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Mössbauer Spectroscopic and Chemical Analysis of the Composition of Sn-Containing Components of Pt–Sn/Al_2O_3(Cl) Reforming Catalyst

V. I. KUZNETSOV, A. S. BELYI, E. N. YURCHENKO, M. D. SMOLIKOV,
M. T. PROTASOVA, E. V. ZATOLOKINA, AND V. K. DUPLYAKIN

Institute of Catalysis, Novosibirsk 630090, USSR

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Based on NGR parameter analyses [δ, Δ, *W*, and $f'(T)$], we have studied the genesis of the states of Sn-containing components of catalysts prepared by impregnating the prechlorinated γ-Al_2O_3 with a solution containing a mixture of complex anions, $[PtCl_3SnCl_3]^{2-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$. At the initial step, Sn-containing compounds interacted with OH or Cl atoms of the support surface. Two types of Sn(IV), three to four states of Sn(II), and several Pt–Sn alloys were identified after reduction of samples with H_2 at 823 K. The amount and composition of Sn(II) components of the catalyst tend to change most dynamically due to a strong interaction of some of the Cl^- ions and Sn atoms with the support lattice. The problems encountered in the application of the method are discussed.

INTRODUCTION

We have previously studied the composition of Sn-containing components of freshly prepared and H_2-reduced (823 K) Pt–Sn catalysts obtained by impregnating prechlorinated γ-Al_2O_3 with a solution of platinum–tin chloride complex in isopropanol (*1*). The catalyst was found to contain significantly larger amounts of Sn(II) chlorine derivatives and smaller amounts of Sn(IV) chlorine compounds as compared to γ-Al_2O_3- (*2*) and $ZnAl_2O_4$-supported Pt–Sn catalysts (*3, 4*). This indicated an active role of the modifying chlorine ions of γ-Al_2O_3 in the formation of catalyst components. We failed to identify the types of Sn-containing and, especially, Sn(II)-containing compounds in more detail because of the restrictions imposed on the decomposition of the total NGR spectrum into individual Lorenz components (ILCs), which meant that the chemical shift (δ) and quadrupole splitting (Δ) of each ILC were varied over the ranges typical of the corresponding individual compounds.

Recently it has been found that modifications of γ-Al_2O_3 by halogenide ions, including Cl^-, is associated with a partial substitution of several types of surface OH groups by Cl^- (*5*). It was of interest to examine in detail the effect of the modifying chlorine ions on the interaction of catalyst components with the surface at all steps of catalyst preparation. With this in mind, it was necessary first, to study the interaction of individual tin compounds, which have no Pt, with the surface under the same conditions.

As found in (*2*), most suitable for this purpose is $SnCl_2 \cdot 2H_2O$. In addition to NGR spectral parameters, δ and Δ, traditionally used to identify catalyst components (*1–4, 6*), we have made an attempt to analyze the linewidths of ILCs (*W*) and the temperature dependence of the probability of resonance γ-quanta absorption by samples (f'). The f'_{77}/f'_{295} ratio is used as a measure of this dependence. In their recent paper Bacaud *et al.* (*6*) took surprisingly high values of Δ for the Pt–Sn alloys at the decomposition of complex NGR spectra of γ-Al_2O_3-supported Pt–Sn catalysts into ILCs. In this connection, it seemed expedient to consider the problem of correct approaches to the decomposition of complex

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NGR spectra into individual components. This paper discusses the above-mentioned problems.

EXPERIMENTAL

Catalyst Preparation Procedure and Elemental Analysis

(*1*) *Support.* Either γ-Al_2O_3 (200 m^2/g BET surface area) or the γ-Al_2O_3 , pretreated with HCl solution in dried isopropanol [γ-$Al_2O_3(Cl)$], was used as support. The amount of Cl so introduced to γ-Al_2O_3 correspond to an equilibrium amount. For this purpose, the introduction was continued until the interaction between the support and the HCl-containing solution did not lead to a decrease in the amount of HCl. Prior to impregnation with the solutions containing Sn compounds, both supports were calcined under vacuum at 873 K for an hour.

(*2*) *$SnCl_2 \cdot 2H_2O$ support system.* Freshly recrystallized $SnCl_2 \cdot 2H_2O$ enriched with ^{119}Sn by 90% was used for the preparation. Both supports were treated with an impregnation solution containing 0.05 *M* $SnCl_2 \cdot 2H_2O$ in absolute isopropanol (3 h, argon atmosphere, intensive agitation). The solution was then removed, and the samples were washed with the solvent and then dried under vacuum ($\sim 1.3 \times 10^{-2}$ N/m^2) at 363 K for 3 h. Samples prepared with γ-Al_2O_3 will be referred to below as A-0 and those with γ-$Al_2O_3(Cl)$, as A-1. The contents (wt%) of Sn and Cl were 0.35 and 0.2 in A-0, and 0.34 and 3.0 in A-1.

The amount of Sn in all samples was determined by atomic absorption spectroscopy. To determine Cl, the samples were treated with water vapor at 1079 K with further argentometric titration of Cl^- in the solution. Sample A-1 was treated with oxygen at 773 K for 3 h. The sample obtained (A-2) contained 0.34% Sn and 1.5% Cl. The sample was then reduced with hydrogen at 823 K for 3 h, after which (A-3) it contained 0.34% Sn and 1.4% Cl. The content of Sn on the support was 10% of its sorption capacity limit. In order to consider the behavior of Pt-unbonded Sn compounds on the surface of γ-$Al_2O_3(Cl)$ under conditions close to catalytic conditions, it was necessary to treat the samples with oxygen and hydrogen. It is well known (*4*) that to remove coke, which is formed during the catalyst operation, the catalyst is subjected to periodic oxidative treatment with oxygen. NGR spectra of the samples of this series (A) are represented in Fig. 1. Parameters δ, Δ, W, and $f'_{77}f'_{295}$ are listed in Table 1.

