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## OBJECTIVE

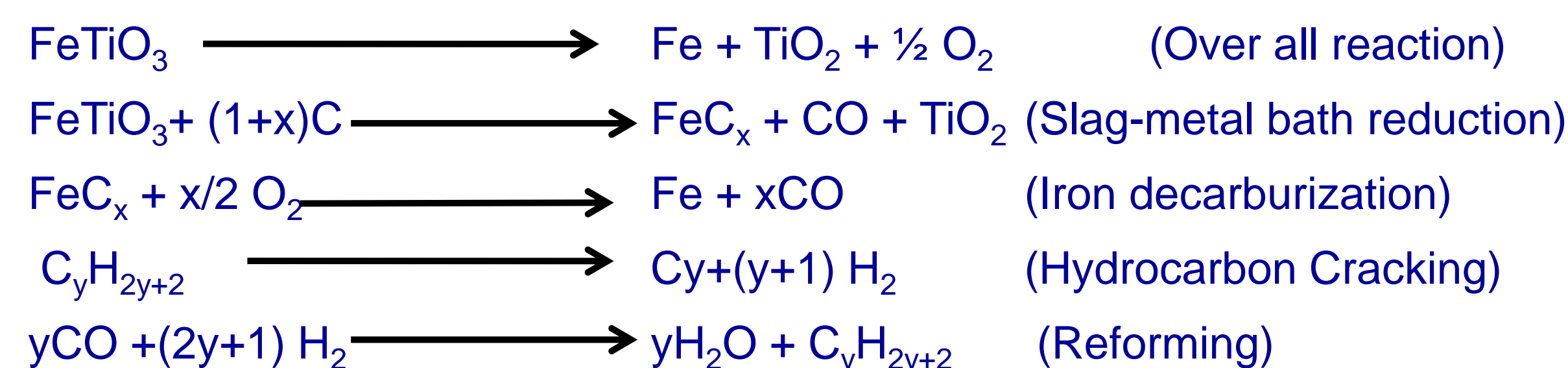
Methanation catalyst development for In-Situ Resource Utilization (ISRU) for NASA's Space Exploration.

## INTRODUCTION



Figure 1 (a) Lunar Regolith, (b) Famous picture by Apollo 11

- O<sub>2</sub> is needed for human exploration and as a propellant.
- The carbothermal reduction process applied to lunar regolith yields O<sub>2</sub>.
- Lunar regolith mainly contains ilmenite (FeTiO<sub>3</sub>).
- Carbothermal reduction of ilmenite.



Catalytic conversion to CH<sub>4</sub> conserves the carbon reagent.

- It is well established that CO dissociation occurs readily with Ni, Co and Ru.
- Graphene Oxide (G.O.) can provide high surface area with tolerance to reducing conditions and resistant to water interference will net better efficiency. Their electronic structure may further aid catalytic activity.

## MATERIALS AND METHOD

MATERIAL'S USED	ABBREVIATION	MATERIAL'S USED	ABBREVIATION
Single Layer Graphene Oxide	SLGO	Phosphorous Pentoxide	P <sub>2</sub> O <sub>5</sub>
Ruthenium trichloride (RuCl <sub>3</sub> ·6H <sub>2</sub> O)	-	potassium peroxydisulfate	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
Ethylene glycol	EG	Potassium Permanganate	KMnO <sub>4</sub>
Nickel Chloride(NiCl <sub>2</sub> ·6H <sub>2</sub> O)	-	Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>
aluminum oxide nanopowder (<50 nm)	Al <sub>2</sub> O <sub>3</sub>	Short multi-walled carbon nanotubes	CNT
Sulphuric Acid	H <sub>2</sub> SO <sub>4</sub>	Hydrochloric Acid	HCl

