

*Supplementary information for*

**Integrating Advanced Fitting Models with Experimental Catalysis to Maximize H<sub>2</sub> Production in Dry Reforming Using Nickel on Metalized-Silica-Alumina Catalysts**

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### **S1. Catalyst Characterization**

The 5Ni1M/SiAl (M = Ir, Pd, Pt, Rh, Ru) catalysts are characterized by surface area and porosity, X-ray diffraction (XRD) techniques, Raman spectroscopy, thermogravimetry and temperature programmed reduction/desorption techniques and X-ray photoelectron spectroscopy. The X-ray diffraction study is carried out by Miniflex Rigaku diffractometer using Cu K<sub>α1</sub> radiation ( $\lambda = 0.15406$  nm) operated at 40 mA and 40 kV. The phase analysis of the catalyst sample is done by X'pert high-score software enriched with the JCPDS database. The surface area and porosity of the catalysts are determined by Micromeritics Tristar II 3020 using the BET and BJH methods, respectively. Nitrogen sorption isotherms are determined at -196 °C after outgassing the 0.25 g of catalyst sample at 250 °C for 3 hours. The reducibility and basicity profile of the catalyst is studied over a 70 mg catalyst sample in a 50–1000°C temperature range by H<sub>2</sub>-temperature-programmed reduction (H<sub>2</sub>-TPR) and CO<sub>2</sub>-temperature programmed desorption (CO<sub>2</sub>-TPD) using Micromeritics AutoChem II instrument. In H<sub>2</sub>-TPR, a 10% H<sub>2</sub>/Ar gas mixture (flow rate of 40 mL/min) is used to reduce the catalyst sample from 50 to 1000°C temperature range (heating ramp 10 °C/min). The amount of H<sub>2</sub> consumed during the reduction is monitored by a thermal conductivity detector (TCD). For CO<sub>2</sub>-TPD, a 10% CO<sub>2</sub>/He gas mixture is allowed to be adsorbed over the catalyst at room temperature. Upon

raising the temperature to 1000°C (heating ramp 10 °C/min), the amount of CO<sub>2</sub> desorption is monitored by TCD. Raman spectroscopy of fresh and spent catalyst samples is investigated over a Laser Raman Spectrometer (JASCO, Japan) using 532 nm beam excitation and 1.6 mW laser intensity. The exposure time was set to 10 seconds with 3 accumulations. The spectra were processed using Spectra Manager Ver.2 software (JASCO, Japan). Thermogravimetry analysis of the 70 mg spent catalyst sample is taken up to 1000 °C (heating ramp 10 °C/min) under air using the Shimadzu-TGA instrument. The weight loss of the catalyst sample is monitored continuously. X-ray photoelectron spectra of the catalysts sample are taken by a ThermoScientific X-ray photoelectron spectrometer using monochromated AlK<sub>α</sub> radiation (energy 1486.6 eV) at 50 eV pass energy and 72 W power. A one-point scale with the C1s peak at 285.0 eV is used for charge correction. The transmission electron microscopy was conducted at 200 kV using an aberration-corrected JEM-ARM200F (JEOL, Tokyo, Japan) with a CEOS corrector (CEOS GmbH, Heidelberg, Germany).

## **S2. Catalyst Performance evaluation**

The DRM reaction experiment is carried out over 0.1 g of catalyst packed in a fixed-bed stainless steel tubular reactor (PID Eng & Tech, Pennsylvania, USA) equipped with a furnace. The inner diameter and length of the reactor are 9.1 mm and 30 cm, respectively. To monitor the reactor's temperature, a K-type thermocouple is positioned at the centre of the catalyst bed. Before the DRM reaction, the catalyst is reduced under hydrogen flow (40 ml/min) at 800°C for 60 minutes. Further, to eliminate any remaining H<sub>2</sub>, N<sub>2</sub> is blown with a 15 ml/min flow rate at 800°C temperature. At a set temperature (700°C for general catalytic reaction at different catalysts), CH<sub>4</sub>: CO<sub>2</sub>: N<sub>2</sub> gas feed (in 3:3:1 ratio) is allowed to pass through the catalyst at 70 ml/min total flow rate and 42000 ccg<sup>-1</sup>h<sup>-1</sup> gas hourly space velocity. The inlet and outlet gas streams are analyzed using online gas chromatography (Shimadzu GC-2014) equipped with a

thermal conductivity detector (TCD) and a combination of Porapak Q and Molecular Sieve 5A columns. The calculation for H<sub>2</sub>-yield and CO yield is as follows:

$$\text{CO Yield (\%)} = \frac{\text{Mole of CO in Product}}{\text{Mol of CH}_4, \text{ in} + \text{Mol of CO}_2, \text{ in}} \times 100$$

$$\text{H}_2 \text{ Yield (\%)} = \frac{\text{Mole of H}_2 \text{ in Product}}{2 \times \text{Mol of CH}_4, \text{ in}} \times 100$$

