



## Red mud as catalyst for hydrocarbon cracking and resultant carbon deposits for water treatment

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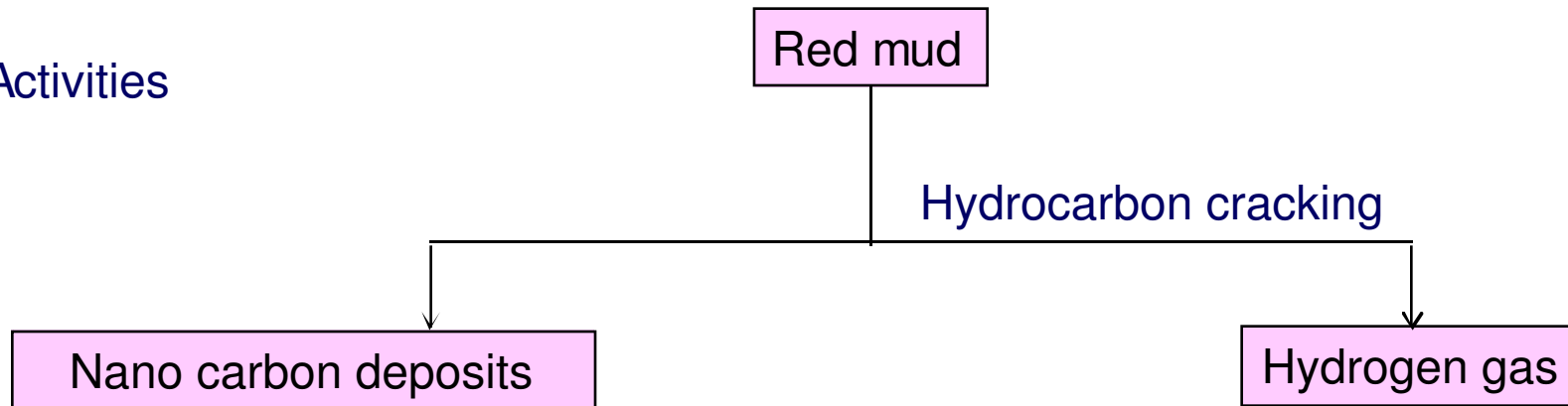
International Seminar on Bauxite Residue, 17 – 19 October 2011, Goa

# Background

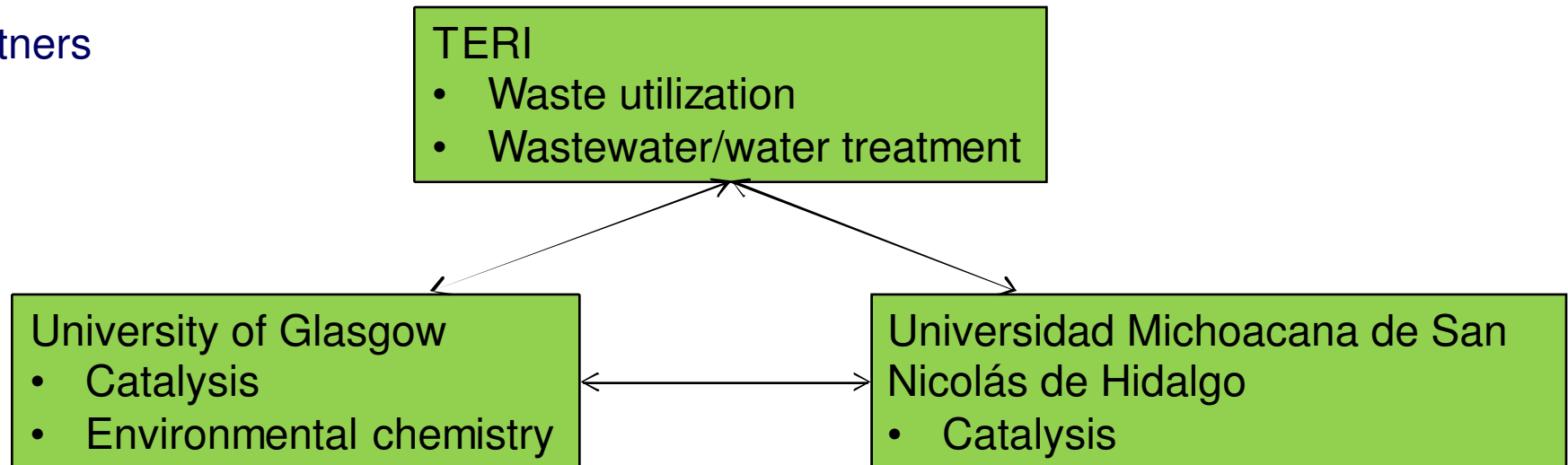
- Many previous studies on application of red mud as catalyst
  - Hydrogenation catalyst
  - Hydrodechlorination catalyst
  - Exhaust gas cleaning
  - Other reaction catalyst
- Motivated by iron content in red mud
- Can be modified by activation, calcination, reduction etc.