## MODIFIED HUMMER'S PROCESS TO PREPARE GRAPHENE OXIDE

- 1g Natural Graphite, 0.5g of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and 0.5 g of P<sub>2</sub>O<sub>5</sub> were added to 1.5 ml of Conc. H<sub>2</sub>SO<sub>4</sub>, thermally isolated and cooled to room temperature.
- Following steps include dilution with 175 ml and washing with D.I water till the pH of the filtrate is neutral and drying over night.
- This oxidized graphite powder of 1g was put in 23 ml cold (0°C) conc. H<sub>2</sub>SO<sub>4</sub>.
- 3g of KMnO<sub>4</sub> was added gradually maintaining the temperature below 20°C.
- This mixture was stirred at 35°C for 2 hours and distilled water 46 ml was added.
- The reaction was terminated by adding 140 ml of D.I water and 2.5 ml of 30% H<sub>2</sub>O<sub>2</sub> solution.
- Material was filtered and subjected to series of washing steps with 1:10 HCL soln. ( 250 ml), ethanol and D.I water to remove metal ions.
- Dried under vacuum to transform into a dry G.O. powder.

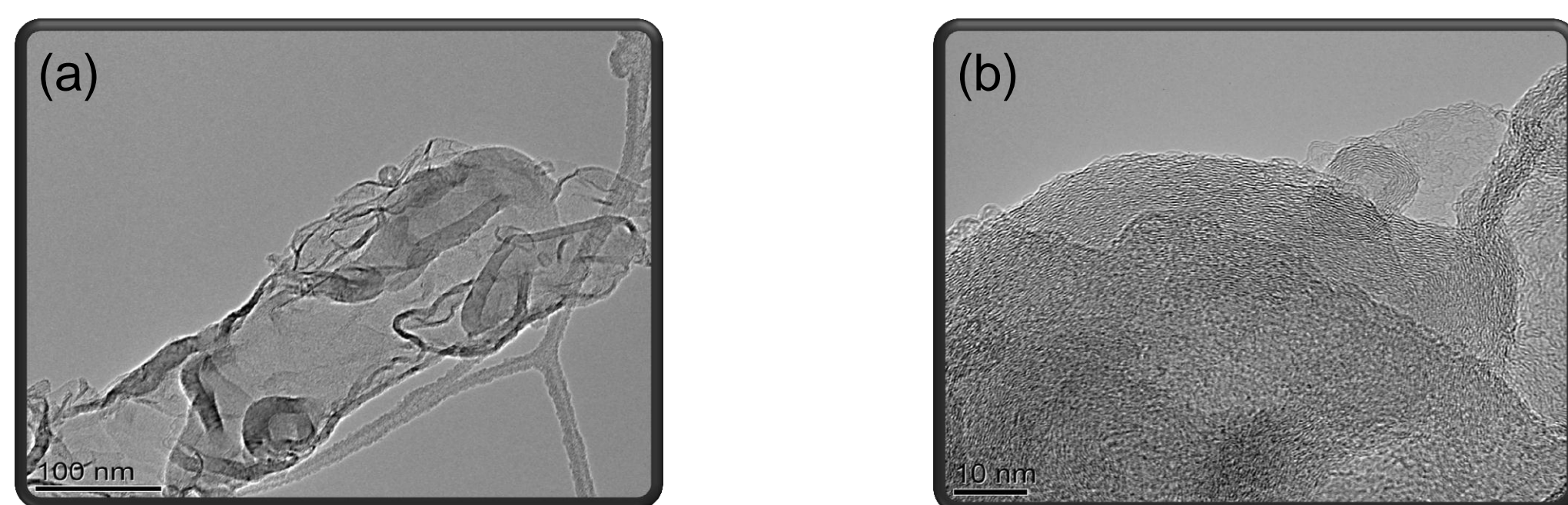


Figure 2. (a), (b) showing the TEM images of G.O. synthesized after Modified Hummer's Process

## Catalyst Decoration: Poly-ol Process

Ruthenium on G.O.(or Al<sub>2</sub>O<sub>3</sub>) and mixed catalyst (G.O./Al<sub>2</sub>O<sub>3</sub> & G.O./ CNT's ) was made by a Poly-ol Process (cation activation process).

