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Hydrogenation Activity and Surface Composition of Perovskite-Type Mixed Rhenium Oxides

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Perovskite-type mixed rhenium oxides having the composition $A_4BRe_2\square O_{12}$ (where A = Ba, Sr; B = Co, Ni; $\square$ = a vacancy in the cation lattice) have been synthesized by solid-state reaction of stoichiometric amounts of the starting oxides and metallic rhenium at temperatures up to 1100°C. It has been shown that the synthesized oxides have high catalytic activity for the hydrogenation of benzene. The sample where A = Ba and B = Ca is inactive for this reaction. In the continuous series of $Ba_{4-x}Sr_xCoRe_2\square O_{12}$ solid solutions, isomorphous substitution of Ba with Sr increases catalytic activity. On $Sr_4CoRe_2\square O_{12}$ and $Sr_4NiRe_2\square O_{12}$, benzene is hydrogenated completely (200–300°C, P_{H_2} = 100–120 atm, t = 2–3 h, 1% of Re). Catalyst activity is increased with increasing ionization potential of A (Ba∠Sr) and B (Ca∠Ni∠Co) cations. On the basis of a phase analysis of the surfaces of $Sr_4CoRe_2\square O_{12}$ and $Sr_4NiRe_2\square O_{12}$ made by thermovacuum electric conductivity curves (TEC), the surface phases formed in the course of the catalysis retain the semiconductor nature of conductivity. XPS of $Sr_4CoRe_2\square O_{12}$ and $Sr_4NiRe_2\square O_{12}$ after catalysis reveals rhenium in reduced Re^{4+} and Re^{6+} states, which is possibly involved in the catalytic sites.

INTRODUCTION

The activity of perovskite-type mixed rhenium oxides with vacancies ($\square$) in the cationic lattice for the hydrogenation of ethyl acetate was reported in Ref. (*1*). This work deals with the catalytic properties of perovskite-type mixed rhenium (VII) oxides with the compositions $Ba_{4-x}Sr_xCoRe_2\square O_{12}$ (x = 0–4.0), $Sr_4NiRe_2\square O_{12}$, and $Ba_4CaRe_2\square O_{12}$, for the hydrogenation of benzene and ethyl acetate. Catalytic activity has been compared with the results of surface-composition investigations by XPS and thermovacuum electrical conductivity curves (TEC).

EXPERIMENTAL

Catalysts

The catalysts $Ba_{4-x}Sr_xB^{II}Re_2\square O_{12}$, where B^{II} = Co, Ni, or Ca, were synthesized under conditions of a solid-phase reaction by the procedures of Ref. (*2*). Stoichiometric amounts of the starting components, namely, $BaCO_3$, $SrCO_3$, CaO, CoO, or NiO, and metallic Re, made up the batch, which was homogenized with addition of acetone and subjected to stepwise heat treatment with repleted intermediate homogenization under the following conditions: 800°C for 48 h, 900°C for 72 h, 1000°C for 96 h, and 1100°C for 96 h. The samples obtained had a black color, while the Ni-containing sample was dark orange. The samples were cooled slowly and characterized by X-ray diffraction using Cu$K\alpha$ radiation. The interplanar distances correspond to the data published for each phase considered (*3*). Surface area was measured by the BET method (N_2 adsorption).

The hydrogenating activity of these samples was compared with the activity of Re_2S_7. The latter was prepared by precipitation of an acidified solution of NH_4ReO_4 with hydrogen sulfide (*4*).

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Procedure

All hydrogenations were run in a 0.15–1 steel autoclave apparatus operated at 75–80 cycles/min. The reactor temperature was controlled at a constant value electronically from a thermocouple sensor in the heater jacket. Reactor temperature and pressure were simultaneously recorded by a thermocouple immersed directly in the reactor. In a run, materials at a catalyst-to-reactant ratio of 0.12–0.69 g of contained rhenium/8.8 g of benzene or 4.5 g ethyl acetate were placed in an open glass tube reactor with a glass pocket for the thermocouple. The autoclave was purged with nitrogen. After sealing and flushing with nitrogen, the autoclave with the reactor was filled with hydrogen at the desired pressure and heated to the predetermined reaction temperature, and agitation was begun, the reaction time being measured from this point. At the end of the reaction period, agitation was stopped and the elapsed time recorded. The autoclave was cooled in air to room temperature. The catalyst was separated by filtration and the product mixture analyzed by GLC with a thermal-conductivity detector (He). The liquid products were analyzed for benzene with a 3 m × 1.5 mm column, packed with P chromosorb with 15% of polyethylene glycoladipinate, 100°C; for ethyl acetate, a 1.8 m × 2 mm column, packed with Porapak Q, 155°C, was used.

