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Kinetics of photoconversion of cyclohexane and benzene by $LnVO_4$ and $LnMo_{0.15}V_{0.85}O_4$ (Ln = Ce, Pr and Nd)

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ABSTRACT

The orthovanadates $LnVO_4$, and molybdovanadates $LnMo_{0.15}V_{0.85}O_4$ (Ln = Ce, Pr and Nd), were synthesized via solid-state method. The crystal structure and the band gap of these compounds were determined by powder X-ray diffraction and UV–visible spectroscopy, respectively. The photocatalytic activities of these materials towards the oxidation of cyclohexane to cyclohexanol and cyclohexanone and towards hydroxylation of benzene to phenol were investigated. A detailed free radical mechanism for the oxidation of cyclohexane has been proposed and the reaction rate coefficients were determined. The hydroxylation of benzene to phenol was modeled using a simple series reaction mechanism. The rate coefficients show that $CeVO_4$ exhibited superior photocatalytic activity and selectivity for the oxidation of cyclohexane to cyclohexanone compared to all other catalysts. For the hydroxylation of benzene, $PrMo_{0.15}V_{0.85}O_4$ yielded high amounts of phenol. The observed trends in photoactivity are in good agreement with the band structure of these compounds.

1. Introduction

Lanthanide orthovanadates belong to the ABO_4 class of compounds. These compounds are of great interest to the scientific and industrial communities due to their useful luminescent and electrical properties and unusual magnetic characteristics [1–6]. These materials have, therefore, been employed as efficient laser diodes, polarizers and sensors for ethanol [7–9]. Lanthanide orthovanadates have also been used as catalysts for dehydrogenation and hydroxylation [10].

These materials have been employed as model systems for investigating polymorphism among ABO_4-type compounds. These compounds are of zircon-type and transform to the scheelite structure at high pressures. However, $LnVO_4$ also crystallizes in the monoclinic monazite structure [2,3], which is preferred because of its higher oxygen coordination number compared to that of the zircon-type [4].

$LaVO_4$ was first synthesized by Ropp and Carroll [11] and then by Escobar and Baran [12]. The hydrothermal synthesis was standardized by Oka et al. [6]. The monoclinic monazite-type $LaVO_4$ does not act as a host for luminescent activators [11,13] and does not work as a catalyst [14]. However, tetragonal-zircon-type $LaVO_4$ exhibits superior catalytic properties [15]. The substitution of Li, Fe, Ce in $LaVO_4$ (A site substitution) results in $Li_{3x}La_{1-x}VO_4$, $La_{1-x}Fe_xVO_4$, $Ca_xCe_{1-x}VO_4$, etc. These compounds are good ion conductors [16], catalysts for CO oxidation [9], and p-type conductors [17], respectively. Similarly, substitution of Mo in $CeVO_4$ (B site substitution) [18] leads to better photocatalytic activity. Thus, the aliovalent cation substitution to A and B sites of ABO_4 compounds results in superior catalytic properties compared to undoped ABO_4. The use of B site-substituted orthovanadates for the photocatalytic hydroxylation of benzene and oxidation of cyclohexane has been investigated for the first time in this study.

Heterogeneous photocatalysis is desirable for the partial oxidation in preference to peroxyacids and peroxides [19,20]. Because molecular oxygen/air is a weak and non-selective oxidant, a good catalyst is needed to activate oxygen. In this study, we have used oxygen for both oxidation and hydroxylation reactions.

The synthesis of cyclohexanone is important because it finds application as an additive in the electronic industry, as a solvent for insecticides and in the manufacture of ε-caprolactum. Cyclohexanone has been synthesized from cyclohexane with cobalt catalyst at high pressure [21], with H_2O_2 [22] and by photocatalysis with V_2O_5 [23]. The synthesis of phenol is an industrially important reaction and has been accomplished using thermal catalysis [24],

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Fenton process [25], semiconductor photocatalysis [26] cation exchange zeolites [27], and substituted titania [28,29]. Thus the syntheses of phenol and cyclohexanone by a "green" photocatalytic process are of great interest.

In the current study, we report for the first time the photocatalytic activity of lanthanide orthovanadates and B site-substituted lanthanide molybdovanadates towards the oxidation of cyclohexane and the partial hydroxylation of benzene. The time evolution of cyclohexane, cyclohexanol and cyclohexanone have been modeled using free radical mechanism and the rate coefficients have been determined. The conversion of benzene to phenol was modeled using a simple series reaction mechanism and the formation and consumption rate constants were evaluated.

2. Experimental

2.1. Materials

CeO_2, Pr_6O_{11}, Nd_2O_3 (Sigma–Aldrich, 99.9%), V_2O_5 (S.D. Fine Chem., India, 99%), and MoO_3 (Sigma–Aldrich, 99.9%) were used as received. Benzene and cyclohexane (S.D. Fine Chem., India, AR grade) were used without further purification. Doubly distilled water was filtered through a Millipore membrane filter prior to use.