# UKIERI red mud project

Activities



Partners

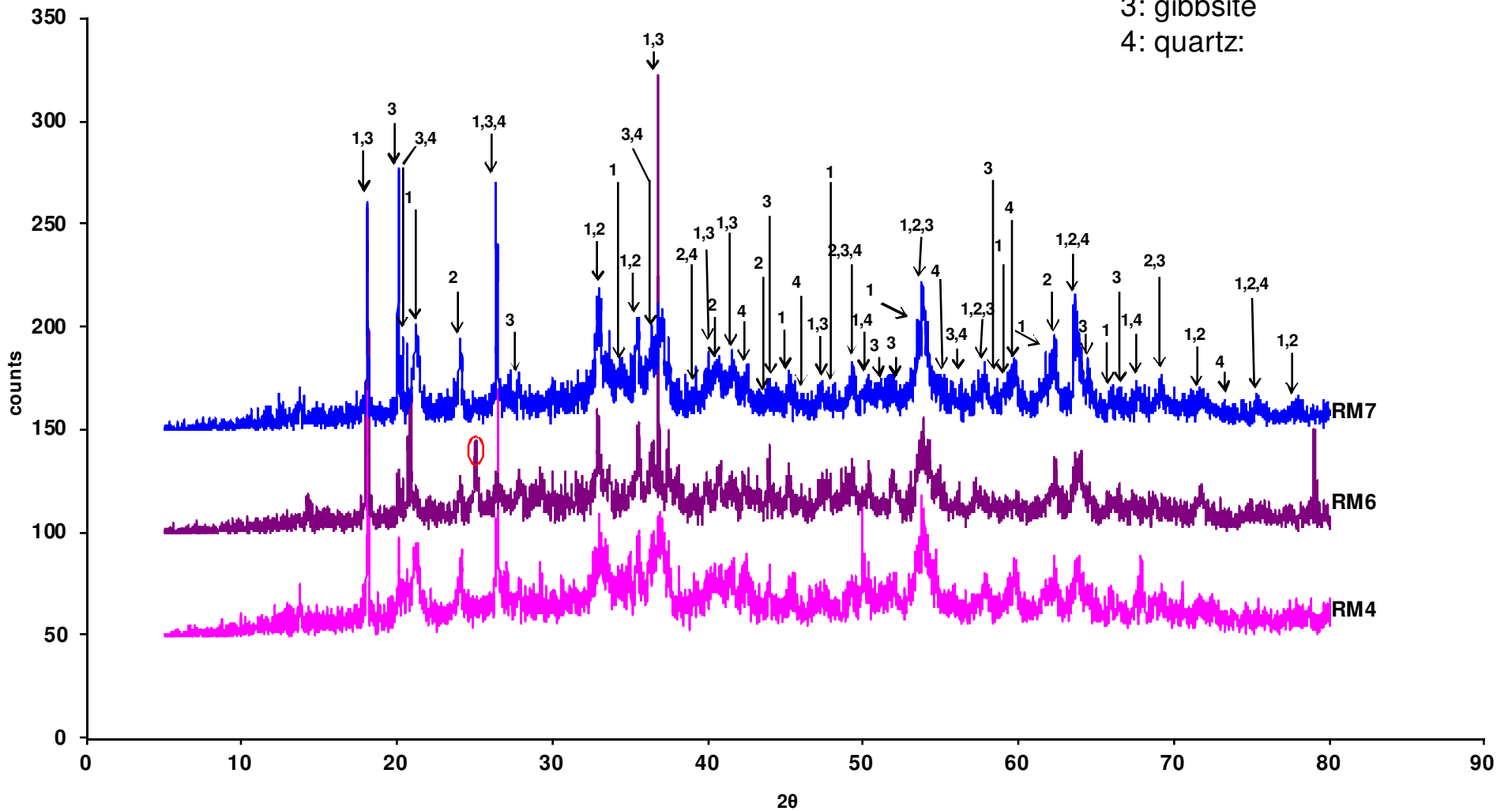


# Red mud properties

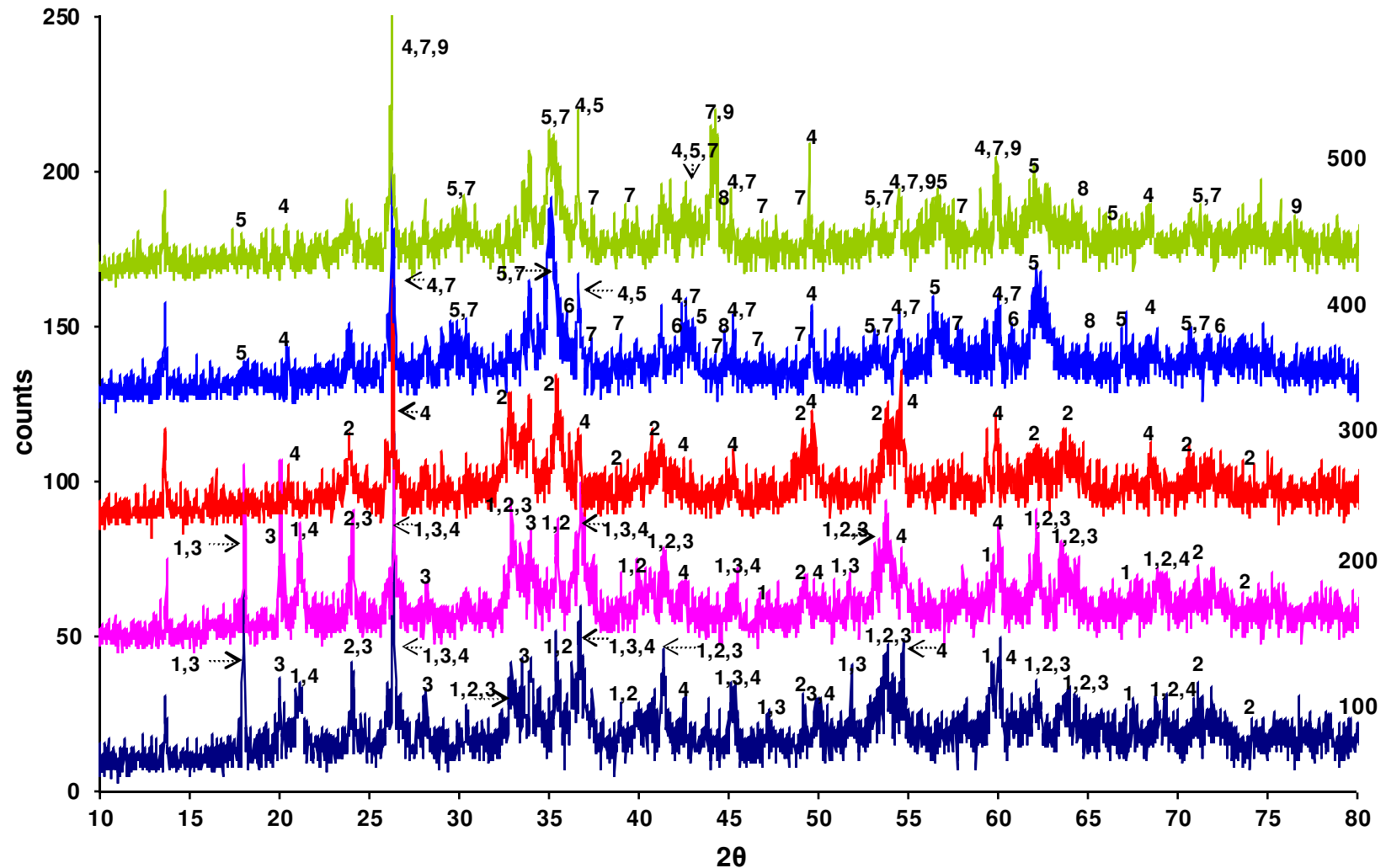
- $\text{Fe}_2\text{O}_3$  main component of all red mud (36-49%)
- Other metal oxides present
  - $\text{Al}_2\text{O}_3$ (9-15%)
  - $\text{TiO}_2$ (0.5-19%)
  - $\text{SiO}_2$  (9-17%)
- Main phase in all samples was hematite
- Goethite, gibbsite and quartz were also present

# XRD of raw red mud

- 1: goethite
- 2: hematite
- 3: gibbsite
- 4: quartz:



