A Comparison of Mesopore Templating Methods for Ceria-Zirconia-Yttria Catalysts

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1.0 Introduction

High surface area mesoporous ceria and zirconia based oxides continue to be in great demand for applications that include emissions abatement, solid oxide fuel cells, electronics, sensors and catalysis. To date, the most cost effective methods for preparing mesoporous materials are via techniques that employ templates or structure directing agents. These templates can be divided into two groups: endo-templates (i.e., soft templates, such as surfactants, dendrimers, and block copolymers) and exo-templates (i.e., hard templates, such as porous carbons and resins).[1-10] This work has critically evaluated the effectiveness of each of these methods to produce highly stable, mesoporous ceria-zirconia-yttria (CZY) mixed oxides with high area surface areas. Specifically, CZY materials were prepared from sol-gel mixtures of the appropriate metal salts using a rage of endo- and exo-templates, and the resulting oxides were evaluated using nitrogen physisorption (BET surface area and BJH Pore Volume), TEM, SEM, TGA, DSC, elemental analysis, and catalytic testing.

2.0 Soft Template Techniques

The general synthesis strategy for all of the materials prepared using soft templates are listed in Figure 1. Three basic procedures are involved: synthesis, drying, and template removal. Four groups of reagents are required for the synthesis step: the metal oxide precursors, solvent(s), hydrolyzing agent or catalyst, and the template. Often, metal alkoxides are used as the metal oxide precursors for sol-gel systems. However, the cost of the CZY alkoxide precursors were higher than desired, so the corresponding inorganic metal salts (e.g., nitrates, carbonates, or oxalates), which are lower in cost, were used instead. Our preference was the nitrate salts because the anion is readily converted to gaseous byproducts upon calcination. Specifically, the list of oxide precursors includes: cerium (III) nitrate hexahydrate, ammonium cerium (IV) nitrate, zirconyl nitrate hexahydrate, and yttrium nitrate hexahydrate. The sol-gel solvent is typically deionized water, but alcohol cosolvents are frequently used, especially with metal alkoxide precursors. Moreover, certain templates are not readily water soluble; for example, the block copolymers and amine functionalized dendrimers have low water solubility. Thus, they are dissolved in water-alcohol mixtures before being added to the other synthesis components. In this work, we used 1-propanol or 1-octanol as the alcohol source. The general synthesis procedure is depicted by the process flow diagram shown in Figure 1.

The two solutions containing either the metal precursors or the soft template (e.g. CTAB) and hydrolyzing agent are prepared separately. The hydrolyzing agent used is ammonium hydroxide, urea, or sodium hydroxide. Both solutions are continuously stirred at room temperature until all solids are dissolved. The precursor salt solution is then mixed with the hydrolyzing agent/CTAB solution and stirred continuously for a 1-4 hr. The synthesis is carried out at pH > 10. Aging of

the resulting sol-gel is carried out in a sealed PFA Teflon reaction vessel that is maintained at a constant temperature. The aging temperature and duration have been found to be very significant factors affecting final oxide properties. The major advantage of this method is the relatively low synthesis temperature condition of the oven. The usual range has been between 70-130 ℃. The aging time also varies from 1-5 days. The samples are removed from the oven and then washed thoroughly with water and centrifuged at least two times. The samples are dried at 110 ℃ for 24 hrs after which the samples were calcined in air at low heating rate to 600 ℃ for 4h.