2.2. Preparation

$LnVO_4$ and $LnMo_{0.15}V_{0.85}O_4$ (Ln = Ce, Pr and Nd) compounds were synthesized from CeO_2, Pr_6O_{11}, Nd_2O_3, MoO_3 and V_2O_5 as cerium, praseodymium, neodymium, molybdenum and vanadium source respectively. A stoichiometric amount of oxide was taken for $LnVO_4$ with a ratio of Ln:V = 1:1. The reactants were ground with an agate motor and pestle. Pellets were made and fired to 700 °C at a rate of 5 °C min^{-1} and held for 6 h. The temperature was then raised to 800 °C at a rate of 10 °C min^{-1} and held for another 6 h in a programmable furnace (FD1540M). Lanthanide oxides (CeO_2, Pr_6O_{11}, Nd_2O_3), MoO_3, and V_2O_5 were taken as the starting materials for the synthesis of lanthanide molybdovanadate ($LnMo_{0.15}V_{0.85}O_4$) with a molar ratio of Ln:Mo:V = 1:0.5:1. Pellets were made and fired at 700 °C with a heating rate of 20 °C min^{-1} and held for 2 h; this was followed by an increase to 800 °C with a heating rate of 5 °C min^{-1}. Further, the resulting compounds [18] were held at 800 °C for 6 h and then cooled to room temperature at the rate of 20 °C min^{-1}. Powder X-ray diffraction patterns of all synthesized orthovanadates and molybdovanadates are shown in Fig. 1.

2.3. Characterization

2.3.1. Powder X-ray diffraction

X-ray datasets were collected on a Philips (Xpert PRO) instrument with a Cu Kα source. The instrument was fitted with an X'celerator detector (PW 3050/60). An absolute scan over the 2θ range of 10–100° with a step size of 0.017° and an effective time per step of 101 s were used during the data collection.

2.3.2. Photocatalytic experiments

2.3.2.1. Photoreactor. The photochemical reactor used in this study comprised a jacketed quartz tube of 3.8 cm i.d., 4.5 cm o.d., and 21 cm length and an outer Pyrex glass reactor of 5.7 cm i.d. and 16 cm in length. A high-pressure mercury vapor lamp (HPML) of 125 W (Philips, India) was placed inside the jacketed quartz tube. Water was circulated in the annulus of the quartz tube to maintain the solution temperature at 35 °C. The outer reactor comprised of an inlet and outlet for oxygen bubbling as shown in the schematic in Fig. 2. The oxygen flow rate was measured with a rotameter (range of 1–100 mL min^{-1}). The outer reactor was sealed with Teflon to maintain a perfect oxygen environment. 100 mL of the organic solution along with the catalyst was taken in the outer reactor and stirred continuously. The lamp radiated predominantly at 365 nm, corresponding to an intensity of 5.9×10^{-6} einstein L^{-1} s^{-1} and a photon flux of 30 W m^{-2} measured using *o*-nitrobenzaldehyde actinometry [30].

2.3.2.2. Photoconversion experiments. For the photo-oxidation of cyclohexane, 100 mL of the solution containing 925 mmol L^{-1} of cyclohexane in an organic solvent was exposed to UV radiation with continuous bubbling of oxygen and vigorous stirring. The effect of different reaction parameters like oxygen flow rate, catalyst loading and solvent medium were studied and are discussed in the following section. For the hydroxylation of benzene, a stock solution of acetonitrile:benzene = 95:5 was made. 20 mL of this stock solution was made up to 100 mL in doubly distilled water. The resultant mixture of benzene, acetonitrile and water was exposed to UV radiation with the same oxygen flow rate and catalyst loading as was used for the oxidation of cyclohexane.

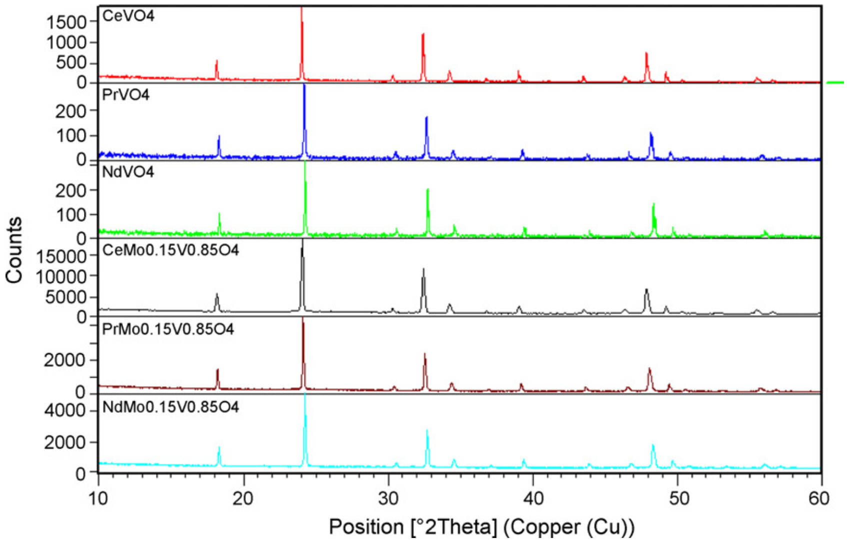

Fig. 1. Powder X-ray diffraction patterns of all synthesized orthovanadates and molybdovanadates.