

THE APPLICATION OF RED MUD AS A PRE-CATALYST FOR THE FORMATION OF FUNCTIONALISED CARBONS

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Abstract

Red mud is an effective pre-catalyst for the cracking of hydrocarbons. This process generates hydrogen and a magnetic carbon composite as products. The latter material has been applied to the treatment of model contaminated water where its magnetic properties facilitate its separation.

Introduction

The cracking of hydrocarbons is a potentially useful route for the production of hydrogen. When iron is applied as the catalyst, a magnetic carbon composite is the resultant product in which the nanotubular forms of carbon are often found. Given the fact that bauxite residue contains a relatively large proportion of iron oxides/oxyhydroxides, it can be viewed as an impure precursor for the preparation of iron catalysts for this reaction. Despite the fact that such systems are generally susceptible to alkali metal poisoning, in a pragmatic sense, we have applied red mud materials directly as pre-catalysts in which no pre-reduction stages are undertaken. Accordingly, the materials are simply exposed to the reactant hydrocarbon streams at the high reaction temperatures employed and reduction occurs, yielding catalytically active reduced iron phases despite the presence of the alkali metal component. In this manuscript, we document some of the features of this process and outline the application of a resultant magnetic containing composite for the decontamination of a model contaminated water source, based upon some of our previous publications in the area. Recent collaborative work between our groups has extended the work to investigate the potential of red mud materials for the preparation of more complex functionalised carbon products and these will be documented in a forthcoming publication.

Summary of Previous Results and Discussion

In general in heterogeneous catalysis, great care is taken to reproducibly prepare catalysts possessing optimal performance. In the case of red mud, the composition of which is both spatially and temporally variable, such an approach is an obvious challenge. However, if sufficient activity is obtained for a reaction involving a cheap resource, the resultant variation of performance by direct application of red mud as a catalytic material may be tolerable. Accordingly, we have undertaken such an approach using red mud as a pre-catalyst for the cracking of hydrocarbons, and in particular methane, which are often viewed as undesirable by-products in operations such as refinery operation and landfill dumping.

The point of variation of composition and resultant influence upon performance for catalytic activity has been illustrated in our study applying three red muds of Indian origin. Their composition, expressed in terms of binary oxides as is common practice is shown below.

Table 1: The composition of three red muds of Indian origin, as presented in reference.¹ RM4 and RM7 were collected from the same site, but with a two year interval. RM6 was obtained from a different site.

Sample code	Major elements										
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	MnO	LOI
RM4	16.40	10.44	42.70	6.44	2.85	1.56	3.72	0.05	0.02	-	15.30
RM6	12.40	10.12	36.40	18.70	2.65	2.52	3.85	0.09	0.02	-	12.80
RM 7	14.60	23.51	36.79	0.74	1.18	0.07	6.08	0.02	0.15	0.12	16.47

Such compositional variation is manifested, to an extent, in terms of differences in the powder x-ray diffraction patterns of the waste materials, shown in the figure overleaf.

By its very nature, catalytic performance is intrinsically sensitive to compositional variation as illustrated by the mass normalised hydrogen formation rate – time on stream profiles from the cracking of methane at 800 °C for the three red mud samples shown below. Whilst the profiles all possess the same general form: a lag period during which the material undergoes reduction, followed by a jump in activity, corresponding to the formation of the reduced catalytically active phase (iron metal and/or iron carbide) and then deactivation associated with the deposition of carbon and correspondingly hindered reactant access, both the period of the lag phase and

also the peak hydrogen production rates are significantly influenced by the phase composition of samples. This aspect is particularly salient when it is considered that the iron content of RM6 and RM7 is close, as are the surface areas of RM4 and RM7.

