

Application of Solid Ash Based Catalysts in Heterogeneous Catalysis

Shaobin Wang

Department of Chemical Engineering, Curtin University of Technology, GPO Box U1987, Perth,
WA 6845, Australia

Supporting Information

Table S1 Structure and description of minerals in fly ash.

Mineral name	Formula	Description
Alkali feldspars	KAlSi_3O_8	A group of minerals consists of framework
Anatase	TiO_2	Polymorph of titanium dioxide
Anhydrite	CaSO_4	Anhydrous calcium sulphate
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$	Calcium aluminium silicate a member of the plagioclase feldspar group
Boehmite	$\gamma\text{-AlO(OH)}$	Polymorph of aluminium oxy-hydroxide
Calcite	CaCO_3	Calcium carbonate
Calcium iron aluminium oxide	$\text{CaAl}_8\text{Fe}_4\text{O}_{19}$	Calcium iron aluminium oxide
Diopside	$\text{CaMgSi}_2\text{O}_6$	Calcium magnesium silicate a member of the clinopyroxene group
Dolomite	$\text{CaMg(CO}_3)_2$	Calcium Magnesium Carbonate
Gehlenite	$\text{Ca}_2\text{AlSi}_2\text{O}_7$	Calcium aluminium silicate a member of the melilite group
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Hydrous calcium sulphate
Hematite	Fe_2O_3	Polymorph of ferric iron oxide
Hydroxyl ellestadite	$\text{Ca}_{10}(\text{SiO}_4)_3(\text{SO}_4)_3(\text{OH})_2$	Metamorphosed limestone
Jarosite	$\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$	Potassium Iron Sulfate Hydroxide
Lime	CaO	Calcium oxide
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	Iron oxide belonging to the spinel group
Magnesioferrite	MgFe_2O_4	Iron magnesium oxide belonging to the spinel group
Magnetite	Fe_3O_4	Iron oxide belonging to the spinel group
Merwinite	$\text{Ca}_3\text{Mg(SiO}_4)_2$	Calcium magnesium silicate
Mullite	$\text{Al}_{4+x}\text{Si}_{2-2x}\text{O}_{10-x}$	High temperature polymorph of aluminium silicate
Nepheline	$\text{Na}_3(\text{Na,K})(\text{Al}_4\text{Si}_4\text{O}_{16})$	Sodium aluminium silicate, a member of the feldspathoid group
Orthoclase	KAlSi_3O_8	Polymorph of potassium aluminum silicate

Periclase	MgO	A cubic form of magnesium oxide
Plagioclase	NaAlSi ₃ O ₈ , CaAl ₂ Si ₂ O ₈	A group of minerals consists of framework
Portlandite	Ca(OH) ₂	Hydrated lime
Quartz	SiO ₂	Low temperature polymorph of silicon dioxide
Rutile	TiO ₂	Polymorph of titanium dioxide
Siderite	FeCO ₃	Iron carbonate
Spinel	MgAl ₂ O ₄	Magnesium aluminium oxide belonging to the spinel group
Stilbite	NaCa ₂ Al ₅ Si ₁₃ O ₃₆ ·14H ₂ O	Hydrated sodium calcium aluminum silicate
Wollastonite	CaSiO ₃	Calcium inosilicate mineral
Bassanite	CaSO ₄ ·0.5 H ₂ O	Monoclinic calcium sulphate
Mica	Na(K) ₂ Al(Mg) ₄₋₆ Si ₈ O ₂₀ (OH,F) ₄	A group of complex hydrous aluminosilicate

