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New Y(La)–M–O Binary Systems (M = Ca, Sr, or Ba): Synthesis, Physicochemical Characterization, and Application As the Supports of Ruthenium Catalysts for Ammonia Synthesis

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Abstract—The effect of the nature of the alkaline-earth metal on the phase composition and specific surface area of new Y(La)–M–O binary oxide compositions (M = Ca, Sr, or Ba) prepared by coprecipitation was studied. These systems were found to contain mixed compounds ($M_2Y_2O_5$, MY_2O_4, and MLa_2O_4), which are different in thermal stability, in addition to individual La_2O_3 or Y_2O_3 phases. The Y(La)–M–O compositions calcined at 450°C were characterized by a more developed specific surface area, as compared with that of individual La_2O_3 or Y_2O_3. An increase in the calcination temperature to 650°C was accompanied by a decrease in the specific surface area of binary compositions. Catalysts prepared by supporting $K_2[Ru_4(CO)_{13}]$ onto the Y(La)–M–O systems were active in ammonia synthesis at 250–400°C and atmospheric pressure. The most active of these catalysts, $K_2[Ru_4(CO)_{13}]$/Y–Ba–O, provided a higher yield of NH_3 at 250–300°C than analogous catalysts prepared with the use of well-known supports (Sibunit, CFC-1, and C/MgO).

INTRODUCTION

The low-temperature modifications of Al_2O_3, SiO_2, and TiO_2 remain the most commonly used supports for preparing catalysts. In recent years, because of the development of the oxidative condensation of hydrocarbons and other organic substances, the need for catalytic systems that exhibit basic properties has been increased. In particular, it was found that alkaline-earth and rare-earth metal oxides can be successfully used as catalysts for these reactions. In this case, Valenzuela *et al.* found that the activity of binary systems, such as Ca–Ce–O, in the oxidative condensation of ethane was higher than that of individual Ca and Ce oxides [1].

The basic properties of a support play an important role in the catalysis of ammonia synthesis. Indeed, Ru/MgO catalysts either in the presence or in the absence of a promoter ($CsNO_3$, $RbNO_3$, etc.) were much more active in this reaction than ruthenium catalysts based on amphoteric or acidic supports (γ-Al_2O_3, SiO_2, activated carbon, etc.) [2–6]. Comparatively recently, highly efficient ruthenium catalysts for ammonia synthesis were reported; these catalysts contained rare-earth metal oxides as promoters [7–9] or supports [10]. The Ru/LnO_x systems (Ln = Ce, La, or Sm) are similar to the Ru–$CsNO_3$/MgO catalyst in activity, although they are free of a cesium promoter [10]. Note that the oxides of La, Ce, Nd, and Y are stronger bases than MgO, but they are weaker bases than the oxides of Ca, Sr, and Ba, as judged from the electronegativities E_f of cations calculated from the equation $E_f = 0.16E_i/r$ (where E_i is the final ionization potential of the cation (eV) and r is the radius of the cation) [11]. Therefore, the addition of CaO, SrO, or BaO to the support (rare-earth metal oxide) can increase its basicity and, consequently, the efficiency of the corresponding catalyst in the synthesis of ammonia. Moreover, it should be borne in mind that the use of individual SrO and BaO as supports is difficult to perform in actual practice because they have low specific surface areas and are prone to the intense absorption of CO_2 from air to undergo quantitative conversion into carbonates.

In this work, we prepared Y(La)–M–O binary compositions (M = Ca, Sr, or Ba) for the first time and determined their chemical and phase composition and specific surface areas depending on the nature of the alkaline-earth metal and on the temperature of calcination. We also studied the activity of catalysts prepared by supporting the $K_2[Ru_4(CO)_{13}]$ cluster on Y(La)–M–O in ammonia synthesis (as compared with the catalysts based on individual Y_2O_3 and La_2O_3).