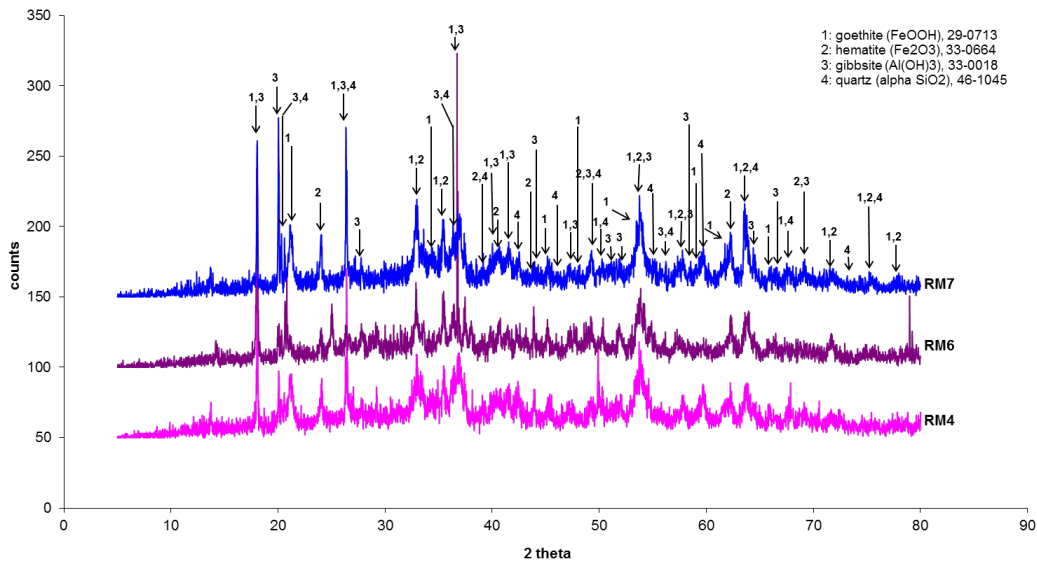


Figure 1: Powder x-ray diffraction patterns (Cu K α radiation) of RM4, RM6 and RM7 red mud samples as presented in reference¹ – figure reproduced with kind permission from the Royal Society of Chemistry

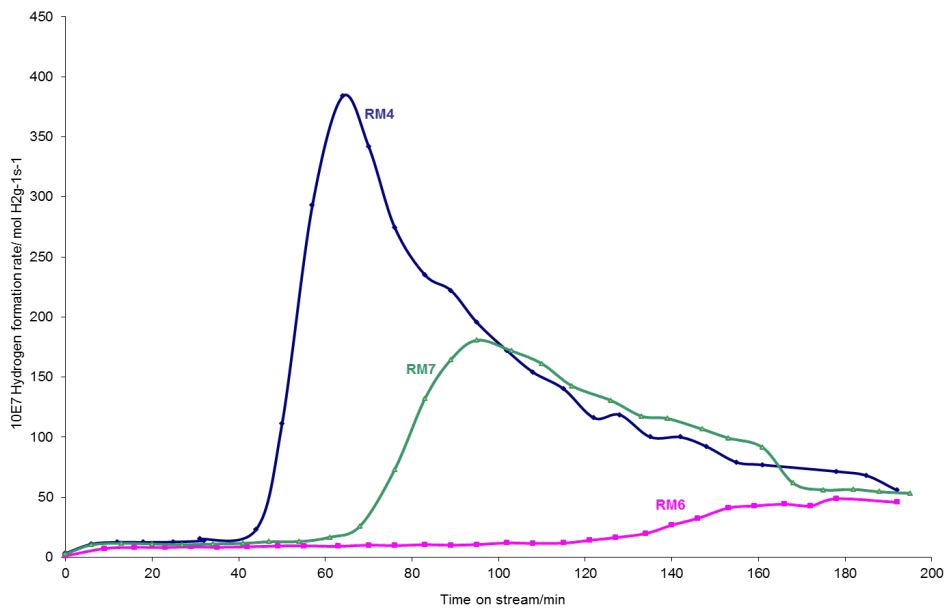


Figure 2: Mass normalised hydrogen formation rates from methane cracking as a function of time on stream. Peak CH₄ conversion rates are 18×10^{-6} , 7.7×10^{-6} and 3.4×10^{-6} molCH₄ g⁻¹ s⁻¹ for RM4 (15 m²g⁻¹), RM7 (14 m²g⁻¹) and RM6 (8 m²g⁻¹). Figure as presented in reference¹ and reproduced with kind permission from the Royal Society of Chemistry

In those cases where peak performance has been obtained, the resultant materials are magnetic carbon containing composites – often comprising graphite encapsulated dense angular particles of iron/iron carbide, as illustrated below:

