

## CATALYTIC CONVERSION OF SYN GAS WITH PEROVSKITES

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### INTRODUCTION

Perovskites, mixed metal oxides of the general formula  $ABO_3$ , have been examined as catalysts for conversion of syn gas to oxygenated organic chemicals. Several of these perovskites have been found to provide moderate to high selectivities to oxygenated organics, particularly methanol and C2OX (acetic acid, acetaldehyde, and ethanol).

### RESULTS AND DISCUSSION

#### CATALYST EVALUATIONS

The perovskites were prepared by co-precipitation with subsequent calcination in air to form pure crystalline phases. The resulting powders (pelleted with  $SiO_2$ ) were evaluated in a U-tube vapor phase reactor. Catalysts were evaluated with 2:1  $H_2:CO$  at 1000 psig. Conclusions are based on results obtained in the CO conversion range of 1-20% (usually 1-10%). Results of catalyst evaluations are presented in Tables I-III.

Perovskites of La with late transition metals and other closely related perovskites were evaluated as syn gas conversion catalysts. The maximum oxygenate selectivities obtained with  $LaCoO_3$ ,  $LaNiO_3$ , and  $LaFeO_3$  were in the range of 24-33%. No oxygenated products were observed with  $LaMnO_3$ .  $LaCoO_3$  and  $LaNiO_3$  underwent runaway methanation, but  $LaFeO_3$  and  $LaMnO_3$  did not. Co, Ni, and Fe are best known as catalysts for producing hydrocarbons (1, 2).

Six substituted derivatives of the above ternary perovskites were evaluated in hopes of finding positive synergism.  $LaNi_{0.5}Fe_{0.5}O_3$  and  $LaMn_{0.5}Ni_{0.5}O_3$  exhibited positive synergism (i. e. higher oxygenate selectivity than the average for the related ternary perovskites).  $LaNi_{0.5}Co_{0.5}O_3$ ,  $LaFe_{0.5}Co_{0.5}O_3$ ,  $LaMn_{0.5}Co_{0.5}O_3$ , and  $LaMn_{0.5}Fe_{0.5}O_3$  exhibited either no synergism or negative synergism when compared to the related ternary perovskites.

Partial substitution of La with Ce and Sr was examined as a means of modifying the catalytic behavior of  $LaCoO_3$ . The maximum oxygenate selectivities obtained with  $La_{0.8}Ce_{0.2}CoO_3$  and  $La_{0.8}Sr_{0.2}CoO_3$  (7-8%) were much lower than the results obtained with the parent system.

$LaCo_{0.5}Ru_{0.5}O_3$ ,  $LaNi_{0.5}Ru_{0.5}O_3$ , and  $LaFe_{0.5}Ru_{0.5}O_3$  were evaluated to determine the effect of partial substitution of Ru for Co, Ni, and Fe and the selectivity patterns typical of Ru in these perovskite lattices. The maximum oxygenate selectivities obtained with these materials (3-14%) are much lower than those obtained with related ternary perovskites. Ru is apparently a poor catalyst for converting syn gas to oxygenates which is consistent with reports that Ru is used in Fischer Tropsch synthesis for producing higher hydrocarbons (2).

$LaNi_{0.5}Ti_{0.5}O_3$  and  $LaFe_{0.5}Ti_{0.5}O_3$  were evaluated to determine the catalytic effects of partial substitution of the B cations by Ti(IV). Both of these materials provided significantly lower oxygenate

selectivities than the related ternary perovskites.

$\text{LaCu}_{0.5}\text{Ti}_{0.5}\text{O}_3$  and  $\text{LaCu}_{0.5}\text{Mn}_{0.5}\text{O}_3$  were evaluated to determine the catalytic behavior of Cu in a perovskite lattice. Both materials exhibited high methanol selectivities (37-38%, maximum). These results suggest that Cu is the catalytic metal in these systems, probably in reduced form. Cu is used in commercial methanol synthesis catalysts.

$\text{NdNiO}_3$ ,  $\text{NdFeO}_3$ , and  $\text{NdCoO}_3$  were evaluated to determine the catalytic effects of replacing La with closely related Nd. The maximum oxygenate selectivities obtained with these perovskites (0-10%) are much lower than those obtained with the analogous La perovskites (24-33%).