### Procedure

- 0.1g of catalyst was dispersed in 32 ml of 0.04M Nickel Chloride-E.G solution and heated to 150°C for 4 hours, vacuum filtered and dried.
- Solid was re-dispersed in 32ml of E.G. 0.3g of Ruthenium Chloride was added.
- pH of the solution was maintained at 8 using 1M NaOH solution.
- Solution was heated to 160°C for 4 hours, vacuum filtered and dried.
- Dried catalyst was dispersed in 10 ml ethanol and impregnated to aluminum foams.

## RESULTS AND DISCUSSIONS

### CHARACTERIZATION

Dispersion of the ruthenium nanoparticles is verified by FE-SEM and TEM and presence of ruthenium by XPS.

### Field Emission-Scanning Electron Microscopy (FE-SEM) IMAGES

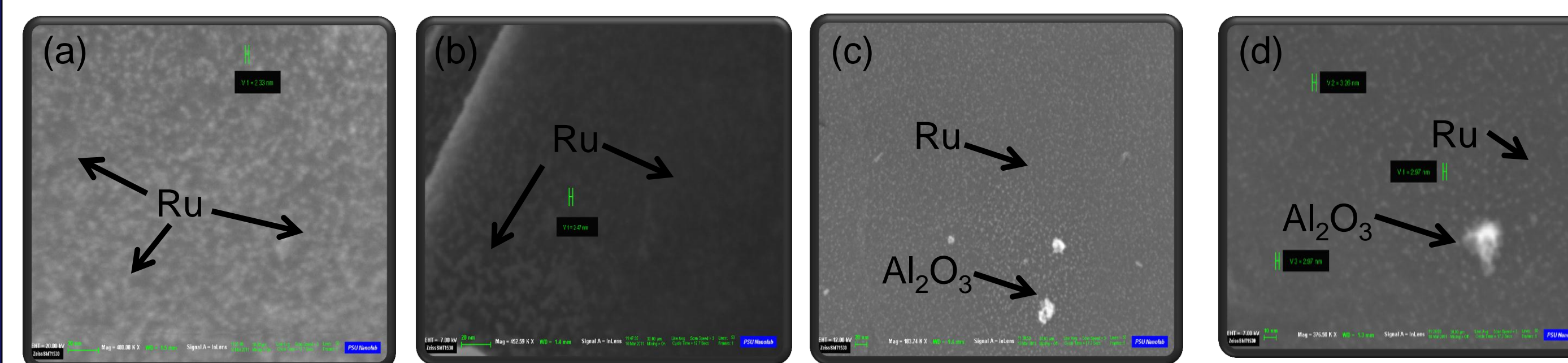


Figure 3. FE-SEM images of Ru nanoparticles supported on (a)&(b) G.O.,(c)&(d) G.O.-Al<sub>2</sub>O<sub>3</sub>