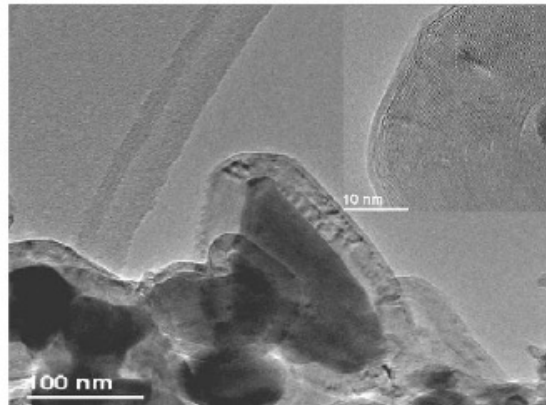


Figure 3: Post-methane cracking reaction TEM image of red mud material as presented in reference² and reproduced with kind permission from Elsevier

Also evident, to a lesser degree are multiwalled carbon nanotubes encompassing dense nanoparticles of iron/iron carbide as well as other morphologies of carbon. The form of carbon produced can be changed by switched the hydrocarbon as illustrated by the cracking of butane for which nanotubes are much more prevalent, albeit with a range of size, as illustrated in the TEM image below:



Figure 4: TEM image illustrating carbon nanotubes formed from butane cracking at 800 °C as presented in reference² and reproduced with kind permission from Elsevier Taking advantage of their magnetic nature for facilitated separation, the composites have been applied to the treatment of model water samples.

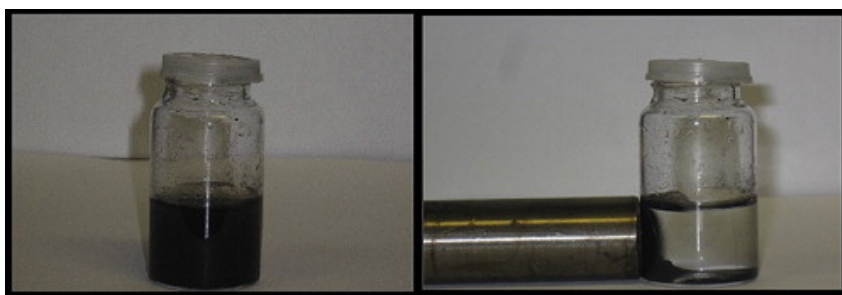


Figure 5: Magnetic separation of the graphite – iron/iron carbide composite generated from the catalytic cracking of methane over red mud. Figure reproduced from reference³ with kind permission from Elsevier

In such studies, comparison has been made between the performance of the magnetic composites, red mud itself and acidified red mud. Upon making a comparison between the affinities of the various materials for the removal of Cu^{2+} , Pb^{2+} and CrO_4^{2-} , as demonstrated in Table 2, below, it can be seen that carbonised red mud is active for the removal of the cations. Whilst, apparently not as good as the red mud itself for Pb^{2+} removal and ineffective for CrO_4^{2-} , it does present the advantage of being less alkaline and also more controllable, as well as the facilitated magnetic separation as detailed above.

Table 2: Langmuir adsorption behaviour of various red mud related samples for the removal of CrO_4^{2-} , Cu^{2+} and Pb^{2+} from model contaminated water samples. RM refers to RM7, ARM RM7 which has been acidified using HCl and CRM to RM7 subjected to methane cracking. Table reproduced from reference³ with kind permission from Elsevier

	pH	Surface area m^2/g	Cr		Cu		Pb	
			mg/g	mmol/g	mg/g	mmol/g	mg/g	mmol/g
RM	11.5	10-15	1.3	0.025	8.9	0.14	133	0.64
ARM	4.5	45-48	1.7	0.033	3.5	0.055	9.0	0.045
CRM	8.2	70	0	0	25	0.39	94	0.45

Conclusions

Providing compromise over both non-optimised performance and also the effects of compositional variability, red muds can be applied as pre-catalysts for the formation of functional carbon materials produced from the cracking of hydrocarbons. Given such hydrocarbons are often viewed as wastes which are sometimes flared leading to

further environmental impact, the combination of two wastes to generate two value added products (hydrogen and the magnetic composites) has been demonstrated.

References

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