



Study the effect of the interaction of reactant-catalyst activation and deactivation of Ni, ReOx / Al₂O₃ catalyst in the process of methane into benzene dehydrocyclohexamerization

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Abstract The effect of reactant–catalyst (R–C) interaction on the activation and deactivation of a Ni, ReOx/Al₂O₃ catalyst during the dehydrocyclohexamerization (DHCH) of methane to benzene has been studied. The R–C interaction involves partial reduction of the catalyst and the buildup of at least two forms of carbon deposit. It has been found that the catalyst activation time shortens with an increase in the amount of carbon deposit remaining after treatment with air. It has been suggested that the catalyst deactivation during the reaction is associated with a decrease in the concentration of bound oxygen.

Keywords Reduction, Chromium(VI), Kinetics, Thermodynamic, Dissolved organic matter

Introduction

The catalytic activation of methane aimed to involve it in processes for the manufacturing of valuable hydrocarbons is of great practical importance, and its successful implementation is unachievable without theoretical research in this area. Unlike the case of Bragin *et al* [1] who conducted methane aromatization in the pulsed mode, a nonoxidative catalytic conversion of methane to benzene under actual catalysis conditions was first accomplished on monometallic and bimetallic alumina catalysts containing 0.3–1.0 wt % Ni, Co, Pt (M), and Re, conventionally named methane DHCH catalysts [2–6]; later, the conversion of methane to benzene and other aromatic hydrocarbons were carried out on MoOx/HZSM-5 and similar systems [7–10]. The formation of an active catalyst is closely related to the reactant–catalyst interaction. This paper is devoted to investigation of the reactant–catalyst interaction on the methane dehydrocyclohexamerization process over M,ReOx/Al₂O₃ catalysts.

Experimental

The object of study was the Ni, ReOx/Al₂O₃ catalyst prepared as in [2]. The reaction was conducted in a catalytic fixed-bed quartz reactor at atmospheric pressure and a temperature of 923 K. The reaction products were analyzed on a gas chromatograph "AutoSystem XL" Perkin Elmer.

Results and Discussion

Contacting methane with the unreduced Ni, ReOx/Al₂O₃ catalyst subjected to standard pretreatment with air (923 K, 1h) leads to the selective formation of benzene (Table 1). This process is accompanied by hydrogen evolution. As is seen from Fig. 1, the reaction is preceded by catalyst activation beginning from the 5th min to 15–20th min, and the



benzene formation rate increases from zero to its maximum value (15×10^{17} C_6H_6 molecule $\text{s}^{-1}\text{g}^{-1}$ cat) and remains at this level until the ~40–45th min of the experiment. The onset time of the decline in the yield of benzene from 14 to 13.5×10^{17} C_6H_6 molecule $\text{s}^{-1}\text{g}^{-1}$ cat (45min of experiment) was taken as the beginning of catalyst deactivation.

Table 1: Methane conversion on Ni, $\text{ReOx}/\text{Al}_2\text{O}_3$; $T = 923\text{K}$, $\text{GHSV} = 1450 \text{h}^{-1}$

Time, min	Conversion, %		Selectivity % C		
	CH_4	O_{bond}^*	C_6H_6	CO_2	C
3	28.0	60.0	-	96	4.0
5	20.0	71.0	8.0	17	75.0
10	18.2	76.0	68	0.0	32.0
15	18.7	78.0	75	0.0	25.0
20	17.9	-	77	0.0	23.0
30	15.8	80.0	80	0.0	20
40	13.4	81.5	87.5	0.0	13.0
60	11.5	85	93	0.0	6.0

* Oxygen in the catalyst composition

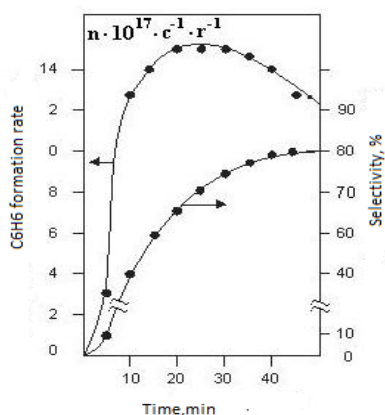


Figure 1: Dependence of the (1) rate and (2) formation selectivity of C_6H_6 formation on the time of the experimental run

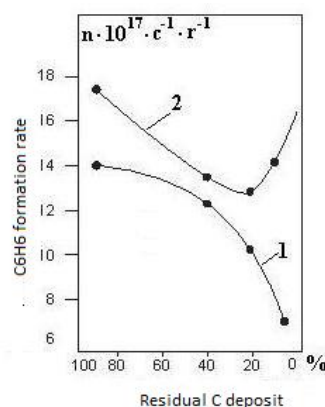


Figure 2: Dependence of the benzene rate upon the residual amount of carbon deposits on the catalyst: (1) the initial rate corresponding to 3 min on stream, and (2) the maximum rate corresponding to the 20th min of the run

The data presented above shows that the decline in the catalyst activity with the on_stream time is not associated with the buildup of carbon deposits on the catalyst surface; rather, this is a result of the decrease in the concentration of bound oxygen. Indeed, the short_term treatment of the deactivated catalyst with air (over 5 min, Fig. 2) on one hand eliminates the effect of catalyst activation due to slight burning out of the carbon deposit forms and, on the other hand, enhances the activity of the sample by increasing the concentration of $[\text{Ni}-\text{O}=\text{ReOx}]$ centers responsible for the formation of C_2Hy from methane molecules. Thus, if the catalyst reactivation is due to the increase in the concentration of bound oxygen necessary for the formation of C_2Hy from two methane molecules, the sample activation time is associated with the buildup on the surface of the required forms of carbon deposits responsible for the stage of oligomerization and dehydrocyclization.

Conclusions

Thus, the Ni, $\text{ReOx}/\text{Al}_2\text{O}_3$ DHCH catalyst is activated by the reactant owing to the partial reduction and coating with



carbon deposits. Bound oxygen participates in the formation of C₂Hy intermediates, and the carbon deposit is responsible for their subsequent oligomerization and dehydrocyclization.

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