

**OPTIMIZATION OF MODIFIED SOL-GEL METHOD FOR THE
FORMATION OF TETRAGONAL PHASE ZIRCONIA IN Zr(IV)/Ce(IV)
CATALYST**

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UNIVERSITI TEKNOLOGI MALAYSIA

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**A dissertation submitted in partial fulfillment of the requirements for the award
of the degree of Master of Science (Chemistry)**

**Faculty of Science
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This dissertation is dedicated to my beloved family and Choong Meng

Thanks for being there when I needed you.

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ABSTRACT

Zirconium-cerium mixed metal oxides is widely used as promoters in automobile emissions control catalyst systems (Three-Way Catalyst, TWC). In order to improve the performance of zirconia-ceria catalysts, a research has been done to develop a zirconia-based catalyst doped with ceria by modified sol-gel method with zirconium oxychloride and cerium (III) nitrate hexahydrate as the precursors. This research investigated the optimum conditions on the formation of single phase tetragonal ZrO_2 . A series of $Zr_{1-x}Ce_xO_2$ catalyst by varying the atomic percentage ratios were prepared in different amount of water and calcinations temperature. The properties of catalysts were characterized with X-Ray Diffraction (XRD), surface area analysis, and Fourier-Transform Infrared Spectroscopy (FTIR). The catalyst showed the best result is selected to test for CO conversion. The $Zr_{0.70}Ce_{0.30}O_2$ catalyst prepared in 5 mL of water dried for two days at 70 °C and calcined at 400 °C for 17 hours gives the optimum condition on the highest formation of single phase tetragonal ZrO_2 . The XRD analysis showed that this catalyst has crystallinity property, consists of tetragonal ZrO_2 as the main phase and average crystallite size of approximately 12.98 nm serve as the active phases for the catalyst. Surface area analysis showed that this catalyst has 35.36 m²/g of surface area. The FTIR analysis showed the existence of surface hydroxyl group on the surface of catalyst. The bands that were assigned to the water deformation mode and hydroxyl deformation mode of surface hydroxyl groups have been eliminated as the calcination temperature increased. The $Zr_{0.70}Ce_{0.30}O_2$ catalyst prepared in 5 mL of water was reported to exhibit the best catalytic activity towards CO conversion, it showed the lowest T_{LO} at room temperature while 100 % CO conversion was achieved at $T_{100} = 320$ °C.

ABSTRAK

Campuran logam oksida zirkonium-cerium diguna secara meluas sebagai penyokong dalam sistem pemangkinan bagi pengawalan bahan pencemar daripada kenderaan bermotor (Pemangkinan Tiga Arah, *TWC*). Demi meningkatkan keupayaan mangkin zirkonia-ceria, satu kajian telah dilakukan untuk menyediakan mangkin berasaskan zirkonia yang didopkan dengan ceria melalui kaedah pengubahsuaian sol-gel di mana zirkonium oksiklorida dan cerium (III) nitrat heksahidrat sebagai bahan pemula. Kajian ini dijalankan bertujuan menyelidik keadaan yang optimum bagi pembentukan fasa tunggal ZrO_2 berstruktur tetragonal. Satu siri mangkin $Zr_{1-x}Ce_xO_2$ telah disediakan dengan mempelbagaikan nisbah peratus atom dan menggunakan kuantiti air serta suhu pengkalsinan yang berbeza. Analisis pencirian dilakukan terhadap mangkin dengan menggunakan teknik pembelauan sinar-X (XRD), analisis luas permukaan dan FTIR. Mangkin yang menunjukkan keputusan yang terbaik dipilih untuk kajian penukaran gas karbon monoksida (CO) kepada CO_2 . Mangkin $Zr_{0.70}Ce_{0.30}O_2$ yang disediakan menggunakan 5 mL air dan dikering pada suhu $70\text{ }^\circ\text{C}$ selama dua hari serta dikalsin pada suhu $400\text{ }^\circ\text{C}$ selama 17 jam menunjukkan keadaan yang paling optimum dalam pembentukan fasa tunggal ZrO_2 berstruktur tetragonal. Analisis XRD menunjukkan mangkin ini terdiri daripada fasa tetragonal ZrO_2 sebagai fasa utama dengan sifat hablur serta purata saiz hablur kira-kira 12.98 nm yang bertindak sebagai fasa aktif mangkin. Analisis luas permukaan menunjukkan mangkin ini mempunyai luas permukaan sebanyak $35.36\text{ m}^2/\text{g}$. Keputusan FTIR menunjukkan kehadiran hidroksil pada permukaan mangkin. Puncak-puncak bagi air, hidroksil telah disingkirkan apabila suhu pengkalsinan meningkat. Penyediaan mangkin $Zr_{0.70}Ce_{0.30}O_2$ dalam 5 mL air memberikan keputusan aktiviti pemangkinan terhadap penukaran gas CO yang paling baik di mana menunjukkan T_{LO} yang paling rendah pada suhu bilik sementara 100 % penukaran gas CO dicapai pada $T_{100} = 320\text{ }^\circ\text{C}$.

