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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Niobium-Containing Catalysts for Oxydehydrogenation of Hydrocarbons and Alcohols

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Abstract—The first methods are developed for introducing niobium(V) into Mg–Al hydrotalcites used as precursors of oxide catalysts for oxydehydrogenation (OD) of alkanes and alcohols. Samples of niobium(V)-containing oxide catalysts are synthesized. Their catalytic properties are studied in oxydehydrogenation of ethane and ethylbenzene to styrene, oxidation dehydrocyclization of octane into ethylbenzene and styrene, and oxydehydrogenation of sec-butanol to ketone (octane-(2)-one). It is ascertained that ethane transformation into ethylene is highly a selective highly process (92–97%) at low temperatures (450–500°C) in the presence of a niobium-containing catalyst; the catalyst is appreciably efficient in ethylbenzene transformation to styrene and dehydrocyclization of *n*-octane to ethylbenzene and styrene, and in oxydehydrogenation of sec-butanol to octane-(2)-one. All the catalysts studied operate stably in OD reactions; no decrease in their activity or selectivity was detected after 50 h operation.

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This work continues studies on the effect of the composition of hydrotalcite-like hydroxo salts used as catalyst precursors on the catalytic properties of oxide catalysts for oxydehydrogenation (OD) of organic compounds.

Earlier [1–5], we have synthesized hydroxo salts having hydrotalcite structure with various compositions (Mg–Al, Mg–Ni–Al, Mg–Ni–Co–Al, Mg–Al–Cr, Mg–Al–Fe), containing nitrate, carbonate, decavanadate, paramolybdate, and metatungstate ions in their anionic interlayers. Oxide catalysts prepared from them were highly selective and provided high yields of target products in the oxydehydrogenation of organic compounds.

This work is aimed at developing a method for introducing niobium(V) to the catalysts and studying its effect on the properties thereof in OD reactions of a number of organic compounds.

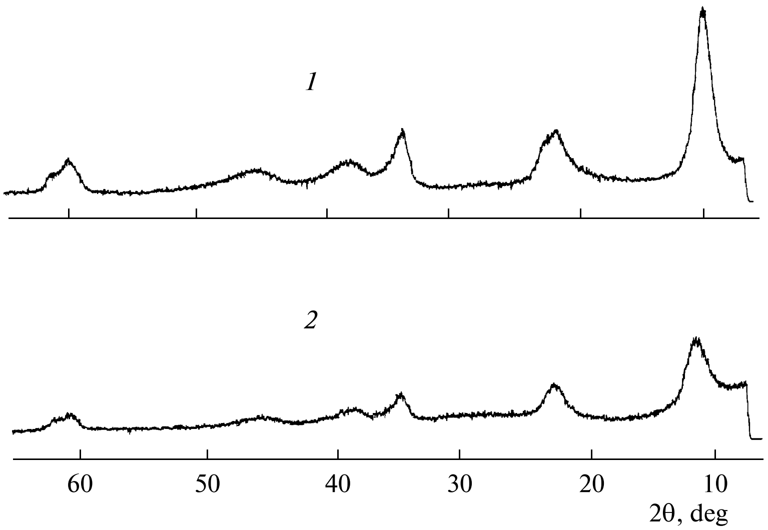
EXPERIMENTAL

Precursors were synthesized by reacting solutions of metal nitrates with potassium hydroxide and potassium carbonate followed by anion exchange of nitrate and carbonate ions for the corresponding polyoxometalates according to the following procedure.

A solution containing potassium hydroxide and potassium carbonate (2 M KOH + 1 M K_2CO_3) was slowly dropped (1 drop/3 s) to a solution containing aluminum nitrate (0.3 mol/L) and magnesium nitrate (0.6 mol/L) at 60°C under continuous stirring until pH changed from 1 to 10. The resultant precipitate, which was a hydroxytalcite-like double hydroxo salt of magnesium and aluminum (figure, curve *1*), was washed with water in a Nutch filter to remove potassium ions until the negative test to sodium tetraphenylborate was obtained.