### Transmission Electron Microscopy (TEM) IMAGES

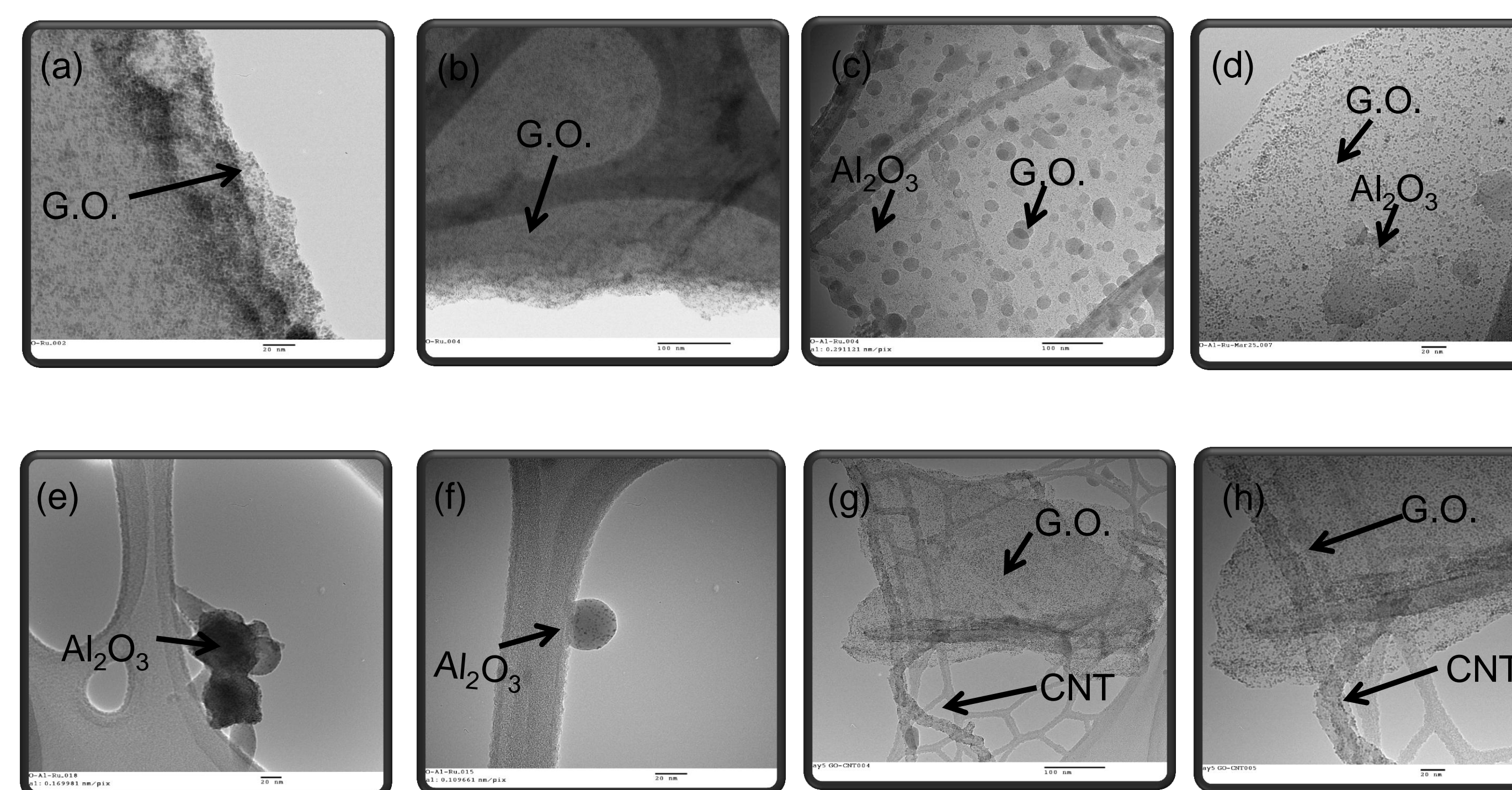


Figure 4. TEM images of Ruthenium nano particles supported on (a)&(b) G.O.; (c)&(d) G.O.-Al<sub>2</sub>O<sub>3</sub>; (e)&(f) Al<sub>2</sub>O<sub>3</sub> and (g)&(h) G.O.-CNT

