The chemical shift of the Sn atom in chloride 3 (δ(^{119}Sn) −33.3, $CDCl_3$ −60 °C) is temperature-independent, which indicates that the central atom retains its coordination state. Therefore, a nonregular mechanism of the stereodynamic process observed involving the cleavage if the coordination O→M bond seems improbable.

Experimental

^{1}H, ^{13}C, and ^{119}Sn NMR spectra of compounds studied were obtained on a Varian XL-400 spectrometer (400.1, 100.6, and 149.2 MHz, respectively) in a pulse mode followed by the Fourier transformation and ^{2}H-stabilization of resonance conditions. Low-temperature studies were carried out in an equimolar mixture of $CDCl_3$ and CD_2Cl_2. ^{1}H and ^{13}C chemical shifts were measured relative to tetramethylsilane as the internal standard. ^{119}Sn chemical shifts were measured relative to tetramethylstannane as the external standard. Free activation energies were determined by the modified Eyring equation.[9]

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Selective dehydrogenation of isopropyl alcohol on low-percentage supported bimetallic rhenium-containing catalysts

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The activity and selectivity of mono- and bimetallic sibunite-supported Re-, Cu-, Ni-, and Pd-containing catalysts in dehydrogenation of isopropyl alcohol to acetone (T = 200—275 °C, v = 1.1 h^{-1}) were studied. The bimetallic Re,Cu-, Re,Ni-, and Re,Pd-catalysts containing 1 or 2% of the metal possess the higher activity and stability than monometallic catalysts.

Key words: supported monometallic Re-, Cu-, Ni-, and Pd-catalysts, bimetallic rhenium-containing catalysts; isopropyl alcohol, dehydrogenation.

The high activity of the carbon-supported rhenium-containing catalysts (30% Re/C) has been observed previously[1] in the dehydrogenation of isopropyl alcohol to acetone. However, this catalyst was rapidly deactivated. In this work, we attempted to develop selective low-percentage rhenium-containing catalysts and found conditions for the dehydrogenation of isopropyl alcohol to acetone.

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Table 1. Dehydrogenation of isopropyl alcohol on 1% monometallic sibunite-supported catalysts (p = 0.1 MPa, υ = 1.1 h^{-1}, in hydrogen flow)

Composition of catalyst*	Conditions		Yield of products (%)	Conversion of Pr^iOH (%)		Selectivity to acetone (%)
	T/°C	t/h		total	to acetone	
Re/Sib	200	1.0	91.4	34.2	26.5	77.0
	250	2.0	86.2	66.6	54.7	82.0
Cu/Sib	200	1.0	94.3	20.5	15.3	74.6
	250	2.0	89.7	52.5	43.7	83.2
Ni/Sib	200	1.0	96.6	15.1	12.1	80.1
	250	2.0	89.1	43.1	33.3	77.3
Pd/Sib	200	1.0	100.0	1.6	1.6	100.0
	250	2.0	100.0	21.5	21.5	100.0
	275	3.0	97.7	37.5	36.4	97.0

* Here and in Table 2, Sib is sibunite.

Experimental

The reaction was studied in a flow-type quartz reactor (l = 350 mm, d = 20 mm) using a catalyst loading of 1.35 g. Isopropyl alcohol (reagent grade, n_D^{20} 1.3776, d_4^{20} 0.7854) was supplied into the reactor using an automated plunger-type dosing apparatus with a flow rate (υ) of 1.1 h^{-1} in a hydrogen flow at T = 200, 250, and 275 °C; the same portion of the catalyst was used. Liquid products were analyzed by GLC (column 3 m × 3 mm filled with polyethylene glycol adipinate (15%) on Chromosorb P) and by refractometry. Sibunite, *i.e.*, granular pyrocarbon with a filled mass of 0.6 g cm^{-3}, a specific surface as measured by nitrogen thermal desorption of 680 m^2 g^{-1}, and a specific surface area estimated by phenol adsorption of 230 m^2 g^{-1}, was used as a support for the catalyst. The size of support granules was 2—3 mm.

The catalysts were prepared by impregnation of sibunite with solutions of NH_4ReO_4, $PdCl_2$, and acetates of nickel or copper. Samples dried at 120 °C were reduced in a hydrogen flow at 500 °C prior to use. We prepared sibunite-supported monometallic catalysts containing 1% Re, Cu, Ni, or Pd, and bimetallic catalysts containing Re and Cu, Re and Ni, or Re and Pd with the concentration of each metal equal to 1 or 2%. The results of studying the catalytic properties of these systems are presented in Tables 1 and 2.

Results and Discussion

The rhenium sample possesses the highest activity in the dehydrogenation of isopropyl alcohol among supported monometallic 1% Re-, Cu-, Ni-, and Pd catalysts. At 250 °C and υ = 1.1 h^{-1}, the yield of acetone on the Re/C catalyst is close to that obtained when the sample containing 30% rhenium is used (T = 195 °C, υ = 0.2 mL min^{-1}).[2]

The catalysts studied can be arranged by activity in the following series: Re/C > Cu/C > Ni/C > Pd/C. Despite a rather high activity, the sibunite-supported 1% monometallic catalysts are not stable in time, and the initial conversion decreases 2—3 times after testing for 3 h.

