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A DFT-assisted mechanism for evolution of the ammoxidation of 2-chlorotoluene (2-CLT) to 2-chlorobenzonitrile (2-CLBN) over alumina-supported V_2O_5 catalyst prepared by a solution combustion method

Ritambhara Dwivedi [a], Prabhakar Sharma [a], Akrati Sisodiya [a], Manohar Singh Batra [b], Rajendra Prasad [a,*]

[a] *Molecular and Heterogeneous Catalysis Lab, School of Chemical Sciences, Devi Ahilya University, Indore 452001, India*
[b] *Post-Graduate Department of Chemistry, Khalsa College, Amritsar, Punjab, India*

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ABSTRACT

Ammoxidation of 2-chlorotoluene (2-CLT) has been carried out over vanadates and supported vanadates in the temperature range 350–450 °C. The catalysts were characterized by XRD, XPS, FT-IR, and Raman and surface area measurement. A maximum yield of 76% of 2-CLBN was obtained at a temperature of 425 °C and a 2-CLT:NH_3:air mole ratio of 1:8:22. DFT computations suggest that the reaction follows a Mars–van Krevelen (MVK) type of redox mechanism. The catalyst is first reduced by ammonia, producing an imine species. The 2-CLT molecule is also adsorbed through a vanadyl oxygen to produce a $CH_2{=}C_6H_5$ species. This moiety is adsorbed over the catalyst through an imine formed on the surface to produce 2-chlorobenzonitrile. XPS spectra of fresh and spent catalysts confirm reduction of the catalyst during ammoxidation.

1. Introduction

Reaction of an organic compound containing a methyl group adjacent to a double bond with dioxygen and ammonia over a solid surface to produce nitriles is called ammoxidation [1,2]. The process can be used to produce a wide range of industrially important nitriles that can be transformed easily to numerous value-added fine chemicals [1–5]. The process of ammoxidation is a vapor-phase single-step ecologically and economically efficient route for synthesis of aliphatic and aromatic nitriles employing cheap raw materials such as air and ammonia. Water is the only byproduct in the reactions [1,5].

Halogen-substituted nitriles produced by ammoxidation are useful in the production of different dyestuffs, herbicides, pharmaceuticals, and pesticides [6–11]. In particular, ammoxidation of 2-chlorotoluene (2-CLT) is an industrially important reaction for producing 2-chlorobenzonitrile (2-CLBN) in a single step. The desired product (2-CLBN) is mainly used for synthesis of dye intermediates, medicines, pesticides, and other fine chemicals [6,7,9].

Ammoxidation of halogen-substituted toluenes in the vapor phase has been studied previously over V—P—O catalysts [6,8–11]. The choice of P/V ratio is found to play a key role in determining the catalytic properties. One-step hydrothermal synthesis and characterization of V—Cr—O nanospheres and their excellent performance in the ammoxidation of 3,4-DCT and 2,6-DCT have been reported by Xu et al. [12]. Performance of Mo-, W-, and La-promoted V_2O_5/Al_2O_3 catalysts for ammoxidation of 2-chlorotoluene to 2-chlorobenzonitrile has been reported by Babu et al. [7]. Vanadium oxide industrial catalysts have been used in a variety of chemical reactions such as selective oxidation, ammoxidation, and oxidative dehydrogenation (ODH) of alkanes to alkenes [13–15]. There are a few reports on the density functional theory modeling of ammoxidation reactions of aliphatic compounds [16–22]. There seems to be no report of ammoxidation of 2-chlorotolune over alumina-supported vanadium catalysts prepared by a solution combustion method [23,24] or transition state modeling of the reaction employing density functional theory (DFT)-level quantum mechanical computations.

The present problem was therefore undertaken to evaluate the performance of supported vanadium catalysts prepared by a solution combustion method and to predict the mechanism of the reaction based on information collected from DFT computations.

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* Corresponding author. Present Address: SSISM, Sandalpur, India.
E-mail address: rjndr.prsd3@gmail.com (R. Prasad).

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2. Experimental

2.1. Preparation of catalyst

All the chemicals employed were of analytical grade and used as such without further purification. Aluminum nitrate (LOBA Chemie Pvt. Ltd.) as Al_2O_3 precursor, ammonium metavanadate (Sigma–Aldrich) as vanadium precursor, and citric acid (Merck) as a fuel were used as received. To prepare alumina-supported V_2O_5 (AV) in molar ratio 90:10, a solution of 16.55 g of aluminum nitrate in 100 ml of water was mixed with another solution prepared by mixing 0.64 g of NH_4VO_4 in 50 ml of water. The final solution was mixed with 17.19 g of citric acid and fired in a microwave oven for 2 min. The material swelled into a green-colored gel. The gel was powdered and calcined in a muffle furnace at 500 °C for 4 h. A dark-green-colored residue was obtained, which was ground in a motor pestle to a fine powder. A series of catalysts were prepared by changing the vanadium content from 5 to 25%. A similar procedure was adopted for preparation of ZrV_2O_7 (ZV) and TiV_2O_7 (TV). The catalysts were designated as MV_X, where M = Al/Zr/Ti, V = vanadium, and *X* is the vanadium percentage in the catalyst.

2.2. Catalyst characterization

XRD measurements of catalysts were made using a Rigaku X-ray powder diffractometer using Cu Kα radiation with wavelength 1.5406 Å as a source. The diffractometer was equipped with a graphite crystal monochromator (for the diffracted beam) and a scintillation counter as detector. The powder XRD data were collected in the 2θ range from 20° to 80° with a scan rate of 0.5° min^{-1}.