# *In-situ* XRD of red mud in methane

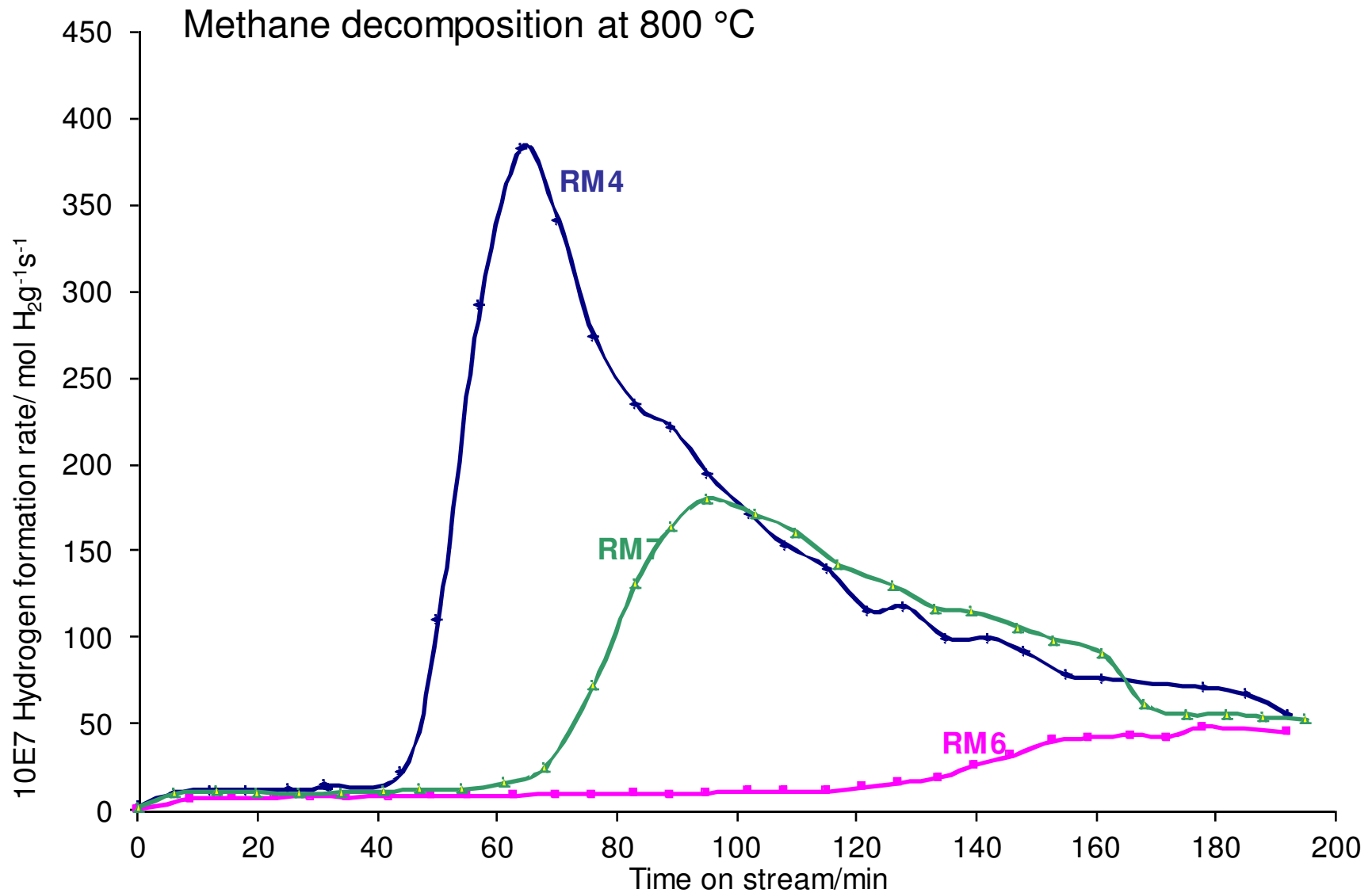


1: goethite; 2: hematite; 3: gibbsite; 4: quartz; 5: magnetite; 6: wustite; 7: iron carbide; 8: iron; 9: graphite

# Catalytic testing of red mud

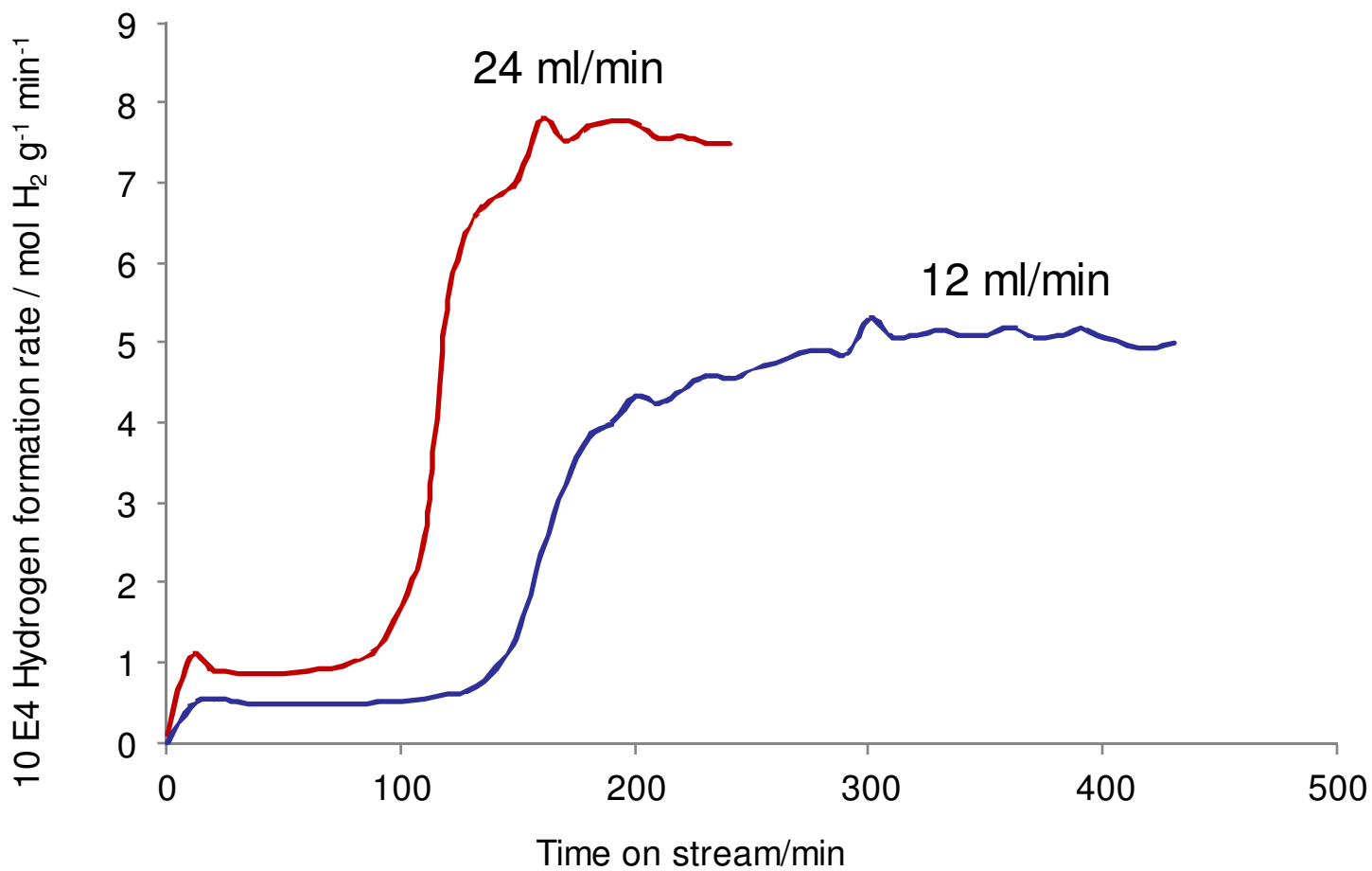
- Testing in fixed bed reactor using different hydrocarbons
- Conditions studied
  - Catalyst weight: 0.4 – 0.5 g
  - Temperature: 700-900 °C
  - Hydrocarbons: Methane, butane, toluene & acetonitrile
  - Inert gas: N<sub>2</sub> and Ar
- RM4, RM6 and RM7 studied

