Natural Kaolin Derived Ruthenium Supported Nanoporous Geopolymer: A Sustainable Catalyst for CO_2 Methanation

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1.Supporting Results:

SI.1: X-ray diffraction pattern of natural kaolin (NK), metakaolin (MK) and geopolymer

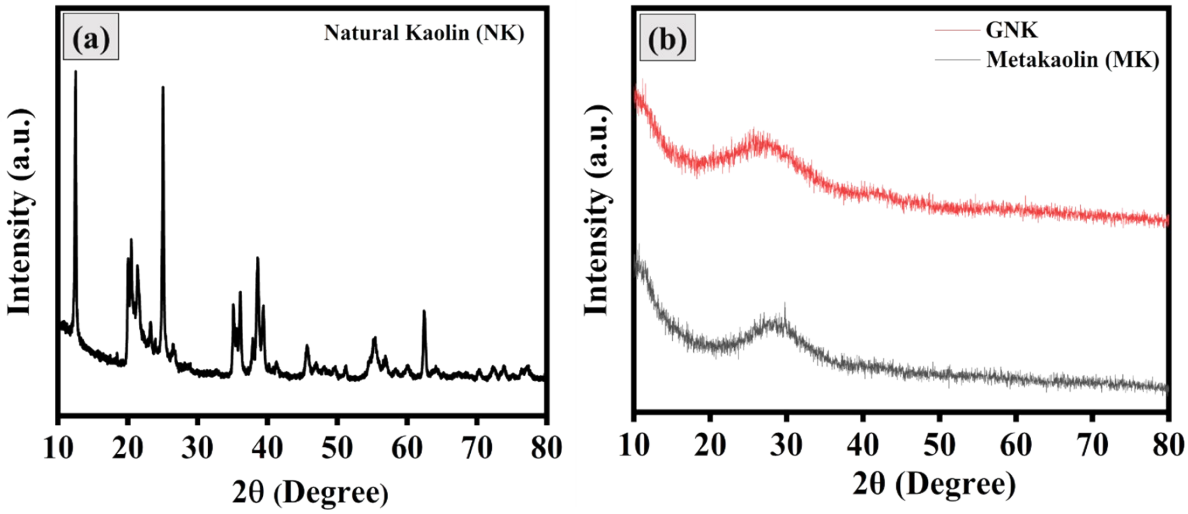


Figure SI 1. XRD of (a) Natural kaolin (b) Metakaolin and geopolymer from natural kaolin **from natural kaolin (GNK)**

SI.2: Fourier Transform Infrared Spectroscopy (FTIR) of GNK

FTIR studies of GNK showing absorption band at 1008 cm^{-1} associated with the asymmetrical stretching of Si-O-Si and Si-O-Al bonds. Further, hydroxyl region shows a broad peak between 2800 and 3800 cm^{-1} due to adsorbed water. Peak at about 1630 cm^{-1} is due to the bending mode of adsorbed water. Another bands at 720 cm^{-1} (Si-O-Si/ Si-O-Al stretching), 560 cm^{-1}

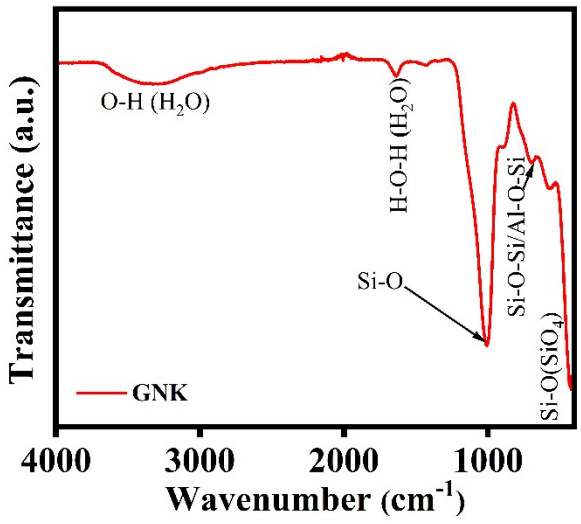


Figure SI 2. Fourier Transform Infrared spectra of geopolymer from natural kaolin (GNK)

(tetrahedral aluminium stretching bands) and 690-440 cm−1 (Si-O-Si/ Si-O-Al bending vibrations) are also present in the GNK.

