Hydrogenation of acetone on technetium catalysts

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The catalytic properties of supported mono- and bimetallic catalysts of the Tc/support, M/support, and M—Tc/support types (M = Pt, Pd, Rh, Ru, Ni, Re, Co; supports are γ-Al_2O_3, MgO, SiO_2) were investigated in the acetone hydrogenation. The main products of this reaction are isopropyl alcohol and propane. The catalytic activity in the acetone hydrogenation of the metals studied decreases in the consequence Pt > Tc ≈ Rh > Pd > Ru > Ni ≈ Re > Co (with γ-Al_2O_3 as the support). The influence of support nature on the catalytic activity was investigated for the Rh—Tc system as an example. A nonadditive increase in the catalytic activity of Rh—Tc/γ-Al_2O_3 in comparison with monometallic catalysts was found. The state of the surface of the catalysts was characterized by the UV-VIS diffuse reflectance spectra.

Key words: acetone, hydrogenation; technetium, bimetallic catalysts; diffuse reflectance spectra.

Supported mono- and especially bimetallic catalysts are widely used as active and selective contacts in various chemical processes.[1] We have shown previously that the bimetallic technetium-containing catalysts exhibit a synergistic effect in the hydrogenation of cyclic hydrocarbons and dehydrocyclization of *n*-hexane.[2] In addition, technetium and Tc-based bimetallic catalysts are active in the hydrogenation of aromatic hydrocarbons.[3] In this work, the catalytic properties of the M—Tc- and Tc-catalysts in acetone hydrogenation were studied. According to the literature data,[4,5] hydrogenation of the carbonyl group can occur on the same active sites as the hydrogenation of the double bond in olefins and aromatic hydrocarbons. The reversible processes of acetone hydrogenation and dehydrogenation of isopropyl alcohol have often been considered as model reactions to reveal the mechanism of catalysis.[6]

Experimental

The catalysts were prepared according to the procedure described previously[2] by impregnation of a support with solutions of the compounds of the corresponding metals (NH_4TcO_4, NH_4ReO_4, $RhCl_3$, H_2PtCl_6, $PdCl_2$, $NiCl_2$, $Ru(OH)Cl_3$, $CoCl_3$). The supports were in the form of granules of 1.5—2.0 mm in a size. After drying in air at 80 °C, the samples were reduced in an H_2 flow for 1 h at 300 °C and then for 6 h at 700 °C. The content of technetium in the catalysts was determined radiometrically, and the contents of the other metals were determined spectrophotometrically. The amounts of supported metals were varied within the limits of 0.05—3.00%.

The following supports were used: Al_2O_3 (S_{sp} = 189 $m^2 g^{-1}$), SiO_2 (KSK-2, S_{sp} = 195 $m^2 g^{-1}$), and MgO (S_{sp} = 57 $m^2 g^{-1}$). The total specific surface area was determined by the BET method by the low-temperature adsorption of krypton. Hydrogen chemisorption was used for determination of the specific surface area of the supported technetium (a comparative method).[7,8]

The catalytic activity was studied in a flow setup at atmospheric pressure. A fresh portion of a catalyst (2 cm^3) was loaded to the U-shape reactor for each experimental run. The acetone feeding rate was constant (30 h^{-1}), and the residence time was 120 s. The reaction products were analyzed by GLC on a Biokhrom-1 chromatograph (flame-ionization detector; helium as the carrier-gas; glass capillary column with PEG-40M).

The UV-VIS. diffuse reflectance spectra were recorded on a Specord M-40 spectrophotometer.

Results and Discussion

As seen in Table 1, the total specific surface areas of the catalysts with different technetium contents are close to each other, however, the specific surface area of the supported technetium (per 1 g Tc, S_{Tc}) sharply in-

Table 1. Specific surface area and dispersion of the Tc/γ-Al_2O_3 catalysts

[Tc] (%)	S_{sp} [a] /$m^2 g^{-1}$	S_{Tc} [b] /m^2 (g Tc)$^{-1}$	Relative dispersion
0.1	85.8	250	0.460
0.2	93.0	214	0.420
1.0	90.0	54	0.073
2.0	86.7	46	0.065

[a] Determined by BET method.
[b] Determined by chemisorption of H_2.