EXPERIMENTAL

The Y(La)–M–O samples were prepared by coprecipitation from a mixture of the aqueous solutions of $Y(NO_3)_3$ or $La(NO_3)_3$ and an alkaline-earth metal nitrate (taken in a certain ratio) with a 2 N KOH solution at specified pH and temperature. The resulting suspension was allowed to stand for 1 h at the specified pH and temperature of precipitation. Next, the suspension was filtered, and the precipitate was washed with distilled water until the absence of nitrates from the filtrate. The

Table 1. Data of chemical analysis of the Y(La)–M–O supports (M = Ca, Sr, or Ba) calcined at 450°C

Sample	Chemical composition		
	MO, mol %	K_2O, wt %	Δ*, % (110–800°C)
Y_2O_3	0	0.03	29.8
Y–Ca–O	5.5	0.04	32.4
Y–Sr–O	5.0	0.71	30.1
Y–Ba–O	6.2	2.40	28.9
La_2O_3	0	0	22.7
La–Ca–O	9.3	0.04	22.3
La–Sr–O	9.0	0.18	21.7
La–Ba–O	4.3	1.72	23.0

* Weight loss as a result of sample calcination from 110 to 800°C in a muffle furnace followed by keeping at 800°C for 4 h.

resulting samples were dried initially in air at room temperature and then in a drying oven at 110°C for 12–14 h and calcined in a flow of dry air at 450 or 650°C for 4 h. The individual Y_2O_3 and La_2O_3 oxides were prepared in a similar manner by adding a 2 N KOH solution to an aqueous solution of $Y(NO_3)_3$ or $La(NO_3)_3$.

The Y(La)–M–O samples synthesized were analyzed by atomic absorption spectrometry [12] to determine MO and K_2O concentrations; the residual amount of nitrate ions was determined according to Kjeldahl [13].

The thermal analysis of the Y(La)–M–O supports was performed with the use of a Q-1500 D derivatograph over the temperature range 20–1000°C in air at a heating rate of 10 K/min. The sample weight was 200 mg; the accuracy of the determination of weight losses was ±0.5%. X-ray diffraction analysis (XRD) was performed on an HZG-4C diffractometer with monochromatic CuK_α radiation; the size of the coherent-scattering regions (CSRs) was calculated from the Selyakov–Scherrer formula [14]. The specific surface area (S_{sp}) of the Y(La)–M–O samples was determined from the thermal desorption of argon [15].

As in our previous studies of ammonia synthesis (for example, see [4, 5]), we used the $K_2[Ru_4(CO)_{13}]$ anionic cluster [16] as a source of active ruthenium particles. To prepare ruthenium catalysts, the oxide support samples (particle size of 0.5–1.0 mm), which were stored in a desiccator in air, were additionally dried in a vacuum at 120°C for 2 h and impregnated with a solution of $K_2[Ru_4(CO)_{13}]$ in THF immediately after drying. The resulting suspension was stirred for 10 min; thereafter, the solvent was removed in a vacuum at 20°C. The ruthenium content of the resulting samples was 5 or 9 wt % (on a support basis). Because $K_2[Ru_4(CO)_{13}]$ is highly sensitive to atmospheric oxygen and moisture, all operations related to the preparation of catalysts were performed in an argon atmosphere or in a vacuum with the use of the standard Schlenk technique.

The catalysts were tested in ammonia synthesis in a glass flow reactor (with a fixed catalyst bed) at 250–400°C and atmospheric pressure. A stoichiometric dinitrogen–dihydrogen mixture was used in all the experiments (gas flow rate of 10 l/h). The catalyst was loaded in the reactor so as to prevent contact between the sample and air. Each sample was halved: one catalyst portion was heated in a flow of H_2 at 500°C for 4 h before testing, and the other portion was tested without pretreatment. The test started at 250°C; next, the reaction temperature was gradually increased to 300, 350, and 400°C and then decreased to 250°C in the reverse sequence. The dinitrogen–dihydrogen mixture and gaseous dihydrogen were purified to remove trace oxygen, moisture, and other impurities by successively passing through columns (50 × 5 cm) packed with A-1 active Al_2O_3, a reduced Ni–Cr catalyst, and synthetic zeolites NaA and NaX. The residual oxygen content of the synthesis gas was no higher than 0.1 ppm, and the moisture content was no higher than 0.5 ppm. The activity of the catalyst was judged from the steady-state concentration of ammonia in a gas flow at a constant flow rate. The concentration of ammonia in the gas flow was determined by measuring the time taken for the ammonia neutralization of a certain volume of an aqueous HCl (or H_2SO_4) solution with a known concentration. The steady-state concentrations of ammonia were obtained by averaging the results of 6–10 measurements and rounding off to two decimal digits. Standard deviations from the average values lied in the range 0.002–0.008 vol %.

