experiments 1 and 2, Table 2) agree well with the results of experiment 3. Increasing the specific velocity of IB introduction from 1 to 1.5 mol L_{Cat}^{-1} h^{-1} (by the corresponding 1.5-fold decrease in the conventional contact time) results in a decrease in its conversion from 47 to 35 %, which is normal for heterogeneous catalytic reactions in a flow-type reactor.

The preparation of benzyl isobutyrate (BIB) from BA and IB *via* reaction (3) together with the data on reaction (2) indicates that the Tishchenko reaction is reversible under the chosen conditions.

The formation of other reaction products in addition to BA and IBA can be easily explained if one takes into account the possibility of the occurrence of their hydrogenation. It can be assumed that hydrogen, which is necessary for hydrogenation transformations, can be formed through the processes of condensation of aromatic compounds, resulting in the formation of high-molecular unidentified products (15—18 %). If this is taken into account, then isobutyl (IA) and benzyl (BnA) alcohols are products of the hydrogenation of IBA and BA, respectively. At the same time, toluene (T) can be considered to result from the hydrodeoxygenation of IA and BnA. The considerable divergence between the theoretical yields of the aliphatic (IBA+IA) and aromatic (BA+BnA+T) products of the catalytic transformation of IB points to the predominant contribution of aromatic compounds to the preparation of high-molecular products.

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Received November 29, 1993;
in revised form May 25, 1994

Catalysis of the transfer of hydrogen from 2-propanol to cyclohexanone by immobilized ruthenium tetrasulfate

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Heterogenized metal complex systems prepared by immobilization of ruthenium tetrasulfate on the surface of silica gel containing γ-aminopropyl groups or on the surface of modified styrene-divinylbenzene copolymer catalyze the transfer of hydrogen from 2-propanol to cyclohexanone in both Ar and air. It has been shown that the activity and stability of the obtained catalysts depend on the concentration of the promoting alkali and on the nature of the support.

Key words: catalysis, ruthenium, modified silica gel, modified polymers, hydrogen transfer, cyclohexanone.

In this work, it has been shown that it is possible for the C=O-group of ketone to be reduced by chemically bound hydrogen (2-propanol) in the presence of a binuclear ruthenium sulfate complex immobilized on silica gel containing γ-aminopropyl groups and styrene-divinylbenzene copolymers modified by 3(5)-methylpyrazole and imidazole groups.

Experimental

Binuclear sulfate $[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$ was prepared according to the method described in Ref. 1. The synthesized complex was immobilized on silica gel containing γ-aminopropyl groups (γ-AMPS) (Silochrom, S_{sp} = 120 m^2/g, concentration of NH_2-groups is 7.10^{-4} mol/g), sample **1**, and on modified

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1494—1496, August, 1994.

styrene divinylbenzene copolymers containing 3(5)-methylpyrazole (Poliorgs-IV, sample **2**) and imidazole (PVB-IM-10T, sample **3**) groups (Table 1). The initial complex was deposited from 2-propanol or methanol with mixing (20 °C) and subsequent washing of the sample in a boiling solvent. All of the deposition and washing procedures were performed in argon. The amount of deposited ruthenium was determined by atomic absorption spectroscopy from the decrease in the metal concentration in the solutions obtained after filtration and washing of the catalysts. The transfer of hydrogen from 2-propanol to cyclohexanol (cHl) was performed according to the procedure described in Ref. 2. The catalyst (0.05 g) was placed in a reactor, Ar was bubbled through the system, and 10 mL of 2-propanol and a promoter (KOH solution in 2-propanol) were added. The reaction mixture was heated up to 82.5 °C with mixing, then a cHl solution ($4.8-9.6 \cdot 10^{-4}$ moles) in 5 mL of 2-propanol was added. The catalyzate was analyzed by GLC on a Biokhrom-21 chromatograph with a flame-ionization detector, N_2 as the gas-carrier, 130 °C, a column of stainless steel of 3×3 mm, and with Triton on a X-545 zeolite as the liquid phase. The catalyst activity was characterized by the initial specific rate of substrate conversion (W_0, mol/g-atom of Ru min), which was graphically determined.

Results and Discussion

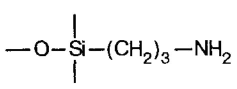
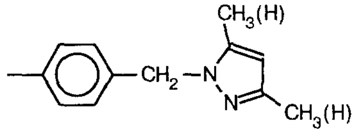
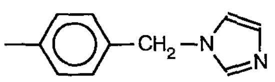
No catalytic activity was observed during the cHl reduction of samples **1**—**3** in boiling 2-propanol in Ar. The complexes catalyzed the hydrogen transfer only when a KOH solution was added to the reaction mixture (an alkali does not catalyze this process in the absence of a metallocomplex). The activity of catalysts **1** and **2** depends on the alkali concentration. It can be seen from Fig. 1, *a* that the reduction of cHl occurs very slowly (W_0 = 0.1 mol/g-atom of Ru min) for the KOH concentration equal to $1.6 \cdot 10^{-3}$ mol/L. Increasing the alkali concentration results in a sharp increase in the reaction rate, which reaches its maximum value at $5 \cdot 10^{-3}$ mol/L (all of the next experiments were performed at [KOH] = $4.5 \cdot 10^{-3}$ mol/L, and a molar ratio Ru : KOH of 1 : 37). Increasing [KOH] further results in a noticeable decrease in the reaction rate, which is probably associated with partial decomposition of the complex by KOH. It should be mentioned that binuclear sulfate $[Ru_2(\mu\text{-}SO_4)_4(H_2O)_2]$ is unstable without a carrier in an alkaline medium: it is hydrolyzed with the detachment of the bridge sulfate groups and subsequent reduction of Ru to the metal, which is inactive under these conditions.