### X-ray Photoelectron Spectroscopy (XPS)

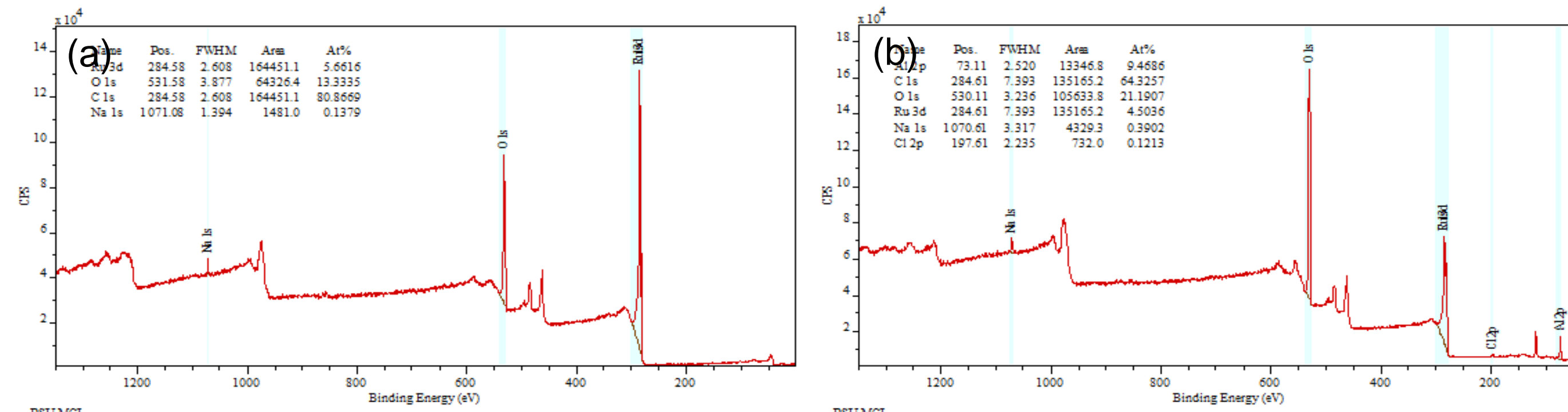


Figure 5. XPS data for (a) Ru/G.O. and (b) Ru-(G.O./Al<sub>2</sub>O<sub>3</sub>)

## Microchannel Reactor

A Microchannel reactor with hierarchical structure was fabricated as follows.

- The metal decorated G.O. (or G.O./Al<sub>2</sub>O<sub>3</sub>) catalysts (Figure 1a) were deposited over a reticulated structure of duodecahedral-shaped cells within a continuous aluminum alloy (Duocel aluminum foam supplied by ERG).
- ERG aluminum foam is a rigid, highly porous and permeable material with mean pore size of 0.5 mm and void fraction of 67-76%.
- Designed specifically for methanation reaction.
- Can provide excellent support for the nano catalysts, mixing of the gases while maintaining low pressure drop.
- Can achieve gas hourly space velocity of 4100 and 16400 h<sup>-1</sup> with high conversion rates.