RESULTS AND DISCUSSION

Table 1 summarizes the results of chemical analysis of the supports calcined at 450°C. Before the addition of a precipitating agent, the solutions of $La(NO_3)_3$ or $Y(NO_3)_3$ and $M(NO_3)_2$ were mixed in a ratio so that the MO content of the final Y(La)–M–O sample was 25 mol % upon the complete precipitation of the alkaline-earth hydroxide. In actual practice, the MO content of Y(La)–M–O was lower than the expected value and varied within a range from 4.3 to 9.0 mol %. The resulting samples also contained the impurities of occluded K^+ (from the precipitating agent) and NO_3^- (from parent nitrates) ions; the fraction of the latter decreased in the course of the thermal treatment of the samples in air. The K^+ content of the Y(La)–M–O samples increased in the order M = Ca < Sr < Ba, which correlated with the pH of the onset of precipitation of the corresponding $M(OH)_2$ hydroxide. Weight loss on calcination (Δ, %) found for the Y(La)–M–O binary systems differed insignificantly from the values of Δ typical of individual Y_2O_3 or La_2O_3, probably because of low MO contents (<10 mol %) of the Y(La)–M–O samples.

Table 2. Results of analysis of the air-dry Y(La)–M–O binary systems (M = Ca, Sr, or Ba)

System	T_{endo}, °C (Δm, wt %)						$\Sigma\Delta m$, wt %
Y–O	160(9.5)	280(3.8)	345(8.0)		530(15.5)		36.8
Y–Ca–O	140(21)	300(8.5)			565(9.0)		38.5
Y–Sr–O	145(19.8)	310(5.5)	400(3.5)	480(2.3)	545(7.0)		38.1
Y–Ba–O	145(39.8)	320(5.8)		485(6.5)			52.1
La–O	120(23.0)	380–400(8.0)			580(6.0)	830(3.0)	40.0
La–Ca–O	150(5.8)	375(8.0)				870(9.8)	23.6
La–Sr–O	155(5.5)	375(8.0)				870(9.0)	22.5
La–Ba–O	140(6.5)	380(7.5)				870(9.5)	23.5

Table 2 summarizes the thermoanalytical data for air-dry Y(La)–M–O samples. All of the samples exhibited a low-temperature endothermic effect at 140–160°C and several high-temperature endothermic effects, the number and position of which depends on the chemical composition of the samples.

The low-temperature endothermic effect was due to the removal of physically adsorbed water, whose concentration in Y–M–O samples (particularly, in Y–Ba–O) was much higher than in La–M–O, as judged from the weight losses. It is likely that the high-temperature endothermic effects were due to the dehydration reactions of the components of the test systems (individual $M(OH)_2$, $Y(OH)_3$, and $La(OH)_3$ and/or the products of interactions between them).

The positions of the endothermic peaks observed in individual Y–O at 280, 345, and 530°C correspond to the stepwise dehydration of yttrium hydroxide

$$Y(OH)_3 \xrightarrow{280°C} Y(O)OH$$
$$\xrightarrow{345°C} Y_2O_3 \cdot H_2O \xrightarrow{530°C} Y_2O_3.$$

The results obtained are inconsistent with data published by Klevtsov and Sheina [17]: the dehydration $Y(OH)_3 \longrightarrow Y(O)OH \longrightarrow Y_2O_3$ occurred at 314 and 474°C, respectively. It is likely that the differences observed are due to the fact that yttrium hydroxide was obtained by a hydrothermal procedure.