In order to carry out the anion exchange with partial replacement of carbonate ions by decavanadate $(V_{10}O_{28})^{6-}$, paramolybdate $(Mo_7O_{24})^{6-}$, and metatungstate $(H_2W_{12}O_{40})^{6-}$ ions, the paste obtained after precipitating and washing was diluted with water to the ratio S : L = 1 : 2, then a solution of potassium decavanadate (0.15 M), or ammonium paramolybdate (0.15 M), or sodium tungstate (0.5 M) was added in an amount depending on the final composition required. The pulp was stirred for 10 min, then nitric acid (0.2 M) was dropped to it until pH reached 4.5 for the exchange of carbonate ion for decavanadate and paramolybdate ions [6, 7] and until pH reached 5.0 for the exchange of carbonate ion for metatungstate ion [8]. The mixture was kept at the required pH value for 10 min for the exchange for decavanadate and paramolybdate ions and for 30 min for the exchange for metatungstate ion; the precipitate was filtered and washed with water to remove potassium, ammonium, and sodium ions.

For introducing niobium into hydrotalcite-like magnesium aluminum hydroxo salt, procedures were



Diffraction patterns for (*1*) hydrotalcite-like magnesium aluminum hydroxo nitrate $[AlMg_2(OH)_6][(NO_3) \cdot nH_2O]$ and (*2*) hydrotalcite-like magnesium aluminum hydroxocarbonate hexaniobate $[AlMg_2(OH)_6][(CO_3)_{0.432}(Nb_6O_{19})_{0.017}]$.

developed for synthesizing potassium polyoxoniobate and introducing it into the hydroxo salt by anionic exchange. For this purpose, we carried out experiments on alloying niobium oxide Nb_2O_5 with potassium carbonate at different molar ratios K_2CO_3 : Nb_2O_5 (7 : 1, 10 : 1, 20 : 1).

The alloying was carried out in platinum bowls first at 900°C (for 30 min), then at 1050°C (for 40 min). The resultant glassy cake was dissolved in a minimal amount of boiling water, cooled, and then thickened under vacuum over concentrated sulfuric acid until crystal were formed; the crystals were washed with water to remove the mother liquor and dried over $CaCl_2/CaO$ in an exiccator.

Analysis of the crystals in all cases showed the molar ratio $K_2O : Nb_2O_5 = 4 : 3$, which corresponds to potassium hexaniobate (“4 : 3 salt”) of composition $K_8[Nb_6O_{19}] \cdot aq$ that was earlier described in literature [9].

To carry out the anion exchange of the carbonate ion of the Mg–Al hydroxo salt for polyoxoniobate ion ($[Nb_6O_{19}]^{8-}$), we used the solution obtained by dissolving the alloy of K_2CO_3 with Nb_2O_5 having the 10 : 1 molar ratio (pH 13.0) and Mg–Al hydroxo salt.

The anion exchange was carried out at three pH values (11, 12 and 13) by acidifying the solution until the required pH value was attained for 6 h at the ratio S : L = 1 : 4. The maximal amount of polyoxoniobate was found to pass into the solution at pH 13, while only a small amount of aluminum (5–7%) passes from the precipitate into the solution and hydrotalcite structure is retained (hexagonal crystal system; a = 3.02 Å, c = 7.7 Å) (figure, curve *2*). Judging from the published data, we have pioneered the synthesis of hydrotalcite-like hydroxo salts containing polyoxoniobate ions.

To ascertain the phase and chemical composition of the hydroxo salts synthesized, we used chemical analysis and X-ray powder diffraction (DRON-2.0, CuK_α radiation).