(*3*) *Pt–Sn catalyst on γ-$Al_2O_3(Cl)$.* Catalysts of series B were prepared by impregnating the support with isopropanol solution containing a mixture of $[PtCl_3(SnCl_3)]^{2-}$ and $[PtCl_2(SnCl_3)_2]^{2-}$ complexes (*7*) with a total concentration of 0.1 *M* using the procedure described in (*1*). After adsorption of the complex on the support for 3 h under the same conditions used for $SnCl_2$ support, the sample was washed with pure isopropanol and dried under vacuum at 363 K. It was subjected to a 3-h treatment, first with oxygen and then with hydrogen at 773 K. The sample (B-1) contained 1.4% Cl. The amounts of Sn and Pt, also determined by atomic absorption spectroscopy, were 0.35 and 0.32% in all samples of series B and C, respectively. Then part of B-1 was subjected to a similar treatment with oxygen at 773 K. To prevent the removal of Cl during heating in oxygen, about 10% (by volume) dichloroethane vapors was added. The amount of Cl in the sample obtained (B-2), indeed, remained at 1.4%. To complete the second oxidation–reduction cycle, sample B-2 was reduced in an atmosphere of H_2 at 823 K for 3 h; the amount of Cl in B-3 decreased to 1.28%. Another part of sample B-1 was subjected to six cycles of treatment in an atmosphere of O_2 and H_2 at 823 K for 3 h. This sample (B-4) contained 1.15% Cl. One of the most probable reasons for the decrease in the amount of Cl in the support from cycle to cycle might be the process of hydrolysis of Al–Cl bonds under the action of small amounts of H_2O. To verify this hypothesis, part of sample B-4 was given a 12-h treatment with a mixture of H_2O and O_2 vapor at 823 K and then a 3-h reduction in an atmosphere of H_2 at the same temperature. The amounts of Pt and Sn in the sample obtained (B-5) remained unchanged, while that of Cl decreased to 0.1%.

A series of samples C was treated under conditions of reforming [H_2 + *n*-heptane mixture (5 : 1) at a total pressure $\sim 10^6$ N/m^2, 823 K): part of sample B-4 was treated for 1 h; as a result, the amount of Cl decreased to 1.1% and 1.2% C[1] appeared in the sample (C-1). The remainder was treated under the same conditions for 9 h, after which the catalyst (C-2) contained 0.9% Cl and 9.8% C. A 3-h treatment of catalyst C-2 with oxygen at 823 K and a subsequent 3-h reduction in an atmosphere of H_2 led to decreases in the amounts of C to 0.1% and of Cl to 0.8% (sample C-3). As in Ref. (*2*), we have considered the possibility of catalyst preparation by successive supporting Sn- and Pt-containing compounds on supports. For this purpose γ-Al_2O_3(Cl) was primarily subjected to a 3-h impregnation with a 0.1 *M* solution of $SnCl_4$ in isopropanol. After removal of the solution, H_2PtCl_6 (0.1 *M* solution in isopropanol) was supported in the same way on the same carrier. Then the sample (P-1) was dried and treated like B-1. NGR spectra were taken for all samples at 77 and 295 K. This allowed us, without determination of absolute values from the ratio of ILC areas, to find f'_{77}/f'_{295}[2] as the parameter that characterizes $f'(T)$ for each Sn compound on the support surface.

(*4*) *NGR spectra.* Spectra were registered as described in (*1*) using a spectrometer with a NTA-1024 multichannel analyzer and $Ba^{119}SnO_3$ as a source of γ-quanta. When treated, the samples were sealed in the ampoules without contact with air. Sample weights were chosen so that at both temperatures of spectrum registration the absorber effective thickness was less than unity. Spectra were displayed on a two-coordinate recorder after accumulation in them of half a million pulses. The experimental error of δ, Δ, and W measurements was ± 0.03 mm/s. All spectra were decomposed into ILCs on a SK-2 curve synthesizer. Examples of such treatment are shown in Figs. 1 and 2. The spectra are in the form in which they are displayed on the SK-2 plotter. Parameters of all ILCs are listed in Tables 1 and 2. The weight percentages of Sn in Sn-containing components of the catalysts, which was found by subtracting from the total amount of Sn in the sample the total area under the NGR spectrum and the areas under ILCs, are shown in Tables 3 and 4. The difference in f' values of Sn compounds was not taken into account.

Electron microscopic studies were carried out using a JEM-100 CX microscope with a resolution of about 3 Å.

RESULTS AND DISCUSSION

Results are compiled in Tables 1–4 and in Figs. 1 and 2 and those of elemental analysis are given under Experimental. Sn-containing components (Tables 1 and 2) were identified by determining δ, Δ, W, and f'_{77}/f'_{295} and comparing them with the known values for various Sn compounds. We have shown previously that the value of f' for Sn(II) compounds and, especially, the dependence $f'(T)$ indicate, first, the rigidity of Sn binding in its first coordination sphere and, to a lesser extent, the type of packing of Sn-containing compounds in the crystals (*8*).

$SnCl_2 \cdot 2H_2O$–γ-Al_2O_3 and $SnCl_2 \cdot 2H_2O$–γ-Al_2O_3(Cl) Systems

The A-0 sample obtained by supporting solvated $SnCl_2$ on γ-Al_2O_3 produces the NGR spectrum shown in Fig. 1. After subtracting two singlets of Sn(V) compounds

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[1] Carbon was determined by the standard microanalysis method.

[2] $S_E = \text{const.} \cdot f' \cdot n$, where $\text{const.} = (\pi/2) \cdot \sigma_0 \cdot W_N \cdot \chi \cdot f$ and n is the number of absorbing nuclei. Hence, it is seen that by taking the $f'T_1/f'T_2$ ratio, we obviate the necessity to determine the absolute values of $f'T$.