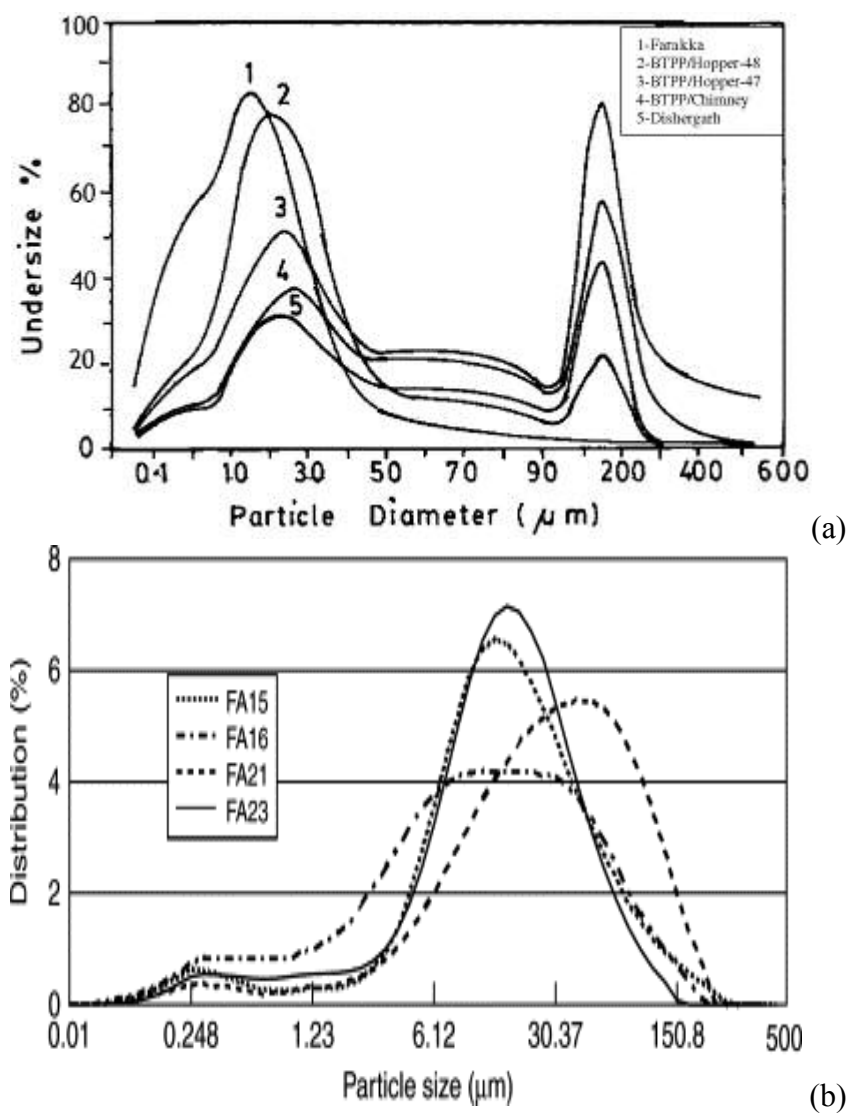


Fig. S1. Particle size distributions (PSD) of fly ashes (a) India (1) (b) Australia (2)

Rice husk ash as catalyst support and catalyst

Chang et al. (3) first reported the application of RHA-based catalysts for CO₂ hydrogenation. They prepared RHA-supported nickel catalysts by incipient wetness impregnation and examined the effects of nickel loading, immersion time, calcination and reaction temperature on catalytic performance. High selectivity (80-90%) for CH₄ formation was found to proceed in the reaction at 350-700 °C. The conversion of CO₂ and the yield of CH₄ depended on calcination conditions while the nickel catalyst activity was independent of immersion time. The CH₄ yield would achieve a maximum value at 500 °C. They also investigated the effect of deposition-precipitation method in preparation of Ni/RHA on catalyst performance. The catalyst exhibited high selectivity (80%) for CH₄ formation when carried out at 400-600 °C, better than silica gel supported Ni catalyst (4). Furthermore, they prepared Ni/RHA catalysts by ion exchange and investigated their performance for the same reaction (5). The results showed that the catalysts prepared by ion exchange yielded finely dispersed and evenly distributed nickel crystallites, making the catalysts exhibiting higher activity than those prepared by incipient wetness impregnation and deposition-precipitation method. The conversion of CO₂ and CH₄ yield increased with an increasing reaction temperature up to 500 °C, but decreased with a further increase in the reaction temperature.

Chang et al. (6) also prepared Cu/RHA catalysts for ethanol dehydrogenation to acetaldehyde at 200-300 °C. These Cu/RHA catalysts displayed higher catalytic activity than those supported on silica gel. Ethanol conversion and turnover frequency (TOF) showed little dependence on copper loading. The activity of catalysts increased with an increase in reaction temperature. Then they (7) investigated the effect of Cr₂O₃ promoter on catalyst performance in the same reaction. The results indicated an optimal Cr content around 2 wt% not only enhanced catalytic activity but also retarded catalyst deactivation due to copper sintering. Despite the lower BET surface area, RHA was superior to commercial silica gel as a candidate for catalyst support in this work, because the surface of the former may possess more unique pores, while the majority of surface pores on the latter are interconnected and thus can be clogged easily. Then they prepared Cu/RHA by the ion exchange method with various copper loadings and calcined at different temperatures. In ethanol dehydrogenation the activity was independent of calcination temperature and had little effect on Cu loading. Ethanol is selectively converted to acetaldehyde at the reaction temperature of 210-270 °C. The Cu/RHA catalysts exhibited higher catalytic activity and lower deactivation rate than Cu/SiO₂ catalysts. The activity of Cu/RHA catalysts was found to depend on Cu surface area (8).