In chemical analysis, potassium was determined gravimetrically in the form of tetraphenylborate; aluminum was determined volumetrically by back titration of excess Trilon B with zinc nitrate with Xylenol Orange; and magnesium, complexonometrically with Eriochrome Black in an ammonia buffer solution masking ammonia with triethanolamine chloride. Vanadium was determined volumetrically by titration of Mohr’s salt in the presence of phenylanthranylic acid as an indicator; molybdenum, gravimetrically with α-benzoin oxime; tungsten and niobium, gravimetrically after performing acidic hydrolysis of the samples (gravimetrical forms were WO_3 and Nb_2O_5).

RESULTS AND DISCUSSION

To prepare the precursors of the OD catalysts, which contain niobium in the form of hexaniobate and other polyoxometalates (decavanadate, paramolybdate, and metatungstate ions), in view of the fact that the latter replace carbonate ion in the interlayer space of hydrotalcite-like Mg–Al hydroxo salt at pH 4.5–5.0 (this value being pH 13 for hexaniobate), we had to use a mixture of two isomorphous phases: hydrotalcite-like aluminum magnesium hydroxocarbonate hexaniobate and aluminum magnesium hydroxocarbonate containing either decavanadate, or paramolybdate, or metatungstate ions, individually or together in various combinations.

The above-mentioned mixture was prepared by stirring for 2 h (to attain homogeneity) of the two starting hydroxo salts in aqueous medium in the ratio S : L = 1 : 2.

Table 1. Composition of the samples of niobium-containing isomorphous hydrotalcite-like salts used as precursors for the oxydehydrogenation of organic compounds

Sample no.	Hydroxo salt mixture
1	$[AlMg_2(OH)_6][(CO_3)_{0.42}(Nb_6O_{19})_{0.02} \cdot nH_2O]$
2	$[AlMg_{1.5}(OH)_5][(CO_3)_{0.424}(Nb_6O_{19})_{0.004}(Mo_7O_{24})_{0.02} \cdot nH_2O]$
3	$[AlMg_{1.8}(OH)_{5.6]}[(CO_3)_{0.33}(Nb_6O_{19})_{0.02}(V_{10}O_{28})_{0.03} \cdot nH_2O]$
4	$[AlMg_{1.5}(OH)_5][(CO_3)_{0.379}(Nb_6O_{19})_{0.004}(V_{10}O_{28})_{0.005}(Mo_7O_{24})_{0.03} \cdot nH_2O]$
5	$[AlMg_{1.6}(OH)_{5.2}[(CO_3)_{0.407}(Nb_6O_{19})_{0.003}(Mo_7O_{24})_{0.02}(V_{10}O_{28})_{0.005}(H_2W_{12}O_{40})_{0.002} \cdot nH_2O]$

Table 2. Composition of the initial isomorphous hydrotalcite-like hydroxo salts used for preparing precursors for the oxydehydrogenation of organic compounds (Table 1) by mixing in the 1 : 1 weight ratio

Sample no.	Niobium-containing hydroxo salt	Niobium-free hydroxo salt
1	$[AlMg_2(OH)_6][(CO_3)_{0.34} \cdot (Nb_6O_{19})_{0.04} \cdot nH_2O]$	$[AlMg_2(OH)_6][(CO_3)_{0.5}] \cdot nH_2O]$
2	$[AlMg_{1.5}(OH)_5][(CO_3)_{0.468} \cdot (Nb_6O_{19})_{0.008} \cdot nH_2O]$	$[AlMg_{1.5}(OH)_5][(CO_3)_{0.38}(Mo_7O_{24})_{0.04} \cdot nH_2O]$
3	$[AlMg_{1.8}(OH)_{5.6}][(CO_3)_{0.34} \cdot (Nb_6O_{19})_{0.04} \cdot nH_2O]$	$[AlMg_{1.8}(OH)_{5.6}][(CO_3)_{0.32}(V_{10}O_{28})_{0.06} \cdot nH_2O]$
4	$[AlMg_{1.5}(OH)_5][(CO_3)_{0.468} \cdot (Nb_6O_{19})_{0.008} \cdot nH_2O]$	$[AlMg_{1.5}(OH)_5][(CO_3)_{0.29}(V_{10}O_{28})_{0.01}(Mo_7O_{24})_{0.06} \cdot nH_2O]$
5	$[AlMg_{1.6}(OH)_{5.2}][(CO_3)_{0.476} \cdot (Nb_6O_{19})_{0.006} \cdot nH_2O]$	$[AlMg_{1.6}(OH)_{5.2}[(CO_3)_{0.338}(V_{10}O_{28})_{0.01}(Mo_7O_{24})_{0.04} \cdot (H_2W_{12}O_{40})_{0.004}] \cdot nH_2O]$

