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Application of industrial waste based catalysts for total oxidation of propane

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ABSTRACT

High metal containing wastes from the aluminium industry, the tannery industry and the electroplating industry were tested as precursors for catalysts. These waste materials were processed using various treatments and tested for the total oxidation of volatile organic compounds employing propane as a model gas. Comparisons were made with unprocessed counterparts in certain cases. Investigations were made in the temperature range of 100–500 °C with a GHSV of 5000 h^{-1}. Characterization of fresh and used catalysts was performed using techniques like BET analysis, X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma optical emission spectrometry (ICP-OES) and thermal analyses (DTA/TG). The results showed that the catalyst obtained from combination of red mud with tannery shavings mixed in high ratio followed by thermal treatment and the unprocessed red mud were the most active. A 50% conversion in the range of 320–380 °C was achieved. In comparison, the other wastes showed lower activity, requiring much higher temperatures for the same conversion.

In view of the low cost involved and easy availability of such materials, their utilization as a source of catalyst can be of interest.

1. Introduction

Wastes originating from various industries are high in metal and metal oxide content and therefore have potential to be used as low cost catalysts. Simple physical and mechanical techniques may be employed to enhance the activity of the material without adding extra cost. Catalytic conversions of certain environmental pollutants like volatile organic compounds (VOCs) are carried over the oxides of transition metals like copper, iron and chromium [1]. Noble metal [2–4] based catalysts are very active for the hydrocarbon total oxidation, however their cost and stability against poisoning by sulfur and halides is an issue. Oxides of transition metals such as Fe, Cr, Mn, Ni, Cu and Co are also active for this reaction and are cheaper [5–9].

The wastes originating from industries like the tannery industry, the electroplating industry and the aluminium industry are high in their transition metal content either due to the raw material or processing and therefore have potential to be used as a source of catalytic materials for such reactions [10–13]. They are free of charge and their activity could be similar to that of mixed metal oxide catalysts prepared from fine chemicals.

Red mud is a by-product of the aluminium industry and has a high percentage of iron oxide. The other components present include oxides of Al, Si, Ti, Ca, Na and others [14–16]. Due to its high alkalinity, it is considered an environmental hazard and requires special disposal methods [17]. Due to its high iron oxide content, there have been various studies testing the potential of red mud as a catalyst [12,18–20]. Red mud in addition to being used as a catalyst also has potential to be used as a catalyst support material [21]. Wastes generated from the tannery industry are high in chromium content and also have a high organic fraction. After the dewatering, dehairing, cleaning and de-fleshing of the hides they are sent for tanning. After classification of the leather it is shaved to generate leather of a constant thickness. The extra shavings may contain about 50% of moisture and approximately 3–5 wt.% Cr content. In addition significant amounts of sodium and calcium may also be present stemming from the chemical treatments employed. The high organic load of the waste gives it a suitable porous structure desirable for a catalyst and the chromium content provides catalytic activity [1]. Tanning of leather is performed with basic chromium sulfate, therefore the chromium in these solid wastes is generally present in the non-toxic +3 oxidation state however it may convert to the toxic state [22] therefore their release in the environment without proper treatment can lead to serious repercussions [23–25]. There have been a few studies on the use of chromium derived from waste material as catalyst [1,25]. Electroplating sludge is generated as a result of the precipitation of the heavy metals from the acidic/alkaline solutions and rinse water generated by electroplating processes. It is a complex solid mixture composed of multiple metals such as copper, zinc, chromium, iron

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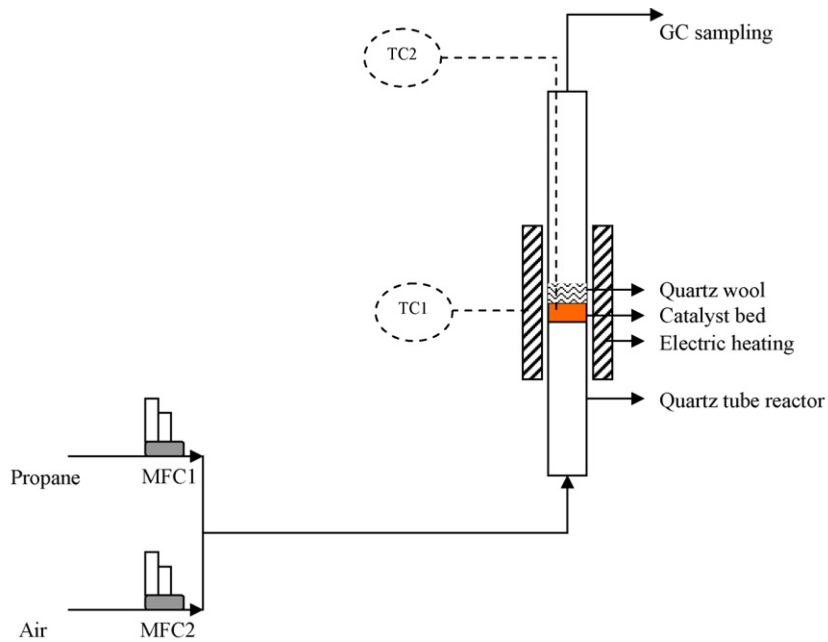

