The Synergistic Effect of Pore Architect and Reducibility in Ceria-Promoted Ni Molecular Sieve for Methane Dry Reforming

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Supporting information S1. Catalyst Characterization:

The N_2 adsorption-desorption profile against relative pressure (P/P_o), surface area, pore volume, and pore diameter of the catalyst sample was obtained from the Micromeritics Tristar II 3020 instrument (Micromatics, USA). The surface area is estimated by the Brunauer-Emmet-Teller equation, whereas pore size distribution is estimated by the nonlocal density function model. The X-ray Diffraction studies of the catalyst sample are carried out Miniflex Rigaku diffractometer (Rigaku, Saudi Arabia) using a $Cu_{K\alpha}$ source (λ= 1.54056 Å) operated at 40 kV and 40 mA. The step size and scanning range of 2θ for analysis were set to 0.01 and 5–100, respectively. The peak search profile is adjusted at minimum significance 2, minimum tip width $2\theta = 0.01°$, Maximum tip width $2\theta = 1°$, and peak base width $2°$ under the minimum second derivative method. Peak search and matched are carried out at a search depth of 10 and a minimum scale factor of 0.1. The diffraction patterns of the sample are matched with the JCPDS database for phase analysis. A laser Raman spectrometer from JASCO in Japan was used for the Raman analysis. It had a 532 nm beam excitation and 1.6 mW laser intensity. The sample was exposed for 10 s at 3 accumulations. The reducibility, basicity, and acidity profile are studied by H_2-temperature programmed reduction (H_2-TPR) and CO_2-temperature programmed desorption by using Micromeritics Autochem II 2920 (Micromatics, USA) and thermal conductivity detector (TCD). For H_2-TPR, 70 mg of the sample was heated up to 900 °C (at a heating ramp of 10 °C/min) under 10% H_2/Ar gas feed (flow rate 40 ml/min). After the interaction of gas feed with a surface, H_2O is formed, which is removed using a cold trap. The change in conductivity due to the consumption of H_2 in TPR or desorption of gases in TPD over the catalyst surface was recorded by a temperature conductivity
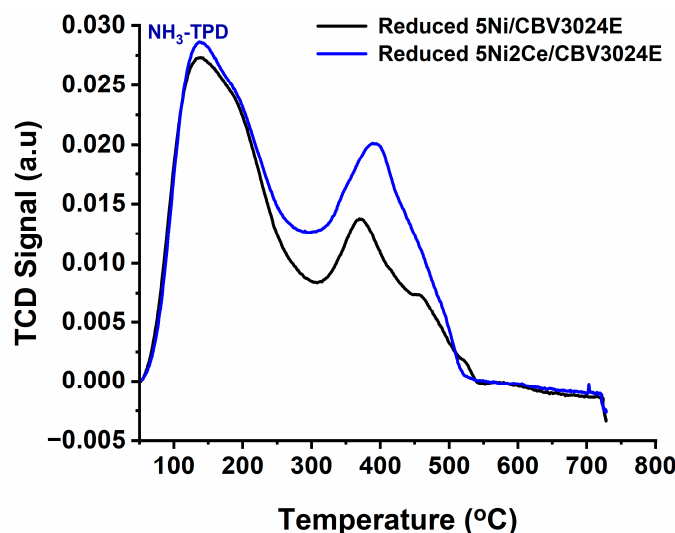
detector (TCD). Fourier transforms infrared (FTIR) spectra of catalyst samples were taken by Prestige-21 SHIMADZU. The amount of carbon deposition on the spent catalysts is evaluated by thermal gravimetric analysis (TGA) in air with a Shimadzu TGA-51. A platinum pan filled with 10–15 mg of the used catalysts is positioned carefully inside the device. It is heated from room temperature up to 1000°C at a 20°C/min^{-1} temperature ramp under an air atmosphere. The change in mass was continuously monitored as the heating progressed.