In order to study the stability of the catalyst (200°C, P_{H_2} = 90–100 atm), hydrogeneration products were sampled over a 2-h period, the catalyst surface being still covered by a thin layer of hydrogenation products. Then a new portion of benzene was introduced. After two runs (4 h) the catalyst was held for 16–18 h at room temperature under benzene. This experiment lasted for several days. The total working time of the catalyst was 22 h.

Phase analysis of the surface was carried out by means of TEC (*5*), which measures the dependences of dc conductivity and its activation energy E_σ on temperature T_{vac} of heating *in vacuo* (100–400°C) and which characterizes various surface phases. XPS values were recorded with an ES-200 B spectrometer. As a standard, we used the C 1*s* line (E_b = 285.0 eV) of the adsorbed hydrocarbons of diffusion pump oil (*6*). Atomic Re/O, Sr/O, and Co/O ratios were determined from corresponding integral intensities with reference to photoionization cross sections, electron escape depth, and coefficients of analyzer transmission for electrons of various kinetic energies. Deconvolution of Re 4*f* spectra was carried out in accordance with the program for Gaussian peak synthesis on a PDP 11/03L minicomputer. After catalysis, samples were transferred to the spectrometer chamber without contact with air under a layer of reaction mixture.

RESULTS

The X-ray diffraction patterns obtained show that all the synthesized phases with B^{II} = Co, Ni are crystallized in the 12-layer perovskite-type structure (sp gr $R3m$, $z = 3$). In the $Ba_{4-x}Sr_xCoRe_2\square O_{12}$ system, a continuous series of solid solutions is formed over the whole range of concentrations between $0 \angle x \angle 4$. Calculated parameters of solid solutions follow the Vegard rule. Compounds with the composition $Ba_4CaRe_2\square O_{12}$ crystallize in a pseudo-eight-layer structure (sp gr $P6_3/mmc$), due to the existence of large cations in the *B*-position (ionic radius of octahedral coordinated calcium is 1.00 Å (*7*).

For the samples of $Ba_{4-x}Sr_xCoRe_2\square O_{12}$ solid solution in the reaction of benzene hydrogenation (T = 200°, P_{H_2} = 100 atm, t = 2 h, 1% of Re), decrease in Ba content from 3.6 to 0.4 leads to an increase in hydrogenation activity; cyclohexane yield increases from 18 to 78% (Table 1). With $Sr_4CoRe_2\square O_{12}$ samples, cyclohexane yield is 80–90% under the above conditions of catalysis. In this way, the presence of barium in the ABO_3 structure appears to hinder benzene hydrogenation. An active $Sr_4CoRe_2\square O_{12}$ sample was used to investigate effect of

TABLE 1

Hydrogenating Properties of Re-Containing Samples

Catalyst	Hydrogenation reactions						
	Benzene[a] yield of C_6H_{12}	Ethyl acetate[b]					
		Composition			Conversion (%)		Selectivity (%)
		H_2O	EtOH	EA	EtOH	Total	
$Ba_{3.6}Sr_{0.4}CoRe_2\square O_{12}$	18						
$Ba_{3.2}Sr_{0.8}CoRe_2\square O_{12}$	20						
$Ba_{2.8}Sr_{1.2}CoRe_2\square O_{12}$	20						
$Ba_{2.0}Sr_{2.0}CoRe_2\square O_{12}$	22	3.9	6.9	89.1	6.6	10.6	60.6
$Ba_{1.6}Sr_{2.4}CoRe_2\square O_{12}$	50						
$Ba_{1.2}Sr_{2.8}CoRe_2\square O_{12}$	52	5.7	13.3	81.0	12.7	19.0	67.0
$Ba_{0.4}Sr_{3.6}CoRe_2\square O_{12}$	78						
$Sr_{4.0}CoRe_2\square O_{12}$	90						
$Sr_{4.0}NiRe_2\square O_{12}$	90; 84	8.2	10.6	81.2	10.2	18.8	54.0
$Sr_{4.0}CaRe_2\square O_{12}$	0						
Re_2S_7	3	4.0	20.9	75.1	20.0	24.9	80.3
$ReO_3(9)$[c]	100						
$Ba(ReO_4)_2$	0						
$Ba_2Y_{1/3}\square_{2/3}ReO_6(1)$		4.5	30.5	65.0	29.2	35.0	83.4