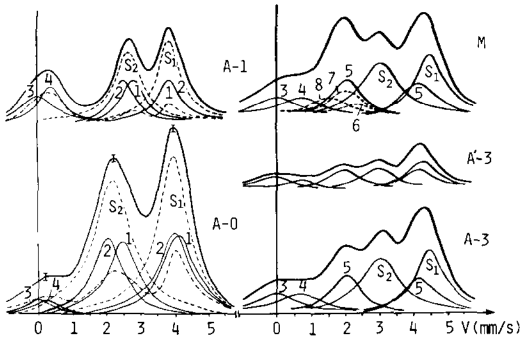


FIG. 1. NGR spectra of the samples of series A. Both components of the doublets are marked with the same figure everywhere. **A-0:** The solid thick line is the sum spectrum of the dried sample at 77 K; the dash-and-dot line, at 295 K; solid thin lines are doublets 1 and 2; and singlets 4 and 3; the dotted line is an asymmetric doublet with components S_1 and S_2, which is the sum of doublets 1 and 2. **A-1:** Components are designated as in A-0. **A-3:** The spectrum recorded at 77 K after reduction of sample A-1, ILCs are shown by solid thin lines (doublet 5-$SnAl_2O_4$); the other designations are as in A-0. **A'-3:** The spectrum of A-3 at 295 K; M is the sum of spectrum A-3 and the spectra of Pt–Sn alloys. Their singlets N 6, 7, and 8 are shown by dots. The maximum scatter of experimental points, typical of spectra of all samples, is shown in the A-0 spectrum.

(Nos. 3 and 4), the spectrum was an asymmetric doublet, whose components S_1 and S_2 were very wide: $W = 1.2–1.3$ mm/s. The asymmetry of components S_1 and S_2 was found to depend upon temperature: f'_{S_1}/f'_{S_2} (77 K) = 1.07 and f'_{S_1}/f'_{S_2} (235 K) = 1.22. Therefore, the registered asymmetry might be explained by the Goldansky–Koryagin effect (*9*). However, very large linewidths that exceeded $2W_{\text{source}}$ ($W_{\text{source}} = 0.39$ mm/s) were evidence that the $S_{1;2}$ doublet was a superposition of at least two doublets. In fact, it can be represented by the sum of two symmetric doublets, Nos. 1 and 2, with different δ and Δ but with the same linewidths, 0.85 mm/s (Table 1). This indicates that $SnCl_2$ molecules interact with two surface OH groups with different proton-donor abilities. According to Ref. (*10*), the f'_{77}/f'_{295} of massive $SnCl_2 \cdot 2H_2O$ is 8. After supporting on γ-Al_2O_3 this ratio decreases to 4.3 for both doublets (Table 1). This decrease indicates the formation of a strong chemical bond between the Sn atom and the surface, as well as the absence of $SnCl_2 \cdot nH_2O$ par-

TABLE 1

Mössbauer Parameters of the Compounds Formed during $SnCl_2 \cdot 2H_2O$ Adsorption on γ-Al_2O_3(Cl) and Further Treatments

Sample type	State and number of the corresponding components of NGR spectrum	NGR parameter			
		δ (mm/s)	Δ (mm/s)	$W_{1;2}$ (mm/s)	f'_{77}/f'_{295}
A-0	$Sn(II)^{ads.}$, doublet 1	3.3	1.5	0.85; 0.85	4.3
	$Sn(II)^{ads.}$, doublet 2	3.0	2.0	0.85; 0.85	4.3
	$Sn(IV)^{surf.}$, singlet 4	0.15	0.6	0.9; 0.9(1.4[a])	3.8
	$SnO_2^{surf.}$, singlet 3	0.05	0.6	0.9; 0.9(1.4[a])	1.6
A-1	$Sn(II)^{ads.}$, doublet 1	3.3	1.15	0.85; 0.85	15.6
	$Sn(II)^{ads.}$, doublet 2	3.15	1.35	0.85; 0.85	15.6
	$Sn(IV)^{surf.}$, singlet 4	0.23	0.6	0.8; 0.8(1.35[a])	3.3
	$SnO_2^{surf.}$, singlet 3	0	0.6	0.9; 0.9(1.5[a])	1.8
A-2	$SnO_2^{surf.}$	0.05	0.7	1.5	1.6
A-3	$Sn(II)^{surf.}$, doublet 3	3.7	1.35	1.15(S_1); 0; 90(S_2)	3.4
	$SnAl_2O_4$, doublet 5	3.2	2.2	0.9; 0.9	2.8
	$Sn(IV)^{surf.}$, singlet 4	0.5	0.6	0.9; 0.9(1.4[a])	2.6
	$SnO_2^{surf.}$, singlet 3	0	0.6	0.9; 0.9(1.45[a])	1.8

[a] Singlet width.

TABLE 2

Mössbauer Parameters on Sn Compounds Formed in Pt–Sn/γ-Al_2O_3(Cl) Catalysts

Compound	Sample for which compound was identified	No. of ILCs according to Fig. 2	NGR parameter			
			δ (mm/s)	Δ (mm/s)	W (mm/s)	f'_{77}/f'_{295}
$Sn(II)^{surf.}$	B-1; B-3; B-5; C-1 ÷ C-3[a]; P-1	Doublet $S_{1;2}$	3.5 ÷ 3.8	1.35 ÷ 1.25	1.15 for S_2; 0.94 for S_1	2.8 ÷ 3.5
$SnAl_2O_4$	B-1; B-3; B-5; C-1 ÷ C-3[a]; P-1	Doublet 5	3.1 ÷ 3.5	2.2 ÷ 2.15	0.9; 0.9	2.7 ÷ 3.2
Sn(II) in lattice	B-3 ÷ B-5; C-1 ÷ C-3; P-1	Singlet 9	4.1	0	1.0	2.0
Pt_3Sn	B-1; B-3 ÷ B-5; C-1 ÷ C-3; P-1	Singlet 8	1.45 ÷ 1.55	0	1.1 ÷ 1.15	2.5 ÷ 3.3
PtSn	B-1; B-3 ÷ B-5; C-1 ÷ C-3; P-1	Singlet 7	1.78 ÷ 1.98	0	1.3 ÷ 1.35	2.5 ÷ 3.8
$PtSn_4$	B-1; B-3 ÷ B-5; P-1	Singlet 6	2.3 ÷ 2.5	0	1.0 ÷ 1.15	2.6 ÷ 3.7
$Sn(IV)^{surf.}$	B-1; B-3 ÷ B-5; C-1 ÷ C-3; P-1	Singlet 4	0.4 ÷ 0.8	0	1.3 ÷ 1.4	1.7 ÷ 2.8
$SnO_2^{surf.}$	B-1 ÷ B-5; C-1 ÷ C-3; P-1	Singlet 3	0 ÷ 0.05	0.6 ÷ 0.65	1.4 ÷ 1.5	1.6 ÷ 2

[a] ÷ indicates admissible variation in the parameter from the first to the second value.

ticles on the surface (*8*). It is seen in Table 2 that as a result of such interaction of $SnCl_2$ with the surface, δ decreases to 3.3–3.0 mm/s and Δ increases to 1.5–2.0 mm/s (for initial $SnCl_2 \cdot 2H_2O$ $\delta = 3.67$ mm/s, $\Delta \sim 1$ mm/s). It is known that the highest values of δ are typical for Sn(II) halogenides. Oxygen-containing Sn(II) compounds have smaller values (*11*).

