CATALYTIC AROMATIZATION OF ETHYLENE AND ETHANE

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The systematic expansion of the raw material supplies for the production of aromatic hydrocarbons (AH) and the development of new and improved methods for the production of these compounds is a significant problem in both scientific research and industrial application. In this regard, clear importance is seen for studies on the dehydrocyclooligomerization of low-molecular-weight olefins and alkanes to form AH, in particular the dehydrocyclo-trimerization of ethylene and ethane to give benzene and other AH which proceeds in the presence of Pt/Al₂O₃ and other M/Al₂O₃ metal–oxide catalysts (M = Rh, Ru, Pd, and Ir) [1, 2]:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH}_2 \\
\text{H}_2 & \quad \text{H}_2 \\
\text{H}_2 & \quad \text{H}_2 \\
\end{align*}
\]

A distinguishing feature of these reactions is their selectivity relative to aromatization (Fig. 1). Pt/Al₂O₃ and Rh/Al₂O₃ have the highest activity and selectivity: The yield of AH in a flow system relative to ethylene passed may reach 10-12%. These catalysts have been studied in greatest detail.

Fig. 1. Activity and selectivity of Pt/Al₂O₃ (I), Ru/Al₂O₃ (II), and Rh/Al₂O₃ (III) catalysts (0.6% M) in the aromatization of ethylene: 1) benzene; 2) toluene; 3) xylenes; 4) total C₆-C₈ AH; 5) total C₉-C₁₂ AH.

The dispersed state of the metal phase plays an important role among the factors which affect the activity of Pt/Al₂O₃ catalysts (PAC). The introduction of various additives into PAC such as Re, Co, Sn, Zr, Sc, Cu, Ru, Ir, and Cl₂, variation of the concentration of these additives and the use of different conditions for the hydrogen reduction and thermal treatment of the catalyst in the air, as well as the use of Al₂O₃ samples differing in specific surface and acidity as the supports has permitted a wide variation of the Pt particle size in PAC ($\gamma = 0.06-1$).* This has allowed study of the effect of particle size and the nature of the additive on the catalytic activity of several series of PAC in the aromatization of ethylene (Figs. 2 and 3).

Figure 2 shows the relationship between the catalytic activity of these samples in ethylene aromatization and their chemisorption capacity. Samples 3-7, 11, and 12 contain $\gamma$-Al₂O₃ as the support and the other catalysts contain $\eta$-Al₂O₃. Marked differences in the action of the support were not found. Of all the catalysts studied, only sample 1 is chlorine-free; all the other catalysts contain from 0.4 to 1.78 mass % Cl. The catalytic activity of sample 1 is markedly less than the other PAC and it has less ability to chemisorb CO than samples 2-7. These findings are in accord with the conclusion that the chemisorption capacity and, thus, the catalytic activity of the metal-alumina catalysts, may be raised significantly by the introduction of a halide.

Figure 2 also indicates that there is a tendency toward increased activity relative to ethylene aromatization with increasing metal dispersion: An increase in the CO chemisorption from 10 to 50 μmole/g catalyst increases the AH yield by a factor of 1.5-2 at 550°C. Analogous behavior is also observed at 600°C.

The formation of carbon deposits on the metal crystallite surface is also an important factor. Indeed, the products of the first pulse of C₂H₄, as a rule, are CH₄ and hydrogen-poor hydrocarbons [1]. The generation of metal-alumina catalysts for ethylene aromatization may be specifically related to coke formation which is very marked on fresh samples.

Other effects are also related to the generation of catalysts for the cyclotrimerization of ethylene. Thus, an x-ray photoelectron spectroscopic study in our laboratory [4] showed that the electronic state of rhodium in the Rh/Al₂O₃ catalyst is significantly altered by the action of the reaction medium. The Rh 3d₅/₂ chemical shift in the x-ray photoelectron spectrum and the catalytic activity of the Rh/Al₂O₃ catalyst depends on the number of ethylene pulses. There apparently is a definite correlation between these two values. A marked positive charge arises on the rhodium clusters with increasing catalytic activity and rhodium is formally converted to the +1 oxidation state. The subsequent decrease in catalytic activity is accompanied by the return of rhodium to a state close to Rh(0).

The dehydrogenation step is one of the important steps in the aromatization of ethylene and ethane. In this regard, the catalytic properties were compared for a large group of modified PAC in the dehydrogenation of cyclohexane and ethylene aromatization. A definite interrelationship was found between these reactions: A large group of samples which are more active in the dehydrogenation of cyclohexane displays relatively high activity in the aromatization of C₂H₆ (see Fig. 3, group A). In contrast, there is no direct relationship between these reactions for catalyst group B. These findings indicate a complex nature for the aromatization of ethylene. The reaction rate is apparently limited in the second group of cat-

* $\gamma$ is the fraction of the platinum on the support surface which is available to the reagents [3].