



The effect of varying the metal ratio in a chromium molybdate catalysts for the oxidative dehydrogenation of *n*-octane



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ABSTRACT

Chromium molybdate catalysts with varying Cr/Mo ratios were synthesized by co-precipitation. The catalysts were characterized using XRD, Raman spectroscopy, TPR, BET surface area measurements, ICP-OES and HR-TEM. X-ray diffraction and Raman studies revealed that the dominant phase in the catalysts was Cr₂(MoO₄)₃. Furthermore, Raman spectroscopy showed that excess Mo and Cr exist as MoO₃ and Cr₂O₃ phases, respectively. The catalytic activation of *n*-octane was investigated from 350 to 550 °C, in a continuous flow fixed-bed reactor with the GHSV fixed at 4000 h⁻¹. Catalytic testing revealed that the conversion of *n*-octane and product selectivity varied with Cr/Mo ratio. At 6% isoconversion (350 °C), the stoichiometric catalyst, i.e. the catalyst with a Cr/Mo ratio of 0.67, produced octenes and carbon oxides as the major products with a selectivity of 51% and 49%, respectively.

1. Introduction

The conversion of light alkanes to their corresponding olefins has attracted much interest in recent years. Currently, olefins are produced via the steam cracking of naphtha and by the dehydrogenation of paraffins. However, these processes have several disadvantages, such as high-energy requirements, coke formation, selectivity control and thermodynamic limitations [1,2]. Recently, oxidative dehydrogenation (ODH) has been investigated as the alternative technology to produce olefins, mainly due to the potential to overcome the major technical problems associated with dehydrogenation [3–6]. Recent studies have shown that the introduction of oxygen moderates carbon deposition on the surface of a catalyst [7,8]. The oxidation of alkanes is known to occur through parallel and sequential oxidation steps, where alkenes are primary ODH products. Carbon oxides (namely CO and CO₂) can form by the secondary combustion of alkenes or through direct combustion of alkanes [9,10].

Mixed metal molybdates, such as bismuth molybdate and iron molybdate have been used in alkene oxidation and methanol oxidation respectively [11–18]. These molybdates are efficient as a redox catalyst, due to its various M=O bonds [19]. It was suggested that these materials are bi-functional in nature [20]. One component, i.e. the M=O bond, is responsible for the dissociation of molecular oxygen. The second component, i.e. the bridging oxygen (M–O–M), is responsible for chemisorption of the hydrocarbon. Subsequently, initiating the C–H

bond breaking and oxygen insertion [20–22]. In the case of bismuth molybdate as a catalyst for conversion of propylene to acrolein, it was proposed that propylene chemisorbed on the Bi–O site to form a surface allyl radical, further oxidized on a Mo–O site [23,24].

According to studies by Wachs et al. [20], who studied various metal molybdates for methanol oxidation, it was found that orthorhombic MoO₃ has saturated Mo atoms on the surface, in contrast to iron molybdate, which has incompletely coordinated surface structures. As a result, MoO₃ was less active towards methanol oxidation compared to iron molybdate [25]. It was also observed by Wachs et al. [17] that the surface metal concentration and Mo coordination influenced methanol conversion. Al-Zahrani et al. [26] have studied that the chromium oxides of different loadings ranging from 0.1 to 20 wt. % on gamma alumina were tested in propane ODH. At 450 °C, 10 wt. % loading exhibited propane conversion of 19%, where the gamma alumina support gave the best performance when compared to other supports such as MgO, TiO₂ and SiO₂. Same authors revealed that the nitrate precursor gave the best results compared to chromate precursors. Similarly, Jibril et al. [27] discovered that Cr-Mo oxide based catalyst supported on alumina showed that propane is oxidatively dehydrogenated to propene. However, CO appeared to be a secondary product produced from propene, whereas, CO₂ exhibited a finite selectivity at low propane conversion, thus suggesting that CO₂ mainly producing from propane. Tyagi et al. [28] reported that the counter metal ion (Cr³⁺) in the chromium molybdate lattice bonded with Mo⁶⁺ in the corners of

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tetrahedral coordinated MoO_4^{2-} units through an oxygen atom, which is chemically isostructural to iron molybdate and bismuth molybdate [29–31]. Furthermore, they revealed that the Cr/Mo ratio has a strong influence on the reducibility, where the lower reducibility leads to lower selectivity to carbon oxides [4,26,32].