SI.3: FESEM Images

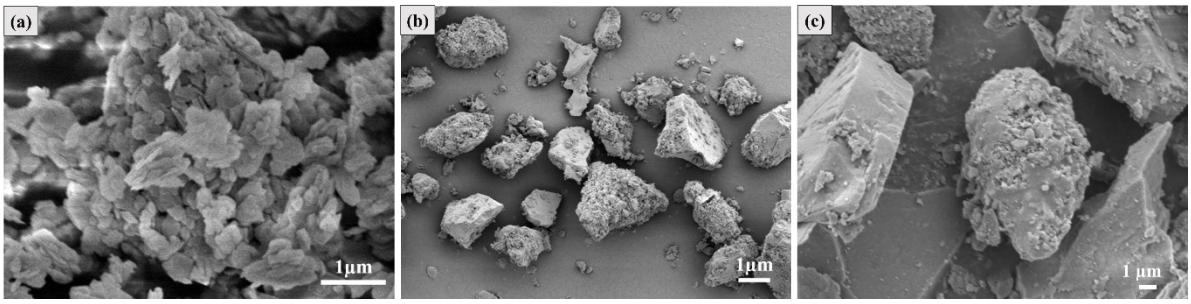


Figure SI 3. SEM Images of (a)Natural kaolin (NK) (b) Metakaolin (MK) (c) geopolymer from natural kaolin (GNK)

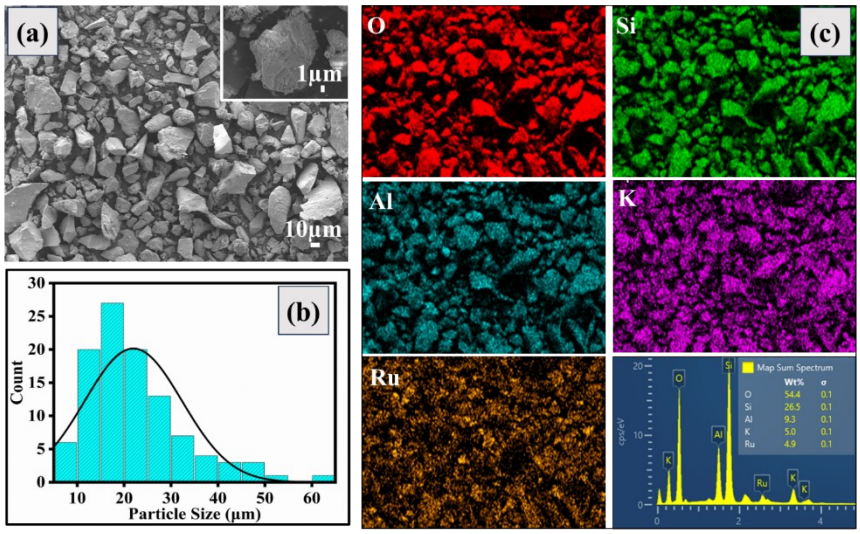


Figure SI 4. a) FESEM image b) Histogram distribution of the particle size c) Elemental distribution and EDX of 1%Ru/GNK

