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Oxidative dehydrogenation and aromatization of *n*-octane over VMgO catalysts obtained by using different MgO precursors and different precursor treatments

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ABSTRACT

VMgO catalysts with a V_2O_5 loading of 15% were prepared by the wet impregnation method. Catalysts synthesis was carried out by employing different MgO precursors (MgC_2O_4 and $Mg(OH)_2$) and different precursors treatments (under vacuum and under static air). The synthesized catalysts were characterized by ICP-OES, BET, powder XRD, SEM, EDX, ^{51}V NMR, H_2-TPR, and NH_3-TPD. The catalysts were tested for the oxidative dehydrogenation of *n*-octane using a continuous flow fixed bed reactor at GHSV of 8000 h^{-1} and *n*-octane/O_2 molar ratio of 0.8. Changing the above synthesis parameters led to the formation of catalysts with different morphologies, textural properties, and acidity. As a consequence, the results of the catalytic testing were also different, and treating the MgO precursors under vacuum induced a general positive effect on the catalytic performance. The aromatization of *n*-octane was predominantly via C1–C6 bonding.

1. Introduction

The merits of the oxidative dehydrogenation (ODH) of the inexpensive alkanes to produce the synthetically more valuable products, such as olefins and aromatics, represents a driving force that motivates the research for developing active and selective catalysts for this purpose. Since the report by Kung and co-workers [1], the usage of VMgO catalysts in attempts to convert short-chain alkanes into the corresponding value-added products such as olefins and dienes was a matter of investigation [2–6]. In fact, they are among the most active and selective catalysts in the oxidative dehydrogenation of short-chain alkanes. Because of its low tendency to form oxygenates and cracking products [1,5,7,8], the VMgO system was considered as a good candidate for the oxidative dehydrogenation of long-chain alkanes such as *n*-octane. Thus, we employed these catalysts for the oxidative dehydrogenation of *n*-octane to produce the corresponding linear octenes and C8 aromatics [9,10].

The challenge in the mixed oxide catalysts, in general, is the preparation of a solid with a high degree of dispersion [11–13]. In the VMgO system, magnesium oxide (basic) is likely to interact intensively with vanadium (acidic), which will eventually lead to a good dispersion of vanadium on the support and presumably a good ODH performance. An interesting feature related to this was that incorporation of vanadium into MgO inhibits the formation of V_2O_5 [6,14]. This oxide, because of its exposed V=O bond, is believed to enhance the formation of oxygenates and total combustion products [1,4,6].

Supports, in general, play an important role in determining the catalyst's properties and hence the catalytic performance [2,4]. Vanadia-based catalysts are believed to be affected by the nature of the metal oxide used as support [2,4,8,15–17]. Magnesium oxide is one of the most important supports used in catalyst preparation. In MgO, the morphological and chemical properties, such as surface area, particle shapes, concentration of edges and corners, and degree of surface hydroxylation were found to be dependent on the method of preparation [18–20]. By analogy, MgO interaction with vanadium during the preparation of VMgO catalysts is likely to be influenced by these properties, and hence lead to the formation of VMgO catalysts with different properties and consequently different catalytic performance. In support of this, it was reported that vanadium supported on MgO with different crystallite sizes showed different catalytic performance during the oxidative dehydrogenation of *n*-butane [21]. It should be added that the degree of interaction between vanadium and magnesium oxide is believed to

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be one of the important factors that determine the properties and the catalytic performance of VMgO catalysts [3,22].

We recently reported on the oxidative activation of *n*-octane over cobalt-substituted ceria and vanadium-supported hydroxyapatite catalysts [23,24]. In contrast, the characteristic feature of the VMgO catalysts, that is their poor tendency to form oxygenates, cracking and isomerization products, makes them good catalysts for the oxidative dehydrogenation of a long-chain alkane, such as *n*-octane, for the production of linear octenes and C8 aromatics; in this oxygen-containing environment, *n*-octane would be susceptible to combustion and cracking. This justifies further investigation of the VMgO system for the oxidative dehydrogenation of *n*-octane, especially since the world production of medium chain length paraffins (C_7–C_{10} linear alkanes) exceeds 1 Mt p.a. Influencing the properties and catalytic performance of VMgO catalysts has been attempted by changing the method of preparation [7,13,25–27], varying the vanadium loadings [1,7,9,28,29], and varying the calcination temperatures and time [28–30]. In this study, we investigated the effects of using different MgO precursors (oxalate and hydroxide) and different precursor treatments on the properties and catalytic performance of the resultant VMgO catalysts. These synthesized catalysts were tested for the oxidative dehydrogenation of *n*-octane to produce linear octenes and C8 aromatics.

2. Experimental

All the catalysts were prepared at a nominal concentration of 15% for V_2O_5 (to the total of the combined V_2O_5 and MgO). This is because a catalyst with this concentration has shown the better performance during the activation of *n*-octane [9].

