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Fly ash supported vanadia catalyst: An efficient catalyst for vapor phase partial oxidation of toluene in a micro-reactor

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ABSTRACT

Synthesis of a highly active solid oxidative catalyst has been reported by loading of vanadium on mechanically activated fly ash through wet impregnation method. The catalytic activity of prepared catalyst was measured by gas phase, solvent free selective oxidation of toluene using molecular oxygen as oxidant in a vapor phase micro-reactor under normal atmospheric pressure. The effects of vanadium weight fractions (3, 8 and 15 wt.%) and reaction temperature (453–553 K) on catalytic activity were investigated. The prepared catalysts were characterized by XRF, BET surface area analyzer, XRD, FTIR, pyridine adsorbed FTIR, Diffuse reflectance UV–vis and SEM techniques. Monolayer vanadia species (monomeric and polymeric) are responsible for the catalytic activity and selectivity of benzaldehyde and benzoic acid. Therefore, an increase of the vanadium concentration in the catalysts above the monolayer coverage results in the decrease of conversion and selectivity in toluene oxidation due to the partial blockage of active monolayer species by crystalline V_2O_5 species. The specific surface area, surface roughness and activity of fly ash were increased by mechanical activation which is being used as an effective support comparable to other silica materials. Thus the overall process is a novel, efficient and promising pathway of cost effective heterogeneous oxidations.

1. Introduction

Fly ash (FA) is a naturally cementitious coal combustion by-product and is extracted by the precipitators in the smokestacks of coal-burning power plants to reduce pollution. It is broadly an alumino-silicate type of mineral rich in aluminium and silica and defined as a heterogeneous mixture of amorphous and crystalline phases with Si, Al, Ca, Fe and Na as the predominant elements and certain elements like B, Mo, S, Se [1–3]. Fly ash having a higher degree of fineness corresponds to larger specific surface area, higher surface energy and more acting faces which illustrate higher activity on its surface. This feature of fly ash makes it suitable to be used as solid catalyst and as active catalytic support material for synthesis of various acid and base catalyzed reactions after suitable mechanical, thermal and chemical activation besides being used for waste water treatment [4,5] and synthesis of building materials [6]. In addition, the use of activated fly ash as a catalyst helps to avoid the use of environmentally unfavorable organic solvents as reaction medium under solvent free conditions which are important in industrial sectors. The use of solid waste FA in catalyst synthesis reduces the cost of bulk production of catalyst as it replaces commercially used costly metal supports viz. SiO_2, TiO_2, ZrO_2, Al_2O_3 etc. In our previous work, the surface activity has been generated over FA after suitable morphological and mineralogical modifications converting it into desired catalytic materials for Friedal–Crafts acylation reactions [7,8], benzylation [9], oil of wintergreen [10] and various types of condensation reactions [11–14] studied under liquid phase conditions.

Vanadium is one of the most abundant and widely distributed metals in the earth's crust. The most dominant non-metallurgical use of vanadium is in catalysis, which represents about 5% of the annual production of vanadium [15]. Generally, bulk V_2O_5 cannot be used as a catalyst because of its poor thermal stability and mechanical strength yet the deposition of vanadium oxide on the surface of active support materials such as SiO_2, Al_2O_3, TiO_2 and ZrO_2 leads to the formation of isolated vanadyl species, polymeric vandate species, and/or small aggregates of V_2O_5 improving the catalytic activity of the active metal oxide phase due to a gain in surface area and mechanical strength [16–18]. The monolayer vanadia species (monomeric and polymeric) are responsible for the catalytic activity and selectivity of the desired products [19]. Supported vanadia catalysts have been widely investigated as promising oxidative catalytic materials for various reactions such as for partial oxidations [20,21], oxidative dehydrogenation of hydrocarbons [22–24], epoxidation of alkenes with peroxides [25], ammoxidation of aromatics and alkylaromatics [26,27], selective reduction of NO_x [28–30], alkylation [31] and polymerization reactions [32] etc.

During the present research work, the application of FA as support is found to enhance the catalytic activity of the active metal oxide