Fig. 1. Scheme for experimental set-up (TC1: thermocouple 1; TC2: thermocouple 2; MFC 1: mass flow controller for propane; MFC 2: mass flow controller for air).

and others. The wastes generated from the electroplating industry cause serious environmental problems due to the presence of a large amount of heavy metals and is considered a hazardous waste [26,27].

The present investigation aims at assessing the potential of utilizing industrial solid wastes such as red mud (RM), tannery shavings (TS) and electroplating sludge (EP) as sources of catalysts for oxidation reactions. The enhancement of catalytic activity of red mud can be achieved by addition of other active components like chromium, copper and nickel oxides. Propane was chosen as a model compound for this study and its total oxidation was examined. Propane is a cheap and stable compound which is easily available and is suitable for VOC combustion studies. The study employs simple thermal and mechanical treatments for processing the waste in an attempt to enhance the catalytic activity of the materials. Reactions were carried out at constant pressure and flow rates in a fixed bed reactor. Characterization of the catalysts was performed using various analytical techniques.

2. Experimental

2.1. Materials

The main material of interest in the investigation was red mud (RM). Three red mud samples were collected from different aluminium companies in India. They were in the form of dry powders with agglomerates. RM4 and RM7 were collected from a site in Tamil Nadu, India with a separation of two years while RM6 tailings were collected from a site in Jharkhand, India. All red mud samples were crushed, dried in an oven and then sieved $\leq$150 μm size.

The tannery shavings (TS) used in the propane oxidation reaction were collected from a tannery company located in Rehau, Southeastern Germany. The collected sample was dried at 110 °C for 24 h prior to analysis. The as received sample was in solid form with high moisture content.

The electroplating sludge from two different batches (EPI, EPII) was collected from an electroplating company located in Delhi, India. They were collected in pre-dried solid form from the company. No treatment was carried out on the sludge.

2.2. Catalyst preparation

2.2.1. Calcined red mud (CRM)

For calcination, the red mud samples were placed in silica crucibles and heated at a rate of 10 °C min^{-1} in static air to 550 °C and held for 4 h. The calcined samples show a colour change to bright red, indicating a phase change. The calcined samples were denoted as CRM.

2.2.2. Red mud and tannery shavings (RMTS)

The red mud samples were mechanically mixed with the tannery shavings in weight ratios of 1:1, 1:3 and 1:6 with a target Cr_2O_3 loading of 2%, 5% and 10%, respectively. The mixing was performed using a manual grinder and the samples were kept for calcination in static air at a temperature of 550 °C using a heating rate of 10 °C min^{-1} and duration of 4 h. The samples were referred to as RMTS.

2.2.3. Metal loaded red mud (MRM)

To load metal from electroplating sludge on red mud, the metal content was extracted using glacial acetic acid. For the extraction, 50 g of the sludge was taken in a flask, mixed with 200 ml glacial acetic acid and boiled at 120 °C for 2 h. This was followed by Soxhlet extraction for 8 h. The residue was dried and weighed. The mass loss in the case of EPI and EPII was 9 g and 16 g, respectively. The volume of the extracted liquid from the two sludges was mixed to get a high metal content in the final solution.

Simple mechanical mixing followed by calcination of red mud and electroplating sludge was not carried out since it does not give a homogeneous material. Instead, the extraction of metals was performed from the electroplating sludge and used for the impregnation of red mud.

For MRM (1), 12 g of red mud was taken in a round bottom flask and 60 ml of the mixed solution was added to it. This mixture was vacuum dried using *vaccubrand PC2001 VARI0 CVC 2000* while revolving at 100 RPM and temperature of 50 °C. The dried material was calcined in static air at a temperature of 550 °C for 4 h using a heating rate of 10 °C min^{-1}. MRM (2) with higher loading was prepared with 10 g of red mud and around 145 ml of mixed solution.