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LIST OF SYMBOLS/ ABBREVIATIONS/ NOTATIONS/ TERMS

A/F	-	Air-to-fuel ratio
θ	-	Half angle of diffracted beam
λ	-	Wavelength of the x-rays
β	-	Peak width
$\langle L \rangle$	-	Particle size
c	-	Cubic
CeO ₂	-	Cerium oxide/ ceria
CO	-	Carbon monoxide
<i>d</i>	-	Interplaner spacing in a crystal
FTIR	-	Fourier-transform infrared
HC	-	Hydrocarbon
m	-	Monoclinic
NO _x	-	Nitrogen oxides
OSC	-	Oxygen storage capacity
PDF	-	Power Diffraction File
RT	-	Room temperature
t	-	Tetragonal
T ₁₀₀	-	100 % conversion temperature
T _{LO}	-	Light-off temperature
TWC	-	Three-way catalyst
XRD	-	X-ray diffraction
ZrO ₂	-	Zirconium oxide/ zirconia

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CHAPTER I

INTRODUCTION

1.1 Air Pollution

Air pollution is the presence of material in air in quantities large enough to produce harmful effects. The undesirable materials may damage, vegetation, human property, or the global environment as well as create aesthetic insults in the form of brown or hazy air or unpleasant smells [1].

Air pollution caused by mobile source had been received much attention by most of the environmentalist. In the last 60 years the world vehicles fleet has increased from about 40 million vehicles to over 700 million, this figure is projected to increase to 920 million by the year 2100 [2]. This will lead to increase of more and more air pollutant. The engine exhaust contains principally three main pollutants, unburned or partially burned hydrocarbons (HCs), carbon monoxide (CO) and nitrogen oxides (NO_x), mostly NO, in addition to other compounds such as water, hydrogen, nitrogen, oxygen, etc. Sulphur oxides, though polluting, are normally not removed by the post combustion treatments, since the only effective way is to reduce them to elemental sulphur, which would accumulate in the system [2].

1.2 Definition and Types of Pollutants

Any solid, liquid, or gas that is present in the air in a concentration that causes some deleterious effect is considered an air pollutant. However, there are several substance that, by virtue by their massive rates of emission and harmful effects, are considered the most significant pollutants [3].

Substances emitted directly from sources are called primary pollutants. The pollutants manufactured in the lower atmosphere by chemical reactions among primary pollutants are called secondary pollutants, they are responsible for most of the smog, haze, and eye irritation and for many of the forms of plant and material damage attributed to air pollution [4].

1.3 Effects of Air Pollution

Carbon monoxide (CO) is a gaseous pollutant which enters the atmosphere from four sources: fossil fuel combustion and industrial emissions, biomass burning, oxidation of CH₄, and oxidation of non-methane hydrocarbon [5].

CO is a colorless and odorless gas. It is very stable and has a lifetime of 2 to 4 months in the atmosphere. High concentration of CO can cause physiological and pathological changes and ultimately death. CO is a poisonous inhalent that deprives the body tissues of necessary oxygen [6].

NO_x in the atmosphere causes environment problems, such as photochemical oxidant and acid rain [7]. Nitrogen dioxide (NO₂) can react with moisture present in the atmosphere to form nitric acid, which can cause considered corrosion of metal surface. Nitrogen oxide (NO) is a colorless gas and its ambient concentration is usually for less than 0.5 ppm. NO is a precursor to the formation of nitrogen dioxide and is an active compound in photochemical smog formation as well [6].

Unburned hydrocarbons in combination with the oxides of nitrogen in the presence of sunlight form photochemical oxidants, components of photochemical smog, that do have adverse effects on human health and on plants [6].

1.4 Catalyst

A catalyst is a substance that increased the rate at which a chemical reaction approaches equilibrium without itself becoming permanently involved in the reaction [8].

Basically, catalysts are considered as chemical compounds capable of directing and accelerating thermodynamically feasible reactions while remaining unaltered at the end of the reaction, whose thermodynamic equilibrium they consequently cannot change [9].

Catalysis is homogeneous when the catalyst is soluble in the reaction medium, and heterogeneous when catalyst is existing in a phase distinctly different from the phase of the reaction medium. In most instances of heterogeneous catalysis, the catalyst is a solid that is brought into contact with gas or liquid reactants to bring about a transformation [9].