2.1. Catalysts synthesis

Magnesium oxalate was prepared by a procedure similar to that reported in [9]. Thus, an aqueous solution of magnesium acetate (40 g in 700 ml) was heated to 50 °C. A hot aqueous solution of oxalic acid, which contained the stoichiometric amount needed to form MgC_2O_4 (25 g in 700 ml), was also heated to 50 °C and added to the acetate solution. The resultant mixture was heated and magnetically stirred for half an hour. The resultant solid (magnesium oxalate) was filtered off using a Buchner funnel. The precipitate so-obtained was washed thoroughly with cold and hot water and placed overnight in an oven operated at 110 °C. MgO was obtained by heating the magnesium oxalate under vacuum at 600 °C for 6 h and was designated MgO(1). In another approach, 15 g of a commercial MgO was placed in a 2000 ml round-bottomed flask that contained 1000 ml of water. This mixture was refluxed (with magnetic stirring) for 8 h. Using a Buchner funnel, the precipitate (magnesium hydroxide) was collected and placed overnight in an oven operated at 110 °C. The resultant $Mg(OH)_2$ was heated under vacuum at 600 °C for 6 h and the magnesium oxide so-obtained was designated MgO(2). Another part of the above prepared $Mg(OH)_2$ was heated in a furnace at 600 °C for 6 h and the resultant magnesium oxide was designated MgO(3).

The prepared magnesium oxides MgO(1), MgO(2), and MgO(3) were used to synthesized three VMgO catalysts, viz., VMgO(1), VMgO(2), and VMgO(3), respectively. The three catalysts were prepared by the wet impregnation method using the procedure that was outlined in [9]. Thus, the above prepared magnesium oxides were impregnated with a clear hot aqueous solution of NH_4VO_3 (greenish yellow in colour) that contained the amount of vanadium needed to give a nominal concentration of 15% for the V_2O_5 to the total weight of both V_2O_5 and MgO. As an example, for the catalyst VMgO(2), 2.3012 g of ammonium metavanadate was dissolved in 800 ml of water and heated at 60 °C till the vanadate was completely dissolved. The hot solution was then added to MgO (10.1045 g) and the resultant mixture was heated, while magnetically stirred, till a paste was formed. The resultant paste was then placed in an oven and left overnight at 110 °C. This catalyst was ground, thoroughly mixed, and calcined at 550 °C for 5 h. Temperature ramping during the calcination was about 1.5°/min. The same procedure was followed for the synthesis of VMgO(1) and VMgO(3) using MgO(1) and MgO(3), respectively.

2.2. Catalysts characterization

The elemental composition of the catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) using an Optima 5300 DV PerkinElmer Optical Emission Spectrometer. For the surface area measurements, catalysts samples were first degassed in a stream of nitrogen at 473 K for 24 h. The BET surface areas were then measured by nitrogen adsorption isotherms at 77 K using the standard multipoint method on a Micromeritics Gemini instrument. The pore volumes were also determined on this Micromeritics Gemini instrument. Powder X-ray diffraction patterns were recorded on a Philips PW1050 Diffractometer equipped with a graphite monochromator and operated at 40 kV and 40 mA. The source of radiation was Co Kα and all data were captured by a Sietronics 122D automated microprocessor. The average crystallite size was calculated by the Scherrer equation using the diffraction line at $2\theta = 50°$. The vanadium magic angle spinning nuclear magnetic resonance (^{51}V MAS NMR) spectra were recorded at 600 MHz on a Bruker Avance III 600 NMR Spectrometer fitted with a Bruker Solid State Probe. A cylindrical zirconia rotor, which contained the packed catalyst sample, was rotated at a speed of 12 kHz during the data acquisition. A pulse length of 2.5 μs and a pulse delay of 1 s were used. Scanning electron microscopy (SEM) images were obtained using a LEO 1450 Scanning Electron Microscope. Samples for these SEM images were coated with gold using a Polaron SC Sputter Coater. Energy-dispersive X-ray spectroscopy (EDX) was carried out using a Jeol JSM 6100 Scanning Electron Microscope equipped with a Bruker EDX Detector. Samples for the EDX were coated with carbon in a Jeol JEE-4C Vacuum Evaporator. Temperature-programmed reduction (TPR) experiments were performed on a Micromeritics 2900 AutoChem II Chemisorption Analyzer. Prior to the reduction, the catalyst (about 0.05 g) was pretreated by being heated under a stream of argon (30 ml/min) at 400 °C for 30 min and then cooled down to 80 °C under the same stream of argon. 5% H_2 in argon was then used as a reducing agent at a flow rate of 50 ml/min. Under these reducing conditions, the temperature was ramped up to 950 °C at a rate of 10°/min. To identify the resultant phases after reduction, powder XRD was carried out on the catalyst samples after the TPR experiments. NH_3-temperature-programmed desorption (NH_3-TPD) experiments were carried out using a Micromeritics 2900 AutoChem II Chemisorption Analyzer. To clean the catalyst's surface, about 0.02 g of the catalyst was first flushed at 350 °C with helium flowing at 20 ml/min for 30 min and the temperature was thereafter brought down to 80 °C. A 4.1% ammonia in helium mixture was then passed (20 ml/min) over the catalyst for 30 min. The system was flushed with helium (30 ml/min) for 30 min to remove the excess ammonia. The adsorbed ammonia was then stripped off by the same stream of helium (30 ml/min) and a temperature ramp of up to 900 °C (at 10°/min), and the desorption profiles were recorded.

2.3. Catalytic testing

The catalytic testing was carried out in a fixed bed continuous flow reactor that operated in a down flow mode. The reactor tube was stainless steel with an internal diameter of 10 mm and a length