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┌──────────────────────┐              ┌──────────────────────────┐
│  Template + solvent  │              │  Metal oxide-ion source or│
└──────────────────────┘              │    Precursor + solvent    │
              ╲                       └──────────────────────────┘
               ╲          ┌──────────┐        ╱
                ╲────────►│  Mixing  │◄───────╱
                          └──────────┘     ( Magnetic stirrer )
                               │
                               ▼
┌──────────────────────┐  ┌───────────────┐
│ Hydrolyzing agent:   │─►│ Precipitation │   ( Magnetic stirrer )
│ Aqueous ammonia      │  └───────────────┘
└──────────────────────┘       │
                               ▼
                          ┌──────────┐
                          │  Aging   │      ( 70 – 130°C )
                          └──────────┘
                               │
                               ▼
                       ┌───────────────┐
                       │ Filtration and│   ( Centrifuge )
                       │   Washing     │
                       └───────────────┘
                               │
                               ▼
                          ┌──────────┐
                          │  Drying  │
                          └──────────┘
                               │
                               ▼
                        ┌────────────┐
                        │ Calcination│    ( 400 – 600°C )
                        └────────────┘
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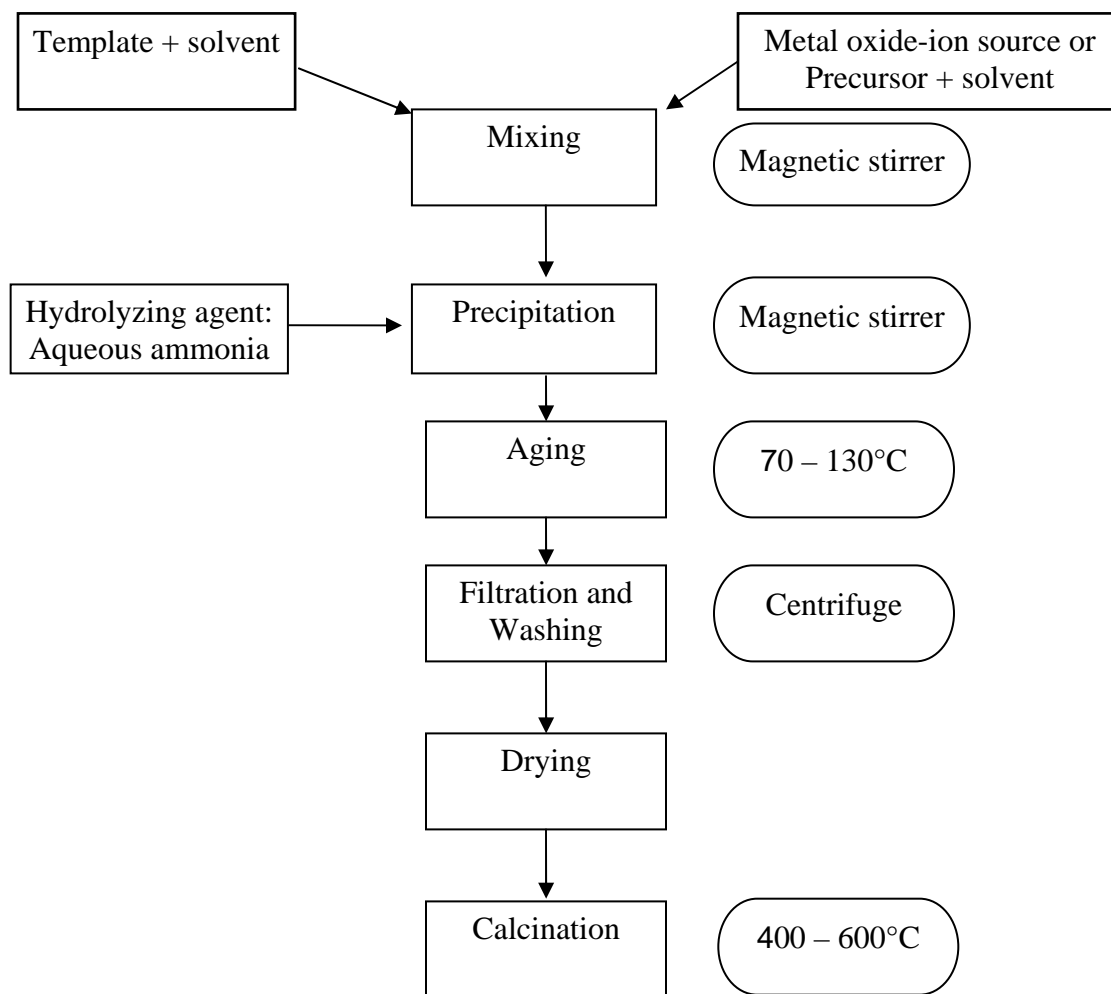
Figure 1: Schematic representation of the synthesis procedures for non-siliceous mesoporous materials prepared using soft template materials, such as surfactants.