In the present contribution, we have aimed to design a catalyst with varied chromium and molybdenum metal ratios. This has been the subject of much debate with the recent studies of the area concluding that the active phase is stoichiometric metal molybdate [17,33]. This study aims to add to this debate by critically analysing the nature of the surface and subsequently, the catalytically active sites.

2. Experimental

2.1. Catalyst synthesis

Catalysts with varying Cr/Mo ratio were prepared by the co-precipitation method. Suitable molar concentration solutions of ammonium heptamolybdate tetrahydrate ($(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, Sigma-Aldrich) and chromium nitrate ($\text{Cr}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, Sigma-Aldrich) were dissolved in 100 cm^3 double distilled water. Both the solutions were added dropwise to the round bottom flask, which is already contained 100 cm^3 double distilled water under continuous stirring. The mixture was maintained at $80\text{ }^\circ\text{C}$ and pH 5–5.5 by adding HNO_3 (1 M solution) or NH_4OH (1 M solution) as needed. After aging for 3 h, filtered the green precipitate, washed with water and dried at $110\text{ }^\circ\text{C}$ overnight. Furthermore, the precursor was calcined at $550\text{ }^\circ\text{C}$ for 6 h [16,34,35]. Bulk chromium and molybdenum oxides were prepared by the thermal decomposition of chromium oxide and molybdic acid, at $550\text{ }^\circ\text{C}$ for 6 h. The Cr/Mo molar ratio of 0.4, 0.5, 0.67, 0.9 and 1.3 were denoted as CM04, CM05, CM067, CM09 and CM13, respectively to easily identify the ratio for the labelled catalyst.

2.2. Catalyst characterization

The catalysts were characterized by various physical and chemical techniques. The phase composition was analyzed by powder X-ray diffraction, using a Bruker D8 Advance instrument with a copper radiation source of wavelength, 1.5406 nm and equipped with a Bruker VANTEC detector. The program used to control the instrument was Ddifrac plus XRD Commander Software. The catalysts were scanned a 2-theta value from 10° to 70° at 0.5 degrees per minute and the long focus line with a voltage and amperage of 40 kV and 40 mA respectively.

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed using a PerkinElmer Optical Emission Spectrometer Optima 5300 DV to determine the molar ratio of the two metals (i.e., chromium and molybdenum), where the sample (0.1 g) was digested using hot sulphuric acid. The calibration was done using 1000 ppm Cr and Mo standards (Fluka, RSA) with appropriate dilutions in the range from 0 to 100 ppm to determine the metal concentration in the catalysts.

Brunauer- Emmett-Teller (BET) surface area and pore volume studies were carried out in a Micromeritics TriStar II multi-point BET surface area analyzer. Samples ($\sim 0.2\text{ g}$) were degassed under a flow of nitrogen one hour at $90\text{ }^\circ\text{C}$, then one hour at $150\text{ }^\circ\text{C}$, subsequently degassed 12 h at $200\text{ }^\circ\text{C}$ using a Micromeritics flow prep 060 sample degas system. The surface area was calculated by using the standard BET multipoint method, relative pressure ratio p/p_0 values from 0.05 to 0.300 and adsorption branch of isotherm at p/p_0 of 0.95 for pore volume calculations.

The molecular structures of various metal oxide species in the chromium molybdate was analyzed using an Advantage 532 series Laser Raman spectrometer with Nuspec software. An argon ion laser line of 532 nm wavelength was used to excite the catalysts with a resolution of 1 cm^{-1} at room temperature.

