Hydrogen Yield from the Partial Oxidation of Methane: Effect Sc Promoter on Supported Ni/MCM41 Catalyst

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Catalyst Characterization S1

We used a Micromeritics Tristar II 3020 to perform surface area and porosity analysis. We estimate the surface area using the Brunauer–Emmet–Teller equation. We degassed the 0.2–0.3 g catalyst samples for three hours at 200 °C to eliminate the adsorbed moisture and volatile gasses. XRD powder patterns were obtained using Cu kα radiation (λ = 0.15406 nm) using a Rigaku (Miniflex) diffractometer that was set to 40 kV and 40 mA. We used the Scherrer equation to determine the sizes of the crystallites. To perform temperature-programmed reduction, oxidation, and desorption, Micromeritics AutoChem II 292 was utilized. We placed a 0.07 g sample in the sample holder for H_2 temperature-programmed reduction (TPR). We then degassed the sample using an argon flow at 150 °C for 60 minutes and cooled it to 25 °C. Next, we used a 10% H/Ar flow to heat the furnace to 1000 °C at a rate of 10 K/min. A thermal conductivity detector (TCD) that tracks the gas mixture at the reactor's exit was able to identify peaks that correspond to the consumption

of H_2 as a function of temperature. We first maintained 70 mg of the sample at 200 °C for one hour under a helium flow, utilizing CO_2 temperature-programmed desorption (TPD) to remove physically adsorbed compounds from the catalyst surface. Next, we fed the sample with 10% CO_2/He gas for 30 minutes at 50 °C, with a flow rate of 30 ml/min. We then increased the temperature to 800 °C with a heating increase of 10 °C per minute. TCD captured the CO_2 desorption signal as the temperature increased linearly. We used a 120 kV transmission electron microscope (TEM), the JEOL JEM 2100F (Akishima, Japan), to capture the shape of the catalyst.

