



Vapor phase catalytic degradation of bis(2-chloroethyl) ether on supported vanadia–titania catalyst

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ARTICLE INFO

Article history:

Received 15 November 2010
Accepted 23 December 2010
Available online 6 January 2011

Keywords:

CEE
TPR
Degradation mechanism
Vanadia–Titania

ABSTRACT

Series of V_2O_5 – TiO_2 catalysts with varying vanadium content are prepared by impregnation method. The catalyst composition is determined by XRD and Smart mapping (SEM–EDAX), respectively. The bulk reducibility of the catalyst is determined by the temperature programmed reduction (TPR). Catalyst activity and stability are elucidated in vapor phase catalytic degradation of bis(2-chloroethyl) ether (CEE). The factors affecting the process parameters such as gas hourly space velocity (GHSV), feed ratios, reaction temperature and vanadium content are studied for getting maximum degradation of CEE. Results reveal that vanadium content and reaction temperature have significant influence on the activity of catalyst, and the optimum vanadium content is identified for maximum degradation. The catalyst having monolayer coverage of vanadia (6% vanadium oxide) gave better performance for the degradation of CEE at 250 °C and the total oxidation is predominant above 200 °C. The GC–MS and ATD coupled GC–MS analyses reveal the degraded products are acetaldehyde, dihydrofurans, carbon dioxide, hydrochloric acid, trace amount of chloroacetaldehyde and chloroethanol, which confirms the proposed degradation path for total oxidation and partial oxidation. A 90% of CEE degradation is achieved at 300 °C and GHSV of 19,000 h^{-1} over 6 wt% of V_2O_5/TiO_2 . A plausible surface mechanism is proposed based on the analyses results.

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1. Introduction

Catalytic removal of industrial toxins gained more interest in many countries due to the stringent environmental policies adopted in present scenario to control the air pollutants, owing to the high toxicity and low human detection limits of these compounds, particularly for polychlorinated organics, dibenzodioxins furans, reduced sulphur compounds, etc. [1,2]. Industrial air emissions treatment is becoming preferred choice to reduce the industrial toxic release inventory before releasing into the environment. There are number of reports on catalytic process for the oxidation of chloro organics, mostly related to the development of catalysts those studies are based on noble metals or transition metal oxides [3]. Nobel metal catalysts are claimed as highly effective, however, their higher cost and poor stability in reaction medium limited their development [4,5].

Supported metal oxides of chromium, manganese, nickel, cobalt, zeolite, titania and silica are widely studied for the environmental cleanup applications, but generally they have low activity and are often subject to deactivation when employed in conversion of chlorinated organics. In order to reduce the halogen deactivation,

sodium carbonate is employed as halogen scavenger for copper and manganese supported catalyst [6]. Chromium trioxide supported on porous carbon is reported as very active catalyst [7,8], however, the high toxicity of chromium oxides imposed serious disposal problems.

Catalytic oxidation of polychlorinated dibenzo-dioxins (PCDD) polychlorinated dibenzo-furans (PCDF) to carbon dioxide, HCl and water is the preferred method for destruction of these compounds [9,10]. The heavier partial oxidation products are reported like chloro benzene diols, chlorinated ethers, dioxins and furans those are ascribed to the parallel operation of combined reactions of condensation, coupling, chlorination and hydrodechlorination reactions in the oxidation of PCDD/PCDF. Toxic gases such as chlorine and phosgene formation are not observed in the oxidative degradation of PCDD/PCDF and only HCl is the main chlorine containing product [11].

The catalytic oxidation of chlorophenols over vanadia–titania catalyst is described in the literature to understand the effect of water and residual chloride. It is also reported that the steady state catalytic activity and product distribution are apparently affected by surface reaction of Cl^- with surface hydroxyl groups and adsorbed chlorinated organics. The phenolate, catecholate, ethers, aldehydes and carbohydrates species are reported as reaction intermediates [12]. Oxidation of dichlorobenzenes and chlorophenols follow the comparable reaction path though the ring breaking is

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the rate determining step in chlorophenols whereas adsorption of dichlorobenzene is rate limiting step [13].

On the other hand vanadia–titania catalysts are identified as effective catalyst for the oxidation of methyl ethyl ketone to acetic acid in presence of water [14]. The activity of the catalyst depends upon the preparation method besides the vanadia content. Isolated monomeric VO_x (vanadium oxide) species are reported to form on TiO_2 at lower vanadia loadings and converts to bulk vanadates with increasing vanadia loading [15]. However, it is opined that dispersive state and the polymeric vanadia phase co-exists at higher loadings. The monomeric and polymeric VO_x species generally termed as monolayer, and is more active for oxidation reactions than bulk/three dimensional VO_x [16–20]. It is reported that the turn over frequencies are decreased with increasing the vanadia surface density in the oxidative dehydrogenation (ODH) reactions [15,16]. Despite the fact that, the 1–5 wt% of vanadia loading catalyst is more efficient with multiple sites, but in case of *n*-butane oxidation, it is not strongly dependent on vanadia surface density.

In addition the vanadia catalyst is recognized for the partial/total oxidations as it has both high activity and selectivity together with strong stability in the chlorine/hydrochloric acid environment [21]. This type of catalyst is well demonstrated for the selective catalytic reduction (SCR) of NO_x (nitrogen oxides) emissions by using NH_3 , thus making the combined removal of NO_x and chlorinated organics/VOCs (volatile organic compounds) possible [22–25].

