Chromium-based catalyst for HFC-125 synthesis: promoters effect

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Abstract. A variation of promoters, including rare-earth elements, allows to control of the specific surface area and, perhaps, oxidation state of chromium and, consequently, catalyst activity and selectivity of chromium-based catalyst for HFC-125. To improve the catalytic properties of the 15% Cr₂O₃ - 85% γ-Al₂O₃ oxide system were added promoters (Ni or Cu or Co) in an amount of 5 wt% in terms of oxides. It was found that additional promotion Cr-Al samples by nickel and copper allow to increase the specific surface area of about 25-40% and the activity increased about 2 times. Modification of cobalt resulted in a decrease of the surface by 20% and the activity decreased by about 2 times.

1. Introduction
Various rare-earth metal oxides were widely investigated as promoters of heterogeneous catalysts for enhancing their activity, selectivity, and stability [1]. In particular, the ceria-containing catalysts use for diesel soot combustion and the reduction NOₓ [2,3] hydrogen purification reactions, namely the water gas shift reaction [4] and etc. It is known, that the promoters affect the textural characteristics: specific surface area, pore diameter, and on the electronic state of the active component. Despite the large number of works, studying the role of promoters in the formation of the main characteristics of catalysts and their role in the formation of the active sites of the catalyst are still unclear.

In recent decades, considerable efforts have been focused on the synthesis of chladones, having zero ozone depletion potential. The most promising in this regard are chladones of the ethane row, namely, pentafluoroethane CHF₂-CF₃ (HFC-125), which is produced by the gas-phase catalytic hydrofluorination of perloroethylene Cl₂C=CCl₂. A fluorination catalyst based on of an amorphous Cr (III) compounds in combination with promoting and stabilizing admixtures of aluminum, magnesium, nickel, zinc and others [5,6]. Rare-earth metal oxides are used as promoters also, namely, lanthanum [7], scandium [8,9], and yttrium [10,11]. However, systematic studies of the mechanism of influence of promoters on the catalytic properties of chromium-containing fluorination catalysts are absent. These issues are of great scientific and practical interest.

In this work, we studied chromium-containing catalyst (~15% Cr₂O₃ - 85% γ-Al₂O₃ ) and the effect of promoters (~5% Ni, Cu and Co) on physicochemical and catalytic properties of the catalysts for the gas-phase hydrofluorination of perchloroethylene to pentafluoroethane (chladone HFC-125). Kinetic regularities of the reaction were also considered.
2. Experimental Part

Catalysts obtained by precipitation of NH₄OH solution from solutions of chlorides of Cr, Al, Ni, Cu and Co. The precipitate was washed, filtered, dried in air at calcined in nitrogen at 330-400°C. The size and volume of pores, the catalyst activity in the reaction of hydrofluorination of perchloroethylene were measured for the samples.

The catalytic activity of samples in the gas-phase fluorination of perchloroethylene (PCE) was performed using the flow-type reactor. A mixture of reagents PCE and HF was fed in U-shaped nickel reactor with a diameter of 3 mm, placed in an oven. After the reactor the mixture entered absorbers, filled with alkali metal carbonate, where formed during the synthesis HCl and unreacted HF were neutralized, thus isolating the water and carbon dioxide. After absorbers sampled gaseous reaction mixture, which mode on-line analyzed by gas chromatography Tsvet-500M (Russia) equipped with a thermal conductivity detector.

The reaction products were identified by CG-MS using a Saturn-2000 system (Varian, United States. According to the results of the chromatographic analysis was calculated mole fraction of PCE and reaction products. The conversion of perchloroethylene X was calculated as the difference between the molar fractions at the reactor inlet and outlet (corrected for the volume change during the reaction) to the mole fraction of PCE in the feed mixture. The selectivity of the reaction products was determined as the ratio of the mole fraction of each product to the sum of molar fractions of all the products in the reaction mixture. The rate constant expenditure of PCE was estimated by the equation for first order reactions

\[ k_{PCE} = -\ln(1 - X)/\tau \]

where \( \tau \) is contact time and \( X \) is PCE conversion.