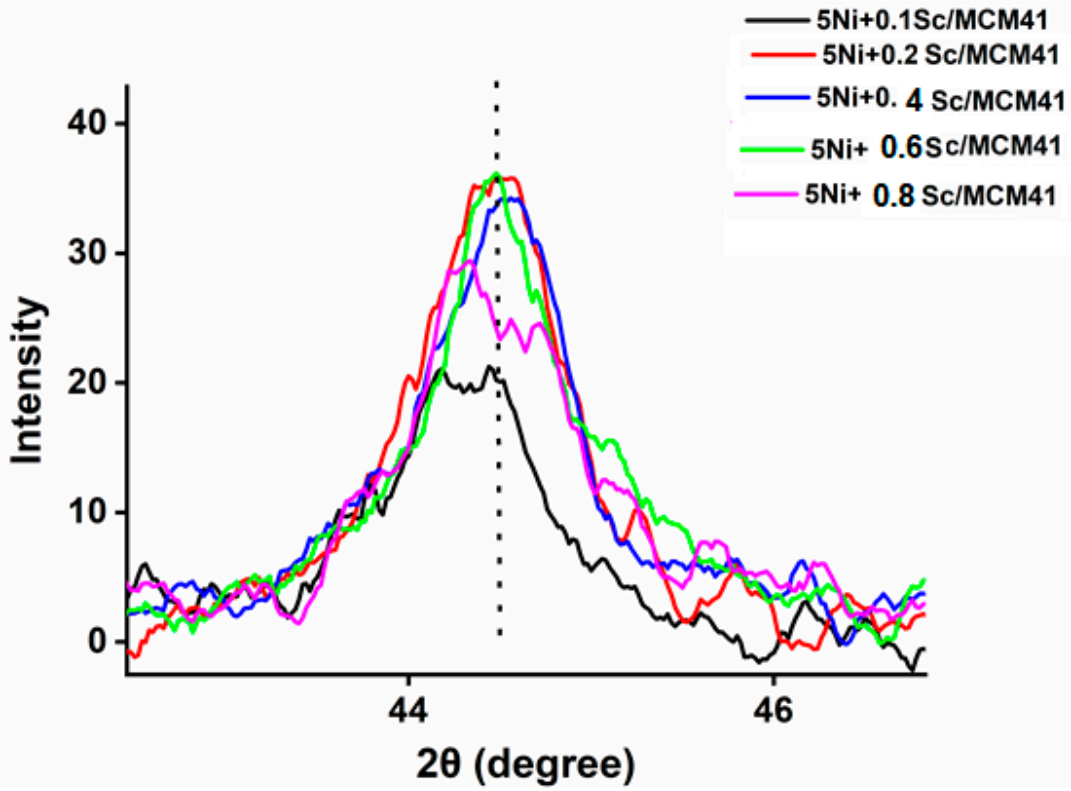

Figure S1. XRD of reduced catalysts in selected Bragg's angle range (showing metallic cubic Ni phase).

Catalytic Activity Test S2

We carried out the partial oxidation of methane (POM) at 650 °C in a fixed-bed stainless steel tubular reactor (PID Eng. & Tech Micro Activity Reference) with a 9.1 mm inner diameter and a length of 30 cm. For each test, quartz wool was placed in the tubular reactor, and on top of this, an amount of 0.1 g of catalyst was deposited. The reactor was then placed within a furnace to control the reaction temperature, and a K-type thermocouple, positioned at the center of the catalyst bed, monitored the reactor's temperature. The catalytic activity tests were performed under atmospheric pressure. After loading the catalyst into the reactor, a pre-treatment process was carried out to remove any adsorbed species and ensure proper activation. The catalyst was initially heated under a flow of pure N_2 at a rate of 20 °C/min until it reached the activation temperature of 800 °C. Once at this temperature, the catalyst was maintained for 1 hour under a H_2 flow of 30 mL/min to achieve complete surface activation. Following the reduction process, the system was flushed with N_2 (40 mL/min) to eliminate any residual hydrogen before introducing the feed gas. After pre-treatment, the reactor temperature was adjusted to 650 °C under a N_2 flow of 15 mL/min. The POM reaction was carried out at 650 °C using a gas mixture of 50% CH_4, 25% O_2, and 25% N_2. The total flow rate was 24 mL/min, and the space velocity was 14,400 mL/(g.h). The reaction products and feed mixtures were analyzed using an online gas chromatography system (Shimadzu GC 2014, Kyoto, Japan) equipped with two columns, namely Porapak Q and Molecular Sieve 5A, arranged in series/bypass connections for the efficient separation of the gas components. A thermal conductivity detector was employed to measure the gas composition, based on the difference in thermal conductivity between the input argon reference gas and the sample gas being analyzed.

This setup enabled the continuous monitoring of key gasses, including H_2 and unreacted feed gas, providing accurate insights into the catalytic performance. The schematic of the experimental setup is shown in Figure S1. We used formulas to compute CH_4 conversion, H_2 yield, CO yield, and the H_2/CO ratio and applied the normalization approach to determine the composition of the effluent gas:

$$\mathrm{CH_4\ conversion\ (\%)} = \frac{\mathrm{CH_{4,in} - CH_{4,out}}}{\mathrm{CH_{4,in}}} \times 100$$

$$\mathrm{H_2\ Yield\ (\%)} = \frac{\mathrm{H_{2,out}}}{2 * \mathrm{CH_{4,in}}} \times 100$$

$$\mathrm{CO\ Yield\ (\%)} = \frac{mol\ of\ CO\ in\ products}{mol\ of\ CH_4\ in\ feed + mole\ of\ O_2\ in\ feed} \times 100$$

$$\mathrm{CO_2\ Yield\ (\%)} = \frac{mol\ of\ CO_2\ in\ products}{mol\ of\ CH_4\ in\ feed + mole\ of\ O_2\ in\ feed} \times 100$$