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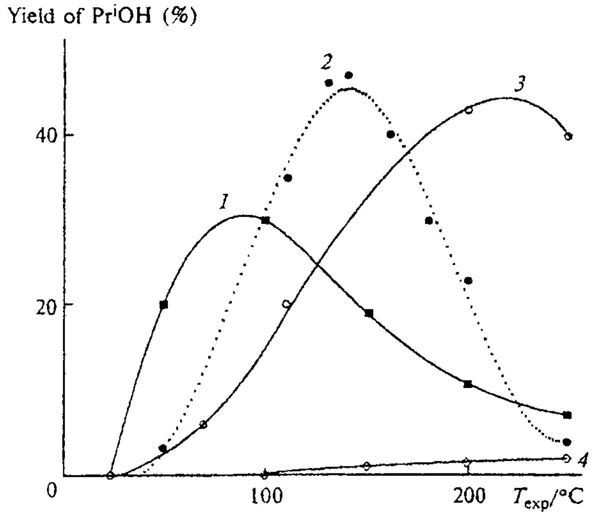

Fig. 1. The effect of temperature on the yield of isopropyl alcohol during acetone hydrogenation over the catalysts 2% Tc/γ-Al_2O_3 (*1*); 1% Tc/γ-Al_2O_3 (*2*); 0.2% Tc/γ-Al_2O_3 (*3*); 0.1% Tc/γ-Al_2O_3 (*4*).

creases at low concentrations. The hydrogen spillover effect seems to be a reason for the increase in S_{Tc} for the 0.1% and 0.2% catalysts.[9,10] The sections of the support adjacent to the metal particles gain the ability of absorbing hydrogen due to the presence of the supported metal. This results in enhanced values of the specific surface area of the supported metal at the technetium concentration <1%. In the systems containing >1% Tc, the spillover effect decreases. Calculation of the relative dispersion from the chemisorption data showed that the catalysts became roughly dispersed with increase in the technetium concentration.

An abnormal behavior of the catalysts with low metal content is seen from the variation of their activity and selectivity in the acetone hydrogenation. The 0.1% Tc/support systems are catalytically inactive (Fig. 1, curve *4*). Over the 0.2% Tc/γ-Al_2O_3 catalyst, the yield of isopropyl alcohol reaches 40% at 200 °C and then decreases with the temperature increasing. The catalysts containing 1% and 2% of technetium are active at low temperatures. However, at $T >$ 100—150 °C their selectivity in respect to isopropyl alcohol drops. This is due to the occurrence at high temperatures of the processes of alcohol dehydration, hydrogenation, and hydrocracking of hydrocarbons to form mainly propene which is then hydrogenated to propane. In addition, other oxygenates (aldehydes, ketones) appear. As a result, the content of isopropyl alcohol in the reaction products decreases.

Thus, the following reactions occur simultaneously in the system under study:

$$Me_2CO \xrightarrow{H_2} Me_2CHOH \xrightarrow[-H_2O]{}$$
$$\longrightarrow MeCH{=}CH_2 \xrightarrow{H_2} MeCH_2{-}Me.$$

With increase in temperature, the yield of propane increases over all the catalysts studied and the selectivity in respect to isopropyl alcohol decreases.

The nature of the support affects the activity and selectivity of the technetium catalysts. As seen in Table 2, the most active are the γ-Al_2O_3-based catalysts, then the systems with MgO follow. The SiO_2-based catalysts are the least efficient, although their specific surface areas are the greatest.

The data on the activity and selectivity of various catalysts which allow one to compare the catalytic properties of technetium and platinum group metals are presented in Tables 2 and 3.

The catalysts studied can be arranged in the following sequence with respect to activity in the acetone hydrogenation: Pt > Tc ≈ Rh > Pd > Ru (support, γ-Al_2O_3; metal content, 0.2%; see Tables 2 and 3) and

Table 2. The effect of support on acetone hydrogenation over Tc catalysts

Catalyst	S_{sp} /m^2 g^{-1}	T_{exp} /°C	Yield of products (%) propane	Pr^{i}OH	σ[a] (%)	α[b] (%)
0.2% Tc/Al_2O_3	93.0	100	9.0	16.0	64.0	25.0
		300	64.0[c]	34.0	34.0	100.0
0.2% Tc/SiO_2	184.3	200	—	—	—	—
		300	5.5	6.0	52.2	11.5
0.2% Tc/MgO	76.4	100	—	—	—	—
		300	5.0	22.0	81.5	27.0
0.2% Rh— 0.2% Tc/γ-Al_2O_3	48.9	100	2.0	63.0	96.9	65.0
		300	55.0[d]	22.5	26.5	85.0
0.2% Rh— 0.2% Tc/SiO_2	219.0	100	—	8.5	100.0	8.5
		300	—	15.0	100.0	15.0
0.2% Rh— 0.2% Tc/MgO	2.4	100	—	16.5	100.0	16.5
		300	16.5	27.5	62.5	44.0

[a] Selectivity to alcohol. [b] Conversion. [c] Yield of propene is 2.0%. [d] Yield of aldehyde is 7.5%.

