INFLUENCE OF REDOX PROPERTIES ON THE ACTIVITY OF IRON OXIDE CATALYSTS IN DEHYDROGENATION OF PROPANE WITH CO₂

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Abstract

Different Fe-containing catalysts (pure Fe₂O₃, Fe₂O₃ supported on active carbon or γ-Al₂O₃, and hydrotalcite-derived Mg-Fe oxides) were examined in the dehydrogenation of propane performed in an Ar or CO₂ atmosphere at 873 K. A promoting effect of carbon dioxide was found for the Fe₂O₃ and Fe₂O₃/AC samples. The catalytic results are discussed in terms of redox properties of the catalysts, determined by temperature-programmed reduction (TPR).

Keywords: Iron(III) oxide catalysts, dehydrogenation of propane, CO₂

INTRODUCTION

Growing demand of the chemical industry for light paraffins requires alternative methods of alkenes production. The easiest route of obtaining alkenes is dehydrogenation of the corresponding alkanes. However, alkane dehydrogenation is a highly endothermic reaction, which requires a supply of heat and is thermodynamically limited [1]. High temperatures, at which the process should be performed, favor side reactions (e.g. cracking), resulting in a low selectivity towards valuable olefins [2]. This effect limits significantly the application of direct dehydrogenation method on commercial scale.

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Due to the above reasons, reactions of alkanes with oxidizing agents, so-called oxidative dehydrogenations, are very attractive alternatives in the synthesis of alkenes. Using an oxidant changes the thermodynamic and energetic effects of the dehydrogenation process. Oxidative dehydrogenation is practically irreversible and exothermic, and can therefore be carried out at low temperatures [3]. A crucial factor influencing the selectivity of the process is, however, the choice of a suitable oxidizing agent. Gaseous oxygen, which is the most widely used oxidant, causes burning of considerable amounts of alkanes to COx due to very strong reactivity. Recently, the use of CO2 as an oxidizing agent has been studied in dehydrogenation of many hydrocarbons, viz. ethane [4-6], isobutane [7], ethylbenzene [8-11].

Taking into account the necessity for utilization of CO2, which has been recognized as one of the major greenhouse gases, and the promising results obtained in oxidative dehydrogenation of ethane and ethylbenzene with CO2, conversion of propane into propene in the presence of carbon dioxide was also proposed. Up till now few papers concerning this reaction have appeared in the open literature. The attention has been mainly focused on using Cr2O3 [12-14], lanthanum vanadate (LaVO4) [15] as well as Ga2O3 [14] as catalysts for dehydrogenation of propane in the presence of CO2. However, it seems that investigations should be directed on the application of iron oxide-based catalysts, which have been found to be very active in oxidative dehydrogenation of other hydrocarbons [7-11].

The present paper reports some results of catalytic performance of unsupported and supported iron(III) oxide catalysts in oxidation of propane to propene in the presence of CO2. Using different types of support enabled to determine the influence of chemical environment of Fe3+ cations in oxide matrix on the catalytic activity of Fe-rich catalysts.

### EXPERIMENTAL

#### Catalysts preparation

Bulk Fe2O3 catalyst was obtained by thermal decomposition of Fe(NO3)3·9H2O at 923 K. The Fe2O3/Al2O3 and Fe2O3/AC catalysts were prepared by the impregnation method using an aqueous solution of iron(III) nitrate. In the case of the Fe2O3/Al2O3 sample the solution of Fe(NO3)3·9H2O was mixed with the support (γ-Al2O3), followed by evaporation under constant stirring and then calcination at 923 K for 3 h in air. The intended content of Fe2O3 in the Fe2O3/Al2O3 catalyst was 5.0 wt.%. Fe2O3 (7.1 wt.%) supported on active carbon (AC) was synthesized using the incipient wetness technique, followed by drying at 453 K for 2 h. Prior to the impregnation commercial carbon (Chemviron-Carbon GmbH) was activated with 90% HNO3 at 363 K for 1 h.