Of the reagents required during the synthesis steps for soft template techniques, the most important is the template source. Three types of soft templates were studied: surfactants, block copolymers and dendrimers.

2.1 Surfactant Template Technique
The most frequently used surfactant for the synthesis of mesoporous materials has been cetyltrimethylammonium bromide (CTAB), a cationic surfactant. Just recently, the first

successful synthesis of mesoporous ceria-zirconia-yttria mixed oxide (CZY) using CTAB as template was reported by Feng[11] *et al.* The synthesis procedure was quite similar to that shown in Figure 1. The final CZY material was calcined at a heating rate of 1 ℃/min from room temperature to 550 ℃ and held for 8hr at this temperature. After calcination, the sample was characterized and the specific surface area for CZY was measured to be 139 m^2/g, and the pore diameter was approximately 6.8 nm. Hung et al. also reported the synthesis of yttria stabilized zirconia (YSZ) using only CTAB as the template. Thermal degradation studies of the YSZ sample revealed that the specific surface area significantly reduced from 137 m^2/g to 3.3 m^2/g upon heating from 600 ℃ to 1200 ℃. Feng[11] *et al.* also reported synthesizing zirconia-yttria mixed oxides (ZYO) with a specific surface area of 200 m^2/g. Kapoor[12,13] *et al.* , using a different synthesis procedure, reported synthesizing mesoporous CZY. In their procedure no hydrolyzing agent was used in the synthesis. However, it is important to note that most transition metal oxide precursor solutions are frequently strongly acidic; thus, they implicitly used the acidic nature of the precursor solution as the hydrolyzing agent. The CZY synthesized had BET surface areas that were between 365 m^2/g and 229 m^2/g depending on the CZY compositions.

Many researchers have used co-solvent or cosurfactant in combination with the surfactant to enlarge the size of the micellar aggregates during the synthesis of silica based mesoporous material[4,14,15]. Cosurfactants are mostly medium chain length alcohols ranging from propanol to 1-octanol[4]. Non-siliceous mesoporous oxide based materials like titanium oxophosphate have also been reportedly synthesized using co-solvents[4]. We used 2-propanol as the cosurfactant.

Another way frequently used to enlarge the size of the micellar aggregates during synthesis of mesoporous materials has been with the addition of micellar swelling agents. Swelling agents are large molecular weight organic compounds that are hydrophobic in nature and tend to be readily soluble in organic solvents. Examples of swelling agents are benzene and mesitylene. The core of the supramolecular aggregates of the surfactant can solubilize these swelling agents. Thus, the swelling agents find their way to the core of the supramolecular aggregates and thereby cause the supramolecular aggregates to swell and experience a slight increase in their diameter. The theoretical basis for this phenomena is well established[4,16]. We found that the physical properties of the CZY samples synthesized using CTAB only, CTAB/1-propanol, and CTAB/1-propanol/benzene as the SDA showed some differences in the BET surface area, BJH pore size distribution and average pore diameter.

2.2 Block Copolymer Template Technique

The block copolymer templated synthesis of mesoporous oxides has been reported extensively in the literature.[17-26] Further, the walls of the mesoporous materials synthesized using block copolymers are known to be thicker than those made from surfactants.[5] The triblock copolymers poly (ethylene oxide)-ploy (propylene oxide)-poly (ethylene oxide) (PEO-PPO-PEO) have been by far the most widely studied. A number of publications on the use of block copolymers as SDA in the synthesis of mesoporous oxides of ceria, zirconia, and yttria have been reported.[27-31] In our lab, we have extended the technique to synthesize CZY. Pluronic P123 triblock copolymer is the block copolymer used during all syntheses. The Pluronic P123 structure directing agent was dissolved in a water-propan-2-ol mixture to synthesize CZY as outlined in Figure 1. The BET surface area and the average pore diameter are 96.0 m^2/g and 3.8 nm, respectively.