The resultant mixture was sufficiently homogeneous, which was attested by the character of sedimentation, and by the data of chemical analysis of the pulp sampled from the top and bottom parts of the sedimentation cylinder (V : Nb, Mo : Nb, and W : Nb ratios were equal in these samples).

To elucidate the effect of Nb(V) on the catalytic properties of oxide catalysts, we synthesized a set of mixtures of hydrotalcite-like isomorphous hydroxo salts (Tables 1, 2).

The samples synthesized (Table 1) were subjected to heat treatment, which consisted in drying the precipitate at 100–120°C until the moisture content was 40%, pelletizing, and igniting in a muffle furnace in an air flow at 100 K/h to 500°C; then, the samples were kept at this temperature for 4–5 h. Catalytic properties of the resultant materials were studied in a flow-through quartz reactor charged with 1–2 mL of the catalyst. The oxidizer used was atmospheric oxygen. To maintain isothermicity, the catalyst was mixed with an equal volume of crushed quartz. The reaction temperature, the alkane flow rate, and the alkane/oxygen ratio in the initial mixture were varied widely. Reaction products were analyzed by liquid chromatography using a column packed with Poropack-Q. The contact gas was analyzed for the unreacted starting compound (ethane, *n*-octane, ethylbenzene, and butyl alcohol), dehydration product (ethylene, styrene, ethylbenzene, and octane-(2)-one), CO_2, and methane. The results of the experiments were used to calculate conversion of the starting compound, selectivity of the reaction, and yield of the target products:

Conversion, % = (moles of converted compound / moles of reagent passed over the catalyst) × 100;

Selectivity, % = (moles of target product/moles of converted compound) × 100;

Yield, % = (moles of target product/moles of reagent passed over the catalyst) × 100.

The catalysts that were synthesized from samples 1–5 (Table 1) were used to study oxydehydrogenation of ethane (Table 3) . The numbering of the catalysts corresponds to the numbering of their precursors (Table 1). The C_2H_6/O_2 ratio (mol/mol) was varied from 1/0.3 to 1/0.5.

The analysis of the results of catalytic studies shows that, over niobium-containing catalysts, the conversion of ethane into ethylene occurs with high selectivity (92–97%) at low temperatures (450–500°C) (Table 3). Rising temperature increases conversion from 19 to 58% with a simultaneous decrease in selectivity to 72–74% (Table 3). Moreover, making the catalyst composition more complex, from Nb–Al–Mg–O via Nb–Mo–Al–Mg–O and Nb–V–Al–Mg–O to Nb–Mo–V–Al–Mg–O and Nb–Mo–V–W–Al–Mg–O, results in an enhancement of catalytic characteristics and a rise in conversion from 12 to 20% and in selectivity from 92 to 97% (Tables 1, 3), the process occurring at low temperatures (450–500°C).

It should be emphasized that unlike over Nb-containing catalysts, the oxydehydrogenation of ethane over catalysts of other compositions (Ni–V–Mo–W–Al–Mg–O, Fe–V–Mo–W–Al–Mg–O) at low temperatures does not virtually occur (conversion is 7–7.5%, selectivity is 40–45%, yield is 2.6–3.3%; Table 4).