Perovskites of barium with platinum group metals were also evaluated as catalysts for syn gas conversion. These materials were prepared by Professor B. L. Chamberland (U. Conn.). Materials prepared by low temperature calcination (< 400°C) were amorphous by XRPD. Materials prepared by re-calcination at higher temperatures ( $\geq 600^\circ\text{C}$ ) were pure crystalline phases by XRPD.

High oxygenate selectivities (almost exclusively methanol) were obtained with  $\text{BaRhO}_3$  and  $\text{BaPtO}_3$  (maximum, 62% and 54%, respectively). Maximum oxygenate selectivities obtained with  $\text{BaIrO}_3$  and  $\text{BaRuO}_3$  were 39% and 14%, respectively. High methanol selectivities have been reported for the related  $\text{LaRhO}_3$  by Bartley (3) and by Watson and Samorjai (4). Supported Pt catalysts have been reported to be selective catalysts for methanol synthesis (2). Supported Ir has been reported as catalysts for both methanol and hydrocarbon synthesis (2). Ru Fischer Tropsch catalysts (2) and our own La-Ru perovskites are mainly hydrocarbon producing catalysts.

#### CATALYST CHARACTERIZATION

Catalysts were characterized to determine the crystalline phase purity of starting materials, to determine if perovskite phases were preserved or decomposed (by reduction) under reaction conditions, and to determine the nature of catalytic sites in these materials. Catalyst samples were characterized by XRPD, EXAFS, XANES, AND ESCA. Results are presented in Table IV.

The "A" cations in these perovskites ( $\text{La(III)}$ ,  $\text{Nd(III)}$ , and  $\text{Ba(II)}$ ) are stable to reduction and catalytically inactive under these conditions. Therefore, the stability of these crystalline lattices to reductive decomposition and the catalytic activity of these materials depends on the late transition metal "B" cations.

The ternary perovskites of La with Co, Ni, Fe, and Mn were pure crystalline phases prior to catalyst testing. EXAFS and XANES results indicated the expected +3 bulk oxidation state for the "B" metals. ESCA analysis of surface "B" atoms indicated oxidation states  $> 0$ , but specific oxidation state (i. e. +2 or +3) could not be assigned.

Recovered materials exhibited a consistent trend. Perovskite lattices of materials not exposed to runaway methanation were preserved. Ni and Co perovskites not exposed to runaway methanation appeared to have been partially reduced (ca. one electron) to form oxide deficient perovskite lattices. Fe and Mn perovskites were unaffected. The oxidation state of surface "B" cations in all of these recovered

catalysts was  $> 0$ .

Perovskite lattices of materials exposed to runaway methanation were destroyed by reduction. During runaway methanation catalyst bed temperatures exceed  $500^{\circ}\text{C}$ . After exposure to runaway methanation the perovskite lattices of  $\text{LaCoO}_3$  and  $\text{LaNiO}_3$  were destroyed. Ni was reduced from +3 to a mixture of +1 and 0, and Co was probably comparably reduced. These results parallel those of Hall and coworkers who reported that hydrogen reduces  $\text{LaCoO}_3$  by one electron at  $400^{\circ}\text{C}$  and by three electrons at  $500^{\circ}\text{C}$  (5). The Fe and Mn perovskites did not undergo runaway methanation under the conditions employed.

Based on these data it appears that the catalytic sites for these materials are higher valent ( $> 0$ ), late transition metal, surface "B" cations in a perovskite or perovskite-like lattices, so long as runaway methanation does not occur. This conclusion applies also to substituted perovskites of La and Nd with Mn, Fe, Co, and Ni.

Six perovskites of the general formula  $\text{LaM}_{0.5}\text{M}'_{0.5}\text{O}_3$  ( $\text{M} \neq \text{M}' = \text{Mn, Fe, Co, and Ni}$ ) were characterized after catalyst testing.  $\text{LaNi}_{0.5}\text{Co}_{0.5}\text{O}_3$  was exposed to runaway methanation and its crystalline lattice was decomposed. The other materials were not exposed to runaway methanation, and their crystalline lattices were preserved.

$\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$  were exposed to runaway methanation, and the crystalline lattices of both materials were destroyed.

$\text{LaCo}_{0.5}\text{Ru}_{0.5}\text{O}_3$  was not exposed to runaway methanation, but  $\text{LaNi}_{0.5}\text{Ru}_{0.5}\text{O}_3$  and  $\text{LaFe}_{0.5}\text{Ru}_{0.5}\text{O}_3$  were. Yet, the perovskite lattices of all three materials were preserved. This contrasts with the behavior of  $\text{LaNiO}_3$ , which underwent lattice decomposition under these conditions. Ru apparently confers added stability to these lattices.