Adam et al. prepared Fe/RHA (9) and In/RHA (10) catalysts via the sol-gel technique. The two types of catalysts showed high activity in the Friedl-Crafts alkylation of aromatic compounds under liquid phase reaction conditions. For Fe/RHA catalysts, two samples were used in the reaction

between toluene and benzyl chloride. The mono-substituted benzyltoluene was the major product and both catalysts yielded more than 92% of the product. Both the ortho- and para-substituted monoisomers were present in about equal quantities. The minor products consisting of 16 di-substituted isomers were also observed in both catalytic products. The catalyst was found to be reusable without loss of activity and with no leaching of the metal (9). They then tested In/RHA in the benzylation of benzene and substituted benzenes under liquid phase reaction conditions (10). In/RHA showed good activity, with 100% conversion and about 90% selectivity towards diphenylmethane (DPM). Catalytic activity with substituted benzenes showed an order of benzene > toluene > ethyl benzene > anisole, which is opposite to that for the classical acid catalyzed Friedel–Crafts type benzylation reaction. This was explained by the postulation of an immobilized activated species adsorbed on the catalyst surface. The catalyzed benzylation fitted well to the pseudo first order kinetic equation. The frequency factor and the activation energy E_a , was found to be $1.02 \times 10^{13} \text{ min}^{-1}$ and $22.9 \text{ kcal mol}^{-1}$ respectively. The catalyst was reused for the benzylation several times without any significant loss in its activity and selectivity.

Endud and Wong (11) synthesized mesoporous silica Si-MCM-48 using RHA and tin modified mesoporous silica MCM-48 with various Si/Sn ratios. The tin-modified materials were used in the catalytic oxidation of benzyl alcohol to benzaldehyde using *tert*-butyl hydroperoxide. The tin modified MCM-48 samples were highly selective giving 100% selectivity towards benzaldehyde in reaction times up to 22 h. The catalytic activity can be correlated with the strong Lewis acidity generated by the presence of tin species in Si-MCM-48. The re-usability of tin modified MCM-48 catalysts demonstrated the catalytic performances of the re-used samples were maintained within 5–10% after two cycles without significant loss of activity. Renu et al. (12) prepared a series of rice-husk-silica supported vanadia catalysts (2–10 wt% V_2O_5) by wet impregnation method and tested their catalytic activity in liquid phase oxidation of benzyl alcohol with H_2O_2 as oxidant. Results showed that upon the addition of vanadia, oxidation took place more effectively and benzaldehyde was obtained as the major product. Activity increased with increase in vanadia loading up to 6 wt% V_2O_5 . However, further increase in vanadia loading to 10 wt% caused a decline in conversion rate and also the benzaldehyde selectivity.

Mohamed et al. (13) used rice husks to prepare two series of ZSM-5 of different Si/Al ratios, namely Z40 and Z80 and incorporated transition metal oxides (V, Co) with ZSM-5 samples by in situ synthesis and by impregnation. These materials were tested for photocatalytic degradation of acid green (AG) dye. The local structures of metal oxides inside zeolites and their photocatalytic activities towards AG were deduced. The degradation rate of Z40 was 16 times higher than Z80 in presence of UV irradiation reflecting the importance of absorbability of silica phase present on Z40 as well as acidity and decreased crystallites size. V and Co impregnated Z (VZ_{imp} , CoZ_{imp}) samples

were found to exhibit higher and unique photocatalytic activities for AG degradation than in situ incorporated ones. CoZ80_{imp} exhibited the highest activity (0.14 min⁻¹) among all samples exceeding CoZ40_{imp} (0.11 min⁻¹) and VZ40_{imp} (0.043 min⁻¹). The enhanced photocatalytic activity of CoZ80_{imp} is attributed to charge transfer excited complex between Co in Z along with AG ligand in addition to increasing the percentages of Co₃O₄ and cobalt silicate moieties over those in CoZ40_{imp} and to the higher surface area of CoZ80_{imp}, comparatively.

