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Propane oxidative dehydrogenation over V-containing mixed oxides derived from decavanadate-exchanged ZnAl–layered double hydroxides prepared by a sol–gel method

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ABSTRACT

The catalytic properties of ZnAlVO mixed oxides derived from decavanadate-exchanged ZnAl–layered double hydroxide (LDH) precursors prepared by a sol–gel method (ZnAlVO–LDH*x*,*y*) were investigated in the oxidative dehydrogenation of propane and compared with those of supported catalysts obtained by conventional impregnation of NH_4VO_3 on ZnO (ZnVO-I,*y*) and ZnAlO mixed oxide (ZnAlVO-I,*y*) supports. The effects of composition and calcination time on the catalytic behavior were particularly examined. Higher propane conversions were achieved at higher vanadium content and calcination time of the precursors. The LDH-derived catalysts were the most active ones in all the temperature range studied (300–425 °C). The order of activity for propane conversion for the different catalyst families varies as ZnAlVO–LDH*x*,*y* > ZnAlVO-I > ZnVO-I and follows the strength of the Lewis and Brønsted acid sites determined by monitoring of pyridine adsorption by Fourier transform infrared spectroscopy, whereas the propene selectivities are close together in agreement with the similar densities of basic sites determined by CO_2–temperature-programmed desorption measurements. It was indeed established that the acidity, rather than the nature of the crystalline phases, the reducibility, or the specific surface area of the samples, governs the catalytic activity.

1. Introduction

Catalytic oxidative dehydrogenation (ODH) of light alkanes and particularly of propane is an interesting route to alkenes, which are useful intermediates for the petrochemical and energy industries [1].

A great variety of catalysts with various compositions have been used in the production of propene from propane by ODH [2–8]. Among them, vanadium-containing catalysts are probably the most broadly studied [1,9–11]. Vanadia dispersed on a variety of supports (SiO_2, TiO_2, ZrO_2, Al_2O_3 and, more recently, graphene) have been indeed reported as catalysts for ODH processes [1,10,12–14]. VMgO mixed oxides, in particular, are among the most active and selective catalysts for the ODH of propane [5,15–19]. The catalytic activity of these materials is closely related to the V content and the composition of the vanadium oxide phase, which can be tuned during preparation, whereas the

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selectivity depends on the nature of the vanadium species at the catalyst surface. Consequently, the development of effective catalysts for propane ODH strongly depends on the preparation method [9,11].

Various methods can be used to prepare metallic vanadates [9,11]. An attractive route to prepare vanadium mixed oxides with highly dispersed vanadium species is the thermal decomposition of layered double hydroxide (LDH) precursors containing the cations to be present in the final mixed oxide materials.

LDH belongs to a large class of synthetic 2D nanostructured anionic clays, having the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}A^{n-}_{x/n}\cdot nH_2O$, where M^{II} and M^{III} stand for divalent and trivalent cations, respectively, and A^{n-} is a charge-balancing anion. The structure is composed of positively charged brucite-like $Mg(OH)_2$ layers in which a fraction of divalent cations is partially substituted by trivalent cations introducing a positive charge balanced by exchangeable anions located in the interlayer region, where crystallization water molecules are also found [20].

LDHs provide high versatility in their composition because of the different nature of the metallic layer components and the balancing anions. This makes them very interesting mixed oxide catalyst precursors. Transition metal-containing LDH-derived mixed oxides with tuned redox and acid–base properties are remarkable oxidation catalysts [21], and those containing vanadium show particular activities and selectivities in the ODH reaction. For instance, Rives et al. [18] have reported the preparation of VMgAlO mixed oxides by calcination of a vanadate-exchanged MgAl–LDH obtained by coprecipitation of the precursor metallic salts. The activity of these LDH-derived catalysts was higher compared with that of the mixed oxides obtained by the impregnation of a MgO support with an aqueous vanadate salt solution.

Compared with the VMgO system, the properties of the VZnO mixed oxides in ODH have been studied to a lesser extent. To the best of our knowledge, no studies regarding VZnO mixed oxides obtained from anion-exchanged LDH precursors have been reported so far, although the substitution of Zn^{2+} for Mg^{2+} leads to different acid–base properties largely involved in the reaction.