# Catalytic activity

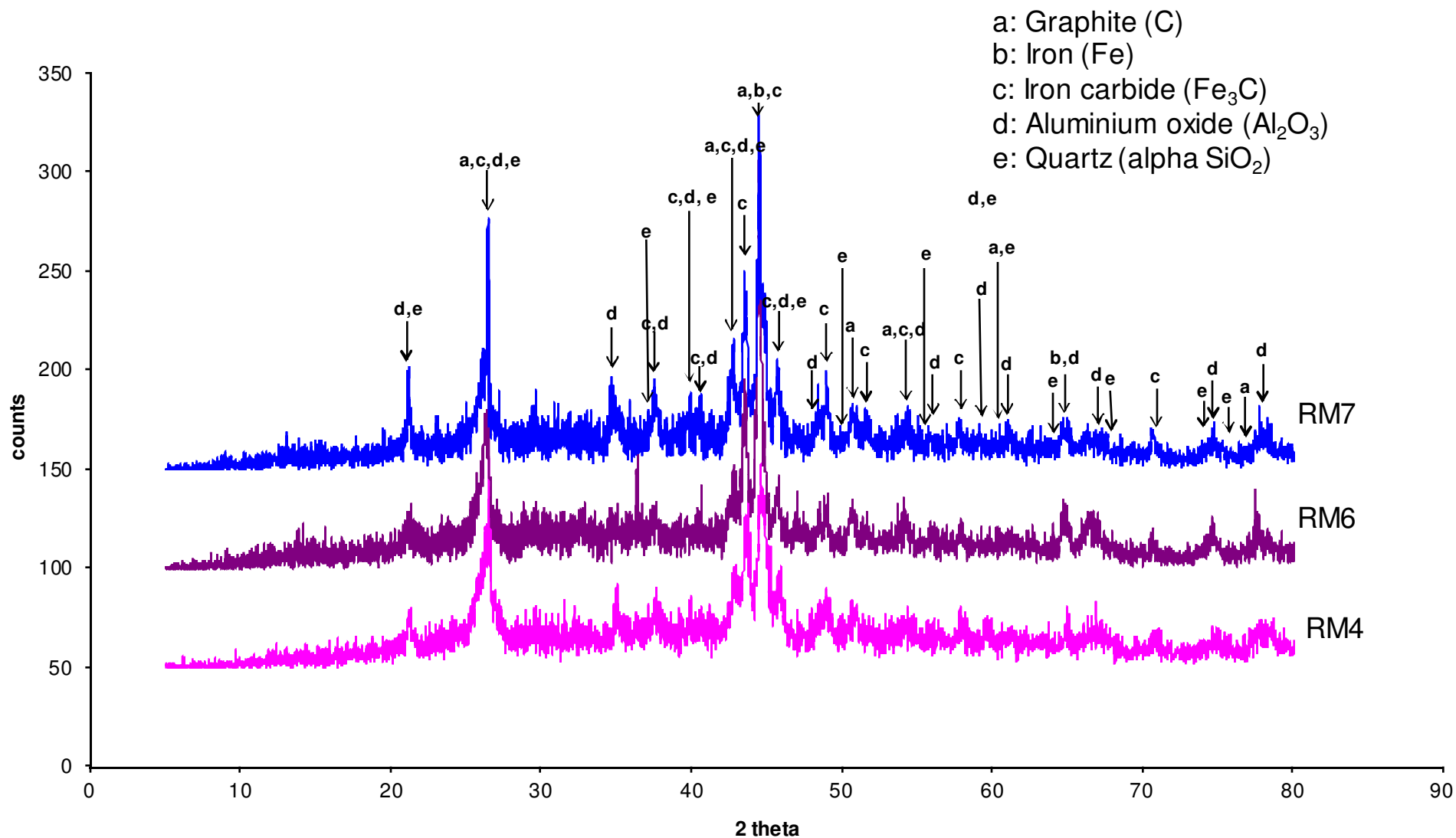


# Catalytic activity (contd.)

Methane decomposition at 800 °C

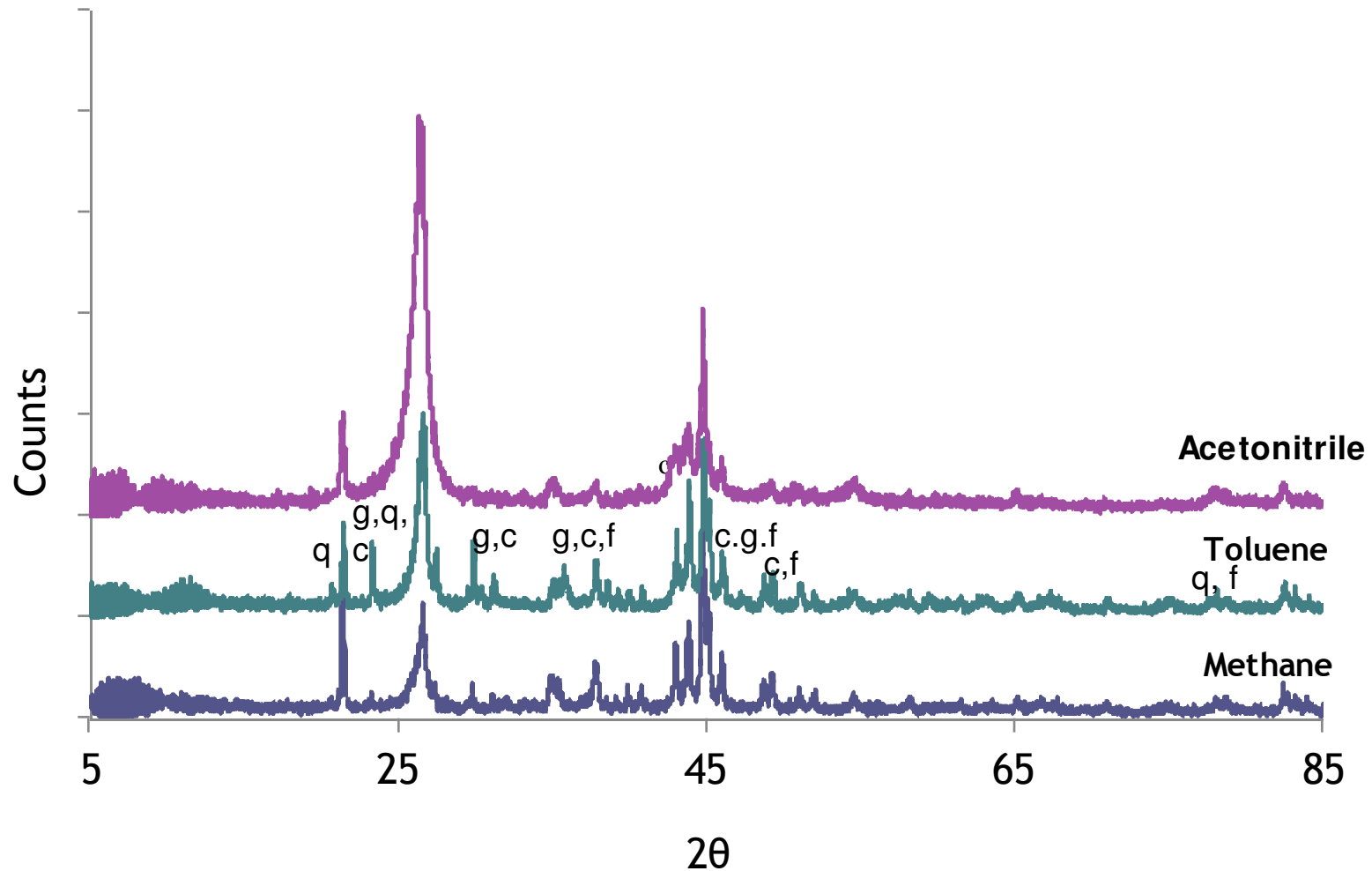


# XRD of post reaction samples



# XRD of post reaction samples

RM7 exposed to different hydrocarbons at 800 °C

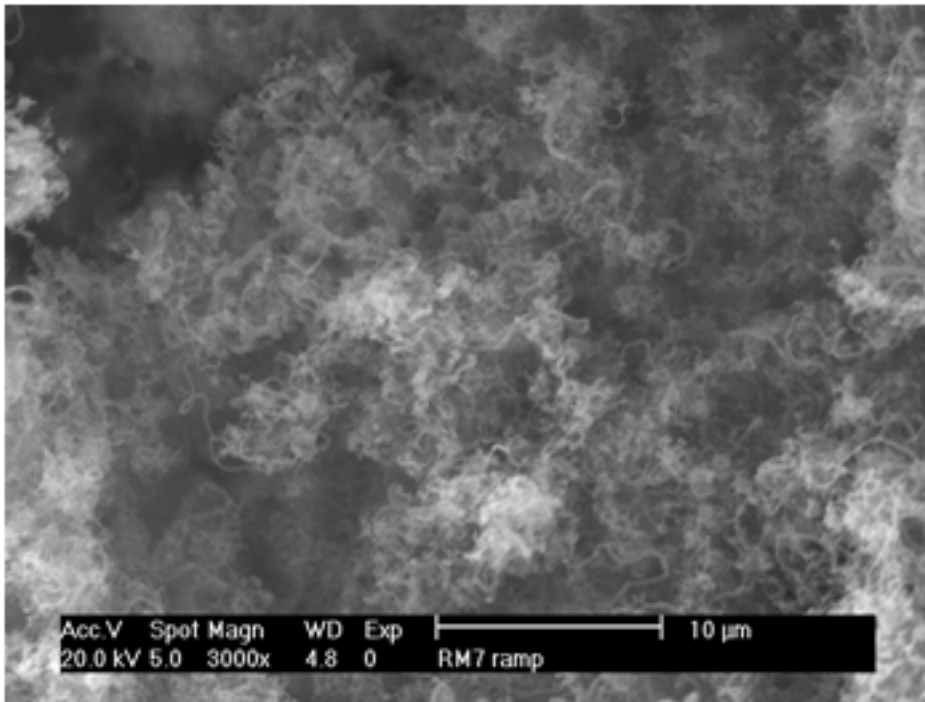


g-graphite, q-quartz  $\text{SiO}_2$ , c-iron carbide  $\text{Fe}_3\text{C}$ , f-iron Fe