1.5 Catalytic Converter

Nowadays, more than 95% of vehicles produced in the world are equipped with a catalytic converter, which for the gasoline-fuelled engines, is almost exclusively based on the so-called three-way catalyst (TWC). TWCs are capable of simultaneously and efficiently converting CO, hydrocarbon (HC) and NO_x into harmless CO₂, H₂O and N₂, provided that the so-called and air-to-fuel ratio (A/F) is constantly kept at the stoichiometry [10]. A typical design of a modern three-way catalytic converter is reported in Fig. 1.1. Basically, it is a stainless steel container

which incorporates a honeycomb monolith made of cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) or metal [2].

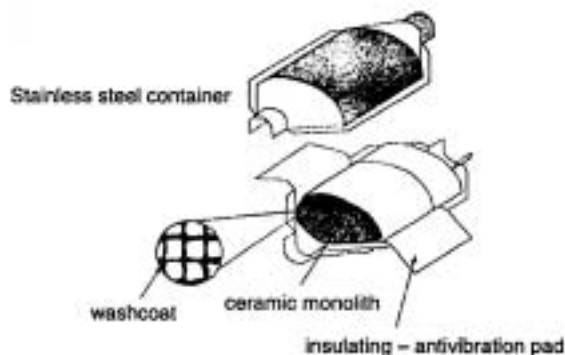


Figure 1.1: Diagram of a typical catalytic converter

1.6 Three-way Catalysts

Automobiles under severe driving conditions such as a long-distance continuous running usually generate high temperature in the catalytic converter, that may cause thermal sintering of both metal active phases and catalyst support, and finally leads to catalyst deactivation. On the other hand, at cool start, the catalyst usually shows low catalytic activity. Therefore, a satisfactory catalytic efficiency at high temperature and a promoted light-off reaction behavior at cool start are demanded for the current three-way catalysts (TWCs) [11].

Three-way catalysts (TWCs) have been widely used to reduce pollutant emissions from gasoline engine powered vehicles [12]. Various three-way catalysts (TWCs) are widely used in car exhausts for the conversion of poisonous gases (CO , NO_x and hydrocarbons) to harmless H_2O , CO_2 and N_2 . These converters, because of their effectiveness, become compulsory part of the modern automobile [13].

The concept of using catalyst to convert CO, NO_x, and HC to less environment active compounds such as nitrogen, water and carbon dioxide was well established practice prior to the need arising on motor vehicles. The principal reactions are shown in Table 1.1 [14].

Table 1.1: Reactions occurring on automobile exhaust catalyst

<p><u>Oxidation Reactions</u></p> $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ $\text{HC} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$
<p><u>Reduction Reactions</u></p> $2\text{CO} + 2\text{NO}_2 \rightarrow 2\text{CO}_2 + \text{N}_2$ $\text{HC} + \text{NO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{N}_2$

Since CO and HC emission are removed by oxidation whereas NO_x may only be removed by reaction with reducing agents, the elimination of all three pollutants can only be achieved by separating the oxidation and reduction functions in appropriate reactors or by design of selective catalyst on which the two reactions may proceed simultaneously [15].

The development of the three-way catalyst (TWC) was dictated by the need to simultaneously convert the HC, CO, and NO_x, present in the automobile exhaust to H₂O, CO₂ and N₂ [16].

1.7 Zirconium Oxide or Zirconia

Zirconium oxide or zirconia is widespread in nature as a trace mineral, baddeleyite. In its pure form, properties such as high hardness, low wear resistance, low coefficient of friction, high elastic modulus, chemical inertness, good ionic conductivity, low thermal conductivity, and high melting temperature have made zirconia a technologically important material. These unique properties enable a wide range of application of zirconia such as structural materials, thermal barrier coatings,

solid-state electrolytes, solid fuel cells, gate dielectrics, oxygen sensors, and heterogeneous catalysts [17].

Since zirconia has a lattice with many vacancies, it is a good ionic conductor at high temperature. These vacancies allowed it to be used as an oxygen sensor to measure the air-to-fuel ratio in internal combustion engines in order to control the emission of NO_x , CO and hydrocarbon compounds [18].

ZrO_2 - based materials have attracted considerable interest in recent decades. In a catalytic sense, they appear to have some advantages in area of practical application over traditional oxides, such as SiO_2 and Al_2O_3 . More significant is the fact that additives can bring about a strong modification of the surface structure of zirconia, in which case substitution of Zr^{4+} with dopant cations results in a rise in anion vacancy concentration and conductivity [19].

The tailored physico-chemical properties of zirconia including structure, redox, and acid-base characteristics make it as an attractive catalyst and catalyst support for a number of reactions [20]. In fact, due to its acid-base bifunctional properties, it catalyses the hydrogenation of different substrates such as for example benzoic acid, carboxylic acids, and carbon monoxide. However, the main use of zirconia is as an efficient support for a variety of catalytic systems [21].