Thus, a decrease in δ for Sn(II) chloride supported on γ-Al_2O_3 allows one to assume that Sn(II) atoms form a chemical bond with an atom of the surface oxygen. In this case appearance of the nonequivalent O atom along with the Cl atom, in the coordination sphere of Sn(II) causes the asymmetry of the $5P_x$, $5P_y$, and $5P_z$ atomic orbital population on Sn, and consequently the observed increase in Δ.

Based on the above results we conclude that the reaction of solvated $SnCl_2$ with nonchlorinated γ-Al_2O_3 occurs as follows:

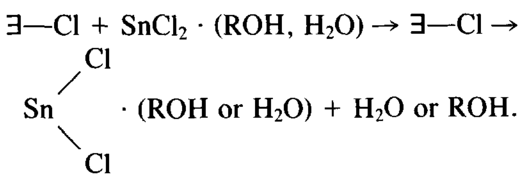
$$\exists\text{—OH} + \text{ClSnCl} \cdot (\text{ROH}, H_2O) \rightarrow \exists\text{—O—Sn—Cl} \cdot (\text{ROH}, H_2O) + \text{HCl}. \quad (1)$$

Furthermore, after impregnation with the $SnCl_2 \cdot 2H_2O$ solution in isopropanol, NGR spectra indicate two states of Sn(IV), in addition to Sn(II) ions bonded to γ-Al_2O_3. Singlet 3 (Fig. 1) has a large W and can be represented as a doublet with δ about 0 and $\Delta \sim 0.6$ mm/s. A similar state of Sn(IV) was interpreted as SnO_2 in (*3, 4*). Besides these parameters, the state of Sn(IV) under consideration has an f'_{77}/f'_{295} ratio which is similar to the ratio typical of the SnO_2 phase (for SnO_2 it is 1.2).

Note that the parameters of this type for Sn(IV) compounds remain nearly the same for all samples of series A. This allows us to conclude that the atoms of Sn(IV) are in a state almost equivalent to that in SnO_2. Singlet 4 (Fig. 1) has a larger value of δ, and nearly the same linewidth, which, like for singlet 3, can be represented as a symmetric doublet with $\Delta \sim 0.6$ mm/s (Table 1). The state of Sn(IV) in this compound is more sensitive to the preparation conditions of the sample, which is evidenced by more pronounced variations of its δ and f'_{77}/f'_{295}. The available data do not allow us to identify this compound of Sn(IV) in more detail [it is given in Table 1 as Sn(IV) on the support surface].

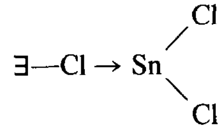
Supporting $SnCl_2 \cdot 2H_2O$ in isopropanol on prechlorinated γ-Al_2O_3 leads to the formation of Sn-containing compounds (Table 1, sample A-1) on the support surface, which have δ and Δ similar to those of A-0; but the f'_{77}/f'_{295} values are considerably different from those of A-0. For doublet Nos. 1 and 2, the sum of which yields an asymmetric doublet $S_{1;2}$ (Fig. 1, A-1), f'_{77}/f'_{295} ratios are even much higher than those of massive $SnCl_2 \cdot 2H_2O$. Such an increase in the temperature dependence of f' of Sn(II) atoms indicates, first, that the corresponding compound does not produce surface particles of the tin chloride phase, but is a specific product of the interaction between solvated molecules of $SnCl_2$ and γ-$Al_2O_3(Cl)$ surface sites. Additional support comes from electron microscopic measurements, which show that molecular distribution of $SnCl_2(ROH, H_2O)$ is most probable because surface particles were not detected. Second, an increase in $f'(T)$ indicates that this interaction produces the compound in which the Sn(II) atom is bound to the surface less rigidly than in the coordination sphere of $SnCl_2 \cdot 2H_2O$.

The observed variations in NGR spectral parameters of Sn(II) on γ-$Al_2O_3(Cl)$ compared to samples on standard γ-Al_2O_3 can reasonably be explained by assuming that the interaction of solvated $SnCl_2$ with this carrier occurs via its coordination with surface Cl^-:



$$\exists\text{—Cl} + SnCl_2 \cdot (ROH, H_2O) \rightarrow \exists\text{—Cl} \rightarrow Sn\begin{matrix}\diagup Cl \\ \\ \diagdown Cl\end{matrix} \cdot (ROH \text{ or } H_2O) + H_2O \text{ or } ROH. \tag{2}$$

Such coordination should bring about low-frequency vibration modes, which are rocking deformation vibrations of $SnCl_2$ relative to surface Cl in the



$$\exists\text{—Cl} \rightarrow Sn\begin{matrix}\diagup Cl \\ \\ \diagdown Cl\end{matrix}$$

fragment and which cause the strong dependence, $f'(T)$ (*8*). Conservation of an approximate constancy of δ as compared to δ of Sn(II) on γ-Al_2O_3 can be accounted for by assuming that coordination with surface Cl atoms occurs via displacement of ROH or H_2O molecules coordinated with $SnCl_2$. Naturally, it is one of the possible explanations. It is evident, however, that the molecules of $SnCl_2$ are bound to the surface sites of γ-$Al_2O_3(Cl)$ more weakly than in the case of γ-Al_2O_3. It should be noted that the interaction via scheme (2) may involve two states of surface Cl atoms with different coordination abilities, because in this case doublet $S_{1;2}$ is asymmetric and decomposes into two symmetric doublets, Nos. 1 and 2 (Table 1, Fig. 1, A-1).