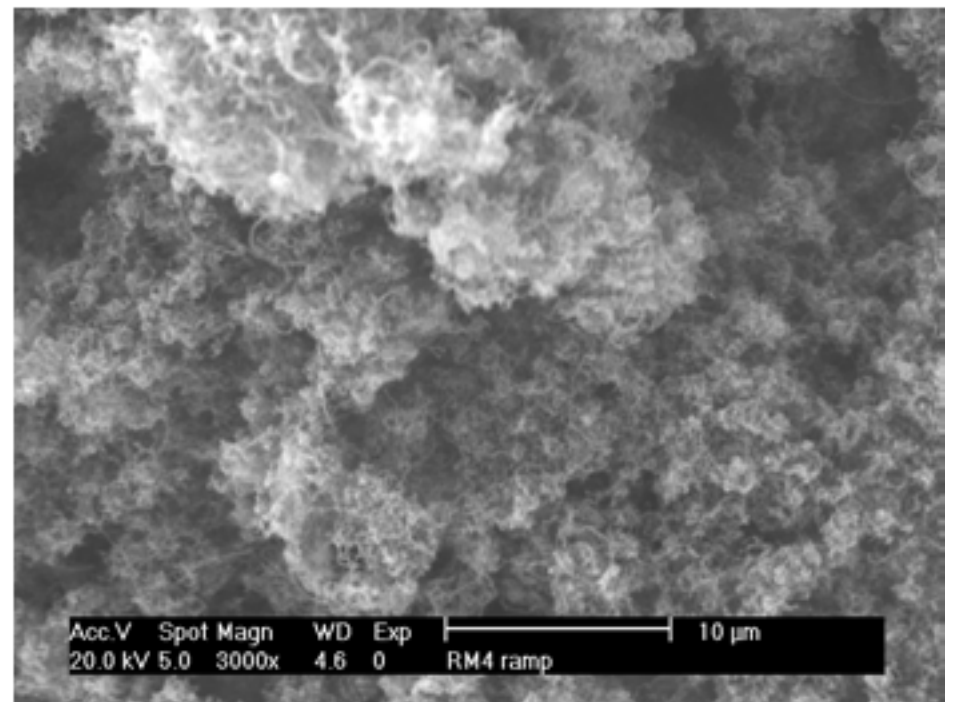
# Magnetic nature of exposed samples



# SEM images of carbon deposits

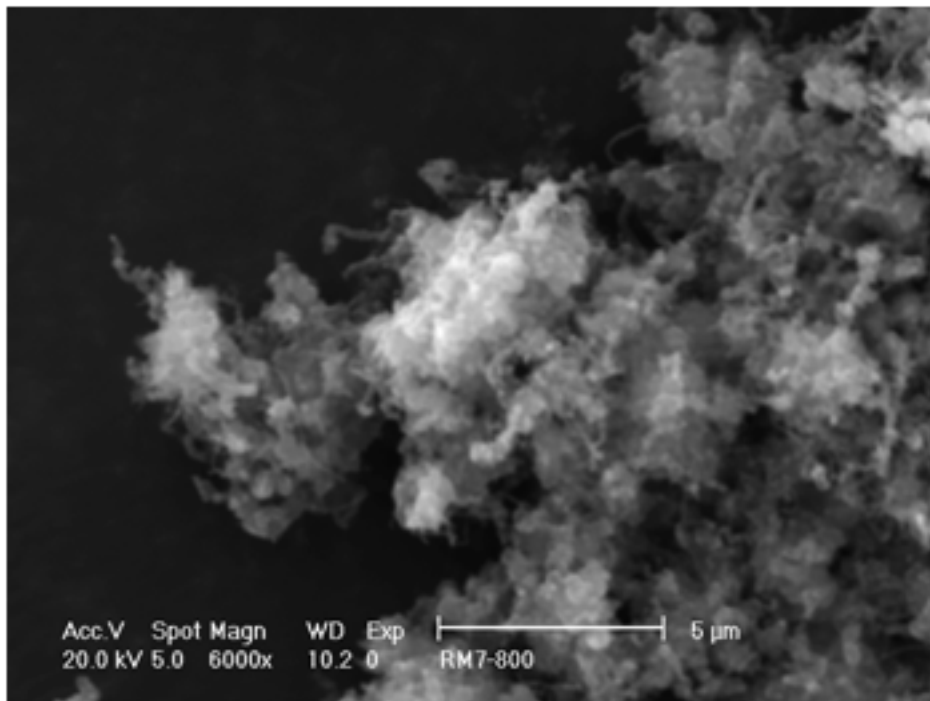


RM7 – insitu XRD in methane

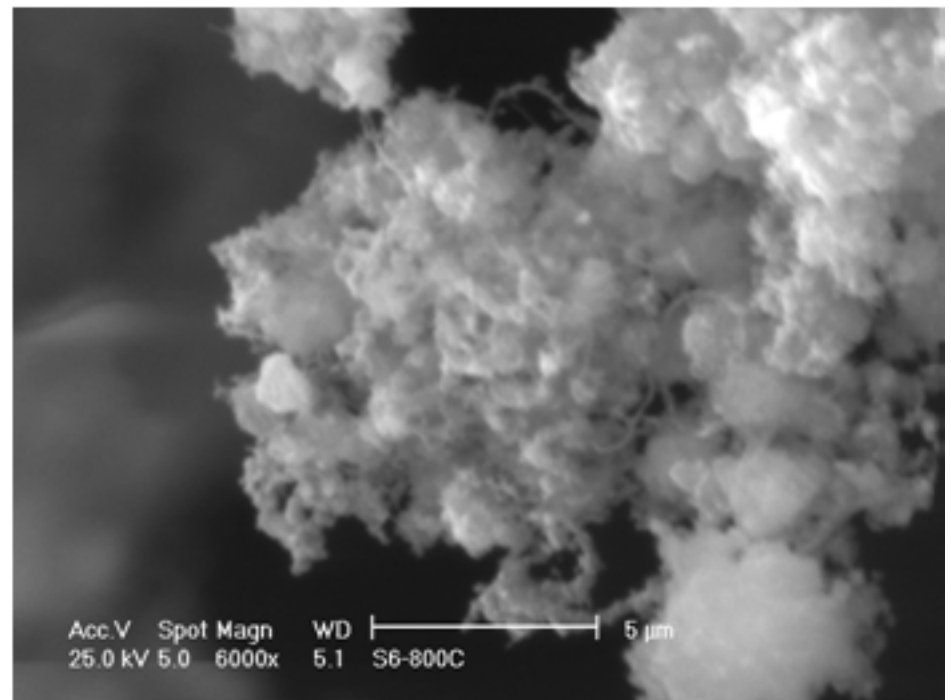


RM4 – insitu XRD in methane

# SEM images of carbon deposits (contd.)

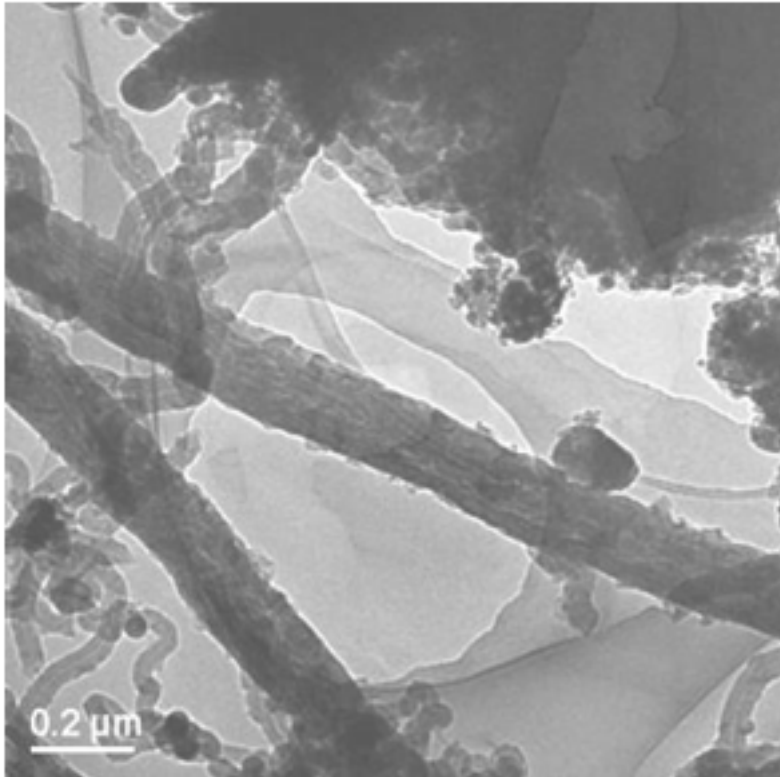


RM7 – reactor run with methane