$\text{LaNi}_{0.5}\text{Ti}_{0.5}\text{O}_3$  and  $\text{LaFe}_{0.5}\text{Ti}_{0.5}\text{O}_3$  were not exposed to runaway methanation. As expected, the perovskite lattices were preserved. The catalytic sites for these materials appear to be higher valent surface cations of Ni and Fe in perovskite lattices.

Neither of the Cu containing perovskites were exposed to runaway methanation. The perovskite structures of both materials were preserved, albeit, with partial reduction. The stability of these lattices is probably due to the reductive stability of Ti(IV) and Mn(IV). The catalytic sites for these materials appear to be lower valent surface atoms of Cu in a perovskite or perovskite-like lattice.

$\text{NdNiO}_3$ ,  $\text{NdCoO}_3$ , and  $\text{NdFeO}_3$  all underwent runaway methanation. Like the analogous La compounds, the Ni and Co perovskite structures were destroyed, but the perovskite structure of  $\text{NdFeO}_3$  was preserved.

The crystalline barium platinum metal perovskites were all pure crystalline phases prior to catalyst testing. The bulk oxidation states of the platinum metals were the expected +4. However, all of these materials except  $\text{BaRuO}_3$  contained surface platinum metal cations in lower oxidation states instead of, or in addition to the +4 state.

Both crystalline and amorphous barium platinum metal perovskites are unstable to syn gas and its products. Platinum metals were reduced to the elemental state, and Ba was converted to  $\text{BaCO}_3$ . It appears that these materials after an induction period are transformed to zero valent platinum metal crystallites on  $\text{BaCO}_3$ .

## CONCLUSIONS

Seven base metal lanthanum perovskites that provide 20-40% selectivity to oxygenates have been found. All of the lanthanum metal perovskites are stable to reductive decomposition if not exposed to runaway methanation and some are stable even if exposed to runaway conditions. The catalytic sites in these materials are thought to be late transition metal surface "B" atoms in higher oxidation states ( $> 0$ ) and in perovskite or perovskite-like lattices. Two platinum metal barium perovskites that provide  $> 50\%$  selectivity to oxygenates (mainly methanol) have also been found. These materials are unstable under reaction conditions and are converted to elemental platinum metals and  $\text{BaCO}_3$ . After an induction period, the catalytic sites for these materials are thought to be the mainly zero valent platinum metal crystallites on  $\text{BaCO}_3$ .

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TABLE I

## CATALYTIC EVALUATION OF PEROVSKITES FOR SYN GAS CONVERSION (a)

PEROVSKITE	GHSV 1/HR	TEMP °C	CO CONV		CO SELECTIVITY, %				STY, G/L.HR	
			%	MeOH	C2OX	HiOX	HC	CO2	OXY	TOTAL
LaCoO3	3944	280	2.3	12.5	10.0	10.6	62.4	4.4	2.1	14.6
		300	9.2	10.3	15.7	0.7	37.9	35.4	9.4	21.5
		320	100.	3.7	3.3		64.5	28.4	91.5	1120.
LaNiO3	2471	320	4.1	20.8	4.7	1.6	55.6	17.3	8.2	24.9
		2434	8.7	10.6	2.9	0.9	62.2	23.5	10.1	59.1
LaFeO3	3000	360	100.				67.4	32.6		748.
		280	3.9	6.4	15.0	2.5	66.5	9.6	7.8	25.0
LaMnO3	3054	300	10.4	4.5	14.0	2.3	66.3	12.8	16.7	63.6
		320	22.8	3.7	8.2	2.1	70.3	15.6	24.7	142.5
LaNi0.5Fe0.5O3	3487	340	4.3				64.3	35.7		33.2
		360	6.2				61.9	38.1		50.0
LaMn0.5Ni0.5O3	3504	340	8.3				62.4	37.6		74.6
		360	9.5	0.9	31.3		54.6	13.1	33.1	55.1
LaNi0.5Co0.5O3	3529	380	15.2	0.6	16.0		66.7	16.8	28.6	111.7
		320	26.4		8.7		73.3	17.9	26.1	212.8
LaFe0.5Co0.5O3	3529	340	2.6	0.8	26.6		61.5	11.9	6.5	15.8
		360	4.5	0.6	15.6		69.3	14.4	6.9	31.3
LaFe0.5Co0.5O3	3529	280	6.5	0.6	10.8	0.4	71.5	17.1	6.9	48.8
		300	2.72	1.4	1.0	0.4	93.6	5.0	0.3	18.3
LaMn0.5Co0.5O3	2958	300	7.4		13.9		73.1	11.3	11.6	50.1
		320	100.				73.2	26.8		1013.
LaMn0.5Fe0.5O3	3769	320	13.6	19.0			73.5	7.5	28.4	80.0
		340	30.2	0.5	8.1		79.4	12.0	26.4	213.2
LaMn0.5Co0.5O3	3769	360	34.0		6.8		77.6	15.5	26.0	266.5
		380	40.6		5.1	0.1	76.3	18.4	24.5	346.9
LaMn0.5Fe0.5O3	3769	320	3.3	0.3	0.3	3.0	76.3	20.4	0.6	20.8
		340	19.3	3.4	0.3	0.2	82.8	13.3	4.2	71.8
LaMn0.5Fe0.5O3	3769	360	22.6	2.0	0.3	0.1	79.9	17.6	4.6	137.
		360	10.4	5.3	4.6	4.0	69.5	16.7	18.6	115.
LaMn0.5Fe0.5O3	3769	360	15.9	3.9	3.7	2.0	69.4	20.9	18.6	170.
		380	19.1	3.3	3.2	1.3	68.8	23.4	19.8	223.