Table 3. Acetone hydrogenation over M/Al_2O_3 catalysts

M	S_{sp} /m^2 g^{-1}	T_{exp} /°C	Yield of products (%)		σ	α
			propane	Pr^{i}OH	(%)	
0.2% Pt	90.1	100	2.0	63.0	96.9	65.0
		200	39.0	18.0	31.6	57.0
		300	86.0	13.5	13.6	99.5
		400	88.0	12.0	12.0	100.0
0.2% Pd	59.4	100	4.0	1.0	20.0	5.0
		200	14.5	18.5	56.1	33.0
		300	39.0	13.0	25.0	52.0
		400	68.0	6.0	8.1	74.0
0.2% Rh	42.3	100	3.0[a]	27.0	88.8	30.4
		200	25.0	45.5	64.5	70.5
		300	42.5[b]	27.0	34.2	79.0
		400	75.0	21.0	21.9	96.0
0.2% Ru	47.4	100	0.5	1.5	75.0	2.0
		200	4.5	14.0	75.7	18.5
		300	24.0	18.0	42.9	42.0
		400	51.0	6.0	10.5	57.0
3% Ni	67.1	200	—	—	—	—
		300	34.0[c]	2.0[d]	8.1	43.0
		400	70.5[e]	8.0[f]	13.0	100.0
1% Re	Not determined	100	—	6.0	100.0	6.0
		200	—	9.0	100.0	9.0
		300	30.0	19.0	38.8	49.0
		400	76.0	12.0	13.6	88.0
2% Co	Not determined	100	—	—	—	—
		200	—[g]	2.0	18.0	11.0
		300	15.0[h]	5.5	20.0	27.5
		400	73.0	6.0	7.6	79.0
1% Tc	90.3	100	2.0	20.0	90.9	22.0
		200	18.0	20.0	52.6	38.0
		300	67.0	13.0	16.3	80.0
		400	87.0	13.0	13.0	100.0

[a] Yield of propene is 0.4%. [b] Yield of aldehyde is 9.5%. [c] Yield of aldehyde is 5.5%. [d] Yield of ethanol is 1.5%. [e] Yield of aldehyde is 16.5%. [f] Yield of ethanol is 8.0%. [g] Yield of aldehyde is 9.0%. [h] Yield of aldehyde is 7.0%.

1% Tc > 3% Ni > 1% Re > 2% Co (support, γ-Al_2O_3; see Table 3). However, the selectivity with respect to isopropyl alcohol over technetium is less than that over the other metals, because more propane is formed over the Tc catalysts than over the other catalysts studied (see Tables 2 and 3).

Bimetallic contacts were studied along with the monometallic catalysts. The most interesting result was obtained for the Rh—Tc/γ-Al_2O_3 system for which a synergistic effect is observed, *i.e.*, a nonadditive increase in the yield of isopropyl alcohol as compared with the corresponding monometallic catalysts (Fig. 2). A synergistic effect is generally seen at low temperatures. With increase in the [Tc]/[Rh] ratio, the yield of the alcohol increases (Fig. 3). Introduction of technetium to other metal systems does not affect significantly the catalytic properties.

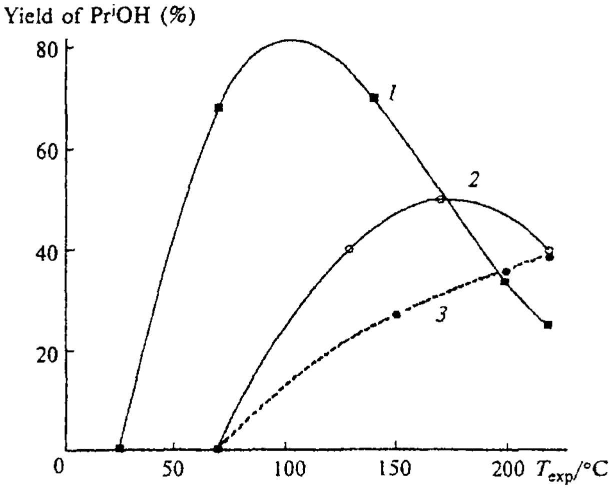

Fig. 2. Synergistic effect in acetone hydrogenation over the catalyst 0.2% Rh—0.2% Tc/γ-Al_2O_3 (*1*) as compared to the 0.2% Rh/γ-Al_2O_3 (*2*) and 0.2% Tc/γ-Al_2O_3 (*3*) catalysts.