Zirconia is also widely used in optical fields because of its high refractive index, large optical band gap, and low optical loss and scatter in the infrared region. It is also useful for making high-reflectivity mirrors, laser gyros and broadband interference filters [22]. Depending on factors such as preparation method, pH, temperature, and kinetic mechanism, synthetic zirconia shows three crystalline phases: monoclinic (m), tetragonal (t), and cubic (c); it has also been shown that a high-pressure orthorhombic form exists [23]. At room temperature, t- and c-phases metastable, while m-phase is stable. t- and c-phases are stable at high temperature. They can be partially or fully stabilized at room temperature by addition a small amount of oxides (e.g. CaO, MgO and types of rare earth oxides) [24].

The monoclinic phase is stable up to 1400 K where it transforms to the tetragonal phase, which is stable up to 1570 K while the cubic phase exists up to the melting point of 2980 K. However, the cubic phase can be stabilized by the addition of divalent cations such as Ca^{2+} , Mg^{2+} or Y^{3+} [20]. Several methods have been developed to stabilize the tetragonal phase at low temperature. These include the addition of dopants (Y_2O_3 , CaO , MgO , CeO_2), or the use of soft-chemistry methods, from which nanocrystalline materials can be obtained [23].

It is known that tetragonal zirconia as a metastable phase exists at well below its normal transformation temperature as a result of the crystalline size effect, the presence of impurities, or the presence of strain at the domain boundaries in polydomain tetragonal particles [25].

Tetragonal- ZrO_2 is used as a catalyst and catalyst support for various gas phase reactions [26]. Several studies have shown that the percentage of tetragonal phase of ZrO_2 (t- ZrO_2) is crucial for the activity and selectivity in catalysis [27]. However, a phase transformation from the tetragonal phase to the less reactive monoclinic phase of crystalline ZrO_2 (m- ZrO_2) during the reaction prevents the further application of ZrO_2 . Therefore, stabilizing the tetragonal zirconia during reaction becomes an important topic in catalysis fields [28]. ZrO_2 stabilized by CeO_2 and other rare earth is known to increase durability and removal efficiency for automotive emission control [29].

1.8 Cerium Oxide or Ceria

Cerium oxide or ceria (CeO_2) has been considered and largely used in the last years as one of the most important promoters of heterogeneous catalytic reactions [30]. Cerium oxide is one of the most important components in high-performance three-way catalyst (TWC) for its ability in enhancing the removal of carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons (HC) [31].

Cerium oxide has been considered of potential interest for solid oxide fuel cells and three-way automobile catalysts because of its good oxygen ion conductivity. Its ability to act as an oxygen buffer and therefore to operate effectively under conditions of oscillating oxygen concentration has promoted its use in automobile catalytic applications [32].

However, pure CeO₂ alone is known to be poorly thermostable. The loss in surface area is usually related to the changes in the pore structure and to crystalline growth. It is, therefore, very important to improve its textural stability. Doping with cations such as Al³⁺, Zr⁴⁺, or Si⁴⁺ may significantly improve the stability of the surface area of ceria at high temperature [33].

Among the lanthanide elements, cerium is the only one that forms stable compounds in a tetravalent oxidation (i.e., Ce⁴⁺) and the coordination number of surface Ce⁴⁺ can vary between four and eight, six and eight being the coordination number of bulk Ce⁴⁺. Furthermore, Cerium ions can behave as a large O₂ trap: due to its low redox potential and cerium ion can easily pass from Ce⁴⁺ to Ce³⁺ [34].

CeO₂ has a cubic fluorite-like structure in which cerium coordinates eight oxygen anions at the corners of a cube, while oxygen is tetrahedrally surrounded by four cerium cations. It has been demonstrated that the Oxygen Storage Capacity (OSC) of cerium oxide is improved by suitable doping with different cationic species and in particular with lanthanum [35].

Agrafiotis *et al* [32] studied deposition of nanophase doped-ceria systems on ceramic honeycomb for automotive catalytic applications. A remarkable enhancement on the catalytic activity of cerium oxide has been observed when the power is of nanophase dimensions because of the large number of lattice defects such as oxygen vacancies present, which provide a large number of active sites for gas-solid catalysis. The number of defects can be increased by partial substitution (doping) of the cerium atoms in the cerium oxide lattice with other metal atoms of lower oxidation state such as Ca or Nd. Because of these properties, doped cerium nano-oxides can act as catalyst themselves, reducing significantly the need for noble metals.

1.8.1 Role of CeO₂ in the TWCs

It is an ambitious task to define the role of the CeO₂ in the three-way catalysis since multiple effects have been attributed to this promoter. Ceria was suggested to [16]:

- (i) promote the noble metal dispersion;
- (ii) increase the thermal stability of the Al₂O₃ support;
- (iii) promote the water gas shift (WGS) and steam reforming reactions;
- (iv) favour catalytic activity at the interfacial metal-support sites, etc;
- (v) promote CO removal through oxidation employing a lattice oxygen;
- (vi) store and release oxygen under, respectively, lean and rich conditions.