Table 3. Results of the oxydehydrogenation of ethane over niobium-containing catalysts of various compositions

Sample no.	Catalyst	Temperature, °C	Dilution, mol/mol C_2H_6/O_2	Conversion, %	Yield, %	Selectivity, %
1	Nb–Al–Mg–O	500	1/0.35	12.0	10.8	92.0
2	Nb–Mo–Al–Mg–O	500	1/0.35	17.0	15.8	92.8
	Nb–Mo–Al–Mg–O	700	1/0.5	57.3	41.4	72.3
3	Nb–V–Al–Mg–O	500	1/0.35	17.0	15.4	92.0
4	Nb–V–Mo–Al–Mg–O	450	1/0.30	19.0	17.1	94.0
5	Nb–V–Mo–Al–Mg–O	700	1/0.50	58.3	42.4	74.3
	Nb–V–Mo–W–Al–Mg–O	450	1/0.30	19.7	19.0	97.0

Table 4. Results of the oxydehydrogenation of ethane over nickel- and iron-containing catalysts

Sample no.	Catalyst	Temperature, °C	Dilution, mol/mol C_2H_6/O_2	Conversion, %	Yield, %	Selectivity, %
1	Ni–V–Mo–W–Al–Mg–O	550	1/1	6.90	2.65	38.7
2	Fe–V–Mo–W–Al–Mg–O	550	1/0.65	7.45	3.30	44.6

Apart from the oxydehydrogenation of ethane over niobium-containing catalysts (Table 1, sample 4), we studied the following reactions:

oxydehydrogenation of ethylbenzene into styrene

$$C_6H_5CH_2CH_3 + O_2 \rightarrow C_6H_5\text{–}CH{=}CH_2 + H_2O + CO_2,$$

oxydehydrocyclization of octane into ethylbenzene and styrene

$$C_8H_{18} \rightarrow C_8H_{16} \rightarrow C_6H_5\,C_2H_5 + C_6H_5CH{=}CH_2,$$

oxydehydrogenation of sec-butanol into ketone (octane-(2)-one).

The results are displayed in Table 5.

As seen in Table 5, the catalyst studied (Nb–V–Mo–Al–Mg–O) (Table 1, sample 4) is sufficiently efficient in conversion of ethylbenzene into styrene and dehydrocyclization of *n*-octane into ethylbenzene and styrene. The yield of styrene reaches 68% with a selectivity of 97–98% at 500°C. In the dehydrocyclization of *n*-octane which has been poorly studied, the total yield of styrene and ethylbenzene reaches 20–25% with a total selectivity of up to 99%.

For the oxydehydrogenation of sec-butanol over the Nb–V–Mo–Al–Mg–O catalyst, optimal conditions were determined for producing octane-(2)-one to provide high yields (up to 67%) and selectivities (96–97%).

Notable is the stable operation of all catalysts studied in oxydehydrogenation; no decrease in activity or selectivity was detected after 50-h performance.

To summarize, efficient niobium-containing catalysts have been developed for selective conversion of alkanes, alkylaromatic alkanes, and alcohols in oxydehydrogenation reactions.

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Table 5. Results of the oxidative conversion of alkanes over the Nb–V–Mo–Al–Mg–O catalyst (Table 1, sample 4)

Sample no.	Starting alkane	Dilution, mol/mol	Temperature, °C	Conversion, %	Selectivity, %
1	Ethylbenzene ($C_6H_5CH_2CH_3$)	$C_6H_5C_2H_5/O_2/H_2O$ 1/1/7	500	70	97.5
2	*n*-Octane (C_8H_{18})	C_8H_{18}/O_2 1/2	500	28.1	89.0
		1/2	500	22.7	90.0
3	Sec-butanol (C_4H_9OH)	C_4H_9OH/O_2			
		1/1	320	45.0	97.0
		1/1	340	55.0	96.8
		1/1	340	70.0	96.0

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