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The oxidative dehydrogenation of propane over potassium-promoted molybdenum oxide/sol–gel zirconia catalysts

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Abstract

The effect of potassium loading on the structural and catalytic properties of MoO_x/ZrO_2 catalysts for oxidative dehydrogenation of propane was investigated. Catalysts have been prepared by modified sol–gel method, and they were characterized by nitrogen physisorption, XRD, FT-Raman spectroscopy, XPS and temperature-programmed reduction (TPR). Catalytic activity measurements have been carried out between 400 and 530 °C under atmospheric pressure. It was observed that potassium addition prevented crystalline $Zr(MoO_4)_2$ formation, suppressing the interaction of molybdenum oxide and zirconia phases, and it also favored the formation of three-dimensional molybdenum oxide and two-dimensional polymolybdates. Both propylene selectivity and yield were enhanced with a certain amount of potassium addition.

Keywords: Oxidative dehydrogenation; Molybdenum oxide; Zirconia; Sol–gel; Alkali promotion

1. Introduction

Conversion of lower alkanes by oxidative transformation to corresponding alkenes has gained importance in recent years [1,2]. Nowadays, propylene is produced by cracking of naphtha and gas oil, and by non-oxidative conversion of propane. On the other hand, the oxidative dehydrogenation (ODH) of propane provides an additional alternative production route for propylene. Furthermore, oxidative dehydrogenation reaction is quite exothermic and the energy requirement can be partially met by the combustion of abstracted hydrogen atoms. In addition, neither coking nor frequent regeneration problems occur. From thermodynamic point of view, up to 100% conversion is possible. However, allylic C–H bond of propylene is weaker than the secondary C–H bond of propane [3], and propylene selectivity is the main problem at high propane conversion levels. This in turn causes a handicap for acidic catalytic surfaces necessary for propane activation, because propylene desorption from surface is not fast enough and even worse it is adsorbed on other sites. In both cases it burns to CO_x while the initial selectivity of propylene is high [4]. Thus, studies on ODH of propane are concentrated on activation mechanism of propane, effect of oxygen type on product selectivity, and the effect of either reaction conditions or catalyst composition on the reaction mechanism [1].

A significant amount of work was carried out for the ODH of propane over molybdenum oxides and metal molybdates [4–11]. For example, Stern and Graselli [9] have determined that among the metal molybdates, nickel molybdate showed the highest ODH performance. An increase in the catalytic activity in the presence of MoO_3 was observed by Cadus et al. [7], Lezla et al. [8] and Miller et al. [12] for $MgMoO_4$ catalysts. But, they also mentioned that if the content of excess MoO_3 units on the surface is higher than a specific amount, activity decreases probably due to forma-

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tion of $Mg_2Mo_3O_{11}$ by the solid-state reactions. Meunier et al. [10] worked with molybdenum oxide-type catalysts with alumina, zirconia and titania supports. They found out that what type of MoO_x species is going to form is determined by the surface molybdenum density as well as the interaction between active component and support. These properties also affect the product selectivity on the ODH of propane [11,13]. Duhamel et al. [14] worked with MoO_3/Al_2O_3 catalysts and reported that hydroxyl groups on the surface of catalysts acted as hydrogen acceptors inhibiting CO_x formation. Chen et al. [15] reported that alkali addition to MoO_x/ZrO_2 catalysts reduced the turnover number, but increased the propylene selectivity. On the other hand, Watson and Ozkan [16] reported that alkali addition up to a certain level increased both propane conversion and propylene selectivity over MoO_3/TiO_2-SiO_2 catalysts prepared by sol–gel co-precipitation method.

Sol–gel method has been frequently employed for high-purity catalyst preparation during the last decade [17]. Some properties such as surface area, pore structure, distribution of active sites, and thermal stability which are the main parameters affecting the catalytic activity, can be controlled. These properties depend on several parameters such as the type of raw materials, solvents, acid/base ratio, amount of water, aging and drying, and calcination conditions [18].