2.3 Dendrimer Templated Technique

Dendrimer templated mesoporous materials abound in the literature.[32-38] Unlike supramolecular aggregates of surfactants and block copolymers that are capable of assuming various forms and shapes; for example, the hexagonal structure of MCM-41, the bilayer structure of MCM-48, and the cubic structure of MCM-50[5], the 4th and 5th generation polypropyleneimine, which are also known as DAB-Am-32 and DAB-Am-64, respectively, are unique in that they do not self-associate like the surfactants and block copolymers. They have a preformed pseudo-spherical structure. The use of DAB-Am-32 and DAB-Am-64 as SDA for the synthesis of silica based mesoporous materials was first reported by Larsen et al.[38] The reason for the use of these particular dendrimers was that Larsen et al. found that their pseudo-rigid structure enabled them to maintain their overall structure better than the more flexible and more common PAMAM dendrimers. Polypropyleneimine dendrimers are currently quite expensive, so their use for the large scale synthesis of porous catalysts is unlikely but their unique structure affords the possibility of examining another type of templating platform. CZY material were synthesized via the same synthesis procedure outlined in Figure 1, with the polypropyleneimine SDA dissolved in 2-propanol.

3.0 Hard Template Techniques

A variety of hard templating synthesis techniques have been examined for mostly siliceous materials, but some non-silica compositions have also been studied.[3,39-44] In general, the synthesis procedure for mesoporous oxides employing hard templates is quite different from that used with soft templates. Figure 2 shows a schematic representation of the synthesis process used when rigid porous materials, which may or may not be functionalized with hydrophilic or hydrophobic groups, are used as structure directing agents.

The precursor solution containing all of the metal precursor salts is mildly heated and stirred continuously. When the precursor solution becomes homogeneous, it is then slowly combined with the hard template by a wet impregnation technique. The solid-solution is properly mixed to ensure complete filling of the interstices and that the solid is laden with the solution. The filtration step can be skipped in most cases but to be sure only the interstices are covered with the precursor solution the solid-solution mixture can be vacuumed filtered. The drying step is occasionally useful if increased loading of the precursor solution are desired, otherwise this step may be omitted. Calcination of the sample is carried out by heating at the rate of 1 ºC/min from room temperature to 600ºC and maintaining this temperature for 4h.
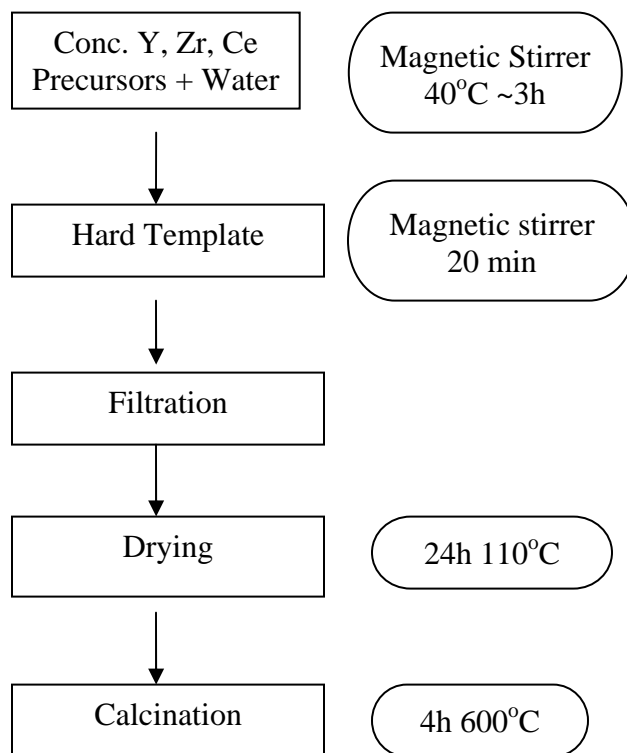
Conc. Y, Zr, Ce Precursors + Water

