

Synthesis, characterization and catalytic activity of Nd₂O₃ supported V₂O₅ catalysts

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Abstract

A series of rare-earth neodymia supported vanadium oxide catalysts with various V₂O₅ loadings ranging from 3 to 15 wt.% were prepared by the wet impregnation method using ammonium metavanadate as the vanadium precursor. The nature of vanadia species formed on the support surface is characterized by a series of different physicochemical techniques like X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), BET surface area, diffuse reflectance UV–vis spectroscopy (DR UV–vis), thermal analysis (TG-DTG/DTA) and SEM. The acidity of the prepared systems were verified by the stepwise temperature programmed desorption of ammonia (NH₃-TPD) and found that the total acidity gets increased with the percentage of vanadia loading. XRD and FTIR results shows the presence of surface dispersed vanadyl species at lower loadings and the formation of higher vanadate species as the percentage composition of vanadia is increased above 9 wt.%. The low surface area of the support, calcination temperature and the percentage of vanadia loading are found to influence the formation of higher vanadia species. The catalytic activity of the V₂O₅-Nd₂O₃ catalysts was probed in the liquid phase hydroxylation of phenol and the result show that the present catalysts are active at lower vanadia concentrations.

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1. Introduction

Metal oxide supported vanadia catalysts are the basic component of several industrial catalysts, which are used for the selective oxidation and ammoxidation of various hydrocarbons and for the selective catalytic reduction of NO_x with NH₃ [1–5]. The catalytic activity of vanadia species depends largely on the nature of the support, as support interaction usually affects the dispersion and redox properties of the active vanadia phases and hence shows differences from bulk V₂O₅. Furthermore, from a reaction point of view, it has been well documented that the selectivity and activity of these supported vanadia catalysts depends on the acid–base properties of the support, calcination temperature and percentage

of vanadia loading apart from its surface acidity. Thus, careful choice of the support, suitable preparation procedure, precise amount of vanadia loaded seems to be the crucial factors in the preparation of vanadia catalysts for a definite reaction. The interesting characteristic properties of vanadia-ceria catalysts [6,7] and its impact in the heterogeneous catalysis scenario focused tremendous attention towards various rare-earth supported vanadia catalysts.

The existence of different surface vanadium oxides on various single oxide supports (TiO₂, SiO₂, MgO and CeO₂) and mixed oxides (TiO₂-SiO₂ and TiO₂-Al₂O₃) has undergone considerable research and refinement during the last few decades since the properties of bulk vanadia is entirely different on a support. Rare-earth supported vanadia catalysts find extensive applications in recent years especially with cerium, since the presence of Ce⁴⁺/Ce³⁺ redox couple made them genuinely interesting in the selective partial oxidation of various hydrocarbons. Au et al. [8,9] reported the preparation of different rare-earth orthovanadates

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and had verified its catalytic activity in the oxidative dehydrogenation reaction of propane. However, literature reveals that reports on vanadia–neodymia mixed oxides are scarce, and hence, it is interesting to evaluate its surface properties and to screen its activity towards different selective oxidation reactions.

Diphenols like catechol and hydroquinone are important chemical materials especially in agro chemical and fine chemical industries. Formation of diphenols from phenol hydroxylation using H_2O_2 as oxidant has become one of the promising approaches due to its minimum environmental pollution, high active oxygen content and the absence of any toxic by-products. This oxidation process is frequently reported as taking place through the decomposition of H_2O_2 with the formation of an unstable electrophilic intermediate, which attacks the phenol nucleus to give a phenoxy ion. The catalysts prepared till date for this reaction are the high surface area titanosilicates [10], molybdovanadophosphates [11], metal complexes [12,13] etc., but had the drawbacks like the difficulty in the separation of catalysts from products, complicated preparation procedure and low product yields. Moreover, literature reveals that simple metal oxides and supported metal oxides like Fe_2O_3 [14], MoO_3 [15], V_2O_5 and TiO_2 colloidal particles [16] and materials with low surface area catalysts like V-Zr-O, Cu-Bi-V-O were active for the hydroxylation of phenol in presence of H_2O_2 [17,18].