In this work, we aimed to investigate the use of alkali-promoted MoO_x/ZrO_2 catalysts prepared by sol–gel method in ODH of propane. The effect of alkali addition on the structure of supporting oxide, the type of MoO_x units and their effect on the propylene yield and selectivity were investigated.

2. Experimental

2.1. Catalyst preparation

Catalysts with 11.5% (wt) MoO_3 content were prepared by sol–gel method. Zirconium (IV) propoxide (70% solution in propanol, Fluka), ethylacetoacetate (Merck), *i*-propanol (Merck), ammonium heptamolybdate (Merck), 25% aqueous ammonia solution (Carlo Erba), and KOH (Merck) were used as starting materials. In the first step of catalyst preparation, zirconium (IV) propoxide was added to *i*-propanol and ethylacethoacetate mixture under vigorous stirring to provide final alkoxide to solvent and ligand agent ratios of 1:3 and 1:2, respectively. Afterwards, ammonia solution, 0.5 M KOH, 0.25 M ammonium heptamolybdate solution and water were added dropwise for 30 min; the molar ratios of water and ammonia to alkoxide were 7:1 and 5:1, respectively. All gels were dried at 120 °C for 8 h and calcined in air at 540 °C for 3 h. K was added according to K/Mo molar ratios of 0, 0.05, 0.15, 0.25, 0.50, and the amount of K in the catalysts was indicated as K0 (K-free), K005, K015, K025, and K050 in tables and figures.

2.2. Catalysts characterization

Nitrogen physisorption measurements were carried out at −196 °C with 150 mg samples by Quantachrome Autosorb 1C after high-vacuum degassing of the catalysts at 300 °C. XRD patterns were obtained from Siemens D type diffractometer by using Cu Kα irradiation ($\lambda = 1.5404$ Å). Raman spectra were recorded using Nicolet Nexus FT-Raman Spectrometer equipped with an InGaAs detector. Raman scattering was excited with a Nd-YAG laser operated between 150 and 1200 cm^{-1} region with 4 cm^{-1} resolution under dehydrated conditions. XP spectroscopy measurements were performed in an ultra high vacuum set-up equipped with a Gammadata-Scienta SES 2002 analyzer with various entrance slits. Monochromatised Al Kα (1486.6 eV; 14 kV; 55 mA) was used as incident radiation. XP spectra were recorded in fixed transmission mode. The energy resolution was determined as 0.5 and 1.5 eV, respectively. Zr $3d_{5/2}$ structure was used as internal standard at 182.2 eV of binding energy. Temperature-programmed reduction (TPR) experiments were carried out with 150 mg samples of 250–355 μm size placed in a quartz micro reactor under atmospheric pressure. Reactor was heated up to 850 °C at a rate of 10 °C/min under H_2/Ar flow of 50 mL/min with a content of 4.7% H_2. Water was eliminated in a cold trap and hydrogen was determined by an on-line Hydros 100 TCD system.

2.3. Catalytic measurements

The ODH reaction of propane was carried out with a fixed-bed U-type quartz reactor. Propane (99.95%, Linde), oxygen (99.99%, Messer-Griesheim) and neon (99.99%, Messer-Griesheim) were fed at atmospheric pressure with the composition of 8:8:59, respectively, to provide a total flow rate of 75 ml/min. Uniform temperature distribution was provided by a furnace with fluidized bed sand bath. Catalysts of 250–355 μm size were diluted with quartz chips at a weight ratio of 1:1 to provide a 2 g catalysts charge. The dead volume of the reactor was filled with quartz chips in order to avoid homogenous reactions. Satochrome on-line GC system with TCD and FID detectors, molecular sieve 5A column for Ne, O_2 and CO, and PoraPLOT Q column for hydrocarbons, CO_2 and H_2O were used for the analysis.

3. Results

3.1. Catalysts characterization

Nitrogen physisorption data of molybdenum oxide catalysts are given in Table 1. Although alkali addition had no significant effect on the surface areas, pore volume/diameter values showed distinct maximum for K015.

The diffractograms of K0 and K050, which show maximum difference, are given in Fig. 1. In the case of K050 catalyst, the most intense peak indicating the formation of