Experiments were performed in the kinetically controlled regime, which has been verified experimentally. The absence of external diffusion limitation was confirmed by varying the feed rate of the reaction. The absence of internal diffusion was determined by performing the experiment at different grain size.

3. Results and Discussion

It is known that individual Cr₂O₃ thermally not stable and at a relatively low temperature (~400°C) crystallizes in the \( \alpha \)-Cr₂O₃, which is accompanied by a decrease of the specific surface. To increase the thermal stability of all investigated samples to Cr₂O₃ was added ~85% Al₂O₃. To improve the catalytic properties (activity and selectivity) in the Cr-Al samples were also added promoter (Ni or Cu or Co) in an amount of 5 wt% in terms of oxides.

It is found that additional promotion Cr-Al samples of nickel and copper increased the specific surface area of about 25-40% (table 1). Moreover, the activity increased about 2 times. Modification of cobalt resulted in a decrease of the surface by 20% and the activity decreased by about 2 times, while maintaining high selectivity. Thus, a direct relationship of the specific surface area of chromium-containing fluorination catalyst with the activity was not observed.

In the literature it is noted that the activity of Cr-catalysts of the gas-phase fluorination depends on chromium oxidation state [6]. We have shown [12] that in Cr-Al catalysts for the fluorination of chromium oxidation state of Cr depend essentially on the conditions of heat treatment: temperature and composition of the gas medium. We have investigated the physicochemical properties of coprecipitated oxide systems 95% of Cr₂O₃–5% Al₂O₃, obtained by heat treatment in nitrogen and air in the temperature range 110-600°C, and their influence on the catalytic activity in the reaction of hydrocorisone perchloroethylene.

Based on the methods of thermal and X-ray diffraction analysis, diffuse reflectance spectroscopy, and specific surface measurements was found that CrO₃.₅ compounds more active than CrO₃.₅. However, getting them in superfine condition is difficult due to the high exothermicity of the oxidation stage, which leads to the decomposition of CrO₃.₅ oxides to CrO₃.₅ with subsequent crystallization and
sintering of decomposition products. The formation of highly dispersed and highly active chromium-containing oxides with stoichiometry CrO\(_{1.9}\) is possible in the two-stage heating of the hydroxide samples, first in nitrogen and then in air at relatively low temperatures:

\[
\text{CrO}_{1.5} \text{(am.)} \xrightarrow{200-370^\circ C} \text{CrO}_{1.9} \text{(am.)} \xrightarrow{370-403^\circ C} \text{CrO}_{1.5} \text{(am.)} \xrightarrow{412-420^\circ C} \alpha \text{-Cr}_2\text{O}_3 \text{(cr.)} \quad (2)
\]

We can assume that the promoter can significantly affect the electronic state of chromium. Perhaps this is the reason the difference in the activity of samples with different promoters. To clarify these issues, it is advisable to carry out studies with a large set of promoters, including rare-earth elements.

**Table 1.** Effect of promoters on the BET specific surface area \((S_{\text{sp}})\), total pore volume \((V_{\text{pore}})\), mean pore diameter \((D_{\text{pore}})\) and catalyst activity \((k \text{ at } 370^\circ C)\), PCE conversion \((X)\) and selectivity towards main products \((S_{\text{sum}})\).