The position and number of endothermic peaks for the Y–M–O systems are somewhat different as compared with individual Y–O. The Y–Ca–O system exhibited endothermic effects at 300 and 565°C; the Y–Sr–O system exhibited endothermic effects at 310, 400, 480, and 545°C; and the Y–Ba–O system exhibited endothermic effects at 320 and 485°C. Taking into account the fact that the dehydration of calcium hydroxide and strontium hydroxide occurs at ~530 and ~650°C, respectively, the above endothermic effects can be hypothetically attributed to the dehydration of the products of interactions between the components of binary systems (solid solutions based on $Y(OH)_3$ or Y–Ca and Y–Sr mixed hydroxides). The absence of a corresponding endothermic effect for the Y–Ba–O sample can be explained by the rapid quantitative conversion of $Ba(OH)_2$ into $BaCO_3$ at the stage of precipitation due to the reaction with dissolved CO_2 and CO_3^{2-} impurities in the precipitating agent (the decomposition temperature of $BaCO_3$ was >1000°C).

In contrast to the above yttrium-containing binary systems, in the La–M–O samples the temperatures of the corresponding high-temperature endothermic effects (375–380 and 870°C) and the weight losses corresponding to these effects were practically independent of the nature of the alkaline-earth metal (Table 2). It can be seen that the dehydration of individual lanthanum oxide is characterized by the occurrence of endothermic effects at 380–400, 580, and 830°C. This is due to the stepwise dehydration of $La(OH)_3$ to La_2O_3 [18]

$$La(OH)_3 \xrightarrow{380–400°C} La(O)OH$$
$$\xrightarrow{580°C} La_2O_3 \cdot H_2O \xrightarrow{830°C} La_2O_3.$$

Because the dehydration temperatures of $La(OH)_3$, La(O)OH, and $La_2O_3 \cdot H_2O$ differ from the temperatures of the endothermic effects observed in the La–M–O systems (Table 2), it is believed that the products of interactions between the components of the binary mixtures are formed even at the stage of $La(OH)_3$ and $M(OH)_2$ coprecipitation, and they undergo dehydration at 375–380 and 870°C.

Table 3 summarizes the XRD data for the Y(La)–M–O samples calcined in a flow of air at 450 and 650°C. From these data, it follows that the phase composition of the samples depends on both the elemental composition and the calcination temperature (T_{calcin}).

The Y–M–O samples calcined at 450°C were the mixtures of Y_2O_3 and $M_2Y_2O_5$ phases, except for the Ba–Y–O sample, in which BaY_2O_4 and $BaCO_3$ were present in addition to Y_2O_3. Yttrium(III) oxide, which is a constituent of Y–Ba–O, is characterized by a cubic structure with the unit cell parameter a = 10.618–10.623 Å, which is higher than the tabulated value for pure Y_2O_3 (a = 10.604 Å) [19]. Note that individual Y_2O_3, which was prepared under conditions analogous to the preparation conditions of Y–M–O and calcined

Table 3. Specific surface areas (S_{sp}) and phase compositions of the Y(La)–M–O samples (M = Ca, Sr, or Ba) depending on the temperature of calcination (according to the thermal desorption of argon and XRD data)*

System	MO content, mol %	450°C			650°C			
		S_{sp}, m^2/g	phase	a, Å	S_{sp}, m^2/g	phase	a, Å	c, Å
Y_2O_3	0	90	Y_2O_3	10.643**	90	Y_2O_3	10.613	–
Y–Ca–O	5.5	130	Y_2O_3	10.618	115	Y_2O_3	10.605	–
			$Ca_2Y_2O_5$	–		CaO	–	–
Y–Sr–O	5.0	100	Y_2O_3	10.618	76	Y_2O_3	10.604	–
			$Sr_2Y_2O_5$	–		SrO	–	–
Y–Ba–O	6.2	110	Y_2O_3	10.623	57	Y_2O_3	10.603	–
			BaY_2O_5	–		$BaCO_3$	–	–
			$BaCO_3$	–				
La_2O_3	0	45	Trace lanthanum nitrate	–	40	La_2O_3	3.945	6.151
			Amorphous phase					
La–Ca–O	9.3	85	X-ray amorphous	–	48	La_2O_3	3.945	6.151
						$CaLa_2O_4$	–	–
La–Sr–O	9.0	95	X-ray amorphous	–	43	La_2O_3	3.945	6.151
						$SrLa_2O_4$	–	–
La–Ba–O	4.3	110	X-ray amorphous	–	31	La_2O_3	3.945	6.151
						$BaLa_2O_4$	–	–

* The unit cell parameters are given for the main phases (in terms of concentration).