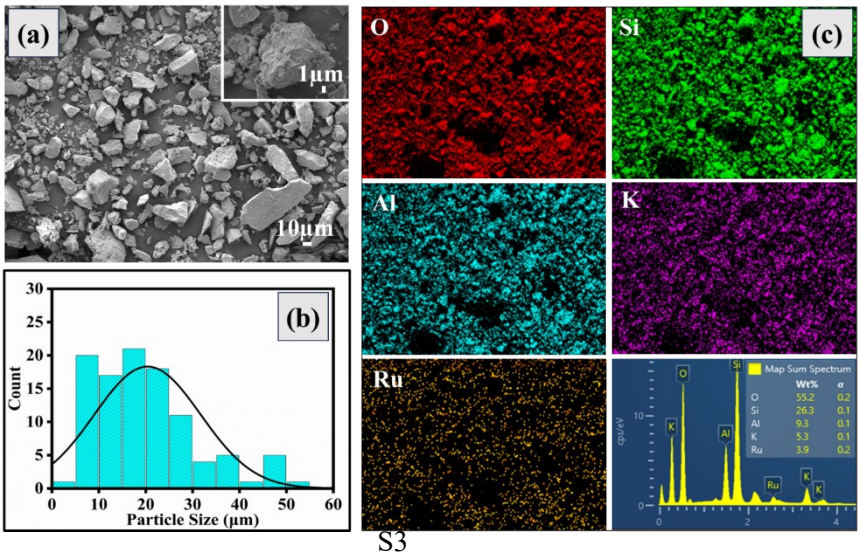


Figure SI 5. a) FESEM image b) Histogram distribution of the particle size c) Elemental distribution and EDX of 3%Ru/GNK

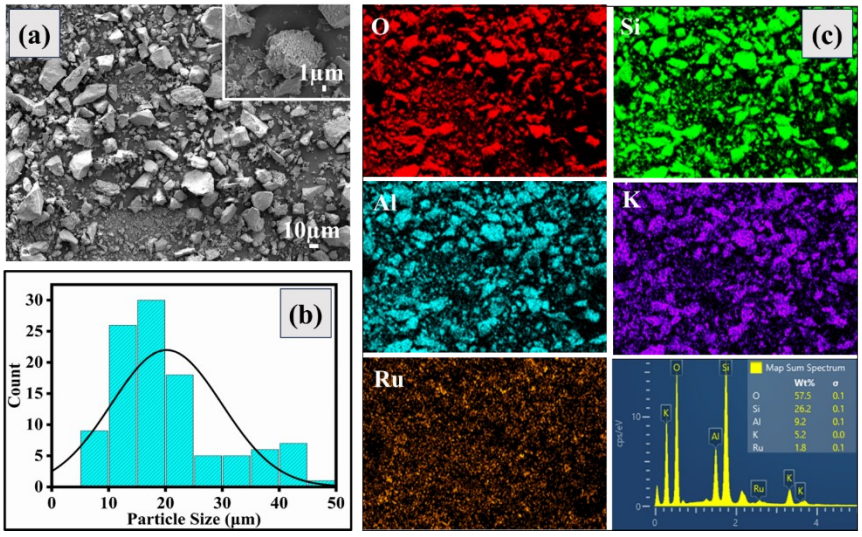


Figure SI 6. a) FESEM image b) Histogram distribution of the particle size c) Elemental distribution and EDX of 5%Ru/GNK

SI.4: XPS Survey Scan

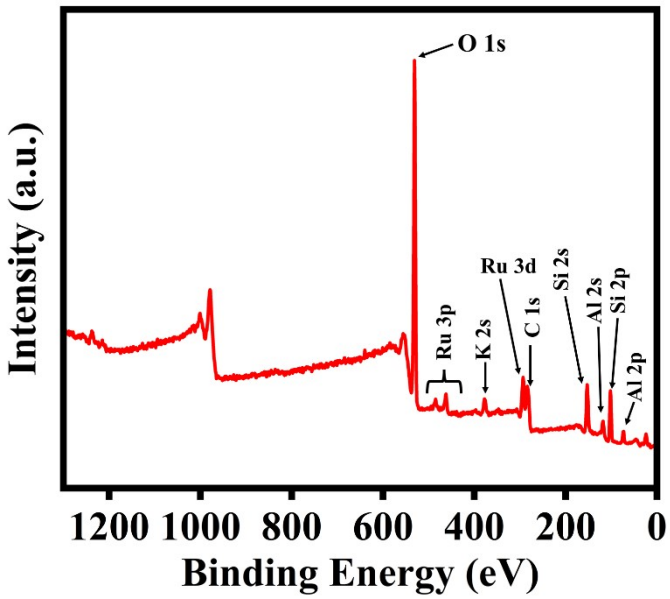


Figure SI 7. X-ray photoelectron spectroscopy (XPS) survey scan of 3% Ru/GNK

SI.5 Hydrogen-Temperature Programmed Reduction (H_2-TPR)

To check out the reducibility of the catalyst H_2-TPR studies were carried out as presented in the SI.6. H_2-TPR of GNK shows two peaks at 286 and 691 ºC. In case of 3%Ru/GNK two peaks are observed at 131 and 331 ºC. The peak at 131ºC corresponds to reduction of RuO_2 to Ru and peak at 331 ºC is arising due the merging of 286 and 691 ºC which was in GNK before the deposition of Ru.