Table 2. Dehydrogenation of isopropyl alcohol on bimetallic rhenium-containing sibunite-supported catalysts (p = 0.1 MPa, υ = 1.1 h^{-1}, in a hydrogen flow)

Composition of catalyst*	Conditions		Yield of products (%)	Conversion of Pr^iOH (%)		Selectivity to acetone (%)
	T/°C	t/h		total	to acetone	
1% Re, 1% Cu, 98% Sib	200 250	1.0 2.0	92.5 85.6	27.7 61.7	21.0 49.0	75.8 79.4
1% Re, 1% Ni, 98% Sib	200 250	1.0 2.0	89.7 80.5	61.5 79.7	53.0 64.0	86.0 80.3
1% Re, 2% Ni, 97% Sib	200 250	1.0 2.0	85.1 86.2	58.6 88.9	45.3 77.7	77.3 87.4
2% Re, 1% Ni, 97% Sib	200 250	1.0 2.0	84.5 80.5	62.8 85.1	48.7 67.9	77.8 79.8
2% Re, 2% Ni, 96% Sib	200 250	1.0 2.0	92.0 83.9	56.4 94.8	50.1 81.5	88.8 85.9
1% Re, 1% Pd, 96% Sib	200 250	1.0 3.0	93.7 81.6	76.1 93.0	55.5 77.2	82.7 83.0

On the sibunite-containing bimetallic catalysts containing 1% Re and 1% Cu, 1% Re and 1% Ni, or 1% Re and 1% Pd, the conversion of isopropyl alcohol to acetone increases considerably as compared to that achieved when the monometallic Cu/C, Ni/C, and Pd/C samples are used. For example, after rhenium was introduced into the palladium-containing catalyst, its activity increases 35 times. The difference in activity of the mono- and bimetallic catalysts is retained at 250 °C. The presence of the second metal increases almost twice the stability of the catalysts. For example, their activity decreases 1.4 times only after testing for 4 h. The high dehydrogenation activity of the supported bimetallic catalysts as compared to the activity of the monometallic contacts is probably related to the fact that in the presence of rhenium, the degree of reduction of the second metal (Cu, Ni, Pd) increases. The activity of 1% bimetallic catalysts in the dehydrogenation increases in the series Re,Cu/C < Re,Ni/C < Re,Pd/C.

The highest effect of the introduction of rhenium was observed for the sibunite-supported Pd-catalyst. The promotion effect of rhenium has been previously observed for palladium-containing alumina-based catalytic systems. The presence of rhenium resulted in an increase in the activity and stability of catalysts in transformations of hydrocarbons and reforming of gasoline fractions.[3]

It follows from the data in Table 2 that the bimetallic catalysts containing 1 and 2% rhenium in combination with 1 or 2% nickel or 1% palladium possess a considerable dehydrogenation activity, and at 200 and 250 °C, the yield of acetone obtained from isopropyl alcohol reaches at least 80% of the equilibrium value.[4] The initial activity of these catalysts almost does not decrease within 6—9 h, and they are characterized by a high selectivity (77—90%).

No phase of crystalline rhenium was observed in the active reduced 2% Re + 2% Ni sample by X-ray phase analysis. This sample can be assumed to exist in the highly dispersed state.

Thus, the developed sibunite-supported bimetallic catalysts containing 1—2% Re in combination with 1—2% Ni or 1% Pd are active and selective in the dehydrogenation of isopropyl alcohol.

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Synthesis and transformations of acyloxy(chloromethyl)phosphonates and acyloxy(chloromethyl)phosphinates

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The reactions of *O*-phenyl chloromethylphosphonochloridate and bis(chloromethyl)phosphinous chloride with sodium acetate afford the corresponding acyloxyphosphonates and acyloxyphosphinates, which are readily transformed due to disproportionation into pyrophosphonates and pyrophosphinates.

Key words: chloromethylphosphonates, bis(chloromethyl)phosphinates, reaction, disproportionation, pyrophosphonates, pyrophosphinates.

Many of the dialkylacyl phosphates (phosphonates and phosphinates) known at present time obtained by the reactions of the corresponding P^{IV} acid chlorides with silver or lead salts of carboxylic acids.[1] The use of sodium or potassium acetates in these reactions gives no positive results. At the same time, we established[2] that chloromethylphosphonochloridates and bis(chloromethyl)phosphinous chlorides exhibit a substantially greater electrophilic activity in nucleophilic substitution reactions than dialkyl chlorophosphates, alkyl(aryl) phosphonochloridates, and dialkyl(aryl) phosphinous chlorides. This suggested success in reactions of chloromethylphosphonates and -phosphinates with sodium acetate. In fact, the reaction of AcONa with *O*-phenyl chloromethylphosphonochloridate (**1**) in MeCN at room temperature results in the almost quantitative formation of *O*-acetyl *O*-phenylchloromethylphosphonate (**2**) (δ_P 14.82), whose structure was confirmed by the data of IR and ^1H and ^{31}P NMR spectroscopy, and the composition was established by elemental analysis.

$$\underset{\mathbf{1}}{PhO(ClCH_2)P(O)Cl} + AcONa \xrightarrow[-NaCl]{}$$

$$\longrightarrow \underset{\mathbf{2}}{PhO(ClCH_2)P(O)OC(O)Me}$$

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