** The tabulated value is 10.604 Å [19].

at 450°C, was characterized by an even higher value of the cubic unit cell parameter (a = 10.643 Å).

The La–M–O samples calcined at 450°C were X-ray amorphous; a trace of lanthanum nitrate was present in the La_2O_3 sample in addition to an amorphous phase. Taking into account the results of thermal analysis, which suggest the dehydration of the reaction product of alkaline-earth and rare-earth metals at 375–380°C, we can assume that the La–M–O binary samples with T_{calcin} = 450°C contain the phases of amorphous lanthanum hydroxide and a solid solution in a highly dispersed state.

An increase in the T_{calcin} of Y(La)–M–O samples to 650°C was accompanied by a change in the phase composition (Table 3). As before, the Y–M–O systems contained two phases: Y_2O_3 and MO (a $BaCO_3$ phase was present in place of BaO in the case of Y–Ba–O). The unit cell parameter of Y_2O_3, which was detected in the Y–M–O samples after calcination at 650°C, was a = 10.603–10.605 Å, which is practically equal to the tabulated value. Individual Y_2O_3 calcined at the specified temperature was characterized by the unit cell parameter a = 10.613 Å, which is higher than the tabulated value. However, in this case the difference between the found and tabulated values of a is less significant than that in the case of Y_2O_3 with T_{calcin} = 450°C. It is likely that the formation of an MO phase in the Y–M–O binary systems calcined at 650°C resulted from the decomposition of an $M_2Y_2O_5$ compound with the formation of MO and MY_2O_4. The phase of MY_2O_4 was not detected by X-ray diffraction analysis, probably because its amount was relatively low (<5%).

In the La–M–O systems, an increase in T_{calcin} was accompanied by crystallization with the formation of La_2O_3 and MLa_2O_4 phases (Table 3). Lanthanum(III) oxide, which is a constituent of the La–M–O systems, as well as individual La_2O_3 prepared under conditions analogous to those for the synthesis of binary compositions, exhibited a hexagonal structure with the unit cell parameters a and c consistent with the tabulated values [19]. The size of La_2O_3 crystallites (CSRs) in the La–M–O binary systems was much smaller than that of individual La_2O_3 (140–160 Å for La–M–O and 250 Å for individual La_2O_3); the size of MLa_2O_4 crystallites in various La–M–O samples lay within the range 90–130 Å.

Thus, thermoanalytical and XRD data allowed us to conclude that the Y(La)–M–O binary compositions contained mixed alkaline-earth and rare-earth metal compounds ($M_2Y_2O_5$, MY_2O_4, and MLa_2O_4) in addition to individual La_2O_3 and Y_2O_3 phases. These mixed compounds consisted of smaller crystallites than the crystallites of La_2O_3 or Y_2O_3 prepared under analogous conditions. On this basis, it would be expected that the Y(La)–M–O systems would exhibit higher values of S_{sp} as compared with the corresponding values for individual oxides.

Table 4. Ammonia synthesis under the action of ruthenium catalysts on individual and binary oxides as supports*

Support	Catalyst amount, g	Ammonia concentration in a gas**, vol %			
		250°C	300°C	350°C	400°C
Y_2O_3	2.20	0.01	0.13	0.68	0.44
Y–Ca–O	2.30	0.02	0.14	0.71	0.41
Y–Sr–O	2.24	0.01	0.15	0.78	0.44
Y–Ba–O	2.10	0.02	0.29	0.81	0.42
Y–Ba–O	2.30***	0.05	0.48	0.86	0.43
La_2O_3	2.21	0.01	0.10	0.61	0.41
La–Ca–O	2.30	0.02	0.20	0.72	0.43
La–Sr–O	2.24	0.01	0.21	0.76	0.43
La–Ba–O	2.26	0.02	0.19	0.73	0.44

* The Ru content of the samples was 1.23 mmol (5 wt % Ru); in the case of the Ru/Y–Ba–O catalyst (9 wt % Ru), the Ru content was 2.24 mmol. The supports calcined at 450°C in a flow of air were used for the preparation of the catalysts.