For sample A-1, as for sample A-0, we observed additionally the signals of two types of Sn(IV) (singlets 3 and 4, Fig. 1). But the amount of Sn(IV) states was higher and the δ of singlet 4 was somewhat higher than in sample A-0. This might also be evidence for participation of Cl atoms in coordination with Sn(IV). Treatment of A-1 with oxygen leads to the complete oxidation of Sn(II) to Sn(IV), which, according to electron microscopic data, remains as extremely dispersed (no particles are detected) as before the oxidation. The NGR spectrum of A-2 (Table 1) has a slightly resolved doublet with $\delta = 0$ and $\Delta = 0.7$ mm/s. The value of f'_{77}/f'_{295} remains similar to that of massive SnO_2. These values of three NGR parameters indicate that the state of Sn(IV) on the surface of γ-$Al_2O_3(Cl)$ treated in oxygen does not differ (at least strongly) from its state in SnO_2 crystals. But the electron microscopic data do not reveal the existence of detectable particles of the SnO_2 phase on the carrier surface. This might be expected proceeding from a low state of surface saturation with tin (see Experimental). Below we shall refer to this state of Sn(IV) as $SnO_2^{\text{surf.}}$ assuming a symmetrical surrounding of Sn(IV) atoms by oxygen atoms.

Reduction of A-2 with H_2 at the same temperatures as the temperature of reforming transforms its spectrum to that of A-3 (Fig. 1) with a wide asymmetric doublet $S_{1;2}$, the linewidths of which are identical to those of A-0 and A-1 spectra. However, this doublet is characterized by a lesser dependence $f'(T)$ and a higher value of δ as compared to A-1. It can also be represented as two symmetric doublets with $W_{1;2} = 0.8$ mm/s, which is evidence that Sn(II) interacts with at least two surface sites different in properties, like in the samples before the reduction treatment (Fig. 1, A-0, A-1). In

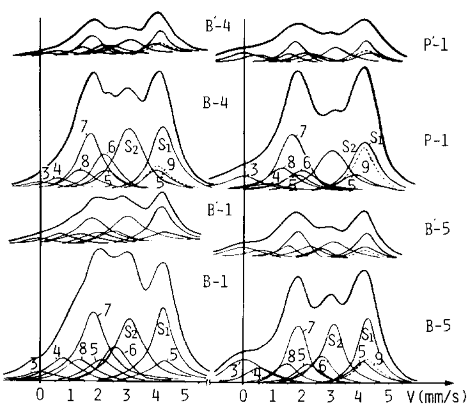


FIG. 2. NGR spectra of Pt–Sn/γ-Al_2O_3(Cl) catalysts. Both components of symmetric doublets are marked by the same figure everywhere. ILCs are designated as in Fig. 1. Spectra B-1, B-4, B-5, and P-1 are taken at 77 K; spectra B'-1, B'-4, B'-5, and P'-1, at 295 K. **B-1:** Sample reduced with H_2 at 773 K after supporting the complexes, drying, and treating with oxygen. **B-4:** sample B-1 after six redox cycles. **B-5:** sample B-4 after 12-h treatment with the mixture of H_2O and O_2 vapor (823 K) and subsequent reduction with H_2 at 823 K. **P-1:** sample obtained by successive supporting of $SnCl_4$ and H_2PtCl_6 (see Experimental).

addition to this doublet, there appears doublet No. 5 with parameters characteristic of $SnAl_2O_4$ (*3*). As for $SnO_2^{surf.}$, the parameters of the corresponding singlet No. 3 remain unchanged. For the second state of Sn(IV) producing singlet No. 4, δ slightly increases, while the temperature dependence of f' decreases.

From all of the above it follows that the effect of the high temperature and reduction atmosphere is primarily a strong change of the state of Sn(II). In fact, instead of the two states of Sn with a typical summed asymmetric doublet $S_{1;2}$ (Fig. 1, A-1), we now have three states [two types of Sn(II) on the surface plus one in the form of $SnAl_2O_4$]. All three states are characterized by a considerably enhanced interaction of Sn with the surface, which is evidenced by a strong decrease in their f'_{77}/f'_{295} as compared to A-1 (Table 1). Moreover, the formation of $SnAl_2O_4$ appears to occur via insertion of Sn(II) into the lattice of γ-Al_2O_3(Cl) and its subsequent transformation. The absence of particles of SnO_2 phases or other Sn(IV) compounds may suggest that Sn(IV) ions insert into the lattice of γ-Al_2O_3(Cl) as well. The spectrum of A'-3 shows the temperature dependence of f' for all Sn-containing components of the sample, whose numerical characteristics are compiled in Table 1.

By summing the spectrum of A-3 with the singlet (*1, 4*) having δ and Δ of Pt_3Sn (No. 6), PtSn (No. 7), and $PtSn_2$ (No. 8) alloys and by varying their intensities solely, it is possible to obtain spectrum M (Fig. 1), which is identical to the spectrum of the Pt–Sn catalyst (compare with Fig. 2, spectrum B-5). This is independent evidence that the latter consists of components whose states are similar to those of A-3 and Pt–Sn alloys.

The data obtained provide no possibility to definitely identify the type of interaction of Sn(II) ions with the support. Still, evaluation of their NGR parameters (Table 1) has made it possible to construct an alternative [compared to (*1*)] model of the decomposition of NGR spectrum of Pt–Sn/γ-Al_2O_3(Cl) catalyst into a ILC (Fig. 2, B-1). The spectrum of B-1 consists of two Sn(IV) singlets, one of which is ascribed to $SnO_2^{surf.}$, an $SnAl_2O_4$ doublet (No. 5) and an asymmetric doublet ($S_{1;2}$) corresponding to Sn(II) ions interacting with the surface and partly preserving the Sn–Cl bonds. At decomposition, NGR parameters of all these components remain similar to those of A-3 (compare Tables 1 and 2). The remaining spectrum was adjusted to the required number of singlets, which have δ and Δ, as well as f'_{77}/f'_{295}, approximately the same as those of individual alloys of the corresponding compositions. We have failed to decompose B-1 and the other spectra into ILCs by taking large splittings for Pt–Sn alloys (*6*) and preserving the above parameters of the remaining Sn-containing components.