$$\frac{H_2}{CO} = \frac{Mole\ of\ H_2\ produced}{Mole\ of\ CO\ produced}$$

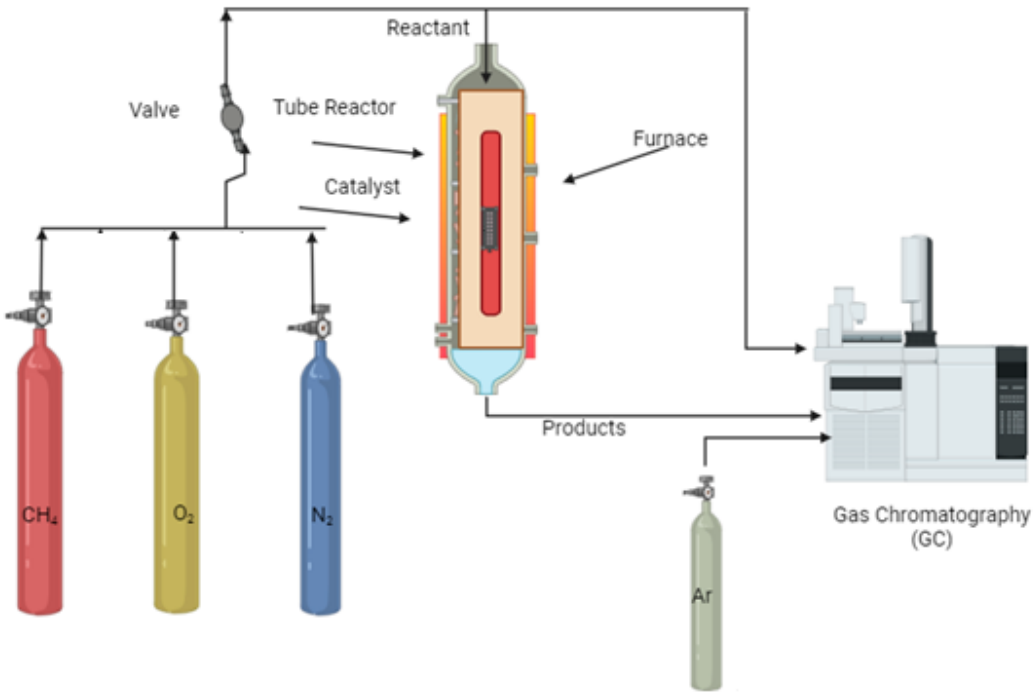

Figure S2 Schematic of the experimental setup**.**

Catalyst Synthesis S3

A 0.1 g catalyst was prepared. It consisted of 4% Ni (0.004 g) derived from $Ni(NO_3)_2 \cdot 6H_2O$.

- **Non-promoted catalyst:** The remaining 96% (0.096 g) was composed of MCM-41 support.
- **Promoted catalyst:** The Ni content remained constant at 4% (0.004 g). The amount of MCM-41 support was reduced proportionally to the wt.% of the Sc promoter. For instance, with 2% Sc (0.002 g), the support weight was adjusted to 0.094 g (0.1 g - 0.004 g Ni - 0.002 g Sc).

Synthesis of the support (MCM-41)

MCM-41 synthesis involves dispersing 18 g of 50 wt.% silica sol in 40 g of water, followed by the addition of 14 g of 25 wt.% tetramethyl ammonium hydroxide (TMAOH) solution and 8 g of trimethyl stearyl ammonium bromide surfactant. Continuous stirring ensures a homogeneous slurry. This mixture is then subjected to hydrothermal treatment at 120 °C for 3 days in a Teflon-lined autoclave. During this process, TMAOH promotes the hydrolysis and condensation of silicate species.

$SiO_2 + 2H_2O \rightarrow Si(OH)_4$

$Si(OH)_4 + Si(OH)_4 \rightarrow Si\text{-}O\text{-}Si + 2H_2O$

The surfactant molecules self-assemble into micelles, around which silica species condense, forming ordered mesoporous structures with uniform pore sizes.