**S3. The basic terms of variance and prediction statistics** are shown below:

(1) Fisher variation (F-value) The F-ratio is defined by the following equation:

$$F_{calc} = \left( \sum_{i=1}^N (y_i - y_{ci})^2 / N - c \right) / S^2 \quad (12)$$

Here,  $S^2$  represents the variance of duplicate readings at the design center, and  $c$  denotes the count of excluded coefficients (either rejected or deemed insignificant in influencing the response) within the regression equation. This comparison is made against the critical F-value, which can be obtained from any statistical tool such as Excel. The degrees of freedom for the numerator (df.n) are determined as  $N - c$ , while the degrees of freedom for the denominator (df.d) are calculated as  $r - 1$ , where  $r$  signifies the number of replications at the design center. This assessment is conducted at a significance level  $\alpha$  of 0.05. The regression equation model effectively fits the experimental data if  $F_{calc}$  is less than  $F_{crit}$ .

(2) A sum of squares due to a fitted model and the sum of square due to errors.

The total variation in the response variable is divided into two components: the sum of squares due to the fitted model ( $SS_{model}$ ) and the unexplained variation, denoted by the sum of squares due to errors ( $SS_{Error}$ ) in Eq (17) [10].

(3)

$$\sum_{i=1}^n (E_i - \bar{E})^2 = \sum_{i=1}^n (P_i - \bar{E})^2 + \sum_{i=1}^n (E_i - P_i)^2$$

$$SS_{Total} = SS_{model} + SS_{Error}$$

“n” refers to the total number of experiments, where,  $E_i$  and  $P_i$  are denote the actual and predicted values, respectively, for the  $i^{\text{th}}$  observation.  $\bar{E}$  represents the mean value of the response variable across all observations.

(4) Determination coefficient  $R^2$  :

$R^2$  assesses the model's goodness-of-fit and its capacity to effectively represent and explain variations in the response variable. It is expressed as shown below:

$$R^2 = \frac{SS_{model}}{SS_{Total}} = 1 - \frac{SS_{Error}}{SS_{Total}}$$

A higher  $R^2$  value indicates a more precise depiction of the relationship between variables, as reflected in a smaller SS-Error.

(5) Absolute percentage error (APE), mean absolute errors (MAE), mean absolute percentage error (MAPE) : Absolute percentage error (APE), mean absolute errors (MAE) and mean absolute percentage error (MAPE) are defined as shown below:

$$APE = 100 * |E_i - P_i|/E_i \% \quad (18)$$

$$MAE = \frac{1}{n} \sum_{i=1}^n |E_i - P_i|/E_i \quad (19)$$

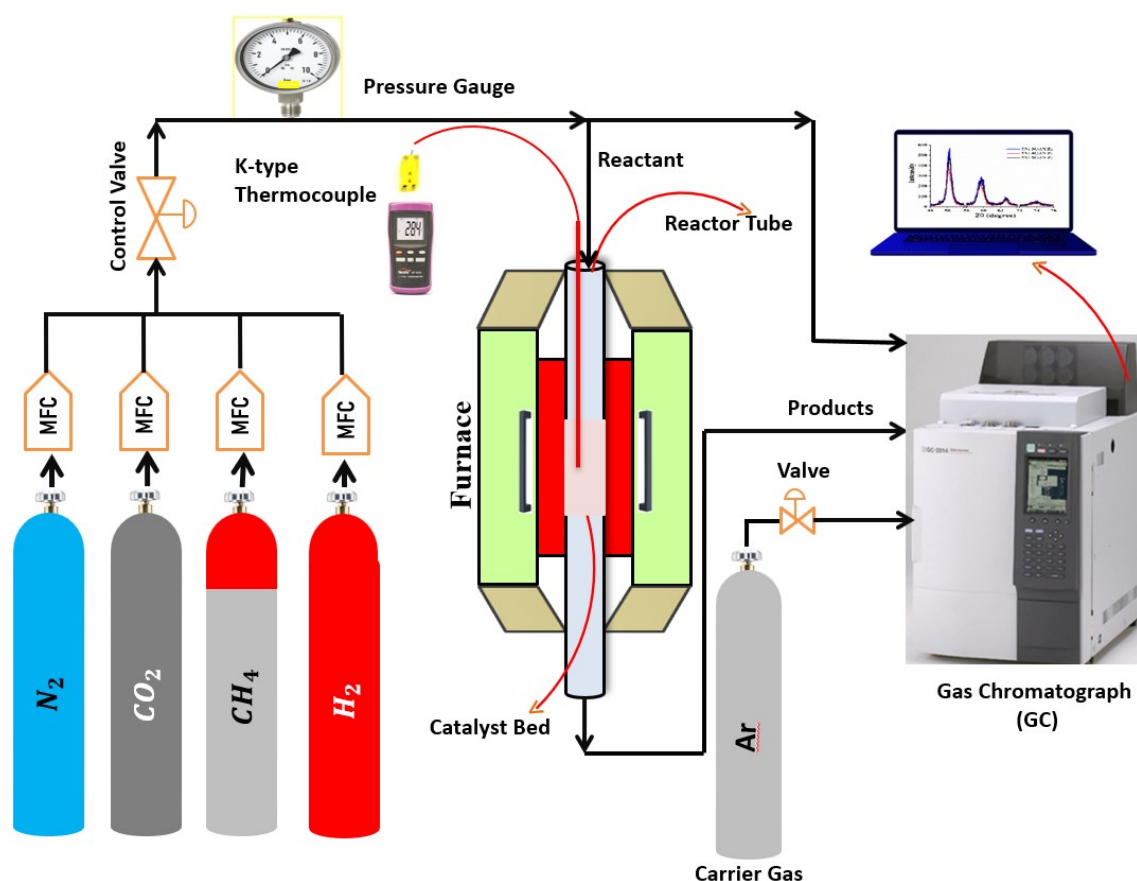
$$MAPE = 100 * \frac{1}{n} \sum_{i=1}^n |E_i - P_i|/E_i \% \quad (20)$$