[a] 200°C; $P_{H_2} = 100$ atm; $t = 2$ h; 1% Re.
[b] 280°C; $P_{H_2} = 100$ atm; $t = 3$ h; 2% Re.
[c] 240°C; $P_{H_2} = 100$ atm; $t = 4$ h; 3% Re.

temperature, amount of Re, hydrogen pressure, and reaction time. For the hydrogenation of benzene as seen in Fig. 1, an increase in temperature from 150 to 180°C is followed by a considerable enhancement in cyclohexane yield from 27 to 90%. At 230°C, $P_{H_2} = 100$ atm, and $t = 2$ h, benzene is reduced to cyclohexane (93–95%). As the Re content increases from 0.5 to 1 wt%, the cyclohexane yield ($T = 230$°C, $P_{H_2} = 100$ atm, $t = 2$ h) increases from 75 to 90%. Further increase in Re concentration to 2.5 wt% has no effect on hydrogenation activity.

A change in pressure from 50 to 100 atm leads to the highest hydrogenation activity, all other conditions being equal. At 230°C, $P_{H_2} = 120$ atm, and $t = 2$ h, benzene is hydrogenated completely. Prolonging the reaction time from 30 to 120 min increases the yield of cyclohexene from 52 to 98%.

A sample of $Ba_{0.4}Sr_{3.6}CoRe_2\square O_{12}$ was tested for stability ($T = 200$°C, $P_{H_2} = 90$–100 atm, 1% of Re). The composition of liquid products was determined every 2 h and substituted with a fresh portion of benzene. For 6 h, catalytic activity remained the same with a 76% cyclohexane yield. In the next 16 h, catalytic activity decreased, and cyclohexane yield was reduced to 35%.

The $Ba_4CaRe_2\square O_{12}$ compound under the chosen conditions ($T = 180$°C, $P_{H_2} = 100$ atm, $t = 2$) has no catalytic activity; neither does $Ba(ReO_4)_2$, which does not possess a perovskite structure.

Perovskites $Ba_2Sr_2CoRe_2\square O_{12}$ and $Ba_{1.2}Sr_{2.8}CoRe_2\square O_{12}$ as $Sr_4NiRe_2\square O_{12}$ ($T = 280$°, $P_{H_2} = 100$ atm, $t = 3$ h, 2% of Re) are less active and selective in the hydrogenation of ethyl acetate than Re_2S_7 and the earlier investigated $Ba_2Y_{1/2}\square_{2/3}ReO_6$ (*1*) (Table 1).