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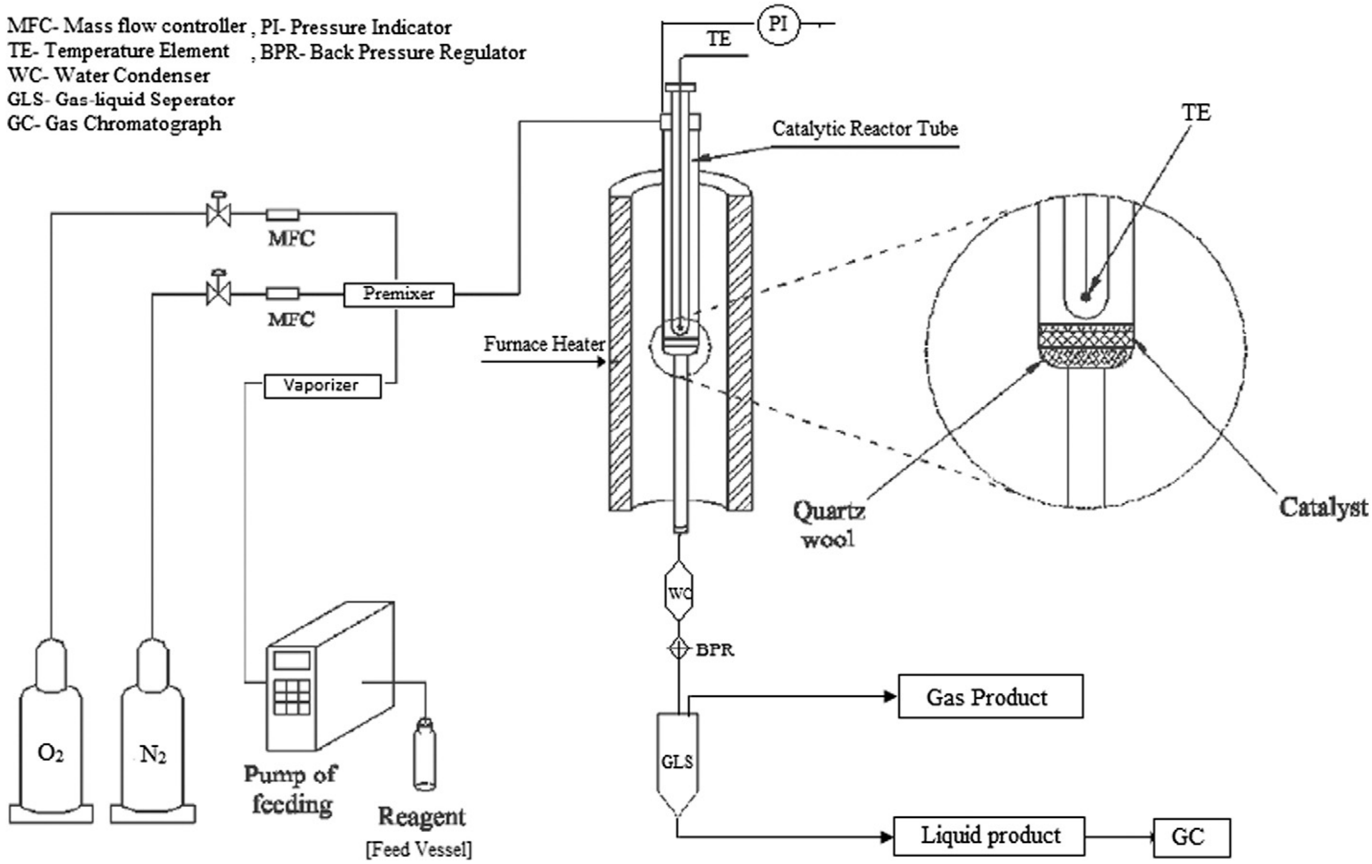

Fig. 1. Scheme of experimental set up for vapor phase oxidation.

component in comparison to the bulk metal oxides. FA is used as an active support for the loading of different wt.% of vanadium (V) content by incipient wet impregnation method. The synthesized fly ash supported vanadia (FAV) catalysts are found to have an efficient metal support interaction and stability at high calcinations and reaction temperatures. The FAV catalysts are effectively used for partial oxidation of toluene to benzaldehyde (BA) and benzoic acid (BAc) under controlled conditions of temperature and pressure in a vapor phase micro-reactor. The monolayer vanadia species remained dominant on activated FA support responsible for high conversion at the optimized reaction conditions. This research gives the FA, as an active catalyst, support material for generating cost effective catalytic systems for industrial scale productions.

2. Experimental

2.1. Materials

Fly ash having SiO_2 (62%), Al_2O_3 (23%), Fe_2O_3 (7%), CaO (1.6%), MgO (0.8%), TiO_2 (1.3%), Na_2O (2.8%) and trace elements (1.5%), analyzed by X-ray fluorescence spectrometer was collected from Kota Thermal Power Plant, Kota (Rajasthan). Ammonium metavanadate and high purity toluene were purchased from Sigma Aldrich.

Table 1
Characterization of fly ash before and after mechanical activation.

Sample	Silica (wt.%)	Crystallite size (nm)	Specific surface area (m^2/g)
FA	62	33	9
MFA-5	62.14	29	11
MFA-10	63.45	25	15
MFA-15	64.27	21	17

FA— fly ash, MFA-5: 5 h mechanically activated fly ash; MFA-10: 10 h mechanically activated fly ash; MFA-15: 15 h mechanically activated fly ash.

2.2. Catalyst preparation

The FAV catalysts were synthesized using incipient wet impregnation method on mechanically activated fly ash (MFA) by the following procedure: Pure fly ash was mechanically activated using high energy planetary ball mill (Retsch PM-100, Germany) in an agate jar using agate balls of 5 mm ball sizes for 5, 10 and 15 h with 250 rpm rotation speed. The ball mill was loaded with ball to powder weight ratio (BPR) of 10:1. 15 h mechanically activated fly ash (MFA-15), possessing high surface area (17 m^2/g), was chosen for further study and was calcined at 800 °C for 3 h for removing carbon, sulfur and other impurities. The requisite amounts (0.13 g for 3 wt.%, 0.36 g for 8 wt.%, 0.68 g for 15 wt.%) of ammonium metavanadate dissolved in hot deionized water were added to 2 g of calcined MFA-15 in 100 ml beaker and stirred overnight. The excess water was evaporated on the water-bath under constant stirring. The impregnated samples were dried at 110 °C for 24 h and calcined in air at 500 °C for 5 h. Catalysts are denoted as FAV-x, where x = 3, 8 and 15 wt.% of the V (vanadium) content.

Table 2
V content and BET surface area for FAV catalysts.

Catalysts	V content (wt.%)	Specific surface area (m^2/g)
FAV-3	1.8	16
FAV-8	5.9	14
FAV-15	12.2	10