$n$  refers to the total number of experiments, where,  $E_i$  and  $P_i$  denote the actual and predicted values, respectively, for the  $i$ -th observation.  $\bar{E}$  represents the mean value of the response variable across all observations.

#### S4. Methodology

The experiment investigated the performance of a 5Ni/1RhSiAl catalyst in converting CO<sub>2</sub> to methane (methanation) using a feedstock gas mixture of CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub> (3:3:1 ratio). The reaction temperature was fixed at 700°C and the gas hourly space velocity (GHSV) was maintained at 42,000 cc/g-cat/h. To optimize the reaction conditions for maximizing the yield of hydrogen (H<sub>2</sub>), a central composite design (CCD) method was employed within the Response Surface Methodology (RSM). Three key factors were analyzed: space velocity, reaction temperature, and the CH<sub>4</sub>/CO<sub>2</sub> ratio. These factors were represented by coded variables (X1, X2, X3) with a range of -1 to +1 (details in Table 2). Table 2 also provides the

actual values corresponding to these coded variables for the mathematical model predicting  $H_2$  yield (Equation 1). The model's applicability was assessed using analysis of variance (ANOVA) and prediction statistics (refer to Table 2 for details).



**Figure S1** Experimental setup for conducting methane reforming.

**Table S1.** The results of background conversions

	Reaction Temp. °C	Conversion %		$H_2/CO$
		$CH_4$	$CO_2$	
No catalyst	700	0.76	0.74	0.18
	800	1.63	2.01	0.41

**Table S2** Predictive and validation results

Variables	T (°C)	SV (L g <sup>-1</sup> cat <sup>-1</sup> hr <sup>-1</sup> )	CH <sub>4</sub> : CO <sub>2</sub>	H <sub>2</sub> /CO	H <sub>2</sub> yield (%)	CH <sub>4</sub> conv. (%)	Run #	Range	Ref.
Optimum conditions (model)	798	26.52 1	0.5	-	97.6	-	18	T=(700- 800°C); Ratio= (0.5–1.0); SV= (22– 42 L g cat <sup>-1</sup> hr <sup>-1</sup>	This work
Optimum conditions (Exp.)	798	26.52 0	0.5	-	95.4	-			
Optimum conditions (model)	800	26.00 0	0.6	-	-	78.3	15	T= (700- 900 °C);  Ratio= (0.2–1.0);  SV= (16– 36 L/ g cat <sup>-1</sup> hr <sup>-1</sup>	[1]
Optimum conditions (model)	784.1 5 °C	33,76	2.52	-	-	96.6	16	T= (700- 800 °C);  Ratio= (1–5);  SV= (10–	[2]

Optimum conditions (model)	850	15.00	TOS =258	0.98	-	-	34	60 L g cat <sup>-1</sup> hr <sup>-1</sup> T= (700-850 °C);  TOS= (150-480);  SV= (9-15 L g cat <sup>-1</sup> hr <sup>-1</sup>	[3]
Optimum conditions (model)	837	14.9	0.98	-	89	-	15	T= (600-850 °C);	[4]
Optimum conditions				-		-		Ratio= (0.5-1.2);	
.(Exp.)	837	14.9	0.92		87.3			SV= (12-52 L g cat <sup>-1</sup> hr <sup>-1</sup>	

#### Ref.

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