Herein, we report the catalytic performance in propane ODH of a VZnAlO mixed oxide obtained via the calcination of a decavanadate-exchanged ZnAl–LDH. The ZnAl–LDH with nitrate as the interlayer anion was first prepared using the sol–gel method, then submitted to exchange with the decavanadate anion, and finally calcined to yield the mixed oxide catalyst. The catalytic performance of these materials was evaluated in propane ODH and compared with that of the VZn(Al)O catalysts prepared by conventional impregnation of either ZnO or ZnAlO mixed oxide supports with a decavanadate aqueous solution. By using these two methods, catalysts with different phase composition, acid–base properties, and reducibilities were obtained, as revealed by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy monitoring of pyridine adsorption, temperature-programmed desorption (TPD) of CO_2, and temperature-programmed reduction (TPR) experiments, respectively, which ultimately led to the different catalytic behavior in propane ODH.

2. Experimental section

2.1. Preparation of the catalysts

All chemicals were from Fluka and used without any further purification. Nitrate-containing ZnAl–LDH with nominal Zn/Al molar ratios of 2 or 3 were prepared using the sol–gel method as follows: 0.05 mol of zinc acetylacetonate $Zn(C_5H_7O_2)_2$ (98%) was dissolved under reflux (at 80 °C) in 100 mL of ethanol with vigorous stirring, and then 8.5 mL of HNO_3 (60%) was added. A second solution containing a suitable amount of aluminum acetylacetonate $Al(C_5H_7O_2)_3$ (99%) (0.025 or 0.0167 mol) in 80 mL of a 1:1 acetone/ethanol mixture was then added dropwise to the former one under reflux at 80 °C with constant stirring. The pH was adjusted to 10 by addition of aqueous NH_3 (33%). The suspension was further refluxed at 80 °C for 24 h and the gel formed was washed several times with ethanol, then with water at 80 °C to remove the unreacted organosalts, centrifuged, and dried overnight at 80 °C, yielding the samples ZnAl–N*x* differing in the nominal Zn/Al molar ratio ($x = 2$ or 3).

The polyoxovanadate-containing samples were prepared by ion exchange from parent nitrate-containing ZnAl–LDH samples. One hundred milliliters of an aqueous solution of NH_4VO_3 (Panreac, 99%) was added to the gel suspension of precursors ZnAl–N2 or ZnAl–N3. The amount of NH_4VO_3 added was that necessary to yield a concentration of $[V_{10}O_{28}]^{6-}$ species 50% larger than that required to balance the positive charge of the brucite-type layer of the LDH. The pH of the mixture was adjusted to 4.5 by slow addition of aqueous HNO_3 (30%), and the solution was stirred for 48 h under nitrogen. The solids were finally filtered, washed with decarbonated water, and dried overnight at 80 °C. The samples were named as ZnAl–V*x*.

The LDH-derived mixed oxide catalysts were prepared by the calcination of the dried ZnAl–V*x* precursors in air at 500 °C for 5 or 24 h, at a heating rate of 10 °C/min, yielding the mixed oxides ZnAlVO–LDH*x*,*y* (y = calcination time in hours). Thermal analyses have shown that this calcination temperature is high enough to yield thermodynamically stable phases.

For the sake of comparison, two additional samples were prepared by conventional wet impregnation of either commercial ZnO (Panreac, 99%; specific surface area = 10 $m^2\ g^{-1}$) or ZnAl–N2 LDH calcined at 500 °C with an aqueous solution containing the required amount of NH_4VO_3 necessary to reach a V/(Zn + Al) molar ratio of ca. 0.6. After impregnation, the solids were filtered, dried overnight at 80 °C, and finally calcined at 500 °C for 5 or 24 h. The dried samples were named as ZnV-I and ZnAlV-I, respectively. The calcined catalysts were named as ZnVO-I,*y* and ZnAlVO-I,*y*, respectively (where I stands for “impregnation” and y is the calcination time in hours).

2.2. Characterization of the catalysts

Zn, Al, and V element chemical analyses were carried out by atomic absorption spectroscopy using an ELL-240 Mark 2 instrument after dissolving the dried samples in HNO_3.

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