Magnetic Stirrer 40°C ~3h

Hard Template

Magnetic stirrer 20 min

Filtration

Drying

24h 110°C

Calcination

4h 600°C

Figure 2: Schematic representation of the synthesis procedure for non-siliceous mesoporous materials prepared using hard templates.

3.1 Activated carbon Template Technique

The earliest report of the use of activated carbon as SDA for the synthesis of mesoporous materials was reported by researchers at the Toyota Central R&D lab in Japan.[44] More recently, the technique has been widely used in the synthesis of a number of metal oxides, including pure single component oxides and mixed oxides containing two or more active metals.[3,39-42] It is important that the ash content of the activated carbon template used be as low as possible and that it should be highly porous and with high surface area. The general preparation method involves dissolving the metal oxide precursors, in this case the nitrate salts of cerium, zirconium, and yttrium, in water. The activated carbon powder is loaded with the precursor solution by the incipient wetness method. The paste is kneaded together properly before it is dried at 110 °C for at least 12 hr. The dried solid is further calcined in air at a heating rate of 1 °C/min to 600 °C and then held for 4h at this temperature. The BET surface area and BJH pore size distribution are measured to be 118m^2/g and 9.0nm, respectively. The TEM images of the resulting calcined oxide show that the CZY particles as relatively agglomerated and crystalline in nature, with the average particle size of the primary particles being approximately 5.0 nm in diameter.

3.2 Polymeric Resin Template Technique

The use of polymeric resins as templates for the synthesis of mixed oxides has been reported in the literature.[45-48] There have been excellent articles written about similar techniques, called opal techniques. This technique is fascinating because it confers a negative replica of its structure

unto the porous metal oxide that is formed. The method of preparation is very similar to that laid out for the activated carbon template. The precursor salts are dissolved in water and the resulting solution is mixed with the polymeric resin. The polymeric resin-precursor solution is then dried in at 110 ºC for at least 12h before being calcined in air at a heating of 1 ºC/min to 600 ºC and then held for 4h at this temperature. The BET surface area and BJH pore size distribution for the CZY sample is 98.0 m^2/g and 3.4 nm, respectively. The TEM images revealed of the resulting oxide particles showed that they are agglomerated and crystalline in nature. The powder X-ray diffraction pattern revealed that the CZY contained nanocrystalline particles.

4.0 Results and Discussion
The CZY sample composition typically used in this study were 45 mol% Ce : 50 mol % Zr : 5 mol% Y. The challenge in the synthesis of ordered mesoporous non-siliceous oxides is two-fold when soft templates are required. First is the control of the kinetics of crystallization of the metal oxide precursors in relation to the self-assembly of the organic template during synthesis. Unlike ordered mesoporous silica based oxides for which the crystallization of the silica precursor and self-assembly of the soft template occur in complete complimentary fashion[49]; the same cannot be said of non-siliceous oxide precursors, which have a tendency to crystallize faster than it would take the soft templates to self-assemble. Second is the rapid collapse of the mesostructure of the non-siliceous oxides during template removal. The goal of this research was to study ways in which we could mitigate or eradicate completely the effects of the above mentioned challenges. Tables 1-3 below show a summary of a fraction of the results obtained during our experimental efforts.