As shown by electron microscopic studies of B-1, its surface has no particles larger than 9 Å; i.e., our samples have nearly the same dispersion of Sn-containing components as that reported in (*6*), where the authors assumed rather unusual parameters for Pt–Sn alloys in the study of the state of the Pt–Sn/γ-Al_2O_3 catalyst. For instance, δ of the Pt–Sn alloy varied over the range 1.85 to 2.13 mm/s, which is typical of an individual massive state, and Δ varied from 0.3 to 5.26 mm/s. The latter value should correspond to the imbalance of the $5P_{x,y}$ and $5P_z$ atomic orbital population on Sn of about 1.7 electrons (*12*).

Note that a value of Δ higher than 3 mm/s (this corresponds to an imbalance of 1 electron) has never been observed for any individual compound of Sn with any atomic composition. It is even more unrealistic if the state of Sn is interpreted as an alloy with the tetrahedral surrounding of a Sn(0) atom by Pt atoms. If the high dispersion of the alloy particles would cause a high value of Δ, δ could not remain unchanged. We have observed (13) the formation of a Pt–Sn cluster species 9 ± 3 Å in size on a SiO_2 surface. Its NGR spectrum was characterized by $\Delta = 2.32$ mm/s and $\delta = 1.43$ mm/s, and a reason for their mutually related change was a strong interaction of Sn with the oxygen atoms of SiO_2 rather than the high dispersion of the cluster. In our case Sn in the Pt–Sn alloys does not seem to interact strongly with the surface. In terms of the Debye crystal the same f'_{77}/f'_{295} as that of massive alloys reflects, most probably, the superposition of two contrary effects: (i) increase of $f'(T)$ with a decrease in size of particles due to the increase in the number of Sn atoms on the alloy surface relative to the number of bulk Sn atoms; (ii) decrease of $f'(T)$ with a strong decrease in the size of particles due to a related decrease in the wavelength of the phonon spectrum (*12*). Practically, we should consider particles of Pt–Sn alloys with an effective diameter less than 10 Å either as clusters or as three-dimensional polymeric molecules, for which $f'(T)$ is a function of the rigidity of Sn binding with the nearest surrounding atoms (*8*). For such particles on the surface of γ-Al_2O_3(Cl) this rigidity is the same as that of massive alloys, as shown by f'_{77}/f'_{295} values measured by us.

Thus, an arbitrary variation of NGR parameters, e.g., Δ, at the decomposition of spectra into ILCs seems to us groundless.

In this connection, it seems expedient to use two models of decomposition. According to the first model, δ, Δ, W remain in the range characteristic of individual compounds with similar compositions. This model was used in (*1, 3, 4*). According to the second model, the interactions of individual compounds with a support are preliminary studied under conditions approximating the reaction conditions. The parameters identified for Sn states remain the same for components resulting from the decomposition of catalyst NGR spectra. This approach was used in part by Berndt *et al.* (*2*) but they considered only the values of δ and Δ. We propose to consider additionally the dynamic parameters of NGR spectra, primarily, the dependence $f'(T)$ in the form f'_{77}/f'_{295}, which is especially sensitive to the character of interaction of Sn atoms with the environment (*8*).

Pt–Sn/Al_2O_3(Cl) Catalyst

As follows from the above-described preparation procedure, $SnCl_3$-containing complexes are supported under conditions identical to those of supporting $SnCl_2 \cdot 2H_2O$. In this case partial hydrolysis of $SnCl_3$ ligands and anchoring of the complex on the surface, which can be described by an equation similar to Eq. (1) (*14*), occur on γ-Al_2O_3. On the γ-Al_2O_3(Cl) support the $SnCl_3$ ligands appear to react with other surface sites. The sample is then dried and subjected to oxidation treatment. All of the Sn transforms to the state that has the same NGR parameters as A-2 (Table 1). We have identified this state as $SnO_2^{\text{surf.}}$.

Treatment of this sample with hydrogen at the same temperature leads to the reduction of most of the Sn(IV) to Sn(II) and Sn(0) (Fig. 2, B-1). As mentioned above, decomposition of such a spectrum into ILCs gives the same set of Sn compounds on the catalyst surface as that obtained by

TABLE 3

Second Model of Decomposition: Amounts (wt%) of Sn-Containing Components in Pt–Sn/γ-Al_2O_3(Cl)

Sample	State							
	$SnO_2^{surf.}$	Sn(IV)$^{surf.}$	Pt_3Sn	PtSn	$PtSn_{2:4}$	$SnAl_2O_4$	Sn(II)$^{surf.}$	Analog of anhydrous $SnCl_2$
B-1	1.2	4.5	8.9	14.7	10.0	14.1	46.6	—
B-2	100							
B-3	3.7	8.6	9.1	12.9	14.6	11.5	35.7	3.9
B-4	2.2	4.1	6.5	17.6	11.8	12.2	39.0	6.6
B-5	9.5	2.9	7.9	14.9	9.0	11.6	37.4	6.8
C-1	1.5	4.6	7.0	16.8	9.2	13.4	40.5	7.0
C-2	1.1	3.1	8.5	17.2	9.4	13.3	38.8	8.6
C-3	0.8	2.3	11.9	14.3	10.6	13.6	37.9	8.6
P-1	6.5	2.6	8.6	18.8	8.4	12.0	31.2	11.9

summing the spectra of A-3 and Pt–Sn alloys (Fig. 1, spectrum M). By further treating the samples of series B and C and sample P-1, their NGR spectra can satisfactorily be represented as the sum of ILCs of the same Sn-containing compounds. Electron microscopic measurements show that the maximum size of particles on the surface of all catalysts does not exceed 9 Å. This relates, first, to the particles of Pt–Sn alloys because they produce the most contrasting pictures. Particles of other Sn compounds are even smaller and most of them appear to represent monomolecular surface coverage. Since under the conditions employed (see Experimental) the state of Sn-containing compounds can change from sample to sample (e.g., the degree of interaction with the surface, etc.), during the decomposition of the spectra into ILCs some variations in their NGR parameters are admitted. The ranges of these variations are shown in Table 2. NGR spectra of a great number of the treated samples, which differ in the number of redox cycles, in the composition of reduction medium, and in the procedure of supporting the Pt–Sn components of the catalyst, can be represented as a sum of NGR spectra of practically the same Sn compounds (to be more precise, states) on the surface. This fact suggests that the Cl-modified γ-Al_2O_3(Cl) support possesses some specific properties that determine the catalyst state under various conditions.

