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Article

Solvent-free selective oxidation of cyclohexane with molecular oxygen over manganese oxides: Effect of the calcination temperature



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ABSTRACT

The effects of calcination temperature on the physicochemical properties of manganese oxide catalysts prepared by a precipitation method were assessed by X-ray diffraction, N₂ adsorption-desorption, X-ray photoelectron spectroscopy, H₂ temperature-programmed reduction, O₂ temperature-programmed desorption, and thermogravimetry-differential analysis. The catalytic performance of each of these materials during the selective oxidation of cyclohexane with oxygen in a solvent-free system was subsequently examined. It was found that the MnO_x-500 catalyst, calcined at 500 °C, consisted of a Mn₂O₃ phase in addition to Mn₅O₈ and Mn₃O₄ phases and possessed a low surface area. Unlike MnO_x-500, the MnO_x-400 catalyst prepared at 400 °C was composed solely of Mn₃O₄ and Mn₅O₈ and had a higher surface area. The pronounced catalytic activity of this latter material for the oxidation of cyclohexene was determined to result from numerous factors, including a higher concentration of surface adsorbed oxygen, greater quantities of the surface Mn⁴⁺ ions that promote oxygen mobility and the extent of O₂ adsorption and reducibility on the catalyst. The effects of various reaction conditions on the activity of the MnO_x-400 during the oxidation of cyclohexane were also evaluated, such as the reaction temperature, reaction time, and initial oxygen pressure. Following a 4 h reaction at an initial O₂ pressure of 0.5 MPa and 140 °C, an 8.0% cyclohexane conversion and 5.0% yield of cyclohexanol and cyclohexanone were achieved over the MnO_x-400 catalyst. In contrast, employing MnO_x-500 resulted in a 6.1% conversion of cyclohexane and 75% selectivity for cyclohexanol and cyclohexanone. After being recycled through 10 replicate uses, the catalytic activity of the MnO_x-400 catalyst was unchanged, demonstrating its good stability.

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1. Introduction

The selective liquid phase oxidation of cyclic hydrocarbons is one of the most widely used industrial processes producing

oxygenates [1]. Because of the importance of cyclohexanol (A) and cyclohexanone (K) in the production of adipic acid and caprolactam, compounds that in turn are used in the manufacture of nylon-6 and nylon-6,6 polymers, the selective oxidation

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of cyclohexane has become a very important reaction [2,3]. In general, there is the trade-off between selectivity and high conversion in hydrocarbon liquid phase oxidation reactions. Thus, conditions generating low conversions (less than 5%) are generally preferable as a means of preventing over-oxidation to form undesired by-products [4–6]. The greatest challenge associated with conventional industrial processes for cyclohexane oxidation is therefore the inherent difficulty in controlling the selectivity for the target products while obtaining a high conversion [7].

To date, a large number of catalysts have been reported for the oxidation of cyclohexane, such as metalloporphyrins [8,9], metal oxides [10–12], molecular sieves [13–16], carbon nanotubes [17,18], metal-organic frameworks materials [19,20], and small organic molecules [21]. Recently, polyoxometalate-based organic-inorganic hybrids demonstrated superior catalytic activity, producing a 29.4% yield of KA oil using H_2O_2 as the oxidant with acetonitrile as the solvent [22]. This same work also investigated changing the structure of the ionic liquid (IL) cation and obtained homogeneous catalysts having the structure $[\text{MimC}_4]_5\text{PMoV}_2$ IL-cation. Using this catalyst, a 28.5% yield of KA oil was obtained from the cyclohexane oxidation. However, a homogeneous catalyst such as this cannot be separated from the reaction mixture and recycled. Therefore, significant research work has been devoted to the development of heterogeneous catalysts for the selective oxidation of cyclohexane as substitutes for conventional homogeneous catalysts.