Table 1
BET surface area of a few supported vanadia catalysts.

V_2O_5 loading (wt.%)	BET surface area ($m^2\,g^{-1}$)	Average particle size (in nm)
AV10 (500)	91.2651	7.35
AV15 (500)	66.9221	7.85
AV20 (500)	57.2605	8.23
AV20 (600)	35.8401	12.15
AV20 (700)	25.2386	19.85
ZV10 (500)	25.8695	15.00
TV10 (500)	14.5708	36.73

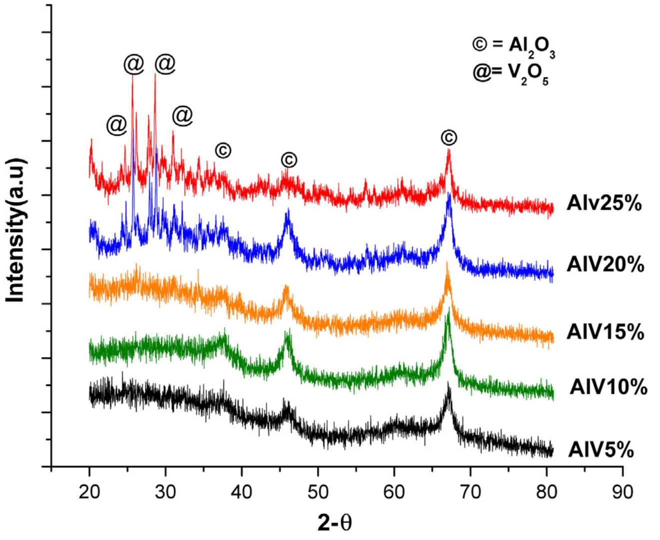

Fig. 1. XRD patterns of V_2O_5/Al_2O_3 catalysts with different V_2O_5 loadings calcined at 500 °C: (@) V_2O_5, (©) γ-Al_2O_3.

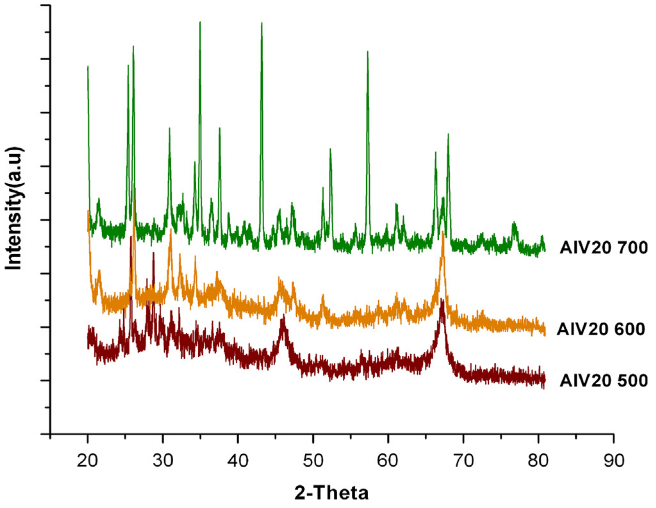

Fig. 2. XRD patterns of AlV20 catalyst at different calcination temperatures.

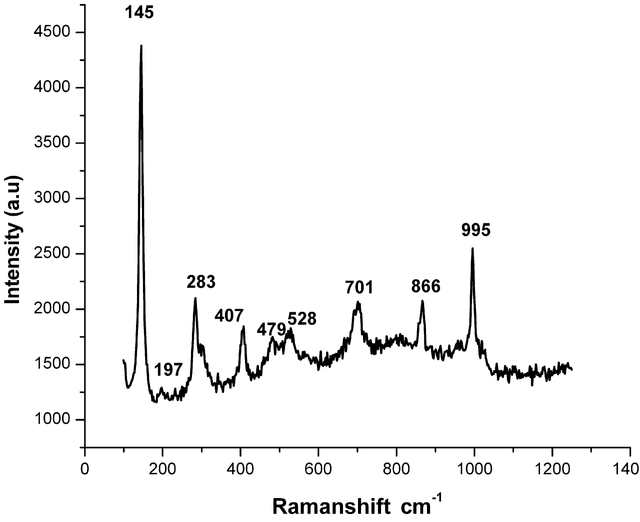

Fig. 3. Raman spectrum of AlV20 catalyst calcined at 500 °C.

Raman records in the range 100–4000 cm^{-1} were made on a Labram HR800 micro Raman spectrometer using a 488 nm wavelength Ar+ laser source at energy 2.53 eV and using Labspec software. Surface area was measured using an ASAP 2020 V3.04 H surface area analyzer in a N_2 physisorption apparatus equipped with a thermal conductivity detector. The pore size distribution was calculated using the BJH method. The FT-IR spectra of the samples were recorded in the range 400–4000 cm^{-1} using a Bruker VERTEX 70.

2.3. Catalytic activity

The activity of the catalysts for vapor-phase ammoxidation of 2-CLT to 2-CLBN was carried out at atmospheric pressure in a fixed-bed, vertical downflow glass reactor placed inside a tubular furnace. The temperature was regulated with the help of energy regulators and metered by a thermocouple inserted in the reactor. Fresh catalyst (1.0 g) was charged into the center of the reactor in such a way that the catalyst was sandwiched between two layers of inert glass beads. The reactant 2-chlorotoluene (2-CLT) was fed using a pressure-equalizing funnel. Air and NH_3 were taken