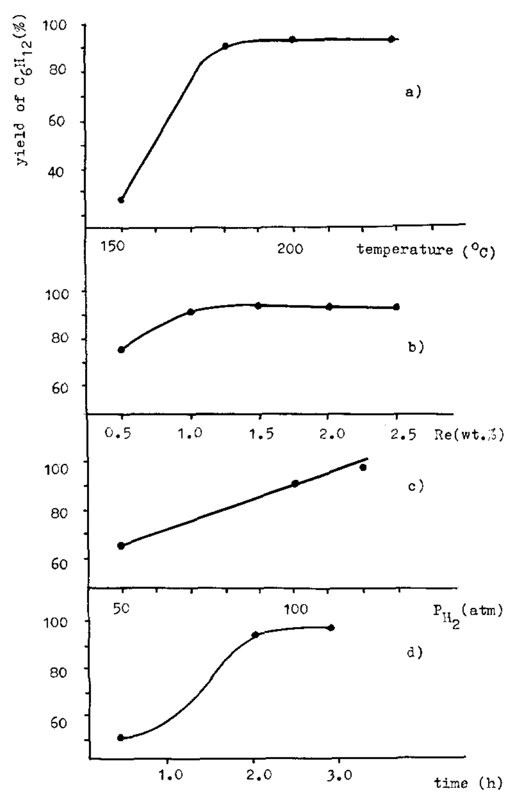

FIG. 1. Yield of cyclohexane (wt%) over $Ba_{0.4}Sr_{3.6}CoRe_2\square O_{12}$ with dependence on (a) temperature (°C) (1% Re, P_{H_2} = 100 atm, t = 2 h), (b) amount of Re (wt%) (T = 230°C, t = 2 h, P_{H_2} = 100 atm), (c) hydrogen pressure (atm) (1% Re, T = 230°C, t = 2 h), (d) time of reaction (h) (1% Re, T = 230°C, P_{H_2} = 110 atm).

In order to clarify which surface phases are responsible for the catalytic activity of the studied perovskites, XPS and TEC experiments were performed on the active samples $Sr_4CoRe_2\square O_{12}$ and $Sr_4NiRe_2\square O_{12}$ and on inactive $Ba_4CaRe_2\square O_{12}$ in the hydrogenation of benzene.

The results of XPS study show (Table 2) that rhenium has a single oxidation state, Re^{7+} in the active $Sr_4NiRe_2\square O_{12}$ and $Sr_4CoRe_2\square O_{12}$ samples. After benzene hydrogenation on $Sr_4NiRe_2\square O_{12}$, where cyclohexane yield was 84%, most of the rhenium (65%) became Re^{4+}. Re content in the studied subsurface layer decreased only 1.5 times. The initial oxidation state of Ni^{2+} did not change, whereas its surface content decreased four times.

After catalysis on $Sr_4CoRe_2\square O_{12}$ (hydrogenation yield reached 79%), rhenium was found in the Re^{6+} state (35.5%) and in the Re^0 state (26.5%). The concentration of surface rhenium was reduced two times. The initial oxidation state of Co^{2+} remained unchanged, whereas its content in subsurface layers dropped to 66%. In both samples, Sr^{2+} oxidation state and its content remained the same before and after catalysis.

TEC curves in Fig. 2 show that in the initial state (Figs. 2a and 2b), the catalytically active $Sr_4CoRe_2\square O_{12}$ sample (curves 1) and the inactive $Ba_4CaRe_2\square O_{12}$ sample

TABLE 2

Electronic State of Components and Surface Composition of a Perovskite before and after Catalysis

Sample	Treatment conditions	Binding energy (eV)									Re/O	Sr/O	Ni/O	Co/O
		Sr $3p_{3/2}$	Sr $3d$	O $1s$	Ni $2p_{3/2}$	Co	Ref $4f_{7/2}$							
							7+	6+	4+	0				
$Sr_4NiRe_2\square O_{12}$	Initial	279.8	133.8	531.3	854.4	—	46.0 (100%)	—	—	—	0.114	0.341	0.0122	—
	After catalysis	279.7	134.4	531.3	854.8	—	46.1 (35%)	—	43.3 (65%)	—	0.074	0.394	0.0028	—
$Sr_4CoRe_2\square O_{12}$	Initial	280.0	134.2	531.4	—	780.9	46.8 (100%)	—	—	—	0.083	0.374	—	0.033
	After catalysis	279.8	134.2	531.4	—	780.0	46.4 (38%)	44.4 (35.5%)	—	40.4 (26.5%)	0.042	0.362	—	0.021

