal contents present in the calcined catalysts

Catalyst	Amount of metal precursor ^[a]			Nominal wt%	Actual wt%
	Ni nitrate	SiO ₂	Mg nitrate	composition	composition
	(grams)	(grams)	(grams)	(Ni:SiO ₂ :Mg)	(Ni:SiO ₂ :MgO)
Ni-SiO ₂	1.49	3.4		15:85:0	13.1±0.5::
Ni-SiO ₂ -MgO[25]	1.49	2.4	5.27	15:60:25	13.8±0.6::22.2±1
Ni-SiO ₂ -MgO[40]	1.49	1.8	8.44	15:45:40	11.5±0.4::35.6±0.6
Ni-SiO ₂ -MgO[55]	1.49	1.2	11.60	15:30:55	12.2±0.6::52.6±0.8
Ni-MgO[85]	1.49		17.93	15:00:85	9.4±0.5:: 61±1

[a] calculated to prepare 2g of the calcined catalyst; [b] determined using ICP-OES analyzer.



Figure S1. N₂ adsorption-desorption isotherms of calcined (a) Ni-MgO, (b) Ni-SiO₂-MgO[55], (c) Ni-SiO₂-MgO[40], (d) Ni-SiO₂-MgO[25] and (e) Ni-SiO₂ samples.



Figure S2. Time dependant (A) CH₄ conversion and (B) CO₂ conversion over Ni-SiO₂-MgO[x] catalysts during bi-reforming of methane reaction. Conditions: W = 0.01 g; CH₄ = 20 mL/min; CO₂ = 10 mL/min; Steam = 20 mL/min; He = 50 mL/min; Reduction temperature = 750°C/1 h; and Reaction temperature = 750°C.



Figure S3. Calculated thermodynamic equilibrium conversion for bi-reforming of methane reaction. Condition: $CH_4 = 20mL/min$, $H_2O = 20 mL/min$, $CO_2 = 10mL/min$ and He = 50mL/min.



Figure S4. Actual and calculated thermodynamic equilibrium CH_4 and CO_2 conversions during bi-reforming of methane reaction. Condition: $CH_4 = 20mL/min$, $CO_2 = 10mL/min$, $H_2O = 20mL/min$ and He = 50mL/min.



Figure S5. Bi-reforming of methane over Ni-SiO₂-MgO[55] at various reaction temperatures

Figure S5 depicts the Bi-reforming of methane (BRM) performance over Ni-SiO₂-MgO[55] at reaction temperature between 650 and 750°C. The result shows that both CH_4 and CO_2 conversions are decreased with decrease in reaction temperature. The H₂/CO values at 650°C is slightly higher than other reaction temperatures, which is possibly due to better water-gas-shift reaction at lower reaction temperature.







Figure S6. Bi-reforming of methane over Ni-SiO₂-MgO[55] catalyst at various CH₄/H₂O ratios.

According to Figure S6 the methane conversions were slightly decreased and CO_2 conversion was increased with decreasing steam amount in the feed is observed. This result shows that the H₂/CO values can easily be tuned by changing the amount of steam in the feed.



Figure S7. DT/TGA profiles for spent Ni-SiO₂-MgO[55] catalyst at various reaction conditions. The carbon formation during reforming reaction is observed at reaction temperature of 650° C and at low steam condition. The carbon formation is negligible for almost all other reaction conditions.









Figure S8. Pyridine-DRIFTS over reduced Ni-SiO₂-MgO[x] catalysts. The pyridine is adsorbed at 150C and desorbed between 150 and 400C in the presence of He gas.









Figure S9. Hydroxyls region of Pyridine-DRIFTS over reduced Ni-SiO₂-MgO[x] catalysts. The pyridine is adsorbed at 150C and desorbed between 150 and 400C in the presence of He gas.





Figure S10. N₂ adsorption-desorption isotherms of (A) reduced and (B) spent (a) Ni-MgO, (b) Ni-SiO₂-MgO[55], (c) Ni-SiO₂-MgO[40], (d) Ni-SiO₂-MgO[25] and (e) Ni-SiO₂ samples.