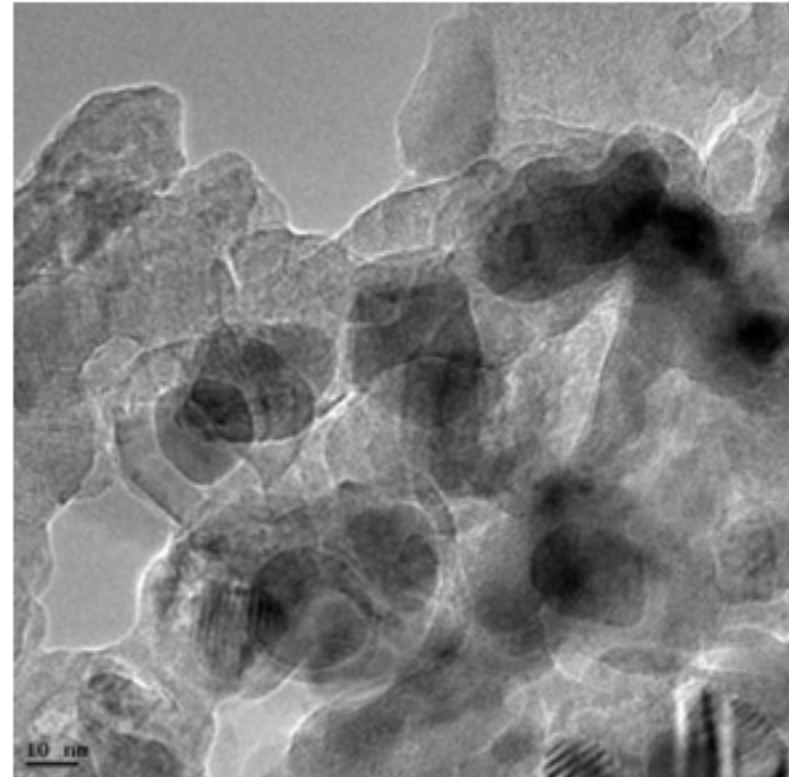


RM7 – reactor run with toluene

# TEM images of carbon deposits

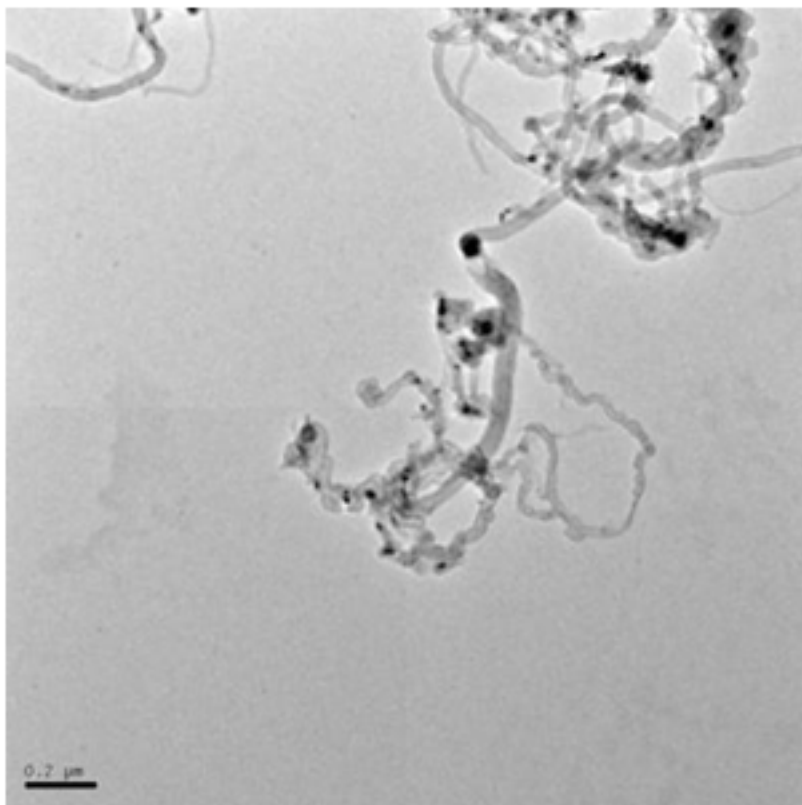


RM7 reactor run with butane

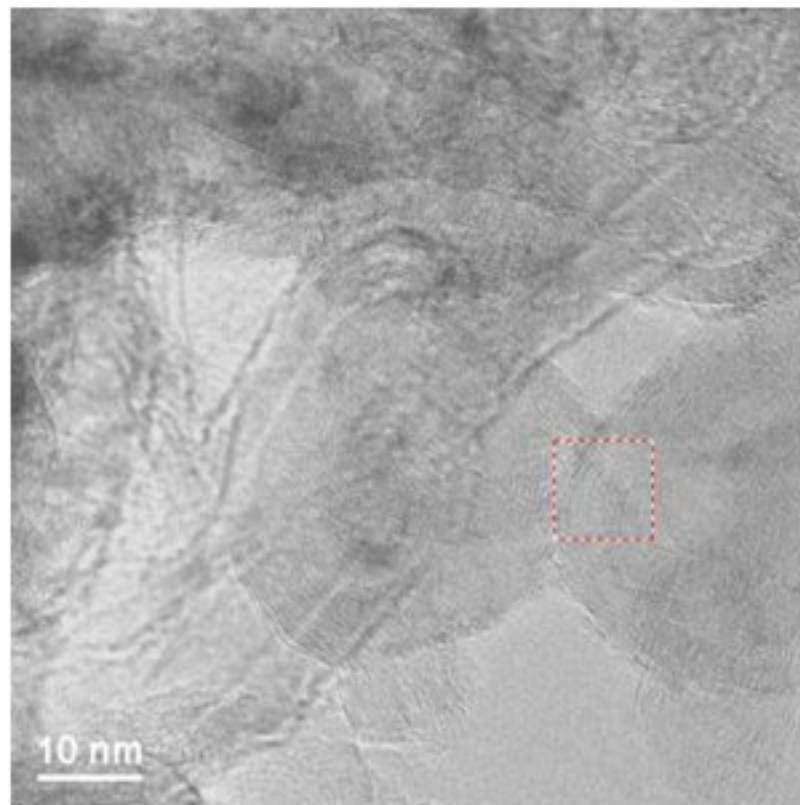


RM7 reactor run with methane

## TEM images of carbon deposits (contd.)



RM4 *in situ* XRD in methane



RM7 *in situ* XRD in methane