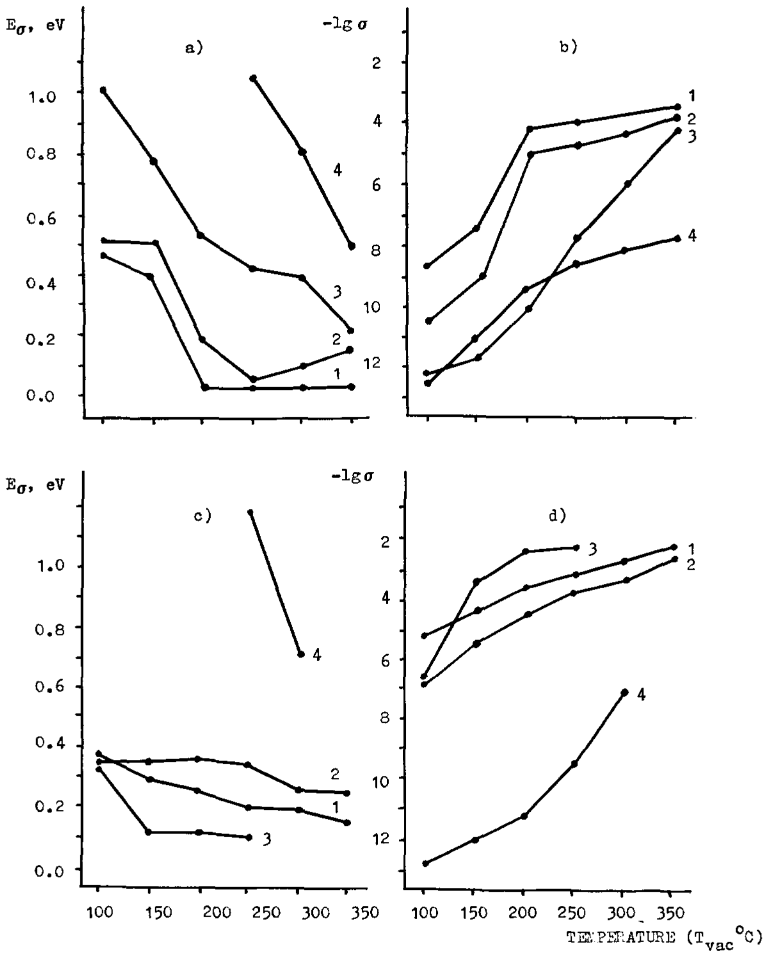

FIG. 2. Activation energy (E_σ, eV). (a,b) and conductivity ($-\lg \sigma$) (c,d) with dependence on: thermovacuum treatment (T_{vac} °C) for samples 1–4 before (a,b) and after (c,d) catalysis. 1-$Sr_4CoRe_2\square O_{12}$, 2-$Ba_4CaRe_2\square O_{12}$, 3-$Sr_4NiRe_2\square O_{12}$, 4-$Ba(ReO_4)_2$.

(curves 2) have a semiconductor type of conductivity and are very close in TEC characteristics. Hence, before catalysis these samples have a similar surface phase composition in terms of electronic properties. This points to the conclusion that the electronic nature of the perovskite surface is first of all determined by Re^{7+} ions in the *B* position, whereas the presence of Co^{2+} or Ca^{2+} ions in the same position cannot make a significant contribution to electrical conductivity; the nature of the cation in the *A* position (Ba^{2+} or Sr^{2+}) is also of no importance for the electrical conductivity of the perovskites studied. In contrast, when Re^{7+} ions are present not in a perovskite structure but rather, for instance, in the barium perrenate structure, the TEC curve is different and conductivity follows the dielectric, rather than the semiconductor, type (curves 4). However, conductivity may be hindered even in the perovskite structure; if Co^{2+} ions are substituted with nickel instead of calcium—as in $Sr_4NiRe_2\square O_{12}$—the conductivity falls sharply (particularly at low T_{vac}), the TEC having another shape (curves 3 in Figs. 2a and 2b) compared to those of $Sr_4CoRe_2\square O_{12}$ and $Ba_4CaRe_2\square O_{12}$. Consequently, Ni ions in octahedral *B*-sites, in contrast to cobalt and calcium, produce a considerable effect on the electrical conductivity of a perovskite structure.