Recently, Wu et al. (14) reported a work using RHA as a catalyst in catalytic ozonation of oxalic acid (OA). It was found that RHA is an efficient green catalyst for oxalic acid removal. Adsorption and ozonation processes were not effective for oxalic acid and its total organic compound (TOC) removal. The addition of RHA catalyst in the ozonation process caused 76.2% OA decomposition and 75% TOC removal in 60 min. Also, 0.25 g/L RHA dosage was found to be optimum for effective removal of oxalic acid. The efficiencies of RHA was compared with other commercially available catalysts, and the order was found to be RHA \approx TiO₂-P25 > FeOOH > SiO₂ > Al₂O₃ > ZnO. Oxalic acid decomposition was enhanced by increasing inlet gaseous ozone concentration from 40 to 120 mg/L. The catalytic ozonation process was more pronounced than the ozonation process alone at pH 3, 7, and 10.

References

- (1) Sarkar, A.; Rano, R.; Mishra, K. K.; Sinha, I. N. Particle size distribution profile of some indian fly ash--a comparative study to assess their possible uses. *Fuel Processing Technology* **2005**, 86 (11), 1221-1238.
- (2) Jankowski, J.; Ward, C. R.; French, D.; Groves, S. Mobility of trace elements from selected australian fly ashes and its potential impact on aquatic ecosystems. *Fuel* **2006**, 85 (2), 243-256.
- (3) Chang, F. W.; Hsiao, T. J.; Chung, S. W.; Lo, J. J. Nickel supported on rice husk ash - activity and selectivity in co2 methanation. *Applied Catalysis a-General* **1997**, 164 (1-2), 225-236.
- (4) Chang, F. W.; Hsiao, T. J.; Shih, J. D. Hydrogenation of co2 over a rice husk ash supported nickel catalyst prepared by deposition-precipitation. *Industrial & Engineering Chemistry Research* **1998**, 37 (10), 3838-3845.
- (5) Chang, F.-W.; Tsay, M.-T.; Liang, S.-P. Hydrogenation of co2 over nickel catalysts supported on rice husk ash prepared by ion exchange. *Applied Catalysis A: General* **2001**, 209 (1-2), 217-227.
- (6) Chang, F. W.; Kuo, W. Y.; Lee, K. C. Dehydrogenation of ethanol over copper catalysts on rice husk ash prepared by incipient wetness impregnation. *Applied Catalysis a-General* **2003**, 246 (2), 253-264.
- (7) Chang, F.-W.; Kuo, W.-Y.; Yang, H.-C. Preparation of cr2o3-promoted copper catalysts on rice husk ash by incipient wetness impregnation. *Applied Catalysis A: General* **2005**, 288 (1-2), 53-61.
- (8) Chang, F. W.; Yang, H. C.; Roselin, L. S.; Kuo, W. Y. Ethanol dehydrogenation over copper catalysts on rice husk ash prepared by ion exchange. *Applied Catalysis a-General* **2006**, 304 (1), 30-39.

- (9) Adam, F.; Kandasamy, K.; Balakrishnan, S. Iron incorporated heterogeneous catalyst from rice husk ash. *Journal of Colloid and Interface Science* **2006**, *304* (1), 137-143.
- (10) Ahmed, A. E.; Adam, F. Indium incorporated silica from rice husk and its catalytic activity. *Microporous and Mesoporous Materials* **2007**, *103* (1-3), 284-295.
- (11) Endud, S.; Wong, K. L. Mesoporous silica mcm-48 molecular sieve modified with SnCl_2 in alkaline medium for selective oxidation of alcohol. *Microporous and Mesoporous Materials* **2007**, *101* (1-2), 256-263.
- (12) Renu, P.; Radhika, T.; Sugunan, S. Characterization and catalytic activity of vanadia supported on rice husk silica promoted samaria. *Catalysis Communications* **2008**, *9* (5), 584-589.
- (13) Mohamed, M. M.; Zidan, F. I.; Thabet, M. Synthesis of zsm-5 zeolite from rice husk ash: Characterization and implications for photocatalytic degradation catalysts. *Microporous and Mesoporous Materials* **2008**, *108* (1-3), 193-203.
- (14) Wu, J. J.; Chen, S. H.; Muruganandham, M. Catalytic ozonation of oxalic acid using carbon-free rice husk ash catalysts. *Ind. Eng. Chem. Res.* **2008**, *47* (9), 2919-2925.