1.9 Catalysis by Zirconia-Ceria

Ceria-zirconia solid solutions comprise an interesting system with great potential for applications in various technological fields. Depending on composition, ceria-zirconia may be used for the manufacture of solid oxide fuel cells, gas sensors, oxygen semi-permeable membranes for steam electrolysis and hot electrodes for magnetohydrodynamic systems [36].

Not long ago, in the middle of 1990s, CeO₂-ZrO₂ mixed oxides has been proclaimed as one of the most perspective materials for application as a component of so-called “three-way catalysts” (TWC) in automotive pollution control. These solids are able to neutralize simultaneously CO, hydrocarbons and NO_x. High catalytic activity of such system combines with enhanced thermal stability and high Oxygen Storage Capacity (OSC). The latter is due to the presence of cerium ions able to change easily their oxidation state depending on the environment [37].

Cerium oxide (CeO₂) is used in automotive emissions control catalysts to regulate the partial pressure of oxygen near the catalyst surface. Despite its widespread use and application, pure cerium oxide has poor thermal stability and is

known to sinter at 1123 K. In order to increase its thermal stability, and ability to store and release oxygen during operation, zirconium is substituted into the cubic structure of ceria. The addition of zirconium to the cubic structure of ceria is reported to increase the oxygen storage capacity of the system while enhancing the thermal stability under high temperatures as compared to pure ceria [38].

In the last few years, it has been effectively shown that $Ce_xZr_{1-x}O_2$ solid solutions in the ceria rich regions ($x = 0.5$) are the most effective redox promoters at low temperature (i.e engine cold start), and so can greatly reduce emissions of CO, NO_x , and hydrocarbon when active metal is dispersed on the surface [39].

Zirconia-rich compositions, $Ce_{1-x}Zr_xO_{2-\delta}$ ($x < 0.3$) find applications as ceramic materials and ionic conductors whereas ceria-rich oxides ($x > 0.3$) are exploited above all as catalytic materials [36].

Mello *et al* [40] studied the performance of Pd / $Ce_{0.75}Zr_{0.25}O_2$ catalyst for the reduction of NO with ethanol and compare with the Pd-Mo catalysts. The Pd / CeO_2 - ZrO_2 sample showed higher activity for the conversion of NO and higher selectivity for N_2 formation when compared to the Pd-MoO₃ / Al₂O₃ sample. The CO chemisorption results showed that the CeZr mixed oxide chemisorbed a higher amount of CO, and this is related to a higher reducibility capacity of this compound when compared to MoO₃.

The CO oxidation on CeO_2 - ZrO_2 mixed oxides prepared via sol-gel technique using urea as a hydrolysis catalyst was studied [41]. Highly uniform nano-size solid solution particles of ceria-zirconia were attained under the conditions of this study (ca 100 °C). The CO oxidation activity of the mixed oxides was found to be dependent on Ce/Zr ratio, which relates to the degree of reducibility. The catalytic activity for CO oxidation decreases with a decrease in Ce/Zr ratio. This might be due to the different in phase compositions of the mixed oxides. It can be postulated that the cubic phase, fluorite structure, which is mainly found in $Ce_{1-x}Zr_xO_2$ (where $x < 0.5$) could be reduced easily than the tetragonal phase found in $Ce_{1-x}Zr_xO_2$ (where $x > 0.5$) [41].

Martorana *et al* [42] reported on the structural modifications of two Pt/ceria-zirconia catalysts in different conditions of flowing gas mixtures and of isothermal treatment temperature; this behavior is compared with that of a metal-free ceria-zirconia sample. In a first phase, oxygen coming from the surface layers of the ceria-zirconia mixed oxide is consumed and no structural variation of the support is observed. After this induction time, bulk reduction of Pt/ceria-zirconia takes place as a step-like process, while the CO₂ production continues at a nearly constant rate. This behavior is totally different from that of the metal-free support in similar reaction conditions, that show a gradual bulk reduction.

Kozlov *et al* [43] investigated the effect of different synthesis methods on the redox property of CeO₂-ZrO₂-Al₂O₃. Related to the important of the preparation method is the observation that enhanced reducibility after redox cycling is only present in bulk oxides using certain preparation methods. Al₂O₃ was able to stabilize the particle size of the mixed oxide during severe redox and thermal treatment.

1.10 Sol-gel Chemistry

Heterogeneous catalysts are often prepared by wet chemistry method such as precipitation, coprecipitation, hydrothermal synthesis or sol-gel process. The main advantages of these low temperature processes are to give solids with large specific surface area and high porosity in the meso and macropore ranges. The solid network is formed, from the solution, via the hydrolysis and condensation of molecular precursors in solution [44].