The shape of the TEC curves changes after catalysis (Figs. 2c and 2d). The initial regions of these curves (at T_{vac} = 100–150°C) correspond to rather low E_b values (0.3–0.4 eV) and small specific resistance ($-\lg_\sigma = 5.5$–7), compared to the values of the starting samples at the same T_{vac} (E_b = 0.5–1.0 eV, $-\lg_\sigma = 8.5$). With reference to XPS, the nature of TEC curves can be connected with partial reduction of the samples during catalysis. It may be that the starting samples are reduced on vacuum heating during electrical conductivity measurement. This is implied by the dramatic changes of $\lg_\sigma$ and E_σ after heating at T_{vac} = 200°C for $Sr_4CoRe_2\square O_{12}$ and $Ba_4CaRe_2\square O_{12}$ (curves 1 and 2 in Figs. 2a and 2b) and at 360°C for $Sr_4NiRe_2\square O_{12}$ (curves 3).

DISCUSSION

Mixed rhenium oxides yield numerous compounds with structures derived from perovskite. The ideal perovskite structure with the general forumula ABO_3 has a cubic unit cell with sides about 3.9 Å and space group *Pm*3*m*, and contains one formula unit. The *B* ions have an octahedral oxygen coordination, and *A* ions have 12-fold coordination. The most useful approach is to consider that this structure is based on that of ReO_3 with corner-sharing octahedra arranged along the cube axis with *A* ions occupying the interstices (*8*). The reaction of benzene hydrogenation on $Sr_4CoRe_2\square O_{12}$ has shown that temperature, pressure, and reaction time are the main factors which affect the yield of cyclohexane.

The $Sr_4NiRe_2\square O_{12}$ compound, where Co^{2+} was substituted with Ni^{2+}, had the same hydrogenation activity under comparable conditions. These two samples exhibited similarity to ReO_3 (*9*). However, in the presence of the latter, higher hydrogen pressure and temperature, and a twofold increase in reaction time are required to attain the same yield.

According to XPS, the $Sr_4CoRe_2\square O_{12}$ sample contains metallic rhenium after catalysis, but electrical conductivity of the semiconductor type remains. It does not become metallic or pseudometallic with $E_g \leq 0$. Hence the Re^0 formed does not create sufficiently large conductive domains on the surface. The maximal coverage of metallic rhenium on the surface of active $Sr_4CoRe_2\square O_{12}$ catalyst can be estimated from Table 2. The specific surface area of the sample is 1.6 m^2/g. Comparison of the atomic ratios of Re/O, Sr/O, and Co/O measured by XPS (Table 2) with the corresponding atomic ratios in the stoichiometric formula $Sr_4CoRe_2\square O_{12}$ (Re/O = 0.167, Sr/O = 0.333, Co/O = 0.083) yields, for the surface composition of this sample in the initial state, the effective formula "$Sr_{4.5}Co_{0.4}ReO_{12}$" and, after catalysis, "$Sr_{4.4}Co_{0.2}Re_{0.5}O_{12}$". Bearing in mind that Re^0 (26.5% of overall rhenium content) cannot be included in the perovskite lattice, the formula would be "$Sr_{4.4}Co_{0.2}Re_{0.37}\square_yO_{12}$." Then, adopting 1.28 Å as the covalent atomic radius of Re and consequently 5.15×10^{-20} m^2 as the surface area occupied by Re atom, we find that metallic rhenium, even if it formed an ideal monolayer, can occupy less than half of the sample's surface area (0.45). Since on real surfaces Re is likely to be sintered into aggregates or microcrystals, the content of metallic Re found by XPS after catalysis is not sufficient to produce metallic conductivity (*10*).

It should be pointed out that partial Re catalyst reduction in the process of catalysis is accompanied by sharp loss of crystallinity.

The X-ray diffractogram for $Sr_4CoRe_2\square O_{12}$ after 22 h of benzene hydrogenation (Table 3) differs from that for the starting perovskite. It contains weak reflections which do not belong to perovskite, oxides, or metallic rhenium. A more definite assignment is difficult, but we conclude that

TABLE 3

X-Ray Data for $Sr_4CoRe_2\square O_2$ after Catalysis (22 h)

d	I/I_0	d	I/I_0
4.62	33	2.39	12
4.55	32	2.34	6
4.13	3	2.08	13
3.92	4	1.99	10
3.53	10	1.96	14
3.45	5	1.82	8
2.84	100	1.62	22
2.83	83	1.59	9
2.71	15	1.42	9
2.45	9		

perovskite long-range order is destroyed during catalysis. However, despite distortions of a long-range order, it is reasonable to assume that the surface can retain stable fragments of the perovskite lattice, which are responsible for the catalytic activity of the samples studied.