a. Pressure = 970-1000 psig, GHSV = gas hourly space velocity, TEMP = temperature, CO CONV = CO conversion, STY = space time yield, MeOH = methanol, C2OX = ethanol + acetaldehyde + acetic acid, HiOX = C3-C6 alcohols, HC = hydrocarbons, OXY = oxygenated organics.

TABLE II  
 CATALYTIC EVALUATION OF PEROVSKITES FOR SYN GAS CONVERSION (a)

PEROVSKITE	GHSV 1/HR	TEMP °C	CO CONV %	CO SELECTIVITY, %				STY, G/L.HR		
				MEOH	C2OX	HiOX	HC	CO2	OXY	TOTAL
La0.8Ce0.2CoO3	3250	280	2.9		1.3	1.6	88.5	8.6	0.7	22.
		300	7.8	4.1	1.2	2.7	83.1	8.9	6.9	62.
		320	40.2	0.7	1.2	1.6	84.5	12.0	12.7	308.
La0.8Sr0.2CoO3	3803	280	2.8		6.9		80.9	12.2	2.1	27.
		300	95.9		0.7	1.0	74.9	23.5	14.1	966.
LaCo0.5Ru0.5O3	2615	320	1.7				94.0	6.0		9.4
		340	5.2				96.9	3.1		26.9
		360	28.3		2.6	0.3	83.7	13.4		5.8
LaNi0.5Ru0.5O3	3015	320	10.0		6.9	.5	87.6	5.0	6.0	57.
		340	19.6	6.7	3.7	.4	82.6	6.7	6.6	130.
		360	52.1		1.3	.5	89.5	8.6	7.9	355.
LaFe0.5Ru0.5O3	2658	300	5.7		12.6	0.9	81.3	5.2	5.5	26.1
		320	11.0		8.5	0.7	79.1	11.7	7.0	59.6
		340	21.7		4.5	1.0	81.9	9.7	8.5	123.
LaNi0.5Ti0.5O3	3337	360	60.7	0.1	1.5	8.5	67.4	22.6	14.7	132.
		360	1.2				69.7	30.3		9.6
		380	1.9				69.7	30.3		15.5
LaFe0.5Ti0.5O3	3189	340	11.4	6.9	10.1	1.3	60.2	21.5		95.5
		360	16.5	4.9	4.7	0.6	64.0	26.9	15.9	143.
		380	20.3	3.1	3.3	0.2	60.5	32.8	12.9	189.
LaCu0.5Ti0.5O3	3323	320	2.9	38.0		0.9	28.7	32.4	13.8	35.6
		340	5.0	32.3		1.6	32.6	33.6	20.7	60.6
		360	7.6	24.1		2.0	35.4	36.8	23.3	88.3
LaCu0.5Mn0.5O3	3361	320	3.4	37.0		29.0	34.0	34.2	14.2	38.2
		340	6.5	28.9		.6	36.3	34.2	21.2	69.4
		360	12.4	20.5		1.3	48.8	29.4	30.0	121.5
NdNiO3	3561	260	2.4				92.8	7.2		15.1
		280	7.0		9.8		90.2		6.0	43.3
		300	73.		0.7		79.6	19.7	3.8	549.
NdFeO3	3060	300	3.3				70.6	29.4		29.6
		320	36.8		2.1	0.7	68.4	28.8	8.3	335
		260	.68				86.2	13.8		5.6
NdCoO3	3494	280	6.1				95.8	4.2		39.7
		300	92.1		0.3		77.3	22.3	3.2	892.