Iglesia et al. [23] reported that Mn species in MnAPO materials can serve as active sites during cyclohexane oxidation when using O_2 as the oxidant. Xu et al. [24] also studied the catalytic activity of MnAPO materials with regard to cyclohexane oxidation, and reported 3.7% conversion of cyclohexane and 64.5% selectivity for KA oil. However, the complicated process required to synthesize these catalysts and the un economical raw materials limit the potential industrial applications of these materials. Various hetero-mixed oxide catalysts have also been studied for the oxidation of cyclohexane, and $\text{WO}_3/\text{V}_2\text{O}_5$ has exhibited high catalytic activity with H_2O_2 as the oxidant [11]. Unfortunately, this approach suffers from the toxicity of the vanadium-based catalyst, and so effective, environmentally friendly, inexpensive and safe catalysts for the oxidation of cyclohexane are still required.

The catalytic oxidation of cyclohexane with oxygen as the oxidant has also been widely studied because of the inherently environmentally friendly nature of this process, although the resulting cyclohexane conversion is generally lower compared with that obtained with H_2O_2 or *tert*-butyl hydroperoxide (TBHP). Yang et al. [18] proposed that cyclohexane oxidation proceeds through a radical mechanism with O_2 as the oxidant. Hence, in some cases, the use of a radical initiator such as H_2O_2 or TBHP in the reaction mixture decreases the induction period and increases the conversion of cyclohexane. Chen et al. [25] also added TBHP to a cyclohexane reaction mixture as a free radical initiator to increase both the reaction rate and the conversion of cyclohexane. Recently, hollow sulfated V-doped TS-1 photocatalysts were evaluated for the selective photooxidation of cyclohexane with molecular oxygen and exhibited high effi-

ciency (TOF = 2.37 h^{-1} , based on the molar amount of V sites) and chemoselectivity (cyclohexanone/cyclohexanol molar ratio = 3.46) [26].

Compared with molecular sieves and metal-organic frameworks materials, transition metal oxides are much easier to prepare and to apply in industrial processes. In the present work, we selected a transition metal oxide (manganese oxide) as the catalyst for the solvent-free oxidation of cyclohexane with molecular oxygen because this oxide is inexpensive, readily available, and environmentally friendly. This study investigated the effect of the calcination temperature on the physicochemical properties of manganese oxide catalysts prepared by a precipitation method. Based on the relationship between the calcination temperature and the resulting physicochemical properties and catalytic performance of the manganese oxide catalysts, we attempted to synthesize a highly effective and stable oxide catalyst for the solvent-free oxidation of cyclohexane with molecular oxygen.

2. Experimental

2.1. Synthesis of catalysts

Manganese oxide catalysts were prepared by a precipitation method using an aqueous $\text{Mn}(\text{NO}_3)_2$ solution as the source of Mn. In a typical procedure, a quantity of a 50 wt% $\text{Mn}(\text{NO}_3)_2$ solution was added to a 250-mL three-neck flask followed by the dropwise addition of an aqueous NaOH solution (1 mol/L) at 60 °C with stirring until the mixture reached a pH of 8. The solution was subsequently held at 60 °C for 4 h with stirring during which time its pH was maintained at 8 by adding the NaOH solution as required. The solid product was collected by filtration, washed several times with de-ionized water, dried at 120 °C overnight, and finally calcined in air at either 350, 400, 450, or 500 °C for 4 h. The corresponding samples are designated as MnO_x -350, MnO_x -400, MnO_x -450, and MnO_x -500, respectively.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Focus X-ray diffractometer with $\text{Cu } K_\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) at a scanning rate of 6°/min. N_2 adsorption-desorption isotherms were acquired on an ASAP 2010 analyzer (Micromeritics) at -196 °C. Prior to these measurements, all samples were degassed at 300 °C for 6 h under vacuum to remove moisture and any volatile impurities. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas of samples. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250 spectrometer with a monochromatized Al K_α X-ray source (1486.6 eV), employing the C 1s (binding energy 284.6 eV) peak of adventitious carbon as a reference. Thermogravimetry-differential thermal analysis (TG-DTA) was carried out using a PerkinElmer Pyris Diamond instrument together with a WCT-2 thermal analyzer at a rate of 10 °C/min in air.

H_2 temperature-programmed reduction (H_2 -TPR) profiles

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