# Carbon content of different samples

Different red mud samples after methane decomposition at 800 °C

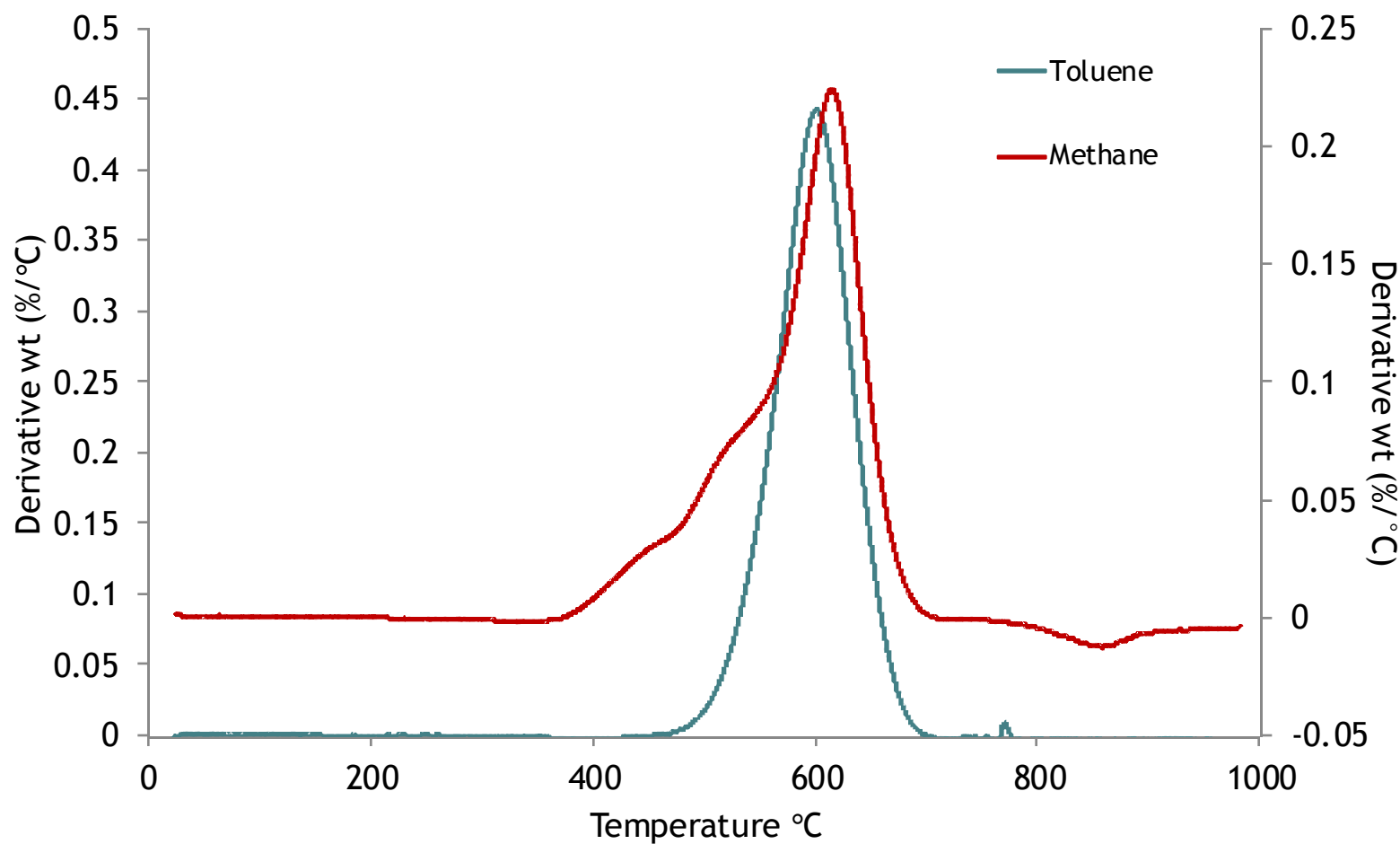
Hydrocarbon	C content (%)	Duration (h)
RM4	47.71	3.5
RM6	43.49	9
RM7	38.06	3.5

RM7 after exposure to different hydrocarbons at 800 °C

Hydrocarbon	C content (%)	Duration (h)
Methane	38.06	3.5
Butane	88.78	8 min
Toluene	26.06	2