a. Pressure = 970-1000 psig, GHSV = gas hourly space velocity, TEMP = temperature, CO CONV = CO conversion, STY = space time yield, MeOH = methanol, C2OX = ethanol + acetaldehyde + acetic acid, HiOX = C3-C6 alcohols, HC = hydrocarbons, OXY = oxygenated organics.

TABLE III  
 CATALYTIC EVALUATION OF PEROVSKITES FOR SYN GAS CONVERSION (a)

PEROVSKITE	GHSV 1/HR	TEMP °C	CO CONV %	CO SELECTIVITY, %				STY, G/L.HR		
				MeOH	C2OX	HiOX	HC	CO2	OXY	TOTAL
BaRuO <sub>3</sub> , Amorph	2381	280	3.5	2.6	3.6	83	10.9	1.2	17.4	
		300	9.6	4.3	3.8	81.5	10.4	4.6	46.3	
		320	34.4	3.2	3.5	83.1	10.2	12.8	158.4	
BaRuO <sub>3</sub> , Cryst	3564	340	80.9	0.2	0.3	79.9	19.4	4.1	550.2	
		260	6.6	1.5	0.6	66.6	19.2	7.5	49.2	
		280	13.4	8.7	1.1	66.9	23.3	8.9	91.9	
BaRhO <sub>3</sub> , Amorph	2556	300	100.	0.4	0.4	71.4	28.2	3.9	1055.	
		240	1.1	54.3	2.4	27.5	14.9	6.9	10.3	
		260	2.5	36.6	8.4	29.8	23.6	11.7	24.8	
BaRhO <sub>3</sub> , Cryst	2483	280	6.7	22.6	10.2	31	38.8	25.4	60.6	
		300	16.7	13.4	10.3	32	44.3	39.2	147	
		260	1.7	62.3	2.2	0.5	22.2	12.8	11.6	16.8
BaIrO <sub>3</sub> , Amorph	2576	280	3.9	46.8	5.0	1.3	28.2	19	19.9	35.9
		300	7.9	29.7	5.9	1.6	43.2	26.2	28.3	73.3
		320	19.0	15.5	6.4	1.6	43.2	33.2	40.8	174.
BaPtO <sub>3</sub> , Cryst	2550	340	49.6	4.7	5.3	1.5	51.5	37	49.1	455.
		280	2.9	29.3	7.7	2.2	43.1	17.6	10.8	24.1
		300	8.7	20.4	5.8	2.1	51.0	20.6	23.1	71.4
BaPtO <sub>3</sub> , Amorph	2540	320	21.4	17.1	5.1	1.4	47.6	28.7	43.7	173.
		340	22.0	8.8	6.2	1.0	61.2	22.8	30.7	162.
		360	34.0	5.1	3	0.9	61.4	29.5	25.6	260.
BaPtO <sub>3</sub> , Cryst	2860	360	4.3	0.2	1.2	0.9	59.8	37.9	0.8	41.
		380	10.0	4.6	0.9	0.9	56.3	37.6	25	55.3
		280	5.7	38.6	4.8	2.2	26.4	28	44.5	78.7
BaPtO <sub>3</sub> , Cryst	2860	300	8.4	48.1	3.4	6.2	19.6	22.6	44.5	78.7
		320	10.6	53.8	4.3	0.4	19.8	21.6	59.5	102.
		340	12.7	49.6	1.9	0.2	25.2	23	63.1	119.
BaPtO <sub>3</sub> , Cryst	2860	360	13.3	39.8	1.9	0.2	31.5	26.6	52.2	120.
		320	2.6	46	1.5	24.2	28.4	14.6	16.3	16.3
		340	4.4	49.1	1.2	0.2	23.6	25.9	25.5	23.5
BaPtO <sub>3</sub> , Cryst	2860	360	6.7	43.8	8.1	0.3	24.2	23.6	38.7	34.7
		380	6.5	37.1	1.8	0.3	32.0	28.9	30.6	45.5

a. Pressure = 970-1000 psig, GHSV = gas hourly space velocity, TEMP = temperature, CO CONV = CO conversion, STY = space time yield, MeOH = methanol, C2OX = ethanol + acetaldehyde + acetic acid, HiOX = C3-C6 alcohols, HC = hydrocarbons, OXY = oxygenated organics, Amorph = amorphous by XRPD, Cryst = crystalline by XRPD.