In the present report, we present our results on the interaction of vanadia species at different loadings with the rare-earth neodymia using a series of different characterization techniques. We extend our studies further to elucidate the nature of vanadia species present in the different loaded samples, its interaction with the support and its role in the phenol hydroxylation reaction. Catalytic data show that the supported catalysts can promote the hydroxylation of phenol to a suitable extent and are stable under the reaction conditions opted.

2. Experimental

2.1. Catalyst preparation

The incipient wet impregnation method was opted to prepare the vanadia-neodymia catalysts used in the study. The support neodymia was prepared via hydroxide method by precipitation from its nitrate solution (neodymium nitrate, supplied by Indian Rare Earth Ltd., Udyogamandal, Kerala) by the dropwise addition of 1:1 ammonia. The resultant mass obtained was then made free from nitrate ions and evaporated in a water bath kept at 110°C for 12 h. The support was calcined in air at 500°C prior to impregnation with an aqueous solution containing ammonium metavanadate (supplied by Merck Chemicals) and oxalic acid in a 1:2 molar ratio. The percentage of vanadium and total amount of impregnating solution were adjusted in order to produce catalysts with

vanadium weight loading between 3 to 15 wt.% [19]. The samples were then dried overnight at 100°C and finally calcined in air at 500°C for 5 h. The catalysts were named according to the weight percentage of vanadia loading and its calcination temperature (for example, the sample 6VN/500 means that 6 wt.% of vanadia was loaded on the support and calcined at a temperature of 500°C). An NdVO_4 sample had been also prepared to check the formation of orthovanadate species at higher loadings and thus considered as a reference compound.

2.2. Characterization

The phase compositions of the prepared catalysts were identified on Rigaku D-Max X-Ray Diffractometer equipped with a Ni filtered $\text{Cu K}\alpha$ radiation at room temperature in the 2θ range of 10° – 60° . IR spectroscopy studies were carried with a Jasco FTIR-5300 instrument in the range of 4000 – 400 cm^{-1} on KBr phase. UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV–2100 recording spectrophotometer in the range 200 – 800 nm . The specific surface area of the catalysts were determined by BET method by nitrogen adsorption at -197°C using a Micromeritics Flow Prep-060 instrument. Thermal analyses were performed by taking 10 mg of samples at a heating rate of $10^\circ\text{C}/\text{min}$ on a Seiko TG V15 Dupont 2100 instrument in air (30 ml/min). The size and morphology of the prepared catalysts were estimated by scanning electron microscope (Jeol Model 5200). Temperature programmed desorption was carried out to determine the strength of acid sites and the total acidity of the catalysts using ammonia as a probe adsorbate. In a typical experiment, 100 mg of the catalyst was placed in a tubular reactor and heated to 200°C under nitrogen flow for approximately 4–5 h. The reactor was then cooled and the adsorption of ammonia was conducted by exposing the sample to ammonia at a flow rate of 10 ml/min for 1 h. The acid strength distribution was then subsequently determined by raising the temperature in steps viz. 100 – 200 , 200 – 300 , 300 – 400 and 400 – 500°C , with the flow of nitrogen.

2.3. Catalytic experiments

2.3.1. Hydroxylation of phenol

The hydroxylation reaction was performed batch wise in a double-necked 50 ml round bottom flask using phenol (2.8 g, 0.0298 mol), water (5 g) and 0.1 g of activated catalyst at a temperature of 80°C . At the beginning of the reaction, 30 wt.% H_2O_2 (0.008 mol) was added in one lot, followed by heating the mixture to the required reaction temperature. The course of the reaction was followed by analyzing the reaction mixture periodically using a gas chromatograph (HP 6890) equipped with a flame ionization detector (FID) and a capillary column (5 μm cross-linked methyl silicone gum, $0.2\text{ mm} \times 50\text{ m}$) and by injecting authentic samples.

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