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> > **Electrical Supplementary Information**

Highly active and stable Ni-Mg phyllosilicate nanotubular catalyst for ultrahigh temperature water-gas shift reaction

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1 Catalysts preparation

All the chemicals were purchased from Sigma-Aldrich Company and did not receive any further treatment before use.

Ni PSNTS were prepared by hydrothermal method. $0.95g \text{ Ni}(\text{NO}_3)_2 \cdot 6H_2\text{O}$ was dissolved into 60ml DI water and 1.3ml sodium silicate solution was added to form precipitation. After 10min stirring, 12g NaOH pellets was added and stirred for another 10min. The dispersion was sealed in an autoclave, heated to 200°C and the temperature maintained for 24h. The as-prepared precipitation was centrifuged and washed with ethanol twice to remove the remaining ions. The produce obtained was finally dried at 60°C in vacuum. The solid was milled into powder and calcined at 600°C for 4h.

Ni-Mg PSNTS were prepared in a similar method. $1.2g Mg(NO_3)_2 \cdot 6H_2O$ and $1.1g Ni(NO_3)_2 \cdot 6H_2O$ were dissolve in a mixture of 30ml DI water and 90ml ethanol. 2.4ml sodium silicate solution was added. After 10min stirring, NaOH pellets were added and stirred for another 30min. The dispersion was sealed in an autoclave, heated to 190°C and the temperature maintained for 48h. The as-prepared precipitation was centrifuged, washed with ethanol twice to remove the remaining ions and dried at 60°C in vacuum. The solid was milled into powder and calcined at 600°C for 4h.

2 Characterization

JEOL TEM and HRTEM-EDS were employed to characterize to morphology of fresh, reduced and spent catalysts. Typically corresponding powders were put into ethanol, treated with sonication for several minutes and dropped onto copper grids.

Wide range XRD (10°-80°) patterns were obtained by Bruker D8 Advance X-ray diffractometer using a Cu K α radiation (λ =0.154056nm) with acceleration voltage of 40kV and beam current of 30mA. Low-angle XRD (0.5°-5°) was conducted in Shimazu XRD-6000 with specific slits for low angle scanning.

 N_2 adsorption-desorption isotherm experiments were performed at 77 K to characterize the textural properties of nanotubes with Micromeritics ASAP 2020 - Physisorption Analyser. Before analysis, the samples were degassed in vacuum at 350 °C for 4 h. The surface area was calculated using BET method and pore volume was obtained using BJH method.

Ni loading was measured with Thermal Scientific iCAP 6000 ICP-OES Analyser. 10mg powder was dissolved in a mixture of 0.5 ml HF (48%), 2 ml HNO₃ (60%) and 2ml H₂O₂ aided by ultrasonic treatment and finally diluted with DI water into a total volume of 40ml. 25, 50, 75 and 100ppm Ni solutions were prepared as standards as well.

H₂-TPR was performed on Thermal Scientific TPDRO 1100 apparatus equipped with a thermal conductivity detector (TCD). Typically, 40mg sample was tested with a flow of 5% hydrogen in nitrogen (25ml/min) with a temperature ramping rate of 10° C/min after degassing with helium for 30min.

Reduction extent was measured as follow: 30mg sample was reduced in a TPR that dwelled in a set temperature for 1h, integrating to get the peak area and converting it into amount of H_2 consumed using a standard calibration factor. Reduced Ni amount was calculate then by assuming a stoichiometry of 1. Reduction extent was obtained via dividing reduced Ni amount by the total Ni amount in the sample.

 CO_2 -TPD and N_2O pulse chemisorption were carried out on the same apparatus. 100mg sample was degassed under helium flow for 30min at room temperature Electronic Supplementary Information (ESI) for Chemical Communications This journal is © The Royal Society of Chemistry 2015

following by reduction with a flow of 5% hydrogen in nitrogen (25ml/min) at set temperature for 1h. After the sample was cooled down to 50° C, CO₂ at a flow rate of 30ml/min was introduced for 1h. Finally, the samples were heated from 50 to 600°C at a ramping rate of 10°C/min after removing physically adsorbed CO₂ under helium gas.

For N₂O pulse chemisorption, 40mg sample was reduced at a set temperature by 5% hydrogen in nitrogen for 1h, and cooled down to 90°C at the atmosphere of helium. Purified N₂O pulses were injected until the eluted peak area was constant. Then the sample was reduced again in a TPR process. The Ni active surface area was calculated from the amount of H₂ consumed in the second reduction by assuming a stoichiometry of 1 and a surface area of 6.5×10^{-20} m² per Ni atom.

3 Catalysis activity test

WGS reaction was conducted in a quartz tube reactor (inner diameter was 4mm) under atmospheric pressure. 25mg catalyst was put into the quartz tube. Before reaction, the catalyst was reduced by hydrogen at a flow rate of 20ml/min for 1h. The composition of produced gas was analyzed by an online GC (Agilent 7820A) equipped with a TCD. CO conversion was calculated by following equation:

 $CO \ conversion = \frac{CO \ flow \ rate_{in} - CO \ flow \ rate_{out}}{CO \ flow \ rate_{in}}$





image	item	Reduction	Reduced	Reduction	Ni active
		peak area	Ni amount	extent	surface area
		(mVs)	(mmol)		(m^2/g_{cata})
Α	Ni PSNTS	520510	0.0588	34%	1.4
	reduced at 500°C				
В	Ni PSNTS	1551640	0.1750	101%	
	reduced at 600°C				
С	Ni-Mg PSNTS	590020	0.0666	93%	1.5
	reduced at 650°C				

Table.S1 Reduction extent and active surface area of reduced Ni and Ni-Mg PSNTS



Fig.S1 (a) wide range XRD profiles of Ni PSNTS and Ni-Mg PSNTS, (b) low –angle XRD profiles of Ni PSNTS and Ni-Mg PSNTS



Fig.S2 TPR profiles of Ni PSNTS and Ni-Mg PSNTS



Fig.S3 Ni PSNTS reduced at 500°C

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Fig.S4 Nitrogen adsorption-desorption isotherm of two PSNTS



Fig.S5 ICP-OES measurement to determine Ni loading



Fig.S6 XRD profiles of reduced and spent Ni PSNTS



Fig.S7 CO₂-TPD profiles of reduced Ni PSNTS and Ni-Mg PSNTS





Mα Ka1 2





Ni Ka1

Fig.S8 EDS of Ni-Mg PSNTS reduced at 650°C





Mg Ka1_2





Ni Ka1