In the same way as for samples of series A, Fig. 2 represents the spectra of individual samples of series B and P-1 at 295 K, which demonstrate $f'(T)$ for all Sn-containing compounds of the catalyst.

In Table 2 it is seen that this dependence becomes almost the same for all states of Sn on the surface. This provides the possibility of estimating the amounts of corresponding catalyst components from the areas under their ILCs without introducing corrections for the differences in f' which cannot be determined accurately. The proposed approximation is acceptable also because we are interested in information about the relative change of Sn-containing components after the sample has been subjected to various conditions rather than in the absolute amounts of these components. The results for all samples studied are compiled in Table 3.

As was noted in the Introduction, in the previous report (*1*) we analyzed the composition of Sn-containing components of sample B-1 according to the first model of decomposition of NGR spectra. The second model used in this work has required a rather complicated, independent analysis of the behaviour of two-valent tin, which is

TABLE 4

First Model of Decomposition: Amounts (wt%) of Sn-Containing Components in Pt–Sn/γ-Al_2O_3(Cl)

Sample	Compound						
	SnO_2	Sn(IV)	Pt_3Sn	PtSn	β-Sn	$SnCl_2 \cdot 2H_2O$	$SnCl_2$ anhydrous
B-1	2.9	10.4	11.5	15.9	11.3	38.1	9.9
B-2	100	—	—	—	—	—	—
B-3	7.6	6.8	13.3	13.4	14.4	29.0	15.4
B-4	3.9	6.4	12.7	13.6	10.3	37.2	15.9
B-5	9.4	7.7	14.1	11.0	5.8	34.7	17.3
C-1	3.8	6.9	13.1	16.1	9.0	34.2	17.7
C-2	0.9	8.6	13.9	17.0	9.6	30.4	19.5
C-3	0.6	8.6	14.2	19.4	7.5	29.2	20.4
P-1	8.5	5.9	14.6	17.7	7.6	19.3	26.5

not bound to Pt, on the support surface under catalyst operation conditions (samples of series A). In order to evaluate in which situations the use of the first (*1*) or the second (this work) approximation is more appropriate, we decomposed the NGR spectra of all samples into ILCs in the first approximation (*1*) and estimated the amounts of Sn-containing components from the areas under their ILCs. The results of this analysis are given in Table 4. From a comparison of catalyst compositions obtained with two models of decomposition it is seen that both models provide qualitatively similar information: two types of Sn(IV) and several states of Sn(II) and Sn(0) in different Pt–Sn alloys. Identification of β-Sn in the first model and of the $PtSn_4$ alloy in the second model should not be regarded as an essential difference because their δ values are similar and their identification by NGR spectroscopy in the case of their coexistence is quite complicated. The quantities of these three groups of surface compounds obtained by the two approaches are also comparable.

Because the first model is simple enough to realize, we recommend that it be used at the initial steps of investigation of the composition of the systems under consideration. The second model, and especially the analysis f'_{77}/f'_{295}, allows one to obtain more detailed information about the types of compounds which can be produced during the course of the interaction of Sn(II), which is not bound to a transition metal, with the surface.

Pt–Sn catalysts on $ZnAl_2O_4$ supports were reported (*4*) to have an ability to rapidly reproduce the composition in many redox cycles. A spectrum of the Pt–Sn/γ-Al_2O_3(Cl) catalyst taken after six redox cycles is illustrated in Fig. 2 (B-4). It is seen that the catalyst composition, namely, initial types of Sn-containing components (see B-1), generally remains the same, but the relative amounts of alloys changed: the amount of $Sn(II)^{surf.}$ decreased slightly, and another type of Sn(II) appeared. This latter type produced singlet No. 9 (Fig. 2, B-4) which is typical of the phase of anhydrous $SnCl_2$ (Table 2). Production of a Sn(II) state similar to $SnCl_2^{anhydr.}$ has also been identified in (*2*). The isolated state of Sn(II) characterized by singlet No. 9 cannot be identified as the phase of anhydrous $SnCl_2$ on the surface because the f'_{77}/f'_{295} of this singlet is rather low. Most probably, this is an alternative (fourth) type of Sn(II) on γ-Al_2O_3(Cl) with symmetric surrounding by Cl atoms in deeper layers of the support surface, similar to the phase of anhydrous $SnCl_2$ (*15*). Subsequent oxidation of catalyst B-4 and reduction (see Experimental) (Fig. 2, B-5) somewhat enhance the concentration of Sn(IV) of both types and decrease the amounts of $SnAl_2O_4$ and $Sn(II)^{surf.}$ in the system.

Because the differences in f' were not taken into account, the obtained numerical estimates of the amounts of each Sn component in the catalyst give only a qualitative idea of their variations. Still, these estimates lead to a conclusion which is very important in practice: subtle peculiarities of the states and concentrations of Sn-containing components change somewhat from cycle to cycle. Data from the elemental analysis indicate that the amount of Cl^- also decreases. In addition, they quite convincingly show that the state of $Sn(II)^{surf.}$ is most dynamic. This indicates that, as for samples of series A, the degree of interaction of Sn(II) not bound to Pt with the support increases from cycle to cycle, perhaps due to a deeper insertion of Sn(II) and Cl^- ions into the bulk. At least this can provide an explanation for the observed weakening of $f'(T)$ of Sn(II).