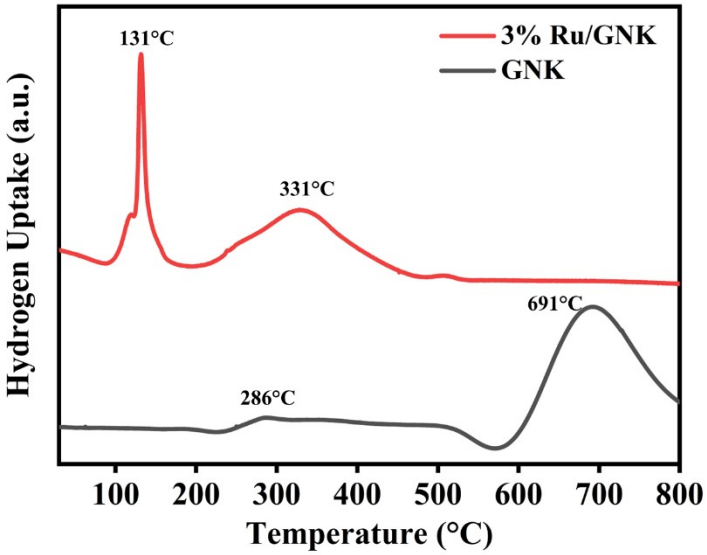


Figure SI 8. H_2-Temperature programmed reduction graph of GNK and 3% Ru/GNK

SI.6: Calibration curve for calculation of number of moles of CO_2 in CO_2-TPD experiment

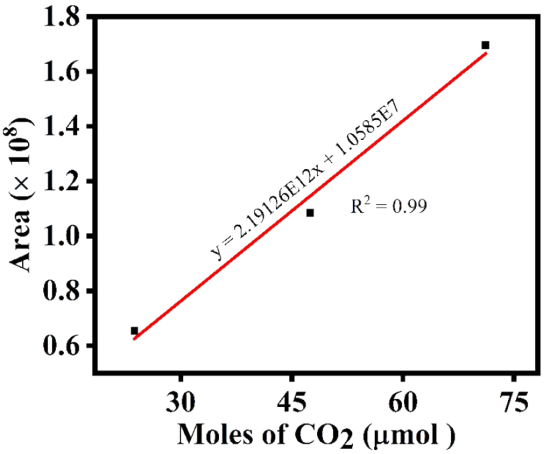
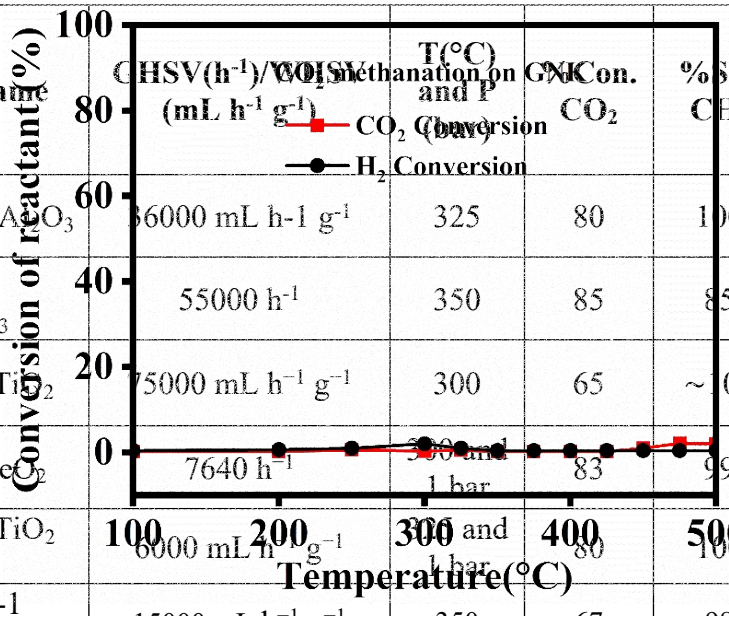


Figure SI 9. Calibration curve for calculation of number of moles of CO_2, graph between area vs moles of CO_2.

