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Oxidative dehydrogenation of propane over cobalt-containing mixed oxides obtained from LDH precursors

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ABSTRACT

Co(x)MgAlO mixed oxide catalysts with cobalt content in the range from 1 to 20 at.%, were prepared by calcination of layered double hydroxide (LDH) precursors at 1023 K. Their characterization was performed using X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), N_2 adsorption, Raman and photoluminescence spectroscopies, TG–DTG and H_2-TPR techniques. The catalytic activities were evaluated in the oxidative dehydrogenation of propane in the temperature range from 723 to 873 K. For all the catalysts the conversion increased when the reaction temperature increased, while the propene selectivity decreased continuously to the benefit of CO_x for Co(20)MgAlO and Co(10)MgAlO catalysts and of cracking products for the other cobalt-containing catalysts. In all the temperature range studied, the catalytic activity increased with increasing the cobalt content in the catalyst in line with the increase of reducibility. The best yields in propene of about 10% were obtained with Co(5)MgAlO and Co(7)MgAlO catalysts for the reaction performed at 873 K. Besides, a comparison of the behavior of Co(3)MgAlO and Co(7)MgAlO catalysts at 823 K showed that, at isoconversion, the propene selectivity was higher for the sample with lower cobalt content. The well-dispersed cobalt species with tetrahedral coordination played a main role in the oxidative dehydrogenation reaction of propane into propene. When the propane-to-oxygen molar ratio was increased from 1 to 4, the conversion decreased while propene selectivity increased continuously and the best propene yields were obtained for a propane-to-oxygen molar ratio of 1.

1. Introduction

A high market demand for propene has been observed in the recent years. The catalytic oxidative dehydrogenation (ODH) of propane into propene has been widely investigated as an alternative to the most largely used pyrolysis processes. A wide variety of catalytic systems have been proposed for this reaction, the most studied being based on vanadium [1–12] or molybdenum [13–21]. Though scarcely studied, other transition metal-based catalytic materials could exhibit comparable catalytic efficiencies [22–31]. Thus, Al-Zahrani et al. [22] showed that Cr, Mn, Zr or Ni oxides supported on γ-Al_2O_3 were reactive in this reaction. The Cr–Al–O mixed oxide led to the higher propene yield (~9%) at 723 K and was more active and selective than a Mo–Al–O mixed oxide catalyst studied as a reference. Jibril et al. [23] studied Kieselguhr-supported transition metal-oxides (metal cations being Cr, Mn, Co, Ni, V and Mo) and showed that Mn- and Co-based catalysts exhibited the maximum propene yields: ~5% and ~4%, respectively, for the reaction at 773 K. Ge et al. [24] investigated lithium salts-promoted Portland cement-supported MnO_x catalysts and showed that they give more than 60% alkane conversion and 80% olefins selectivity at 923 K for ODH of ethane and propane to ethylene and propylene, respectively. Jalowiecki-Duhamel et al. [25] studied Ce–M–O mixed oxides (M = Ni, Cu, Co, Cr, or Zn) and showed that Ce–Ni–O was the most efficient catalyst yielding 5.4% of propene at 648 K. Wang et al. [26] studied the ODH of ethane and propane over LiCl-promoted NiO/sulfated zirconia catalysts. They were very active and selective in both reactions leading to 73.5% ethylene yield at 923 K and 10.4% propylene yield at 873 K, respectively. More recently, Wu et al. [27] showed that TiO_2-doped nickel oxide yielded 12% propene from propane at 573 K.

Cobalt supported catalysts also shown high efficiency in ODH of light alkanes. A Co(7.6 wt.%)/TiO_2 catalyst has been found active in the ODH of ethane with an ethylene yield of 13.2% at 823 K [28].

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