The dependence of the reduction rate on the cHl concentration is also extreme with a maximum in the range of $1.2-1.6 \cdot 10^{-2}$ mol/L (Fig. 1, *b*). The rate of the hydrogen transfer abruptly decreases when the cHl concentration further increases. Retardation of the process seems to be caused by the attachment of the catalyst at a complex with cHl, like in the case of fixed binuclear Rh(II) complexes.[3]

It can be seen from the data of Table 1 that the nature of the matrix has a substantial effect on catalyst activity: the rate of hydrogen transfer in the presence of the complex fixed on a silica gel significantly exceeds the rate of the process catalyzed by ruthenium sulfate bound to a polymer (catalyst **2**). Unlike catalysts **1** and **2**, sample **3** turned out to be inactive due to its instability to an alkali: the immobilized ruthenium tetrasulfate was washed into solution from the carrier surface and the Ru was subsequently reduced to the metal.

It is interesting that the activity of these catalysts did not decrease in air. A similar phenomenon has been

Table 1. Transfer of hydrogen from 2-propanol to cyclohexanone in the presence of immobilized ruthenium tetrasulfate ($1.3 \cdot 10^{-6}$ g-atom of Ru, $10 \cdot 10^{-5}$ moles of cHl, $4.9 \cdot 10^{-5}$ moles of KOH)

Catalyst	Ligand	Carrier	W_0/mol(g-atom of Ru min)$^{-1}$ in an atmosphere of	
			Ar	air
1	 $-O-\overset{|}{\underset{|}{Si}}-(CH_2)_3-NH_2$	γ-AMPS	9.1	8.2
2		Polyorgs-IV	1.2	0.9
3		PVB-IM-10T	0.0	0.0

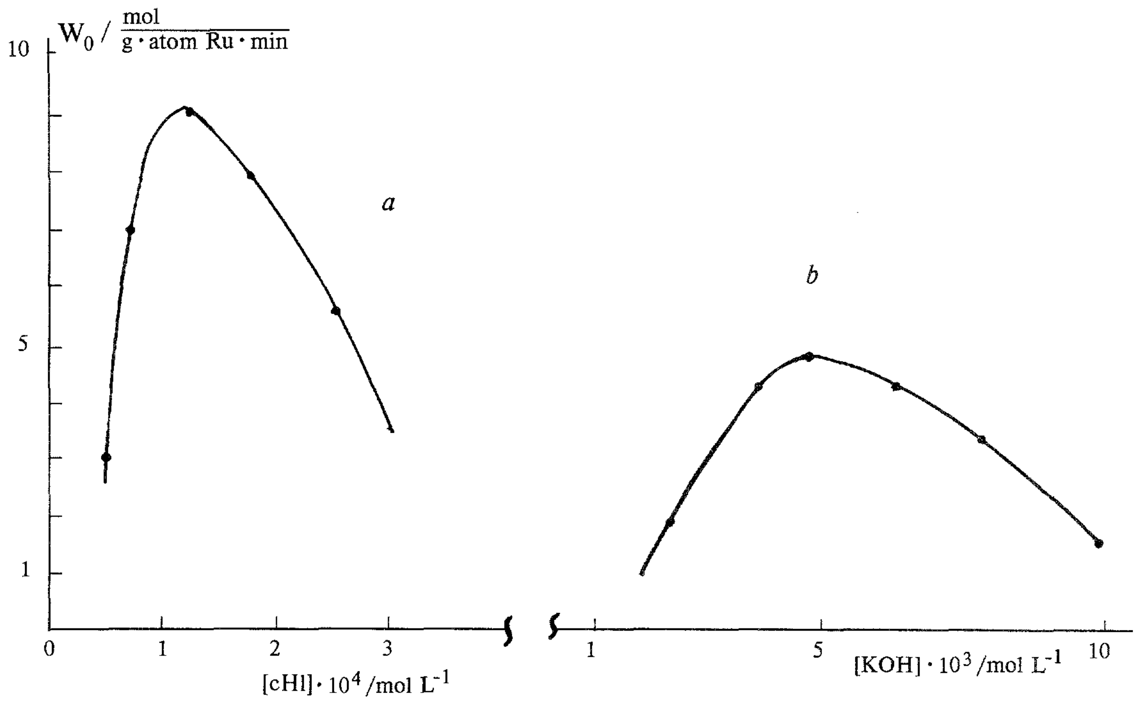


Fig. 1. Effect of the cHI (*a*) and KOH (*b*) concentrations on the initial rate of cHI reduction by 2-propanol in the presence of catalyst **1** ($1.3 \cdot 10^{-6}$ g-atom of Ru, 15 mL of 2-propanol, 82.4 °C, $4.9 \cdot 10^{-5}$ mol/L KOH (*a*), 10^{-4} mol/L cHI (*b*))

previously observed for the reductive hydrodehalogenation of *p*-bromotoluene *via* the transfer of hydrogen from $NaBH_4$ in 2-propanol.[4] The data obtained agree well with the hydride-ionic mechanism of hydrogen transfer suggested in Ref. 5, which involves oxidative addition of an alcohol and coordination of a ketone molecule to form a six-membered intermediate compound.

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Received February 8, 1994