Modified by MgO Silica Gels and Aluminium Oxide as Active Acid-Base Catalysts for Oxidative Dehydrogenation of Ethylbenzene

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Introduction

The investigation of the catalytic properties of γ-Al_2O_3 and SiO_2 in the reaction of the oxidative dehydrogenation (OD) of ethylbenzene (EB) has shown that the treatment of γ-Al_2O_3 by the different acids (H_3BO_3, H_3PO_4) increases an activity of the catalyst while alkaline additives, on the contrary, decreases it [1]. In the case of silica gels the introduction of calcium oxide in the small amounts increases SiO_2 activity in OD of EB.

The aim of the present paper is a study of the influence of magnesium and/or phosphorus oxides concentrations on the activity of silica gels possessing by the different texture characteristics and aluminium oxide undergone to calcining at different temperatures.

Materials and methods

Catalysts were prepared by impregnation of SiO_2 with the different texture characteristics and $AlO(OH)\cdot xH_2O$ of boehmite type by the aqueous solution of magnesium nitrate and/or phosphoric acid. Contents of MgO and phosphorus in the composition of the catalyst were 2-10 mol.% and 5 wt.%, respectively. The samples were dried at 100-110^{0}C for 4-5 hours. Catalysts were characterized by DTA/TG and IR-spectroscopy. The texture characteristics of the samples were determined according to isotherms of methanol adsorption and by chromatographic method according to heat desorption of nitrogen.

The catalytic reaction has been carried out on a flow apparatus with the fixed bed of catalysts at 500^{0}C, ratio EB:air = 1:6 mol/mol, LHSV = 0.5 h^{-1}. Before tests, catalysts have been activated in air flow at 500-520^{0}C for 3 hours. The reaction products were analyzed by chromatographic method.

Results and discussion

Activity of the initial silica gels with the different texture characteristics rises with increasing of average pores radius (ř) from 1.1 to 7.0 nm. At 500^{0}C ethylbenzene conversion increases from 23.3 to 47.0%, while styrene yield increases from 18.5 to 36.3% [2]. Modification of silica gels by MgO increases activity of silica gels and it is appreciably shown in the case of macroporous SiO_2 (Fig.1). The sizes of silica gel pores influence also on a duration of the initial reaction period during of which styrene yield is increased and then stabilized (Fig.2). At OD of EB over aluminium oxide EB conversion at 500^{0}C is 51.0% at selectivity on styrene 84.0%. Influence of MgO on activity of aluminium oxide depends on preliminary calcining temperature of $AlO(OH)\cdot xH_2O$. Impregnation of $AlO(OH)\cdot xH_2O$ calcined at 550^{0}C for 5 hours by magnesium nitrate solution noticeably does not increase activity of the catalyst while at high concentrations of MgO decreases it. Promoting effect of

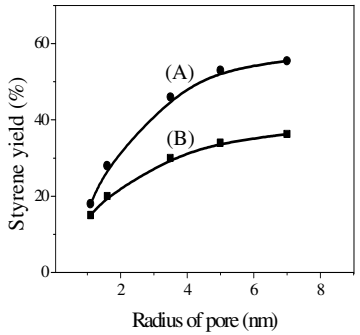

Figure 1. The dependence of styrene yield on average silica gels pores radius
A) 5% MgO/SiO_2; B) SiO_2

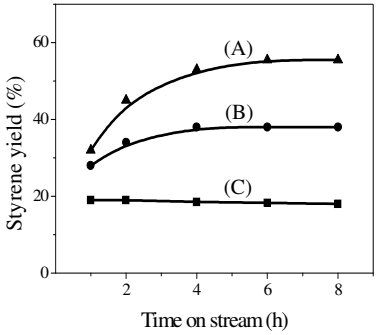

Figure 2. The dependence of styrene yield on TOS over 5% MgO/SiO_2
A) ř = 7.0 nm; B) ř = 3.5 nm; C) ř = 1.1 nm

MgO is shown at impregnation of $AlO(OH)\cdot xH_2O$ undergone only to drying at temperatures below 150^{0}C. In this case the extremal dependence of styrene yield on MgO content in a composition of the catalyst is observed, maximum of which is equal to 4% MgO. EB conversion over this sample is 64.0%, selectivity on styrene is 87.0%. It appears that after $AlO(OH)\cdot xH_2O$ calcining at high temperatures the changes in texture structure of aluminium oxide occur that results in the change of the interaction nature of magnesium nitrate with aluminium oxide.

Modification of MgO/γ-Al_2O_3 by phosphoric acid leads to increasing of EB conversion up to 69.0% and selectivity to 89.0%. Taking into account that at initial period of the reaction formation and accumulation of carbon deposits (CD) occurs over the catalyst surface and in stationary period OD of EB takes place over the catalytic system CD/catalyst, it can be supposed that the purposeful and balanced action of the modifiers of acid and base nature favours the formation of more active catalytic system. Moreover a maximal yield of styrene over such the catalytic systems is observed at optimal CD quantity. The modifiers of acid and base nature in an optimal ratio exert a regulating influence on CD amount and thereby promote the achievement of higher indexes of a process as compared with the initial oxides of silicon and aluminium. This is confirmed by DTA/TG studies of the catalysts of the different composition coked in the reaction conditions.

Thus the composition, texture characteristics and acid-base properties of the catalysts on the basis of silica gels and aluminium oxide exert an important influence on forming and regulating of the quantity of CD which together with the catalyst are the operating catalytic system in OD of EB.

References

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