Synthesis of the supported active metals

Ni (M.wt) = 58.69 g/mol;

$Ni(NO_3)_2.6H_2O$ (M.wt) of the precursor = **290.81 g/mol;**

4% of Ni in the catalyst corresponds to = 4/100 x 0.1g = 0.004 g;

The amount of the precursor to give 4% of Ni is = (290.81x 0.004)/58.69 = 0.0198g;

The weight of the support (MCM-41) = 0.1-0.0198 = 0.0802g;

For the preparation of the non-promoted catalyst; 0.0198g of Ni precursor is impregnated using the wet method in 0.0802g of MCM-41 to obtain the 4Ni/MCM-41 catalyst;

For the promoted catalyst, the scandium is prepared using its precursor ($Sc(NO_3)_3$) and the Ni from its precursor ($Ni(NO_3)_2.6H_2O$);

Sc = **44.96g/mol;**

$Sc(NO_3)_3$ = **230.97 g/mol;**

For instance: 2% of Sc in the catalyst corresponds to = 2/100 x 0.1g = 0.002 g;

The amount of the Sc precursor to obtain 2% of Sc is = (230.97x 0.002)/44.96= 0.0091g;

Thus, for the preparation of the 2% Sc-promoted catalyst; 0.0198g of Ni precursor and 0.0091g of Sc precursor are impregnated using the wet metho in 0.0711g of MCM-41 to obtain the 4Ni+2Sc/MCM-41 catalyst.

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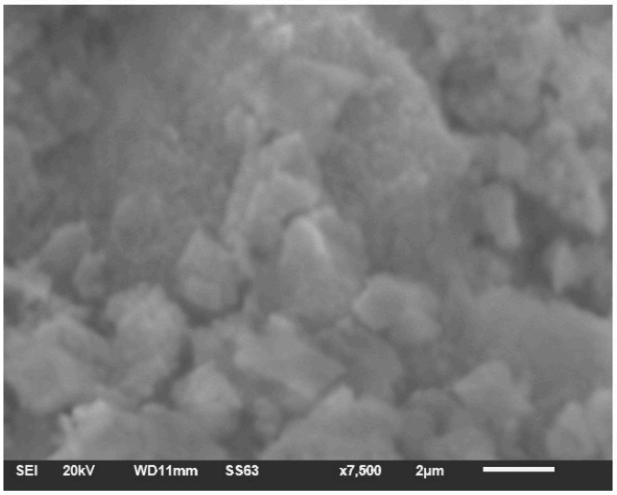

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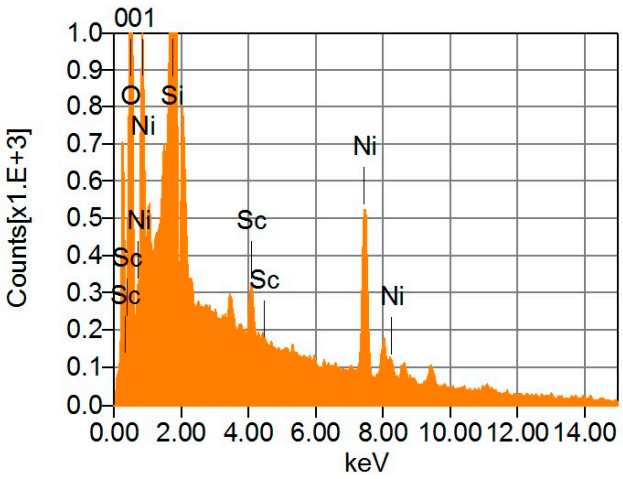
Mag. : x 7,500
Date : 2024/12/17
Pixel : 640 x 480



Acquisition Condition
Instrument : 6010LA
Volt : 20.00 kV
Current : ---
Process Time : T4
Live time : 41.38 sec
Real Time : 54.22 sec
DeadTime : 24.00 %
Count Rate : 15308.00

Formula	mass%	Atom%	Sigma	Net
O	50.56	65.32	0.05	405508
Si	44.87	33.02	0.06	1569287
Sc	0.39	0.18	0.01	8599
Ni	4.18	1.47	0.03	32945
Total	100.00	100.00		

Figure S3. EDX elemental profile.