Temperature programmed reduction (TPR) profiles were obtained

using a Micromeritics Autochem II 2920 chemisorption analyzer. Approximately, 0.05 g of the catalyst sample was placed in a U-shaped quartz tube using quartz wool to hold the catalyst particles inside. Prior to reduction, the catalysts were pretreated by heating to $400\text{ }^\circ\text{C}$ under a stream of helium (30 mL/min) for 30 min and the temperature was decreased to $80\text{ }^\circ\text{C}$ under the same stream of helium. The reduction experiments were carried out using 5 vol. % hydrogen in Argon as the reducing agent with a flow rate of 30 mL/min . At these conditions, the sample temperature was raised from the room temperature to $800\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C/min}$. The degree of reducibility was calculated using the amount of hydrogen utilized during reduction and relating that to the reducible metal oxides present, assuming total reduction. An example of the calculation using catalyst CM067 has been added to the supplementary information.

For high-resolution transmission electron microscopy (HR-TEM), ethanol was added to the fresh catalyst and sonicated for 10 min. The samples were coated on $200\text{ }\mu\text{m}$ mesh copper grid covering with a thin layer of formvar and dried under a flexi desk lamp to form holes in grids. Images were captured using a JEOL JEM2100 HR TEM instrument made by Joel, Japan. Electron source used in the instrument is a lanthanum hexaboride filament (LaB_6) at an acceleration voltage of 200 kV . Particle size measurements were done using iTEM and ImageJ software. The catalysts surface structure and morphologies were observed using a Zeiss Ultra Plus field emission gun scanning electron microscope (FEG-SEM) with a Smart SEM Software. Samples were placed on aluminum stubs using a double side carbon tape and they coated at $20\text{ }\mu\text{A}$ sputter current with gold for 30 s, by using Q150R series high vacuum Quorum sputter coater which is fully automated. The Aztec software was used for EDX analysis coupled to Oxford instruments where they act as a detector and X-ray source.

2.3. Catalytic testing

The gas phase reactions were carried out using a continuous flow fixed bed reactor functioning as down flow mode. A stainless-steel reactor tube with a 10 mm internal diameter and 300 mm in length was used to load the catalyst. All voids in the reactor tube filled with carborundum (40 grit, Polychem). 1 ml ($\sim 0.8200\text{ g}$) of the catalyst with a particle size between $1000\text{--}600\text{ }\mu\text{m}$, placed between two cotton wool plugs, where the vicinity of the hotspot of the reactor tube. All the reactions were carried out at the temperature range of $350\text{--}550\text{ }^\circ\text{C}$, at $50\text{ }^\circ\text{C}$ intervals. Carbon to oxygen molar ratio was adjusted using air, which is oxygen source and nitrogen as diluent inert gas and *n*-octane concentration in the gaseous mixture was 11% (v/v). The high precision isocratic pump (Lab Alliance Series-II) was used to deliver *n*-octane into the system and gases conveyed using air and nitrogen rotameters (AALBORG, USA). The reactor line temperature of $140\text{ }^\circ\text{C}$ was obtained using glass fiber heating tape. The liquid products and the unreacted octane were collected in a catch pot cooled to about $\sim 2\text{ }^\circ\text{C}$ and the volume of the gaseous components was measured by a wet gas flow meter (Ritter Drum-Type Gas Meter).

The product stream (both liquid and gases) from the reactor were analyzed by Shimadzu-2020 gas chromatograph (GC) with Restek 1-Pona capillary column (50 m length and $0.25\text{ }\mu\text{m}$ diameter), equipped with flame ionization detector (FID). The gases products were injected into a Perkin Elmer Clarus 400 GC with thermal conductivity detector (TCD) and Perkin Elmer Clarus 560 GC containing TCD for oxygen quantification, where they equipped with Supelco Corboxen capillary columns with different series 1010 and 5A respectively, and with dimensions ($30\text{ m} \times 0.53\text{ mm} \times 30\text{ }\mu\text{m}$). A Perkin Elmer Clarus 500 GC-MS was used to identify unknown products from the reaction.

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