The sol-gel process is a useful synthesis approach for the preparation of amorphous, as well as structurally ordered materials. Through sol-gel process, it is possible to control the properties of the synthesized samples, such as porosity and surface area to obtain homogeneous matrices [45].

The sol-gel is also considered to be the most practical method for the fabrication of porous ceramic membranes. During the sol-gel process, the properties of the sol, the surface and pore structure of the support, the method of preparing gel membrane and its drying and firing conditions are the key factors influencing the pore structure and performance of membranes [46].

The sol-gel process for preparing oxide glasses is attractive as the preparation is accomplished at room temperature without high-temperature melting or hot pressing. Since the preparation are conducted in solutions, the homogeneity attained in the initial reaction mixture can also be retained. The synthetic procedure for sol-gel preparation based on acid or base catalyzed hydrolysis of alkoxy-silane precursors in aqueous solution, followed by condensation, gelation, aging, drying, and densification. The technique is capable of providing specialty glasses with optically active organic or inorganic materials embedded in the matrix, which often have high optical purity and excellent dielectric effects while possessing transparency over a wide visible range. Thus, glasses prepared by the sol-gel process are attractive candidates for optical and electro-optical applications [47].

The sol-gel technique works well for the synthesis of complex metal oxides with high phase purity because the polymerizing gel traps the various metal ion components spatially, permitting precipitation from solution where all the metal ions occupy near-neighbor positions in the gel matrix, upon further processing and high temperature calcinations, the resultant amorphous mixture of metal oxides, hydroxides, and metal salts decomposes with M-O-M bond formation, while having to diffuse only a few angstroms to their lattice positions in a homogeneous solid solution. Furthermore, the gel matrix isolates the individual metal oxide particles, giving rise to nanostructured grains after the high temperature calcinations to form the finished metal oxide [48].

There is considered evidence that sols, or colloidal oxides, can play a critical role as precursors to the primary particles of crystalline or amorphous oxides [49]. Sols have played a very critical role in the ability to prepare catalytic oxide structures, such as washcoats on monolith structures, as the sol structures play a

critical role as the binder phase between aggregates of oxides within such structures [49].

Sol structures can, however, just as likely be mere spectators in the crystallization processes which form the final structures within gelled sols. A case can be made that the term sol-gel is very misleading, in that although sols may be formed as intermediate structures in some cases, they are clearly not necessarily transformed into the primary particles, or elementary structures, within the gelled oxide [49].

Gel synthesis involves polymerizing molecular precursors into a three dimensional network and subsequently converting the wet gel into a xerogel by removing the solvent [50].

In the sol-gel route synthesis, a stepwise reaction scheme has been undertaken to control the ratio of hydrolysis to condensation rates. In general, the rate of hydrolysis is fast compared to that of condensation in strong acidic condition. Therefore, a well-ordered hexagonal arrangement of mesopores is formed at low-pH in acidic conditions. Meanwhile, in neutral or basic conditions ranging from pH 7 to pH 9, the rate of condensation is faster than that of hydrolysis, and eventually the materials prepared by a single-step reaction at high pH display gel-like structure without mesopores. It is hence an interesting attempt to synthesize ordered mesoporous materials by two-step sol-gel route at lower acidic pH followed by a higher pH [51].

As in previous work [52, 53], modified sol-gel method is used to prepare a zirconia based catalyst in this study. Modified sol-gel is a method which varies the technique to prepare a sol-gel as well as reaction condition.

1.10.1 The Advantages of Sol-gel Approach Over the Traditional Methods of Preparation

Sol-gel processing provides a new approach to the preparation of supported metal catalysts. A well-defined pore size distribution can be obtained using this approach. The potential advantages of sol-gel processing include: purity, homogeneity, and controlled porosity combined with the ability to form large surface area materials at low temperature [54].

The advantage of the sol-gel method of synthesis is that virtually any metal oxide system can be examined, and no special apparatus or equipment is required. Besides, its advantages are the formation of ceramics of high purity and good control over microstructure and particle morphology in the synthesis, typically at room temperature [48].

1.10.2 Effects of Variables on the Chemistry of the Sol-gel Synthesis

The important variables which must be considered in the synthesis of supported metals by the sol-gel method include pH, water/metal alcoxide ratio (R), gelation temperature, metal loading, addition of dopants, solvent removal, and pretreatment conditions [55].

A large number of studies have been performed in an effort to understand the effect of water on the properties of the gel. When non-stoichiometric amounts of water were added, an analysis of the reaction products showed that the extent of polymerization was largely depends on the number of moles of water, which was added [54]. When the H_2O / alcoxide ratio is increased, the time required for the formation of the gel is also observed to increase. This same result is also obtained when pH is decreased [54]. An increase in the H_2O / alcoxide ratio clearly leads to an increase in the pore diameter. The surface area appears to go through a maximum when the H_2O / alcoxide ratio is close to that corresponding to stoichiometry [54].