Supporting information S2. Catalyst Activity Test:

A fixed bed steel reactor made by PID Eng & Tech, with dimensions of 9.1 mm in diameter and 30 cm in length, is used to conduct the DRM reaction experiment. 0.1 g of catalyst is packed in the reactor which is encircled by heating. For measuring the temperature of the catalyst bed, a K-type thermocouple is located axially at the centre of the catalyst bed. The catalyst must be reduced for one hour at 600 °C in a stream of flowing hydrogen gas (at a flow rate of 30 ml/min) before it can be used. Using a combination of CH_4, CO_2, and N_2 at flow rates of 30 ml/min, 30 ml/min, and 10 ml/min, the DRM reaction was conducted over a reduced catalyst at 800°C and 1 atm pressure. The gas hourly space velocity of gas feed is 42,000 cm^3/g$_{cal}$.h. An online gas chromatography system, which includes a thermal conductivity detector (TCD), Porapak Q columns, and a molecular sieve 5A, is used to examine the gas streams entering and leaving the system. The following is the formula for determining the H$_2$-yield and CO yield:

$$H_2 \text{ Yield (\%)} = \frac{Mole\ of\ H_2\ in\ product}{2x\ Mol\ of\ CH_4,\ in} \times 100 \qquad (S1)$$

$$CO \text{ Yield (\%)} = \frac{Mole\ of\ CO\ in\ product}{Mol\ of\ CH_4,\ in + Mol\ of\ CO_2,\ in} \times 100 \qquad (S2)$$

Figure S1. NH$_3$-Temperature Programmed desorption of reduced 5Ni/CBV3024E and reduced 5Ni2Ce/CBV3024E catalysts

Table S1. The comparative study of catalytic activity in terms of H_2 yield over different catalyst systems.

Sr No.	Catalyst Name	Method	Weight of Active Metal (wt.%)	CW (%) in mg	I.D. (mm)	RT (°C)	Feed gas ratio CH_4: CO_2: Inert Gas (in mL) / min			GHSV (L/h g_{cat})	TOS (h)	Y_{H_2} (%)	Ref.
1	5Ni/MgO+ZrO₂	WI	5	100	9.1	600	3	3	1	42	7	46	48
2	5Ni/Zr	WI	5	50 + 450 mg SiC	7	600	1	1	2	30	50	17	49
3	5Ni1Ce/Zr	WI	5	100	9.1	700	3	3	1	42	7	47	20
4	Ni/CZ28	WI	5	100	10	700	1	1	0	30	3	34	50
5	La$_{1.95}$Sr$_{0.05}$Zr$_{1.44}$Ni$_{0.56}$O$_{7-d}$	PM	-	75	6	900	1	1	0	24	45	54.6	51
6	Ni/LaZr- Macropores	UHL	5	100	4	400	1	1	8#	7.2	100	56	52
9	5Ni2Sr/WO₃+ZrO₂	WI	5	100	9.1	700	3	3	1	42	7.8	57	53
10	5Ni/15YZr	WI	5	100	9.1	700	3	3	1	42	7	55	54
11	5NiSr/15YZr	WI	5	100	9.1	700	3	3	1	42	7	62	54
12	Ni/CeY	WI	5	-	6	750	1	1	0	18	0.5	63	55
13	5Ni/AlSi	WI	5	100	7	700	1	1	0	18	5	40	56
14	Ni-SiPd-OA	WI	0.2	100	6	700	2	2	0	24	6	48	57
15	5Ni-Mg/MCM-41	WI	5	60	9	700	1	1	1	60	4	43	58
16	NiCu/Al₂O₃	WI	10	-	5	750	1	1	0	24	0.5	65	59
17	NiCo/Al₂O₃	WI	10	-	5	750	1	1	0	24	0.5	60	59
18	5Ni3SiAl	WI	5 (Ni)	100	9	700	3	3	1	42	7	62	60
19	Ni/CaAl	WI	10	50	8	850	3	2	5*	120	0.5	40	61
20	Ni/MgAl	WI	10	50	8	850	3	2	5*	120	0.5	36	61
21	Ni-FeAl	SC	15	30	20	800	1	1	1**	3	20	60	62
22	**5Ni/CBV3024E**	**WI**	**5**	**100**	**9.1**	**800**	**3**	**3**	**1**	**42**	**7**	**43**	**This Study**
	5Ni2Ce/CBV3024E	**WI**	**5**	**100**	**9.1**	**800**	**3**	**3**	**1**	**42**	**20**	**70**	

CW: Catalysts Weight, I.D.: Initial Diameter of fixed bed tubular flow reactor, Method: SC = Solution combution, WI: Wet impregnation method, CP: Co-Precipitation method, UHL: Urea Hydrolysis Method, PM: Pechini Method, RT (°C): Reaction Temperature, CT (°C): Calcination Temperature, GHSV: Gas Hourly Space Velocity, TOS: Time on Stream, Y_{H2} (%): Hydrogen Yield (%), SP-OA : SP: Mesoporous SiO₂ (316 m²/g, pre diameter = 11.81 nm), OA: Oleic acid assisted, #: Sign dedicated to ether, * = Carrier gas He, **= Carrier gas Ar