SI.7: CO_2 methanation on geopolymer from natural kaolin (GNK) support only



Catalyst Name	GHSV(h^{-1})/WHSV ($mL\ h^{-1}\ g^{-1}$)	T(°C) and P (bar)	% Con. CO_2	% Sel. CH_4	% Yield CH_4	Ref.
Ru/7% CrOx/Al_2O_3	36000 mL h-1 g^{-1}	325	80	100	-	1
3wt% Ru/Al_2O_3	55000 h^{-1}	350	85	85	-	2
5 wt%Ru/r-TiO_2	75000 mL h^{-1} g^{-1}	300	65	~100	-	3
5 wt%Ru/CeO_2	7640 h^{-1}	300 and 1 bar	83	99	-	4
2.5 wt%Ru/TiO_2 (001)	6000 mL h^{-1} g^{-1}	325 and 1 bar	80	100	-	5
10wt%Ni-1						6

Figure SI 10. Catalytic activity test for CO_2 methanation reaction on support GNK only showing CO_2 conversion and H_2 consumption with temperature. Reaction Conditions: Amount of catalyst = 50mg, P = 1 atm, T = RT to 500 °C, GHSV = 20,000 h^{-1} and (H_2/CO_2) ratio = 4.

Table SI. 1 Comparison table of activity of the catalyst with literature

CeO_2-ZrO_2 (CeZ) nanocomposites	48000 h^{-1}	325	42	98	-	[7]
30Ni−20Ce/MTK_M	14,000mL h^{-1} g^{-1}	350	61.2	98	-	[8]
Ni-P-SGS	12000 mL $g^{-1}h^{-1}$	400	80.2	99.2	-	[9]
15%Ni/Fly ash zeolite type X	12,000 h^{-1}	450	53	-	-	[10]
3%Ru/GNK	20,000 h^{-1}	350	51.6	97.7	41.8	**This Work**

Table SI. 2 Comparison table of activation energy for CO_2 methanation

Catalyst Name	Activation energy, E_a (KJ/mol)	Temperature Range (°C)	References
Ru/TiO_2	69-76	150-200°C	[11]
Ru/Al_2O_3	22.4 ±2.8	50-200°C	[12]
Ru/Al_2O_3	84	275 - 335°C	[13]
30Ni–20Ce/MTK_M	55.1	250-400°C	[8]
Ni/CeO_2	94.9–106.0	T = 473-511 K	[14]
$0.5\%Ru/SiO_2$	72	T = 502 and 563 K	[15]
$0.5\%\ Ru/Al_2O_3$	71	T = 502 and 563 K	[15]
3%Ru/GNK	63.6	175-275°C	**This Work**

Equations for calculations CO_2 conversion, H_2 consumption, CH_4/CO selectivity and CH_4/CO yield -

$$\text{Conversion of } CO_2(\%) = \frac{nCO_{2in} - nCO_{2out}}{nCO_{2in}} \times 100 \qquad \text{(Eq.1)}$$

$$\text{Selectivity of } CH_4 \text{ or CO}(\%) = \frac{nCH_4 \ or \ nCO}{nCH_4 + nCO} \times 100 \qquad \text{(Eq.2)}$$

$$\text{Yield of } CH_4 \text{ or CO}(\%) = \frac{nCH_4 \ or \ nCO}{nCO_{2in}} \times 100 \qquad \text{(Eq.3)}$$

$$\text{Carbon Balance } (C_B) = \left[1 - \frac{nCO + nCH_4 + nCO_{2out}}{nCO_{2in}}\right] \times 100 \qquad \text{(Eq.4)}$$

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