The synthesis of solid catalysts using sol-gel processing may be performed under acid condition (pH 1.5-6), basic conditions (pH 8-11) or neutral conditions (pH 7). Different catalysts can be used to perform the hydrolysis reactions [54]. Under strongly acidic conditions, hydrolysis occurred very rapidly and that gel formation times were increased substantially. Hydrolysis is slower and the polymerization is catalyzed by the base. Under these conditions, gelation times are considerably slower [54].

The reaction pH is very important in determining the final properties of the material which is synthesized. Under basic conditions, the particles which are initially formed have a diameter of approximately 1 nm. These particles increase in size during the synthesis. The resultant gel tends to be mesoporous or macroporous. When the reaction is performed at a pH of 7, the particles in the sol vary between 2.5 and 20 nm. For this reason, the resultant gel has a non-uniform pore size distribution. Under acid conditions the particles in both the sol and the gel are very uniform. They vary in size between 0.5 and 3.0 nm and in general have very high porosities. It is also important to note that the pore volume corresponding to meso (2-50 nm) and macro (>50 nm) pores increase at the expense of micropores (<2.0 nm) with increasing pH [54].

In the sol-gel process, drying is regarded as an important procedure in the determination of the performance of resultant xerogels [56]. Among the many drying techniques, thermal drying is employed most frequently for convenience, and a preceding ambient drying is usually performed. It is assumed that shortening the ambient drying period, along with shortening the total drying procedures, can tailor the characteristics of the resultant xerogels [56].

In some cases, the gel is aged before drying. Aging can take the form of a "redispersion treatment" which allows dissolution and precipitation of material for a degree of "fine tuning" of the network's structure. The solvent is subsequently removed by either (i) evaporative drying or (ii) a supercritical drying step. Supercritical drying has the advantage of eliminating the liquid/vapor interface during drying that could otherwise lead to partial collapse of the network structure-

most notably loss of surface area and pore volume-due to high differential capillary pore pressures [57].

1.10.3 Preparation of Catalysts by Sol-gel Method

The preparation of supported metal catalysts by sol-gel method is unique because the metal precursor is mixed homogeneously together with the molecular precursor of the support, resulting in a greater degree of control over the final properties of the catalyst [55].

There are two types of sol-gel method depending on the chemical nature of the precursors such as inorganic based sol-gel method and organic based sol-gel method. Inorganic based sol-gel method involved inorganic salt which easily dissolved in water whereas organic based sol-gel method involved organometallic salts/ complexes such as alkoxides which can be dissolved in organic solvent.

Sol-gel processing in which metalorganic precursors are mixed with metal precursors to form a homogeneous solution. The metalorganic is hydrolyzed through the addition of water carefully controlling the pH and the reaction temperature. As hydrolysis and polymerization occur, colloidal particles or micelles with an approximate diameter of 10 nm are formed. These particles continue to increase in size until a metal oxide gel (alcogel) is formed. The solvent can be eliminated by heat treatment in air to form a xerogel. The metal oxide gel (hydrogel) is formed by using inorganic salt as a precursor. The solvent can be dried to form a xerogel [54].

Most zirconia compounds can be used as precursors of zirconium oxide in the sol-gel process. These precursors of zirconia can be classified as zirconium alkoxides (zirconium propoxide, zirconium tetra-n-butoxide etc.) and inorganic zirconium salts (zirconium oxychloride, zirconium acetate etc.) [46].

When zirconia is prepared using the sol-gel method, the tetragonal phase can be stabilized at low temperature, depending on pH and the type of catalyst used in the synthesis. The OH groups retained in the bulk in this method favour stabilization of the tetragonal phase, whereas when positive ions are present (e.g., H^+ , Li^+ , Na^+) the monoclinic phase is produced at low temperature [23].

The crystalline properties of zirconia synthesized by the precipitation and sol-gel methods were comparatively studied [18]. Both synthesis methods gave rise to nanocrystalline zirconia. The samples calcined at 800 °C and prepared by the precipitation had average crystalline sizes less than 18 nm, which were two times smaller than the corresponding value obtained in the sol-gel samples. Both tetragonal and monoclinic nanocrystalline phases had atomic defects in concentrations that depended on the synthesis method and annealing temperature.