In particular, vanadia–titania based catalysts are employed commercially for the oxidation of chlorinated aromatic compounds. This process is studied in recent years by several research groups with highly toxic chlorinated aromatic model compounds. Chlorinated benzenes are cited as model compounds for these purposes [10,26,27]. On the other hand, CEE is used in pesticide industries as an intermediate for the production of insecticides. These chemicals are usually toxic and potential carcinogens in nature [28]. In contrast, the use of model compounds those are possessing Cl and O (halogen and ether groups) functionalities like CEE is relatively rare. Thus, in the present study CEE is used as probe molecule to understand the degradation path under gas phase catalytic oxidation over vanadia TiO_2 catalysts. The gas phase pyrolysis of CEE is reported in a static reactor to track the mechanism of the thermal degradation path. The vinyl chloride, methyl chloride, ethylene and carbon oxides are reported as major products. Most of these studies are emphasized on the batch reaction process to understand the mechanism and kinetics [29,30]. There is no systematic study of these compounds so far to understand the structure activity relationship and it is still debatable. The present study is focused on the catalytic oxidative degradation of CEE over V_2O_5 – TiO_2 catalyst and the influence of reaction temperature, reducibility of catalyst, and vanadia content on the activity and selectivity. This study is also focused on the tracking of reaction mechanism using GC–MS and Automated Thermal Desorption (ATD) coupled with GC–MS.

2. Experimental

2.1. Preparation of the catalyst

Titania supported vanadia catalysts of different compositions were prepared by wet impregnation method (Table 1). Vanadium pentoxide (0.12 g) was dissolved in 10 ml of H_2O_2 (30%) at 3 °C under ice bath to control the exothermicity and the pH of the vanadia precursor solution was 1.2. The requisite amount of this solution was used to impregnate on TiO_2 support (Aldrich). The solution was slowly added to the TiO_2 support under constant stirring and the pH of the solution was monitored continuously. After adding the solution to the TiO_2 support, the pH of the excess

solution was observed as 2. The excess solution was evaporated and dried at 120 °C in air for 10 h followed by calcination at 400 °C for 4 h in air. These samples were designated as VT1, VT2, VT3, VT4 and VT5 catalysts containing 2, 4, 6, 8 and 10 wt% of vanadium, respectively.

2.2. Characterization

The calcined samples were characterized for the N_2 BET surface area, pore size distribution, X-ray diffraction and SEM–EDAX analyses. X-ray diffraction patterns of calcined catalysts were recorded on a Regaku X-ray diffractometer using $\text{Co K}\alpha$ ($\lambda = 1.78897$) radiation. Surface area and pore size distribution measurements were performed on ASAP 2020 (Micromeritics, USA) by nitrogen adsorption at liquid nitrogen temperature using multipoint BET method. Pore size distribution was measured by BJH desorption method. Temperature programmed reduction (TPR in 5% H_2 in Ar) and temperature programmed desorption of CEE (TPD) were performed on Micromeritics (ASAP 2920) sorption unit. For thermal desorption experiments, CEE was allowed to adsorb on (100 mg) of catalyst at 30 °C under comparable reaction conditions without using any oxidizer for 1 h and charged into the U-tube reactor for thermal desorption studies. TPD was performed by heating the sample from 30 to 400 °C at a rate of 10 °C/min using helium as carrier.

Surface micrographs of vanadia catalysts were obtained by SEM (JEOL JSM 5800, SEM–EDAX) instrument. Samples for EDAX (Oxford INCA system) analysis were coated with thin carbon tape in order to avoid charge influence. Quantitative surface vanadia distribution was performed by smart map acquisition.

2.3. Activity studies

The vapor phase catalytic oxidation of CEE was carried out using a fixed-bed continuous flow reactor (12 mm ID 30 mm length) interfaced with an online GC. The CEE (AR grade 99% Aldrich), nitrogen and air (Baruka Gases, India Ltd., 99.8%) gases were used in this study. The gas flow rates were maintained by mass flow controllers (Sierra Instruments Inc., flow accuracy $\pm 1\%$). A precise infusion pump (KD Scientific 2000) was used to maintain the CEE flow rate into the preheating chamber. The CEE flow rate was maintained at a rate of 0.5 mL/h in to the preheater, where the air stream and diluting gases were mixed in the mixing chamber. All the gasses streams were also preheated before entering to the reactor at 150 °C to avoid any condensation of CEE. V_2O_5 – TiO_2 catalyst diluted with glass beads was packed in glass reactor with glass wool and mounted on to the electrically heated furnace with profile controller (West 6400 profile controller, UK) for reaction studies. The reaction was studied in the temperature range of 150–300 °C, with gas hourly space velocities from 4000 to 30,000 h^{-1} and the oxygen to CEE mole ratio were varied between 5 and 12.

Samples from reaction product stream were introduced into the GC/FID (Nucon Eng., India) equipped with Valco six port valve. Separation of the product stream was done by using BP-10 capillary column (30 m \times 0.25 mm) for partial oxidation products and reactants. The CO and CO_2 were analyzed by CO (SR 94 electrochemical based detectors), CO_2 (IR based detectors P90 Technovation Analytical Instruments Ltd., India) sensors, respectively. The initial concentration of CEE was measured for each set of experiment by using a by-pass line. Qualitative analysis was done by GC–MS (Agilent 6890N) equipped with mass-selective detector using BP-10 (30 m \times 0.25 mm). Dihydrofurans and acetic acid were observed as major products at lower temperatures and carbon oxides were the major products at higher temperatures. Trace amount of other products was also observed (<5%), and were identified but not quantified in the present study.

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