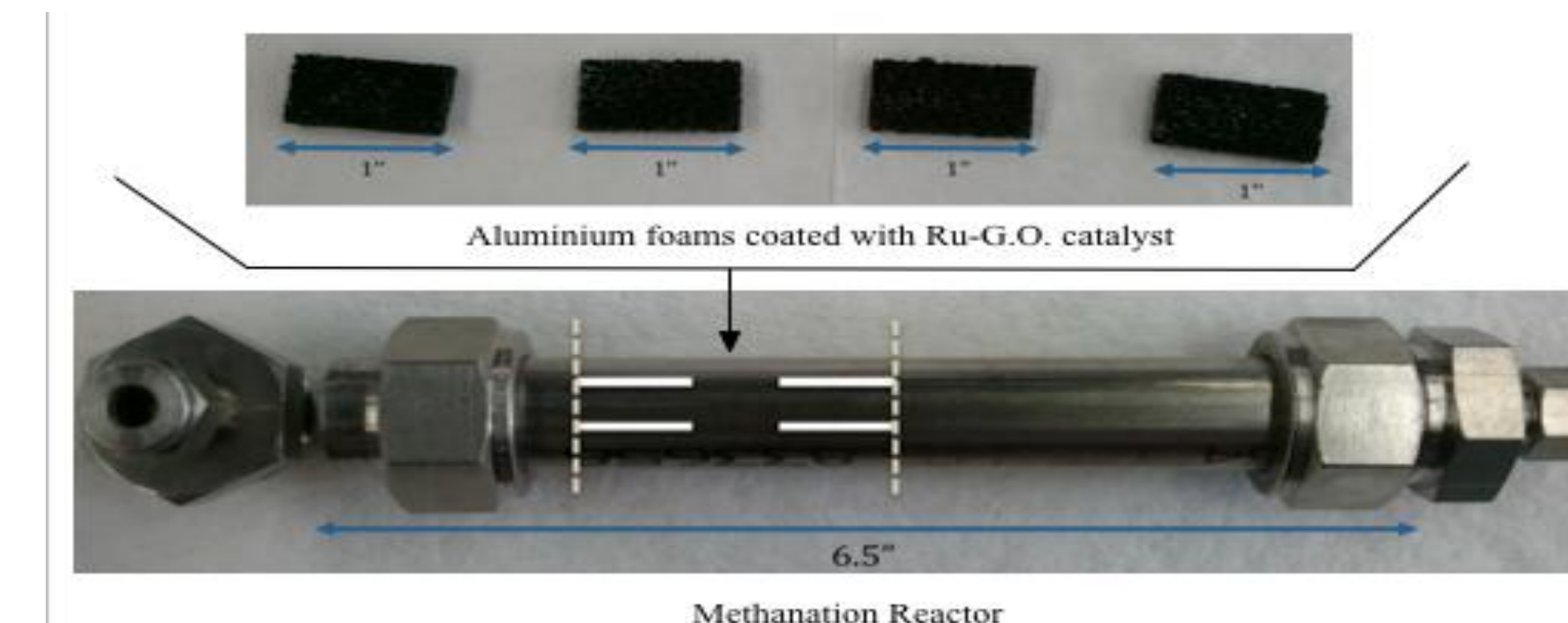


Figure 6. Illustration of the micro-channel methanation reactor

## SUMMARY

- Graphene Oxide (G.O.) was synthesized by modified hummer's process.
- Ruthenium decoration on the catalysts was done by a Poly-ol process.
- G.O. was successful in using as a support for uniform distribution and metal density of ruthenium verified by the FE-SEM, TEM and XPS results.
- FE-SEM and TEM micrographs showed uniform decoration of Ruthenium on G.O., Al<sub>2</sub>O<sub>3</sub>,G.O./Al<sub>2</sub>O<sub>3</sub> and G.O./ CNT's. The average particle size of Ruthenium was 2.7 nm.
- XPS results also confirms the presence of Ruthenium.
- Micro channel methanation reactor was developed specifically for these nano catalyst systems.
- These nanostructured, hierarchical catalytic systems can facilitate thermal equilibration, offer high surface area, and maximize catalyst exposure with reduced pressure drop.

## LITERATURE CITED

- 1) Robert J. Gustafson; Eric E.Rice and Brant C. White; *AIP Conf. Proc.* **2005**, 746, 1224-1228
- 2) Araki, M.; Ponec, V., *J. Catal.* **1976**, 44, 439-448.
- 3) Sachtler; J. W. A.; Kool, J. M.; Ponec, V., *J. Catal.* **1979**, 56, 284-286.
- 4) W. S.Hummers; R. E. Offeman, *J. Am. Chem. Soc.* **1958**, 80, 1339.
- 5) Lu, J., *Carbon* **2007**, 45, 1599-1605.
- 6) Ebbesen, T. W.; Hiura, H.; Bisher, M. E.; Treacy, M. M. J.; ShreeveKeyer, J. L.; Haushalter, R. C. *Adv. Mater.* **1996**, 8, 155-157.
- 7) Satishkumar, B. C.; Vogl, E. M.; Govindaraj, A.; Rao, C. N. R. *J. Phys. D* **1996**, 29, 3173-3176.
- 8) Wang, Y.; Johnson, B. R.; Cao, C.; Chin, Y.-H.; Rozmiarek, R. T.; Gao, Y.; Tonkovich, A. L. Y. Wang, Y.; Hollady, J. D.; (Eds), *Micro reactor Technology and Process Intensification, ACS symposium series* **2005**, 914, 102-118.
- 9) Sirijaruphan, A.; Goodwin, J. G.; Rice, R. W.; Wei, D.; Butcher, K. R. *Appl. Catal. A: Gen.* **2005**, 281, 1-9.
- 10) Chin, Y.C.; J. Hu, Cao, C.; Gao, Y.; Wang, Y. *Catal. Today* **2005**, 110, 47-52.
- 11) [http://en.wikipedia.org/wiki/Lunar\\_soil](http://en.wikipedia.org/wiki/Lunar_soil)

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## For Further Information

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