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Influence of rhenium additives on the activity of Cu/sibunite catalyst in transformations of isopropyl alcohol

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The dehydrogenating and dehydrating properties of the Cu(2%)/sibunite catalyst with rhenium additives were studied in the transformations of isopropyl alcohol at 200—270 °C. The catalyst containing 0.25% Re was found to possess the maximum dehydrogenating activity at 200 °C.

Key words: supported copper- and rhenium,copper-containing catalysts, dehydrogenation, dehydration, isopropyl alcohol, acetone, propylene, sibunite.

It has previously[1] been found that the introduction of the 1% Re additive enhances the activity of the Cu(1%)/Sib catalyst (Sib is sibunite) in the transformation of isopropyl alcohol into acetone, and low Cu,Re/Sib catalysts are active in the selective dehydrogenation of methanol to methyl formate (MF).[2] The addition of 0.25% Re favors an increase in the dehydrogenating activity and stability of the Cu(4%)/Sib catalyst.

In this work, the possibility to enhance the dehydrogenating activity of the Cu/Sib catalyst in the decomposition of isopropyl alcohol by rhenium additives was explored.

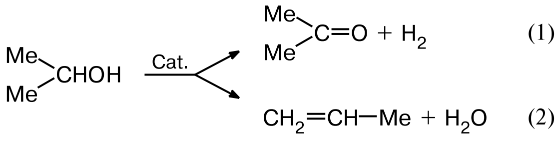
Experimental

The reaction was studied under the atmospheric pressure in a flow-type set with a quartz reactor (350×20 mm). The weight of the catalyst sample was 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 system with a space velocity of 1.1 h^{-1} in a hydrogen flow. Experiments were carried out at temperatures of 200, 235, 250, and 270 °C using the same portion of the catalyst in each experiment. The duration of each experiment was 30 min. Liquid products were analyzed by GLC (column 3 m×3 mm packed with 15% polyethylene glycol adipinate on Chromosorb P) and by refractometry. For analysis of gaseous products, a column (2 m×3 mm) packed with Polisorb was used. Sibunite (granular pyrocarbon with a filled mass of 0.6 g cm^{-3}) served as the support for the catalyst. Its specific surface measured by nitrogen adsorption was 680 $m^2 g^{-1}$, and that measured by phenol adsorption was 230 $m^2 g^{-1}$. The granular size of the support was 2—3 mm.

Catalysts were prepared by the impregnation of sibunite with solutions of NH_4ReO_4 and copper acetate. Samples were dried at 120 °C before experiments and then reduced in a hydrogen flow at 400 °C. Six samples containing 2% Cu were prepared: one sample without an additive (**1**), four samples with an additive of Re (0.25, 0.5, 1.0, and 2.0%) (**2—5**), and one sample with the Cu(2%)+Re(0.25%)/Sib composition (**6**). For the preparation of sample **6**, the support was impregnated with copper nitrate instead of acetate. The degree of conversion of isopropyl alcohol was taken as a measure of catalytic activity. Selectivity was determined from the fractions of acetone and water in the liquid catalyst.

Results and Discussion

The results illustrating the catalytic properties of samples **1—6** are presented in Table 1. The liquid products of isopropyl alcohol transformation on the monometallic (no rhenium) catalyst contain acetone and water along with the unreacted alcohol, and the gaseous products contain propylene and hydrogen. Two reactions occur under the chosen conditions at 200 °C: dehydrogenation to form acetone and hydrogen (1) and dehydration to form propylene and water (2).



Cat. is catalyst

The total conversion of the alcohol is 15.3%, and the acetone : water ratio is equal to 3.3. When the temperature increases from 200 to 270 °C, the total conversion of the alcohol on the monometallic catalyst increases

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Table 1. Transformation of isopropyl alcohol on catalysts **1—6**