That the fragments of perovskite structure remained unchanged can be deduced from the following facts:

1. The hydrogenation activity varied from sample to sample (Table 1), while the complete degradation of perovskite structure to Re oxides could lead to the formation of catalysts with nearly equal activities.
2. The electronic state of Co and Ni did not change under the conditions of the catalytic experiments, whereas the complete degradation of the perovskite structure could result in reduction of the corresponding oxides to metals.

It is worth noting that $Ba(ReO_4)_2$, which has no hydrogenation activity, is not reduced under conditions of catalysts (curves 4 in Figs. 2a and 2b, and the corresponding curves 4 in Figs. 2c and 2d). This means that catalytic activity is related to rhenium in perovskite structure, which is capable of reduction under reaction conditions up to a certain oxidation state. However, this partial rhenium reduction is a necessary but by no means sufficient condition for the formation of the active surface. Indeed, the surfaces of the perovskite samples studied are reduced to approximately the same degree and yet not all the samples are active. The phase of metallic rhenium also appears to have no decisive effect on activity, since there is not metallic rhenium in active $Sr_4Ni Re_2\square O_{12}$.

It is possible that Re^{6+}- or Re^{4+}-containing sites, which are formed on the partially reduced surface, are active in catalysis. Activity of these sites would, of course, depend on the geometrical structure and the chemical composition of the nearest surrounding Re ions. The octahedra of oxygens in the crystalline structure of the compounds studied (*3*) can be described as strings of three face-sharing octahedra (the middle octahedron of the three shares two faces) linked together by octahedra which share only corners. In the $Ba_{4-x}Sr_xB^{II}Re_2\square O_2$ structure, Co, Ni, or Ca ions of the unit cell are placed in the octahedra which share corners only. The six rhenium ions are placed in the octahedra on both sides of the Co, Ni, or Ca-containing octahedra. The octahedra which share pairs of faces are left vacant.

Vacant octahedra are somewhat smaller than those occupied by rhenium and have an excessive negative charge. It can be postulated that these vacancies facilitate hydrogenation, acting as the specific "traps" for hydrogen. Experiments have shown that the efficiency of these traps is greater when the ionization potentials of the atoms surrounding their cation positions *A* and *B* are large, i.e., when the greater disclosure of the vacant octahedra takes place.

The activity of catalysts in the framework examined increases in the order Ba (ionization potential 5.210 eV (*11*) → Sr (5.692) for cations in the *A* position, and Ca (6.111) → Ni (7.633) → Co (7.860) for cations in the *B* position. In addition, the introduction of Ca into position *B* with its much higher ionic radius (1.0 Å vs 0.7 Å for Ni and 0.65 Å for Co) in an octahedral surrounding and its smaller ionization potential compared to those of other atoms results in the contraction of vacant octahedra due to purely geometrical factors and does not favor disclosure of vacancies.

When *A*-type cations are substituted in the perovskite structure, the geometric factor should also be considered. That is why the replacement of Sr by Ba (ionic radius 1.44 and 1.60 Å, respectively) is accompanied by the loss of $Ba_4CaRe_2\square O_{12}$ activity.

SUMMARY

As discussed above, the mixed rhenium oxides $A_4BRe_2\square O_{12}$ (where A = Ba, Sr; B = Co, Ni) with a perovskite structure possess considerable catalytic activity in benzene hydrogenation. In the continuous series of $Ba_{4-x}Sr_xCoRe_2\square O_{12}$ solid solutions, isomorphous substitution of Ba by Sr increases activity. Benzene is completely hydrogenated on $Sr_4CoRe_2\square O_{12}$ and $Sr_4NiRe_2\square O_{12}$. The active catalyst surface retains a semiconductor nature and contains Re in reduced states (Re^{4+} and Re^{6+}), which are possibly involved in the active sites.

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