Table S1 H_2-TPR-O_2-TPO-H_2-TPR cyclic experiments.

H_2-TPR-O_2-TPO-H_2-TPR Cyclic Experiments								
Physisorption Techniques	Catalysts Name	Catalysts- Weak Interaction with Nickel		Catalysts- Moderate Interaction with Nickel		Catalysts- Strong Interaction with Nickel		Total Quantity (cm^3/g STP)
		Temperature 0-300 (°C)		Temperature 300-600 (°C)		Temperature 600-1000 (°C)		
		T (°C)	Quantity (cm^3/g STP)	T (°C)	Quantity (cm^3/g STP)	T (°C)	Quantity (cm^3/g STP)	
H_2-TPR (First)	4Ni/MCM41	-	-	397	12.23	-	-	15.53
		-	-	592	3.30	-	-	
	4Ni+0.2Sc/MCM41	-	-	476	7.72	990	0.012	17.79
		-	-	627	10	992	0.040	
		-	-	-	-	995	0.016	
	4Ni+0.4Sc/MCM41	-	-	474	6.20	646	11.15	17.70
	4Ni+0.6Sc/MCM41	-	-	447	6.74	649	11.79	18.53
	4Ni+0.8Sc/MCM41	-	-	434	1.47	649	13.14	14.61
O_2-TPO	4Ni/MCM41	45-50	0.017	351	7.79	642-700	0.46	9.16
		129-162	0.031	527	0.35	700-750	0.59	
		-	-	-	-	803-900	0.123	
	4Ni+0.2Sc/MCM41	-	-	338	1.93	730-764	0.140	8.20
		-	-	345	0.027	820-899	0.484	
		-	-	356	1.43	900-950	0.549	
		-	-	427-491	1.39	-	-	
		-	-	504-514	2.26	-	-	
	4Ni+0.4Sc/MCM41	43	0.012	347-371	3.58	638-698	0.26	7.98
		58	0.005	420-499	1.38	701-798	0.32	
		-	-	501-530	1.75	800-900	0.44	
		-	-	-	-	900-948	0.228	
	4Ni+0.6Sc/MCM41	46	0.017	518-535	0.422	615-684	0.016	3.80
		280-285	3.30			734-763	0.030	
	4Ni+0.8Sc/MCM41	197	0.006	348	7.59	714	0.2527	8.37
		210	0.0046	544	0.488	782	0.0098	
		-	-	-	-	826-894	0.021	

Physisorption Techniques	Catalysts Name	Catalysts- Weak Interaction with Nickel	Catalysts- Moderate Interaction with Nickel	Catalysts- Strong Interaction with Nickel

Table S2 A comparison of the present work activity with the results mentioned in the previous literature.

Sample	Catalyst Weight (mg)	CH_4/O_2	Reaction Temperature (◦C)	CH_4 Conversion (%)	H_2 Yield (%)	Ref
V-MCM-41	50	0.9	600	-	53	[58]
10% Ni-MCM-41	50	0.9	800	83	-	[59]
Co/meso Al_2O_3	-	2.0	750	85	-	[60]
Co/MgO	1.5-15		850	91	-	[61]
Co/MgAl	100		750	50	-	[62]
Co/ZrO_2–Al_2O_3	150	2.0	700	65	-	[63]
Ni/SiO_2	50	0.5	700	80	90	[64]
Ni Ce/SiO_2	50	0.9	500	60	60	[65]
Fe-MCM-41	10	0.9	500	40	33	[66]
4Ni+0.2Sc/MCM41	100	2.0	650	63.9	60	Present work
4Ni/MCM41	100	2.0	650	58.5	56	Present work