

Transition metal-containing mixed oxides catalysts derived from LDH precursors for propane oxidative dehydrogenation

Gheorghita Mitran¹, Nathalie Tanchoux², Adriana Urda¹, François Fajula², Didier Tichit² and Ioan-Cezar Marcu^{1*}

¹University of Bucharest, Faculty of Chemistry, Bucharest, 030018, Romania

²Institut Charles Gerhardt, Matériaux Avancés pour la Catalyse et la Santé (MACS), Montpellier, 34296, France

*e-mail address: ioancezar.marcu@g.unibuc.ro

Introduction

The oxidative dehydrogenation of propane is an attractive alternative to the conventional catalytic or thermal dehydrogenation, for obtaining propylene, a largely used starting compound in chemical industry. Nevertheless, the catalytic oxidative dehydrogenation of propane with high yields remains a challenge [1]. In this work the catalytic activity of transition metal-based mixed oxides obtained from LDH precursors have been compared in this reaction

Experimental

Transition metal-based mixed oxides, noted MMgAlO with M = Mn, Fe, Co, Ni, Cu, or Zn, were prepared by thermal decomposition of layered double hydroxide (LDH) precursors. The transition metal content, as atomic percent with respect to the cations, was kept at 5 %. XRD, N₂ adsorption, EDX, TG-DTG and H₂-TPR experiments were used to characterize the catalysts. Catalytic tests were performed in a fixed bed quartz tube down-flow reactor using a propane-air mixture in the temperature range from 450 to 600°C.

Results/Discussion

The XRD analysis showed that the precursors exhibit the characteristic structure of LDH materials and the final catalysts that of the Mg(Al)O mixed oxides with the periclase-like structure. In addition, MnAl₂O₄, FeAl₂O₄ and Fe₂O₃ and ZnAl₂O₄ phases were also detected for MnMgAlO, FeMgAlO and ZnMgAlO, respectively. The specific surface areas of the MMgAlO catalysts were in the range of 134 – 172 m²/g. Two domains separated at ca. 350°C were observed in the TPR profiles. Reductions in the low temperature domain (< 350°C) can be assigned to metal oxide particles weakly interacting with the support. The peaks in the high

temperature domain (350°C – 800°C) likely accounted for the reduction of aluminate mixed oxide phases in agreement with the composition of the samples.

The highest propene yields were obtained in all cases above 550°C where the catalysts can be ranked in the order: CoMgAlO > MnMgAlO > NiMgAlO > ZnMgAlO > FeMgAlO > CuMgAlO. The selectivity vs. conversion curves for CoMgAlO, MnMgAlO and NiMgAlO catalysts at 550°C and a propane-to-oxygen molar ratio of 2 are presented in Figure 1. For the reaction over Co- and Mn-based systems, the extrapolation to zero conversion showed that propene is the only primary product. These results suggested that, in these cases, total oxidation products (CO_x) were formed rather by oxidation of propene than by direct oxidation of propane. No close correlation could be observed between the reducibility and the catalytic behaviour of the samples suggesting that the reducibility is not the only determining parameter.

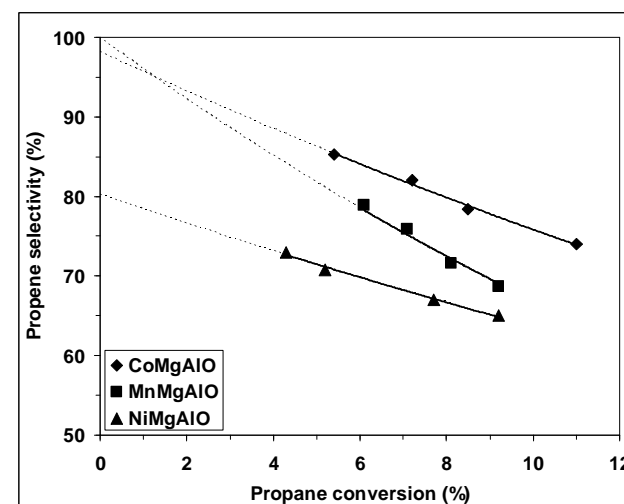


Figure 1. Selectivity vs. conversion curves for MnMgAlO, CoMgAlO and NiMgAlO catalysts.

Because of its highest performance, the Co-based system has been further studied. A series of Co(x)MgAlO mixed oxides, with x ranging from 1 to 20 %, has been prepared using the same method, characterized and tested in the oxidative dehydrogenation of propane. The propane conversion increased continuously with increasing the Co content in the catalyst, while the propene selectivity passed through a maximum for Co(3)MgAlO.

References

1. F. Cavani, N. Ballarini and A. Cericola, *Catal. Today*, **127**, 113 (2007).