# TGA of post reaction samples

RM7 exposed to hydrocarbon at 800 °C

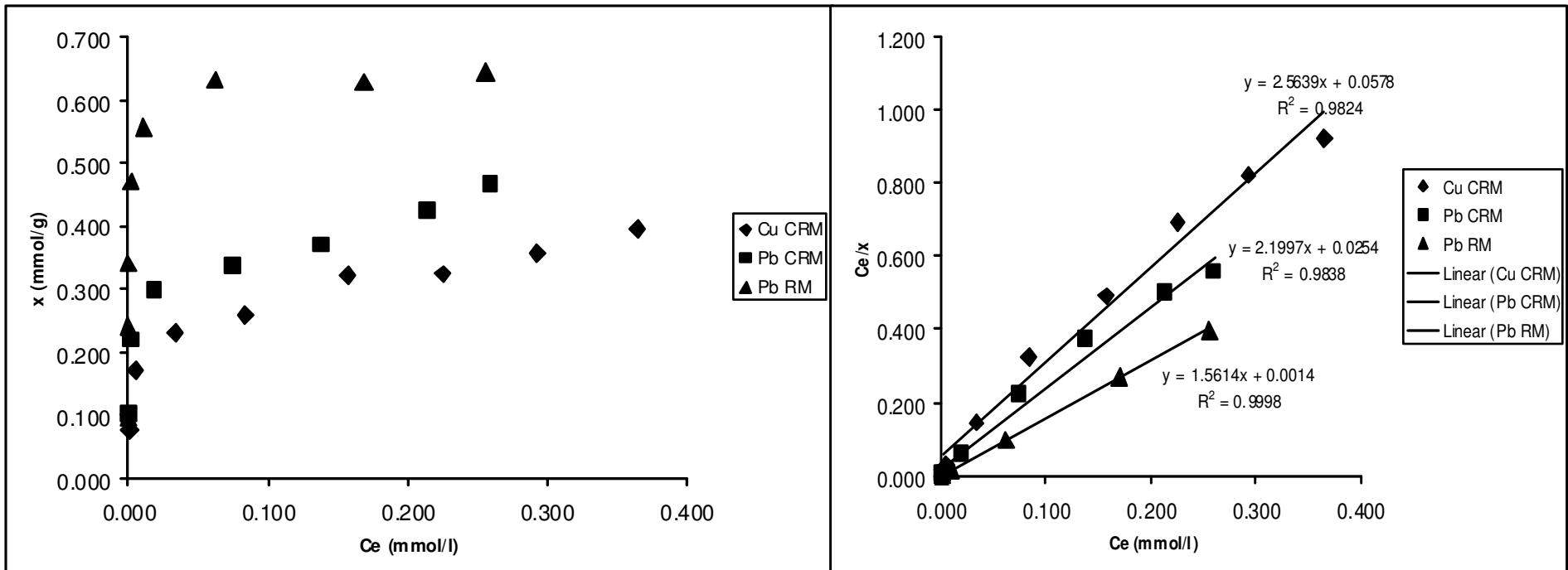


# Application of spent catalyst as adsorbent

- Adsorption of phenol on red mud
  - As-received
  - Calcined                      At 400 °C in air for 2hrs
  - Neutralised                      Repeated washing with water
  - Acid treated                      Mixed with HCl (pH 4), dried at 105°C overnight
- Heavy metals adsorption on red mud
  - As-received
  - Carbonised                      Exposed to CH<sub>4</sub> at 800 °C
- Analysis
  - Heavy metals                      AAS (Perkin Elmer AA 400/100)
  - Phenol                              Spectrophotometer (Aquamate)

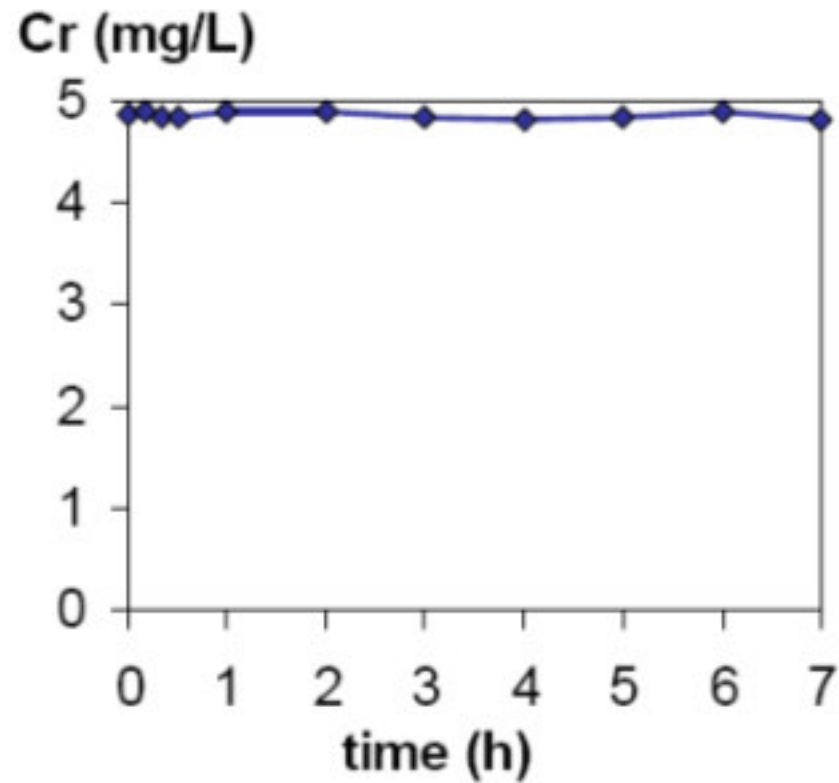
# Adsorption isotherms

Adsorption isotherms of Pb (II) and Cu (II) on CRM and Pb (II) on red mud



# Adsorption isotherms (contd.)

Absence of chromium (VI) uptake by CRM



## Adsorption isotherms (contd.)

- Pb (II) and Cu (II) adsorption on carbonized red mud (CRM)
  - Adsorption capacity for Pb (II): 0.45 mmol/g (94.3 mg/g)
  - Adsorption capacity for Cu (II): 0.39 mmol/g (24.8 mg/g)
- Adsorption of Pb (II) on as received red mud
  - Adsorption capacity: 0.64 mmol/g (133 mg/g)
- CRM found to be ineffective for adsorption of Cr(VI)
- Phenol was not adsorbed on acid treated and as-received red mud

# Summary

- Fe containing components undergo stepwise reduction from haematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) and finally form iron (Fe) and iron carbide ( $\text{Fe}_3\text{C}$ )
- Carbon deposited is in the form of graphite and magnetic in nature
- The amount and type of carbon deposited is dependent on the metal particle and the hydrocarbon used
- Less deposition of carbon on exposure to toluene and methane compared to butane
- Presence of  $\text{TiO}_2$  in red mud reduces the activity

## Summary (contd.)

- Adsorption of phenol under alkaline and neutral conditions was negligible
- RM and CRM have the ability to adsorb Pb (II) and Cu (II)
- Cr (VI) adsorption does not take place on CRM
- Magnetic nature of CRM can facilitate its separation

## Selected publications

- M. Balakrishnan, V.S. Batra, N. Gupta, J.S.J. Hargreaves, B. Krumlova, U. Kurien, G. Pande, I.D. Pulford, J.L. Rico, EUROACAT X Congress, 28 Aug-2 Sept 2011, Glasgow, UK
- M. Balakrishnan, V.S. Batra, J. Hargreaves and I.D. Pulford, Green Chemistry (2011) 13, 16
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