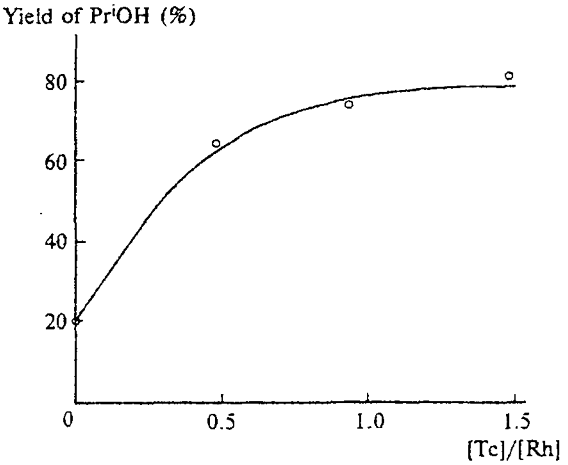

Fig. 3. Dependence of the yield of isopropyl alcohol in acetone hydrogenation over Rh—Tc/γ-Al_2O_3 catalyst on the [Tc]/[Rh] ratio at 100 °C ([Rh] = const = 0.1%, the content of Tc (%) varies).

As in the case of the monometallic Tc catalysts, the nature of a support affects the activity of bimetallic contacts. The data in Table 2 for the Rh—Tc systems show that the Al_2O_3-based catalysts are the most active, then the MgO-based catalysts follow, and the Rh—Tc/SiO_2 systems are the least efficient in spite of the great specific surface area of the support. The dependence of the activity of the Tc catalysts on the nature of the support has been observed previously in the dehydrogenation of cyclic hydrocarbons and alcohols.[2,11] The presence of the ionic species of technetium (in the case of γ-Al_2O_3 and MgO) is the main reason for the effect mentioned. The effect of the nature of the support on the activity and selectivity of the Tc catalysts in acetone hydrogenation is likely due to the same reason.

Table 4. The diffuse reflectance spectra of the catalysts 0.1% Rh, 0.1% Tc, and 0.1% Rh—0.1% Tc on various supports

Support	Catalyst	T_{treat}/°C [a]	λ_{max}/nm
Al_2O_3	Rh	~20[b]	422, 544
		700	—
	Tc	700	247, 294
	Rh—Tc	~20[b]	251, 291, 433
	Rh—Tc	700	250, 298, 417, 505
MgO	Rh	700	341, 500, 730
	Tc	700	248, 294
	Rh—Tc	700	261, 318, 344, 505, 720
SiO_2	Rh	700	344
	Tc	700	252, 305
	Rh—Tc	700	255, 291, 344

[a] The temperature of the samples treatment.

[b] Unreduced sample.

The state of the surface of the catalysts studied was characterized by the UV-VIS diffuse reflectance spectra. Table 4 presents the maxima of the bands for the Rh—Tc catalysts. The spectra are seen to be dependent on the support nature. Thus, bands for Rh/γ-Al_2O_3 after treatment at 700 °C are not seen, whereas three bands are observed in the spectrum of Rh/MgO. No diffuse reflectance bands are observed for the Tc/SiO_2 catalyst, and the bands concerning TcO_4^- are retained for Tc on the other supports. The bands in the spectra of the bimetallic catalytic systems are typical of ionic metal species; in addition, their shift relative to the spectra of the monometallic catalysts is observed. Thus, the bands due to the presence of the technetium ions are bathochromically shifted. The position of the bands concerning rhodium ions with different degrees of oxidation depends on the nature of the support. The change in the reflectance spectra of the supported bimetallic catalysts allows one to suggest the interaction of the metals either with each other or with the support. Apparently, as in the case of dehydrogenation of naphthenes, the nonadditive increase in the activity during the acetone hydrogenation is due to the formation of additional catalytic sites at the expense of the formation of compounds of the Rh_xTc_y type.[11]

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