** The equilibrium concentrations of ammonia (vol %) at atmospheric pressure and various temperatures were the following: 2.18 at 300°C, 0.86 at 350°C, and 0.44 at 400°C.

*** 9 wt % Ru.

Indeed, it can be seen in Table 3 that the values of S_{sp} for the Y(La)–M–O binary compositions with T_{calcin} = 450°C found as a result of adsorption measurements are higher than the values of S_{sp} for individual Y_2O_3 and La_2O_3 obtained under analogous conditions. Moreover, the S_{sp} of samples based on Y_2O_3 was higher than that of samples containing La_2O_3. An increase in T_{calcin} to 650°C had practically no effect on the value of S_{sp} for the individual oxides of Y and La; however, it resulted in a considerable decrease in this value for binary compositions. As a result, in all cases except for M = Ca, the value of S_{sp} for the Y(La)–M–O binary compositions after calcination at 650°C became comparable with or even lower than the S_{sp} of Y_2O_3 or La_2O_3.

The oxide support samples prepared were subsequently used as the supports of ruthenium catalysts for ammonia synthesis. The preliminary tests of the catalysts demonstrated that they were characterized by an extremely low rate of attaining a steady-state activity, especially at 250 and 300°C. In the case of yttrium-containing systems, the time taken for attaining steady-state conditions in the synthesis of ammonia can be significantly shortened by the preheating of a supported sample in a flow of dihydrogen at 500°C for 4 h. For the catalysts on lanthanum-containing supports, a steady-state rate can be attained comparatively rapidly only in a repeated test cycle. In this case, preheating in a flow of dihydrogen at 500°C resulted to a decrease in the activity.

Table 4 summarizes the results of testing the catalysts in ammonia synthesis. The oxide supports calcined at 450°C were used for the preparation of these catalysts. An increase in the calcination temperature to 650°C, which resulted in a decrease in the specific surface area of a binary oxide (see above), decreased the efficiency of the catalysts.

Data obtained indicate that the rate of ammonia formation increased on going from individual Y_2O_3 and La_2O_3 to the corresponding binary oxide supports (Table 4). With the use of yttrium-containing binary systems, the activity of catalysts at 300 and 350°C increased with the order number of the alkaline-earth metal (Y–Ca–O < Y–Sr–O < Y–Ba–O), that is, in the order of increasing basicity of the oxide. However, in the case of lanthanum-containing binary supports, the efficiency of samples in the synthesis of ammonia was only slightly affected by the nature of the alkaline-earth metal.

The Ru/La–Ca–O and Ru/La–Sr–O catalysts exhibited a higher activity in the hydrogenation of dinitrogen at 300°C than the corresponding yttrium analogs Ru/Y–Ca–O and Ru/Y–Sr–O. However, if CaO and SrO are replaced with BaO in binary oxides, the rate of the synthesis on the Ru/Y–Ba–O yttrium-containing catalyst became higher than that on the analogous Ru/La–Ba–O lanthanum sample not only at 300°C but also at 350°C. This Ru/Y–Ba–O yttrium-containing catalyst (5 wt % Ru) was found to be the most efficient among all the catalysts tested in this work, and its activity can be additionally improved by an increase in the Ru/support ratio from 5 to 9 wt % (Table 4). On this catalyst (2.3 g; 9 wt % Ru), a steady-state concentration of ammonia in a gas flow at 250 and 300°C was as high as 0.05 and 0.48 vol %, respectively, whereas the process of ammonia synthesis completely reached an equilibrium at 350 and 400°C. The above Ru/Y–Ba–O catalyst is much superior to the previously described analogous ruthenium catalysts on Sibunit [20], CFC-1 [5], and carbonized magnesium oxide [21] in activity at 250–300°C, and it is superior to the catalyst on MgO [5] in activity at 250°C.

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