INFLUENCE OF POTASSIUM OXIDE ON
DEHYDROGENATING ACTIVE SITES OF
ALUMINOCHROMIUM CATALYSTS

K. I. Slovetskaya, A. M. Rubinshtein,
E. A. Timofeeva, É. G. Aleshin,
and V. É. Ivankovskii

In numerous studies, surveys of which are given in [1-3], it has been shown that an addition of K₂O
in amounts up to ~3% to aluminochromium (AC) catalyst increases their dehydrogenating activity and inhibits reactions proceeding on the oxygen centers. It is noted that the role of K₂O is not limited to a change
in the acidity of the catalysts. The influence of K₂O on the amount of the microcrystalline phase, Cr₂O₃,
the carrier of active sites in reduced catalysts, and on the formation of chromates and bichromates in the oxidized catalysts, is suggested.

In this work an attempt was made to determine the influence of K₂O on the number of dehydrogenating active sites and on the number of hydrocarbon molecules reacted on one active site per unit time. It was
shown earlier [4, 5] that the chemisorption and dehydrogenation of n-alkanes on AC catalysts occur on active sites containing Cr²⁺. Therefore, the number of sites can be judged according to the number of Cr²⁺
ions in the catalyst. A comparison of the activities related to one center of the catalyst, containing and not containing K₂O, permitted the detection of an influence of K₂O on the chemical nature of the center.

EXPERIMENTAL

AC catalysts were prepared by impregnation of A1₂O₃ with a solution of (NH₄)₂CrO₄, while alumino-
chromopotassium (ACP) catalysts (0.4 and 3.7 mole% K₂O) were prepared by impregnation of A1₂O₃ with a
mixture of (NH₄)₂CrO₄ and KNO₃ solutions. The ratios of Cr₂O₃ and A1₂O₃ in all the catalysts are the same;
5.8 mole % Cr₂O₃ per 94.2 mole % A1₂O₃. The specific surface of the catalysts is 120-188 m²/g, dry weight
0.48-1.2 g/cm³. More details on the preparation of the catalysts, their characteristics, and the procedure
of experiments on the dehydrogenation of n-hexane were described in [6, 7]. In [7] the yields of hexenes and benzene from n-hexane, obtained at 521-524°C on catalysts (0.48 g) diluted with quartz sand, and at volume velocities of delivery of the hydrocarbon 2.7-37.5 h⁻¹, were cited in [7]. The rates of formation of benzene W₀ under conditions of a zero-order reaction (Fig. 1) were calculated according to these data, and the rates of formation of hexenes and benzene together (Wₓ) were determined by the method of graphical differentiation, with a 13.5% summary yield (Σ) of hexenes and benzene. Moreover, according to the kinetic equation in integral form

\[ \Sigma U = - \beta U \ln (1-\Sigma) - \alpha V_c \]

where α and β are constants; U is the rate of delivery of hexane, ml/h; V_c is the volume of the catalyst;
we calculated the constant α (Fig. 2 and Table 1) and the constant β = 1. Since Eq. (1) is insensitive to peculiarities of the mechanism, in this case we shall not consider them, regarding α as the constant of
Eq. (1), characterizing the summary rate of the dehydrogenation of n-hexane [8]. It should be noted that
under the conditions of the experiments, side reactions occur to a small degree [6]. The yield of branched hydrocarbons on ACP catalysts at Σ < 20% was 0-1.5%, on AC 1-2.5%, while the yield of dienes on both catalysts was 1-2%. Cracking practically did not occur. Analysis of the catalysts for n-hexane was carried out on a chromatograph with a katharometer [stationary phase tricresyl phosphate (TCP)]. Since on
TCP certain isohexenes emerge in the same peak as the n-hexenes, isohexanes, and n-hexane, for certain AC and ACP catalysts the reaction products were also analyzed on a chromatograph with a flame-ionization detector (stationary phase squalane and triethylene glycol dibutylate). The difference in the results obtained is small and does not affect the basic conclusions of the work. The amount of Cr\(^{2+}\) in catalysts subjected to the same treatment as in the catalytic experiments with n-hexane was determined by titration with iron ammonium alum [4].

**DISCUSSION OF RESULTS**

The dehydrogenation of n-hexane on oxide AC catalysts is a consecutive process, including a step of formation of hexenes from n-hexane, followed by conversion of the hexenes to benzene [3]. The first step in the process can be judged according to the summary rate \(W_\Sigma\), since the hexenes constituted 70–90\% of the total yield of hexenes and benzene, and also, evidently according to the constant \(\alpha\). The subsequent stages of dehydrogenation of hexenes to benzene can be judged according to the rate of formation of benzene. The values of \(W_\Sigma\), \(W_b\), and \(\alpha\) are cited in Table 1, and their dependences on the content of Cr\(^{2+}\) in Fig. 3. It is noteworthy that \(W_\Sigma\), \(W_b\), and \(\alpha\) increase with increasing Cr\(^{2+}\) content in the catalyst, both ACP (3.7\% K\(_2\)O) and AC without K\(_2\)O or with a low content of K\(_2\)O (0.4\%), which we combined into one group. At the same content of Cr\(^{2+}\), i.e., with the same number of centers, ACP catalysts are substantially more active than AC. This pertains to the conversion both of hexane to hexenes (see Fig. 3a, b) and to the subsequent steps of conversion of hexenes to benzene (Fig. 3c). Thus, on one active site of the ACP catalysts, more hydrocarbon molecules are dehydrogenated per unit time than on one active site of AC catalysts. This is in all probability associated with changes in the chemical nature of the dehydrogenating center when K\(_2\)O is introduced into the catalysts. As was indicated above, potassium chromates and bichromates can be formed in ACP catalysts. It is extremely probable that in the reduction of the catalysts part of the potassium ions, not consumed for the neutralization of the acid centers of Al\(_2\)O\(_3\), remain in the Cr\(_2\)O\(_3\), introducing Cr\(^{2+}\) ions into the coordination sphere, changing its electron donor properties, and thereby influencing the chemisorption and subsequent dehydrogenation of the hydrocarbons. It should be noted that the introduction of K\(_2\)O into the catalysts does not change the rates of the dehydrogenation of hexane to hexenes and subsequent conversion of hexenes to benzene to the same degree. For example, in the sequence from the AC catalysts T-1 to the ACP catalyst TS-1, both \(W_\Sigma\) and \(\alpha\) increase 2.3-fold, and \(W_b\) 3.5-fold. This difference in the change in the rates affects the selectivity of the reaction \(\gamma\) (ratio of the yields of hexenes

---

*Since the method of graphical differentiation by which \(W_\Sigma\) was determined gives large errors, no full quantitative correlation was observed between \(W_\Sigma\) and \(\alpha\).