Rossignol *et al* [58] studied the preparation of zirconia-ceria solid solutions ($Zr_{1-x}Ce_xO_2$) with $0 \leq x \leq 1$) by two different methods: conventional “coprecipitation” and “modified sol-gel” preparation. Both the structure and the texture of those solids depend on the synthesis and the zirconium precursor. For solids prepared by the modified sol-gel method, with a surface area of $60 \text{ m}^2\text{g}^{-1}$, a new cubic phase ($Zr_{0.25}Ce_{0.75}O_2$) is obtained, while an orthorhombic zirconia phase was identified for solids prepared either by coprecipitation or sol-gel methods. The sol-gel method was particularly efficient for preparation of Ce-Zr-O mixed oxides with high cerium contents.

Lopez *et al* [59] investigated the improvement of structural and morphological properties of Mn-Zr mixed oxides by sol-gel method with varying Mn/Zr ratio in the entire compositional range. This procedure allows an excellent control over relevant properties of the synthesized materials, namely compositional homogeneity, purity, and porous structure.

Aguilar *et al* [23] reported a systematic analysis of the crystallization process of amorphous sol-gel samples and the thermal behavior of zirconia cogelled with silica, in the complete ZrO_2 - SiO_2 system range, annealing the samples with long thermal treatments at temperature between 100 °C-1400 °C. ZrO_2 - SiO_2 mixed oxides

prepared using the sol-gel technique are promising catalysts, or catalyst supports, in petrochemical processes. For example, it has been shown to be useful in the *n*-hexane isomerization reaction to high octane, employing bifunctional zirconia-silica catalysts in products such as 2,2-dimethylbutane and 2,3-dimethylbutane.

Farias *et al* [45] investigated on the sol-gel synthesis of alumina and 1:1 mixed oxides of Al₂O₃-ZrO₂, SiO₂-TiO₂, ZrO₂-TiO₂ and Al₂O₃-TiO₂. Due to their species with acidic sites of different types (mainly Brønsted sites for SiO₂ and Lewis sites for the other oxides) and strengths, the mixed oxides are interesting matrices from a catalytic point of view.

1.11 Statement of the Problem and the Needs of the Study

The automobile exhaust is identified as one of the major sources of air pollution [29]. Due to incomplete combustion of fuel, automobiles emits toxic gases such as carbon monoxide (CO), hydrocarbon (HC), and nitrogen oxides (NO_x) to the environment. The way to reduce these toxic gases released to the air is by converting them simultaneously to non-toxic gases and to do this, a three-way catalyst is developed. Tetragonal ZrO₂ is used as catalyst and catalyst support for various gas phase reaction [26]. Several studies have shown that the percentage of tetragonal phase of ZrO₂ is crucial for the activity and selectivity [27].

Since the tetragonal phase of ZrO₂ can serve a good catalytic site, therefore this research will be carried out to study the optimum condition on the highest formation of single phase tetragonal ZrO₂. This research will be concentrated on the preparation of the three-way catalyst based on zirconium oxide using modified sol-gel method.

1.12 Research Objectives

The objectives of this research are:

1. To prepare a single-phase tetragonal zirconium oxide doped with cerium oxide catalyst by modified sol-gel method.
2. To elucidate the physical characteristics of catalyst using various analytical methods for further understanding of the properties of the catalyst consisting of single-phase tetragonal zirconia.
3. To evaluate the performance of the catalyst obtained towards CO conversion/ oxidation.

1.13 Scope of Research

This research is carried out to study the optimum conditions on the highest formation of single phase tetragonal ZrO_2 . Three parameters will be studied in this study to prepare a single phase tetragonal zirconia doped with ceria catalyst, viz amount of water, amount of dopants and calcination temperatures. In this study, the precursors will be dissolved in a minimum amount of water to prepare a catalyst. A series of $Zr_xCe_{1-x}O_2$ catalysts will be prepared by varying the atomic percentage ratios, over the composition range from 5%-50% of cerium loading. The calcination temperature start at 400 °C will be chosen based on previous studies on catalyst based on metal oxides, which reported that the catalysts were mostly active at this temperature [60].

The physical properties of catalysts will be characterized with X-Ray Diffraction (XRD), surface area analysis, and Fourier-Transform Infrared Spectroscopy (FTIR). The best atomic percentage ratio of catalyst for the highest formation of single phase tetragonal ZrO_2 will be selected for further study on the catalytic activity towards CO conversion.

Other characterization techniques can be used for further understanding of the properties of the catalyst. Nitrogen adsorption analysis at 77 K should be carried out to determine the types and shapes of pores for catalysts. The chemical composition of the prepared model catalysts can be analyzed with Auger electron spectroscopy (AES) to characterize the surface species segregation compared with the bulk composition. Besides, the catalyst systems can also be further analyzed with X-ray photoelectron spectroscopy (XPS) to verify surface composition and elemental oxidation states [35].

Finally, the catalytic activity of $Zr_{0.70}Ce_{0.30}O_2$ catalyst towards the oxidation of CO and hydrocarbon with the reduction of NO_x is suggested to carry out in order to get better performance of the three-way catalyst.

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