| Sample | Catalyst composition | \(S_{\text{sp}}\) (m\(^2\)/g) | \(V_{\text{pore}}\) (cm\(^3\)/g) | \(D_{\text{pore}}\) (nm) | \(k_{370}\) (s\(^{-1}\)) | \(X\) (%) | \(S_{\text{sum}}\) (%) |
|--------|----------------------|-------------------------------|-------------------------------|---------------------|-----------------|-----------|-----------------|
| 1      | 15%Cr\(_2\)O\(_3\) 85%Al\(_2\)O\(_3\) 5%NiO | 245                           | 0.6                           | 35                  | 0.15            | 33        | 96              |
| 2      | 10%Cr\(_2\)O\(_3\) 85%Al\(_2\)O\(_3\) 5%CuO | 310                           | 0.5                           | 30                  | 0.28            | 57        | 95              |
| 3      | 10%Cr\(_2\)O\(_3\) 85%Al\(_2\)O\(_3\) 5%CoO | 340                           | 0.45                          | 30                  | 0.27            | 54        | 100             |
| 4      | 10%Cr\(_2\)O\(_3\) 85%Al\(_2\)O\(_3\) 5%CoO | 200                           | 0.45                          | 40                  | 0.08            | 21        | 100             |

The overall reaction of the perchloroethylene hydrofluorination to pentafluoroethane is written as follows:

\[
\text{C}_2\text{Cl}_4 + 5 \text{HF} = \text{C}_2\text{HF}_5 + 4 \text{HCl} \quad (3)
\]

**Figure 1.** Concentrations of main (a) and by-products (b) along the reactor high.

1 – CCl\(_2\)=CCl\(_2\), 2 – CF\(_3\)=CFCl, 3 – CF\(_3\)=CHCl\(_2\), 4 – CF\(_3\)=CHFCl, 5 – CF\(_3\)=CHF\(_2\), 6 – CF\(_3\)=CH\(_2\)Cl, 7 – CF\(_3\)=CCl\(_3\), 8 – CF\(_3\)=CFCl\(_2\), 9 – CF\(_3\)=CF\(_2\)Cl.
However, the process includes a large number of possible reaction routes and, apart from its main products, might yield the products of side-reactions like isomerization, elimination and disproportionation. The reaction mixture contained the following main products: CFCl=CCl$_2$ difluorodichloroethylene isomers CFCl=CFCl and CF$_2$=CCl$_2$, difluorotrichloroethane CF$_2$Cl–CHCl$_2$, trifluorodichloroethane isomers CHCl$_2$–CF$_3$ and CHFCl–CF$_2$Cl, tetrafluorochloroethane isomers CF$_3$–CHFCl and CHF$_2$–CF$_2$Cl, pentafluorochloroethane CF$_3$–CF$_2$Cl, and pentafluoroethane CF$_2$–CHF$_2$.

Besides, the following by-products were formed: trifluorotrichloroethane CF$_2$Cl–CFCl$_2$, trifluorochloroethane CH$_2$Cl–CF$_3$, tetrafluorodichloro ethane CF$_2$Cl–CF$_2$Cl, tetrafluoroethane CHF$_2$–CHF$_2$ and its isomer CF$_3$–CH$_2$F.

Typical distribution of the reaction products is shown in Figure 1. Analysis of experimental data obtained on samples with different promoters (Table1) testified that despite the difference in the activity and selectivity the scheme the products formation is identical. The observed dependence shows that the process of perchlorethylene hydrofluorination proceeds via complex parallel-series scheme, which can be represented in a form similar to that given in [13, 14] for the Cr-Mg catalyst:

![Simplified reaction pathway of PCE hydrofluorination.](image)

This scheme consists of ten reactions. It includes consecutive substitution of fluorine for chlorine, and by-product formation, as a result of reactions of the trifluorodichloroethane CHCl$_2$–CF$_3$ and tetrafluorochloroethane CF$_3$–CHFCl disproportionation.

4. Conclusion

A variation of promoters, including rare-earth elements, allows to control of the specific surface and, perhaps, oxidation state of chromium and, consequently, catalyst activity and selectivity.

To improve the catalytic properties of the 15% Cr$_2$O$_3$ - 85% γ-Al$_2$O$_3$ oxide system were added promoter (Ni or Cu or Co) in an amount of 5 wt% in terms of oxides. It was found that additional promotion Cr-Al samples of nickel and copper increased the specific surface area of about 25-40% (table 1) and the activity increased about 2 times. Modification of cobalt resulted in a decrease of the surface by 20% and the activity decreased by about 2 times.

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