Composite oxide materials for automotive catalyst applications

John G. Darab * MEL Chemicals Inc., 500 Barbertown-Point Breeze Road, Flemington, NJ 08822 * corresponding author: jdarab@melchemicals.com

Introduction

Traditional three way catalytic (TWC) converters used in automotive exhaust abatement schemes are typically made by multiple wash-coating cordierite honeycomb monoliths with combinations of aluminum oxide or doped aluminum oxide, oxygen storage component (OSC) oxides such as cerium- and other rare earth-doped zirconium oxide, and platinum group metals (PGMs). Within this mixture, consider for the moment just the oxygen storage component. There is an ever increasing need to increase the thermal durability of the OSC as catalytic converters are required to be exposed to increasing operating temperatures.

One way to improve the thermal stability of oxygen storage materials is to prepare them as a composite with aluminum oxide or doped-aluminum oxide. Zirconium oxide, typically the majority oxide of an OSC material, does not form a solid solution with aluminum oxide; however, by dispersing the two components on a fine scale may allow for the improvement in thermal durability of the overall OSC properties of the composite.

Of considerable recent interest is a new type of composite material with specific compositions consisting generally of about 40-70wt% Al_2O_3 with the balance typically being made up of CeO₂, ZrO₂, and stabilizers such as La₂O₃, Pr₆O₁₁, etc. As indicated above, for these types of composite materials, it is desirable to have the components mixed as homogeneous as possible, and it is because of this that the manner in which the first steps in making such materials, steps involving the co-precipitation of a composite hydroxide and its subsequent treatment, become critical to defining the final properties of the material.

Materials and Methods

All of the materials discussed here were made at the 5-10kg scale at MEL Chemicals Inc. and are in the form of a calcined fine oxide composites. With the exception of aluminum nitrate nonahydrate (typically Honeywell), all the intermediates came from the MEL Chemicals Inc. plant and included acidic aqueous solutions of zirconium oxynitrate, zirconium oxychloride, cerium nitrate, any other rare-earth nitrates used in the preparations.

An Al/Zr/Ce/RE-hydroxide composite hydroxide was first prepared by coprecipitation from an appropriate starting solution made from the above mentioned raw materials and 25% sodium hydroxide solution at a constant pH of ~9-10 and ambient temperatures. The composite materials discussed here were finished by hydrothermally treating at controlled pH and temperature followed by filtration and washing steps then eventually drying and calcining at 850°C for 4 hours. Details can be found in reference 1.

Results and Discussion

For a constant pH precipitation at a pH of \sim 9-10 at ambient temperatures, the aluminum hydroxide component will most likely be in the from of amorphous Al(OH)₃. Subsequent specific hydrothermal treatment should transform the Al(OH)₃ to boehmite, AlOOH, which allows for the formation of more favorable aluminum hydroxide phases during

calcination, such as γ -Al₂O₃. The other oxides in the composite will generally combine to form a CeO₂-REO-ZrO₂ solid solution finely dispersed through the alumina component. However, some of the CeO₂ and REO will also partition to the alumina component, both during the initial co-precipitation and during post precipitation processing, providing excellent stability to the alumina component and to the composite as a whole.

Space precludes presenting all the compositions made in this work (see references 1 and 2 for examples); however, the composition and textural properties of four selected compositions, indicated simply as Materials 7, 8, 13, and 16 are presented in **Table 1** as indicative examples. Not included in **Table 1** for space limitations are the impurity levels, which is another important aspect to this work. For example, Material 13 has 0.01 wt% SO₄, 11 ppm Cl and 96 ppm Na, all of which would pass typical specification limits for OSC materials. If processed differently the textural properties can sometimes be improved; however, this usually comes at a cost of greater impurity levels, often exceeding typical specification limits.

ıbl	le	1	. Cha	acterist	ics of	selecte	d com	posite	mat	terials	s prej	pared	l 1n 1	this	work	[2	Ľ].
-----	----	---	-------	----------	--------	---------	-------	--------	-----	---------	--------	-------	--------	------	------	----	-----

CHARACTERISTIC	UNITS	UNITS MATERIAL					
		8	7	13	16		
CeO ₂	wt%	4.6	4.9	29.7	10.4		
Pr_6O_{11}	wt%	0.0	6.2	3.9	0.0		
Nd_2O_3	wt%	0.0	0.0	0.0	2.5		
La_2O_3	wt%	8.2	0.0	0.0	2.4		
ZrO ₂	wt%	41.1	41.9	22.3	34.9		
Al ₂ O ₃	wt%	46.1	47.0	44.1	50.7		
As-calcined BET:							
SA	m ² /g	96	123	94	93		
Total PV	cm ³ /g	0.34	0.52	0.51	0.57		
950°C/2h aged BET:	_						
SA	m ² /g	65	74	79	76		
Total PV	cm ³ /g	0.28	0.45	0.49	0.55		
1100°C/2h aged BET:	_						
SA	m²/g	31	37	48	44		
Total PV	cm ³ /g	0.16	0.36	0.40	0.44		

Significance

The results obtained from some of the composite oxide automotive catalyst materials made using a method previous developed by the author have been presented here. A more complete review of the method of manufacture, additional materials prepared, and the properties of these materials will be presented.

References

- Darab, J.G. Composite oxides or hydroxides comprising alumina, zirconia and optionally ceria and/or rare earth oxides for automotive catalyst applications and method of manufacturing, EP1838621 (B1), 2011.
- Darab, J.G. Composite oxides or hydroxides comprising alumina and zirconia for automotive catalyst applications and method of manufacturing, US793904, 2011.