

OXIDATIVE DEHYDROGENATION OF n-BUTANE OVER $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ AND $\text{Cr}_2\text{O}_3/\text{SiO}_2$ CATALYSTS

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Five samples of Cr_2O_3 (5, 8, 10, 12 and 15 wt.%) supported on $\gamma\text{-Al}_2\text{O}_3$ and four samples of the same oxide (4, 6, 8 and 10 wt.%) supported on SiO_2 as well as $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts modified by CaO (1.0, 1.5, 3.0 and 4.5wt.%) have been prepared and studied. Physico-chemical characteristics of the studied catalysts were determined by methods: BET, XRD, TPR, Hydrogen Titration and Ammonia Adsorption. Activity of the catalysts was investigated in the reaction of oxidehydrogenation (ODH) of n-butane at different temperatures and values of mol ratio $\text{CO}_2/\text{n-butane}$ from 1 to 4 in a microflow reactor. The optimal temperature for catalyst calcination has been found to be at the range 600 - 625°C. For $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts the sample with 10wt. % Cr_2O_3 gave the highest activity at 550°C and mol ratio $\text{CO}_2/\text{n-butane}$ of 2. For $\text{Cr}_2\text{O}_3/\text{SiO}_2$ catalysts the sample with 8 wt.% Cr_2O_3 gave the highest activity at 500°C and the same mol ratio of $\text{CO}_2/\text{n-butane}$. Both the systems $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ and $\text{Cr}_2\text{O}_3/\text{SiO}_2$ have been found to express high activity in the studied reaction in the presence of CO_2 , but Cr_2O_3 on $\gamma\text{-Al}_2\text{O}_3$ has been shown to be more suitable carrier for giving effective catalysts in the reaction. The factors defining the activity and selectivity in this reaction are volume velocity of the feed, the ratio of $\text{CO}_2/\text{n-butane}$ and the concentration of chromium oxide. Also the acidity of carriers must be at an appropriate level.

Addition of CaO to $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ samples gave some interesting results. From the results of XRD and TPR studies it seems that the interaction between chromium oxide and calcium oxide led to an enrichment of active centers Cr^{5+} . Also it has been shown that CaO probably is a stabilizing factor for $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts in keeping the activity and selectivity at higher temperatures (up to 625°C) due to the presence of several formations between this oxide and alumina such as $\text{CaO}\cdot 6\text{Al}_2\text{O}_3$, $\text{CaO}\cdot\text{Al}_2\text{O}_3$, $5\text{CaO}\cdot 3\text{Al}_2\text{O}_3$. Besides it has been indicated that this oxide reduced the acidity of alumina that was a reason of the activity enhancement. The optimal content of CaO for promoted catalysts is 3 wt.%. With this content of CaO at 625°C and mol ratio $\text{CO}_2/\text{n-butane}$ of 2 the conversion of n-butane, selectivity and efficiency in butene formation have been found to depend on the regime (temperature and time) of catalyst reduction. The

sample, calcined at 625°C and reduced at 300°C, gave higher selectivity but lower efficiency (lower activity), compared with the sample, reduced at 480°C. Also the duration of catalyst reduction is seems to play some role in defining the values of its activity and selectivity.