Table 1. Effect of Synthesis Temperature on the Physical Properties of CZYs Made from Different Combination of Structure Directing Agent and Calcined at 600ºC for 4h

Sample	BET Surface Area (m^2/g) Hydrothermal Treatment Temperature (ºC)				Avg. Pore Diameter (nm) Hydrothermal Treatment Temperature (ºC)			
	70	90	110	130	70	90	110	130
CZY/no Template	102	93	101	84	3.7	3.7	4.7	3.6
CZY/CTAB	80	94	94	107	4.7	4.7	3.3	5.4
CZY/CTAB/1-Propanol	85	87	89	121	6.3	5.4	4.6	2.2
ZY/CTAB/1-propanol/benzene	81	98	92	95	4.1	4.8	5.3	3.3

From Table 1, it is observed that the effects of hydrothermal treatment temperatures on the physical properties of the CZY are quite moderate to say the least. A significant impart though of the hydrothermal treatment temperature is on the aging time. At high hydrothermal treatment temperatures, crystallization of the CZY occurred much faster as expected.

On the other hand, the use of hydrolysis retarding agents like acetylacetone (ACAC) or triethanol amine (TEA) on the physical properties of the CZY synthesized using CTAB and P123 soft template was significant as shown in Table 2. While ACAC led to an increase in the BET surface area from 82 to 106 m^2/g and from 58 to 78 m^2/g for CZY synthesized via CTAB and P123, respectively; however, TEA led to a decrease in the BET surface area of the CZY samples from 82 to 14 m^2/g and from 58 to 44 m^2/g for CZY synthesized via CTAB and P123 SDA's.

Table 2. Effect of Hydrolysis Retarding Agents on the Physical Properties of CZY's made from Different Structure Directing Agent and calcined @ 600ºC for 4h

CZY Template	BET Surface Area (m^2/g) 20ºC/min Heating Rate During Calcination	Avg. Pore Diameter (nm) 20ºC/min Heating Rate During Calcination
CTAB	82	6.2
CTAB/ACAC	106	5.3
CTAB/TEA	14	3.8
DAB-AM-32	97	3.0
DAB-AM-64	40	2.8
P123	58	2.8
P123/ACAC	78	3.6
P123/TEA	44	3.6

Table 3 suggests that carrying out the calcination of the templated CZY samples at higher heating rates lowered BET surface area of the CZY sample than when it was calcined at lower heating rate. When heating rates was increased from 1 to 20ºC/min, the BET surface area of the resin and activated carbon templated CZY decreased from 98 to 78m^2/g and 118 and 103m^2/g, respectively. For P123 templated CZY, the BET surface area similarly dropped from 96 to 78m2/g and 50 to 44m2/g for the ACAC and TEA treated samples, respectively.

Table 3. Effect of Heating Rate on the Physical Properties of CZY made from Different Structure Directing Agent and calcined @ 600ºC for 4h

CZY Template	BET Surface Area (m^2/g)		Avg. Pore Diameter (nm)	
	Heating rate (ºC/min)		Heating rate (ºC/min)	
	1	20	1	20
CTAB	78	82	6.2	6.2
CTAB+acac	106	106	5.4	5.3
CTAB+TEA	9	14	3.8	3.8
P123+acac	96	78	3.8	3.6
P123+TEA	50	44	3.8	3.6
Resin	98	78	3.4	3.4
Activated Carbon	118	103	9.0	9.0

5.0 Conclusion

The results shown above are our attempt at providing the following answers: does hydrothermal treatment temperature help in slowing down the rates of non-siliceous oxide precursor crystallization during synthesis; which is a better hydrolysis retarding agent between acetylacetone and triethanol amine; and what heating rates best preserve the mesostructure of the synthesized CZY during calcination? In conclusion, we summarize our findings as follows: at high temperatures the crystallization rates increases; acetylacetone is a much better hydrolysis retarding agents than triethanol amine; and adopting a calcination protocol that uses a low heating rate helps to minimizes the heat evolution rates, thus, preventing hot spots during calcination. The CZY synthesized using the various templates all showed that we successfully made mesoporous oxides even though there is little evidence they are highly ordered. It is hoped that attempts in the future would be focused on making highly ordered mesoporous non-siliceous oxides with appropriate combination of hydrolysis and condensation retarding agents, and suitable calcination protocol.

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