Catalyst	Content of Re (%)	T /°C	Composition of liquid products (wt.%)			Total conversion (mol.%)	Conversion (mol.%) to		Selectivity of transformation of Pr^{i}OH		Acetone : water
			Me_2CO	H_2O	Pr^{i}OH		Me_2CO	H_2O	Me_2CO	H_2O	
1	0	200	11.6	1.1	87.3	15.3	11.7	3.6	76.6	23.4	3.3
		235	28.6	1.8	69.6	33.8	28.1	5.7	83.1	16.9	4.9
		250	33.6	1.7	64.7	38.4	33.0	5.4	86.0	14.0	6.7
		270	37.7	1.8	60.5	42.7	37.0	5.7	86.7	13.3	6.5
		200*	10.1	1.1	88.8	14.0	10.4	3.6	74.5	25.5	3.0
2	0.25	200	18.2	1.0	80.8	21.5	18.3	3.2	85.0	15.0	5.7
		235	39.2	1.7	59.1	43.9	38.6	5.3	87.8	12.2	7.1
		250	45.1	2.4	52.5	51.1	43.6	7.5	85.4	14.6	5.8
		270	56.4	2.8	40.8	62.4	53.8	8.6	86.3	13.7	6.3
3	0.5	200	23.9	2.0	75.1	29.4	23.1	6.3	78.6	21.4	3.6
		235	46.8	2.4	50.8	52.6	45.2	7.4	85.9	14.1	6.0
		250	49.7	2.2	48.1	54.8	47.9	6.9	87.4	12.6	6.9
		270	57.3	2.4	40.3	62.6	55.2	7.4	88.1	11.9	7.4
4	1.0	200	23.0	2.6	74.4	30.4	22.3	8.1	73.3	26.7	2.7
		235	37.3	3.6	59.1	46.1	35.2	10.9	76.0	24.0	3.0
		250	45.1	3.6	51.3	51.5	39.5	12.0	76.0	24.0	3.0
		270	53.6	4.1	42.3	62.0	49.8	12.2	80.3	19.7	4.1
5	2.0	200	35.1	3.1	61.8	43.3	33.9	9.4	78.3	21.7	3.6
		235	51.0	7.2	41.8	64.8	44.5	20.3	68.7	31.3	2.2
		250	59.2	8.9	31.9	71.8	50.0	24.2	67.5	32.3	2.1
		270	65.4	9.7	24.9	80.1	54.2	25.9	67.6	32.4	2.1
		200*	43.5	3.4	53.1	51.5	41.1	10.4	79.9	20.1	3.9
6**	0.25	200	48.4	3.2	48.4	55.7	46.1	9.6	82.7	17.3	4.8
		235	73.2	4.6	22.2	80.3	66.8	13.5	83.3	16.7	4.9
		250	78.9	3.4	17.7	85.2	74.1	11.1	87.0	13.0	6.7
		275	80.5	6.4	13.1	89.0	71.0	18.0	79.7	20.3	3.9
		200*	38.3	2.4	59.3	44.5	36.8	7.7	82.6	17.4	4.8

* After the operation of the catalyst for 2 h at higher temperatures. In other cases, data were obtained 30 min after the beginning of experiment.

** Catalyst prepared from copper nitrate.

from 15.3 to 42.7% and the selectivity for acetone formation increases from 76.6 to 86.7%. Correspondingly, the acetone : water ratio increases from 3.3 to 6.7. An initial activity of the Cu(2%)/Sib catalyst 200 °C was nearly completely restored when the temperature of the sample operated at 270 °C for 2 h was finally reduced to 200 °C.

The introduction of rhenium additives enhances the activity of the catalyst. The total conversion of the alcohol at 200 °C increases from 15.3% on monometallic Cu catalyst **1** to 43.3% on sample **5** with 2.0% Re. The maximum increase in the dehydrogenating activity is observed for the rhenium content 0.25% (samples **2** and **6**). The acetone : water ratio increases on these catalysts to 5.7 and 4.8, respectively.

Catalyst **2** also exhibits[2] the maximum activity and selectivity for the dehydrogenation of methanol to MF.

An increase in the rhenium content noticeably changes the direction of Pr^{i}OH transformation.

When the temperature increases from 200 to 270 °C, the total conversion of the alcohol on the most active catalyst **5** (Cu(2%)+Re(2%)/Sib) increases from 43.3 to 80.1%. However, its dehydrogenating activity decreases, while the dehydrating activity increases: the selectivity with respect to acetone decreases and that for water (propylene) increases. On this catalyst, as on the sample containing 0.25% Re, the ratio of the products of reactions (1) and (2) typical of the catalyst operated at 200 °C is completely restored when an operating temperature in excess of 200 °C after 2-h time-on stream is reduced to 200 °C. This implies, evidently, that the low (Cu,Re)/Sib catalysts do not loose their activity during alcohol transformation due to the presence of such reducing agents as H_2 and H_2O in the reaction mixture. They prevent the deposition of coke or other deactivating products on the catalyst surface.

Rhenium, being a metal with a comparatively high melting point, does not undergo recrystallization during catalysis and, therefore, favors an increase in the stability of the metal-supported catalyst.[3] This fact has first[4] been demonstrated for the bimetallic (Pd,Re)/Al_2O_3 and (Pt,Re)/Al_2O_3 catalysts for reforming (see Refs. 5—7). The present work shows that the rhenium additive improves the dehydrogenating properties of the Cu(2%)/Sib catalyst.

Thus, the introduction of rhenium into the carbon-supported copper catalysts allows the purposeful change in the selectivity of isopropyl alcohol transformation.

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