The Deactivation of Polyoxide Catalysts and Their Regeneration

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Abstract—The mechanism of adsorption of SO$_2$ as a component of discharge in the air on Pt- and Pd-containing catalysts has been studied. The conditions of their poisoning and regeneration have been defined. Methods of TPD, IRS, mass-spectrometry, and chromatography were applied for this research. The study of SO$_2$ adsorption and its interaction with oxygen on Pt(Pd)/Al$_2$O$_3$ catalysts at the temperature range of 300–500°C has shown that the formation of the molecular-adsorbed forms of SO$_2$ (I and II) and tightly covalently bound sulfate (III form) and ionic sulfate (form IV), responsible for the catalysts’ poisoning occurs. Decrease of the Pt (Pd)-containing catalysts’ poisoning was put into effect by their modification with the group of transition elements consisting of Co, Cr, and Ce. The regeneration of the catalysts was carried out by a heat treatment of samples at 700°C and above. The opportunity is shown for 99–100% Pt and Pd extraction out of the dead catalysts and the recycled Al$_2$O$_3$ carrier.

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INTRODUCTION

The gas emissions of industrial enterprises and motor transport containing sulfur, carbon, and nitrogen oxides; high-toxic organic compounds and strong smelling hydrocarbons; soot; and other admixtures have a pernicious effect on the environment. The most widespread method of their deactivation is the full oxidation (or reduction) in the presence of a catalyst. One of the main problems connected with the use of catalysts is considered to be activity loss due to catalyst poisoning. For example, a significant decrease of activity is typical of catalysts, produced on the basis of precious metals (Pt, Pd) or transition metals oxides (Co, Cr, Mn, and so on).

Sulfur dioxide [1–3] can adsorb on the Al$_2$O$_3$ carrier as sulfite and sulfate surface structures.

Individual oxides of transition metals (Mn, Cr, Co, Fe, and so on) [4–7] are more subjected to poisoning by sulfur dioxide than mixed catalysts produced on their basis [8–10].

Mixed oxides of transition metals are less active than catalysts on the basis of Pt-group metals and they are cheaper. Among oxide-mixed catalysts the Cr- and Cu-containing contacts are characterized by high activity in the oxidation reaction of CO and hydrocarbons [8–9, 11–13].

Catalysts on the basis of precious metals are more proved against sulfur. In addition they are able to save their catalytic activity in the oxidation reaction of CO and hydrocarbons [14, 16]. The addition of sulfur-resistant metal oxides (Cr, Ce, Co, Cu–Cr, and so on) to catalysts containing precious metals leads to the formation of new types of high-active and stable mixed gas cleaning catalysts in sulfur dioxide’s presence. However, in scientific literature there are no data about catalyst poisoning by sulfur dioxide in dependence on the nature of admixture of different transition metals. Besides, the mechanism of surface sulfate complexes formation and their characteristics are not discussed.

The regeneration of gas cleaning catalysts which lost its activity due to SO$_2$ poisoning after long-term operation is of interest. High-temperature (at 400–1000°C) heating of a sample is more often used for regeneration to decompose surface sulfite–sulfate complexes and accumulated sulfate on the Al$_2$O$_3$-carrier [7, 17]. However, the decomposition of these complexes and the restoration of original activity of contacts are not always possible to reach.

EXPERIMENTAL

A study of γ-Al$_2$O$_3$-supported catalysts and those obtained using the tabletting method following by the adsorption of SO$_2$ + O$_2$ was carried out with the IKS method but all questions were not resolved. In this case, the absorption band of aluminum oxide (lower then 1100 cm$^{-1}$) in IR-spectrums overlaps the absorption bands of sulfate complexes. Thus, the prepared and pounded catalyst’s samples have been stirred up in isopropanole to get the fine fraction and then precipitated on optical KBr glass, using the method of [18]. The following day the plate covered with hard film of the catalyst was carefully extracted and dried up in the air. Then, it was put into a quartz glass cell with windows made of NaCl (or KBr). Infrared spectrums were regis-
The work was aimed at studying the mechanism of the individual and the mixed interaction of $O_2$ and $SO_2^{ads} + O_2$ and Pt-and Pd-catalysts, and the mechanism of surface sulfate structures formation and how the nature of metals influences this process.

TPD-spectrums, obtained after $SO_2$ adsorption and the interaction of $SO_2^{ads} + O_2$ and $\gamma$-$Al_2O_3$- and Pt(Pd)/$Al_2O_3$-catalysts at a temperature of $400^{\circ}C$ are shown in Fig. 1. In the TPD-spectrum are peaks in four temperature regions (K) (I) 300–700, (II) 500–850, (III) 700–1100, and (IV) 920–1300 which correspond to the decomposition of four forms of adsorption complexes of sulfur dioxide in the temperature range of 300–1300 K. For example, there are three forms of adsorbed sulfur dioxide (Fig. 1, curve I, TPD peaks I, II, III) at $\gamma$-$Al_2O_3$ with a temperature of $300^{\circ}C$.

After blowing-in of oxygen the I form of sulfur dioxide disappears, and only the II and II forms remain (curve 2, TPD II, III) at the constant $T_{max}$ of latter ones; i.e., in the presence of oxygen the new surface complexes of sulfur dioxide does not form on $\gamma$-$Al_2O_3$.

The sulfur dioxide is adsorbed at $300^{\circ}C$ on a Pt/$Al_2O_3$-catalyst, as well as on $Al_2O_3$ in three forms (Fig. 1, curve 3, TPD I, II, III). As a result of the interaction of adsorbed sulfur dioxide and oxygen, the I form disappears completely from the TPD spectrum (curve 3, TPD I, $T_{max}$ = 460 K); the II form disappears partially (curve 3, TPD II, $T_{max}$ = 673 K); the III form considerably rises (curve 4, TPD III, $T_{max}$ = 973 K); and the new IV form appears (curve 4, TPD IV, $T_{max}$ = 1050 K).

On a Pd/$Al_2O_3$ catalyst the sulfur dioxide is also adsorbed at $300^{\circ}C$ ($573 K$) as two forms (Fig. 1, curve 5, TPD II, and III). Under these conditions, the I form, typical for $Al_2O_3$, is absent on the Pd/$Al_2O_3$ catalyst. In addition, on the Pt-catalyst under the oxygen blowing-in the sulfur dioxide of the II form comes into the reaction. As a result, it disappears from the spectrum (curve 5, TPD II). Simultaneously, the III form rises (curve 6, TPD III, $T_{max}$ = 850 K) and the new, IV form appears (curve 6, TPD IV, $T_{max}$ = 1063 K).

Essential changes observed in the TPD spectrums of the Pt(Pd)$Al_2O_3$ catalyst in contrast to the individual $Al_2O_3$ catalyst are connected to the participation of Pt and Pd in the oxidation reaction with oxygen of adsorbed sulfur dioxide (I and II forms). As a result of this reaction the $SO_3$ is formed. One part of the $SO_3$ interacts tightly with metals; the other part migrates on a carrier. The given process can be simply represented in the following way:

\[ M + SO_2 \rightarrow MSO_2, \]  
\[ 2M + O_2 \rightarrow 2MO, \]  
\[ MO + MSO_2 \rightarrow 2M + SO_3 \quad (MSO_3), \]  
\[ MO + SO_3 \rightarrow MOSO_3, \]