TABLE IV

## CHARACTERIZATION OF PEROVSKITES RECOVERED AFTER CATALYST EVALUATION

PEROVSKITE (a)	MAX RXN TEMP, °C (b)	XRPD (c) STRUCTURE PRESERVED	OTHER PHASES	EXAFS/XANES, BULK OXID STATE		ESCA, SURFACE OXID STATE	
				FRESH	USED	FRESH	USED
LaCoO <sub>3</sub>	RUNAWAY	NO					
LaCoO <sub>3</sub>	300	YES, (PR)		+ 3	+ 2	> 0	> 0
LaNiO <sub>3</sub>	RUNAWAY	NO		+ 3	+ 1, 0		
LaNiO <sub>3</sub>	340	YES, (PR)					
LaFeO <sub>3</sub>	320	YES		+ 3	+ 3	> 0	> 0
LaFeO <sub>3</sub>	360	YES					
LaMnO <sub>3</sub>	380	YES		+ 3	+ 3	> 0	> 0
LaFeO <sub>3</sub> .5CoO <sub>3</sub>	380	YES					
LaNiO <sub>3</sub> .5CoO <sub>3</sub>	RUNAWAY	NO					
LaNiO <sub>3</sub> .5FeO <sub>3</sub>	380	YES					
LaMnO <sub>3</sub> .5CoO <sub>3</sub>	380	YES					
LaMnO <sub>3</sub> .5NiO <sub>3</sub>	380	YES					
LaMnO <sub>3</sub> .5FeO <sub>3</sub>	380	YES					
LaO <sub>8</sub> CeO <sub>2</sub> CoO <sub>3</sub>	RUNAWAY	NO					
LaO <sub>8</sub> SrO <sub>2</sub> CoO <sub>3</sub>	RUNAWAY	NO					
LaCoO <sub>3</sub> .5RuO <sub>3</sub>	360	YES					
LaNiO <sub>3</sub> .5RuO <sub>3</sub>	RUNAWAY	YES					
LaFeO <sub>3</sub> .5RuO <sub>3</sub>	RUNAWAY	YES					
LaNiO <sub>3</sub> .5TiO <sub>3</sub>	380	YES					
LaFeO <sub>3</sub> .5TiO <sub>3</sub>	380	YES					
LaCuO <sub>3</sub> .5TiO <sub>3</sub>	380	YES, (PR)					
LaCuO <sub>3</sub> .5MnO <sub>3</sub>	380	YES, (PR)					
NdNiO <sub>3</sub>	RUNAWAY	NO					
NdFeO <sub>3</sub>	RUNAWAY	YES					
NdCoO <sub>3</sub>	RUNAWAY	NO					
BaRuO <sub>3</sub> , Amorph	360	NO	BaCO <sub>3</sub> , Ru(0)				
BaRuO <sub>3</sub> , Cryst	RUNAWAY	NO	BaCO <sub>3</sub> , Ru(0)	+ 4	0	+ 4	+ 4, 0
BaRhO <sub>3</sub> , Amorph	RUNAWAY	NO	BaCO <sub>3</sub> , Rh(0)				
BaRhO <sub>3</sub> , Cryst	RUNAWAY	NO	BaCO <sub>3</sub> , Rh(0)	+ 4	0	+ 3	0
BaIrO <sub>3</sub> , Amorph	380	NO	BaCO <sub>3</sub> , Ir(0)				
BaIrO <sub>3</sub> , Cryst	380	NO	BaCO <sub>3</sub> , Ir(0)	+ 4	0	+ 4, + 3	+ 3
BaPtO <sub>3</sub> , Amorph	380	NO	BaCO <sub>3</sub> , Pt(0)				
BaPtO <sub>3</sub> , Cryst	380	NO	BaCO <sub>3</sub> , Pt(0)	+ 4	0	+ 4, + 2	+ 2, 0

(a) Amorph = amorphous by XRPD, Cryst = crystalline by XRPD.

(b) Runaway indicates that the catalyst bed temperature has exceeded 500°C.

(c) PR indicates that the perovskite structure has apparently been partially reduced through the formation of oxide vacancies, but the lattice has been essentially preserved.