The catalysts treated by the reaction mixture (series C) have essentially similar compositions and almost the same proportion of components as the catalyst subjected to several cycles of reduction with hydrogen. This proves that the peculiarities of variations of catalyst states established for series B are also valid for real conditions of reforming. The main substance of the reaction medium that participates in the catalyst formation is H_2. Interestingly, after the reduction, the catalyst obtained by supporting H_2PtCl_6 over γ-Al_2O_3(Cl) with preadsorbed $SnCl_4$ produces an NGR spectrum (Fig. 2, P-1) that indicates the same qualitative composition as sample B-5, which was made from $SnCl_3$-containing complex of Pt, but of different quantitative composition. It differs from sample B-1 by the presence of Sn(II), which is similar in δ to anhydrous $SnCl_2$, and the amount of which is larger than in samples B-5 and C-3. Another quantitative difference is a smaller amount of $Sn(II)^{surf.}$. Thus, the preliminary supporting of $SnCl_4$ on γ-Al_2O_3(Cl) seems to promote a more complete interaction of Sn(II) with γ-Al_2O_3(Cl) at subsequent reduction. Separate supporting of Pt and Sn components has almost no effect on the composition and amount of Pt–Sn alloys.

From the data on the relative content of Sn compounds in the catalyst and from the elemental analysis for Cl it follows that excess Cl ions do not interact with Sn on the surface, and their removal after hydrolysis of the Al–Cl bonds does not affect the state of the remaining Sn compounds. This indicates that excess Cl^{-1} ions on the surface play an important role in the primary act of interaction of the compounds with the support surface, "making" them react with sites of a certain nature. It is even the first thermal treatment that seems to lead to a rather strong bond between Sn and these sites. Subsequent redox cycles do not substantially change the topology of disposition of most Pt and Sn atoms and surface atoms of γ-Al_2O_3(Cl) interacting with them.

CONCLUSIONS

1. The state and the properties of the support surface play a most important role in the formation of Pt–Sn catalysts. Cl^- ions that modify the properties of the γ-Al_2O_3 surface change the character of interaction of supported Sn chlorides and $SnCl_3$-containing complexes with the surface, which further determines the specificity of the state of Sn in the catalyst.

2. The reforming Pt–Sn/γ-Al_2O_3(Cl) catalysts under consideration are multicomponent, highly dispersed products of the interaction of Sn(IV), Sn(II), and Sn(O) with the support surface and Pt. The latter forms nearly all possible alloys with Sn. After a rather large number of redox cycles, Sn(IV) compounds and Pt–Sn alloys are reproducibly formed on the catalyst surface; their amounts are slightly changed. The amount and composition of Sn(II) compounds tend to change most dynamically. The change is associated with a strong interaction of some of the Cl^- ions and the Sn with the support

lattice. Some of the Cl^- ions are lost at HCl due to hydrolysis of the Al–Cl bonds. Sn(IV) ions are also quite rigidly bound in the surface layer of the lattice, whereas tin in the alloys does not interact noticeably with the lattice. Dispersion of the catalyst particles does not decrease from cycle to cycle, which is additional evidence that the support plays an important part in the formation of the catalyst.

3. During the NGR study of the states of Sn-containing components of such catalysts, the analysis of the corresponding spectra is connected with the necessity to decompose them into individual Lorenz components. The parameters of these components should be varied with great caution. For the first, rough analysis it is recommended that the parameters of ILCs be similar to those of individual Sn compounds in similar states. A more detailed analysis of the state of Sn on the support with various simpler Sn compounds such as $SnCl_2 \cdot 2H_2O$ is needed. To identify the compounds formed at all steps of catalyst preparation, it is necessary to use all measurable parameters of NGR spectra [δ, Δ, W, and $f'(T)$].

REFERENCES

1. Kuznetsov, V. I., Yurchenko, E. N., Belyi, A. S., Zatolokina, E. V., Smolikov, M. A., and Duplyakin, V. K., *React. Kinet. Catal. Lett.* **21,** 419 (1982).
2. Berndt, H., Mehner, H., Volters, S., and Meisel, W., *Z. Anorg. Allg. Chem. B* **429,** 47 (1977).
3. Grey, P. R., and Farha, F. E., "Mössbauer Effect Methodology, Proceedings of Annual Symposia," Vol. 10, p. 47. Plenum, New York/London, 1976.
4. Pakhomov, N. A., Buyanov, R. A., Yurchenko, E. N., Chernyshev, A. P., Kotelnikov, G. R., Moroz, E. M., Zaitseva, N. A., and Patanov, V. A., *Kinet. Katal.* **22,** 488 (1981).
5. Paukshtis, E. A., Soltanov, P. I., Yurchenko, E. N., and Jiratova, K., *Collection of Czekoslovak Chemical Communications* **47,** 2044 (1982).
6. Bacaud, R., Bussiere, P., and Figueras, F., *J. Catal.* **69,** 399 (1981).
7. Shitova, N. B., Alt, L. Ya., Perevalova, V. I., Belyi, A. S., and Duplyakin, V. K., *React. Kinet. Catal. Lett.* **23,** 17 (1983).
8. Yurchenko, E. N., Kuznetsov, V. I., and Burgina, E. B., *Teor. Exp. Khim.,* No. 2, 194 (1985).
9. Suzdalev, I. P., Goldanskii, V. I., Makarov, E. F., Plachinda, A. S., and Korytko, L. A., *Zh. Exp. Teor. Fiz.* **46**(II), 1424 (1965).
10. Bryukhanov, V. A., Delyagin, N. N., Opalenko, A. A., and Shpinel, V. S., *Zh. Eksp. Teor. Fiz.* **43,** 432 (1962).
11. Greenwood, N. N., and Gibb, T. C., "Mössbauer Spectroscopy." Chapman & Hall, London, 1971.
12. Shpinel, V. S., "Rezonans gamma-luchei v kristallakh." Nauka, Moskva, 1967.
13. Shepelin, A. P., Chernyshev, A. P., Kovalchuk, V. I., Zhdan, P. G., Yurchenko, E. N., Kuznetsov, B. N., and Yermakov, Yu. I., *Kinet. Katal.* **22,** 716 (1982).
14. Yurchenko, E. N., Kuznetsov, V. I., Melnikova, V. P., and Startsev, A. N., *React. Kinet. Catal. Lett.* **23,** 137 (1983).
15. Van den Berg, J. M., *Acta Crystallogr.* **14,** 1002 (1961).