

EFFICIENCY COMPARATOR: CARBON MONOXIDE CONVERTER EMISSION BY METALLIC OSMIUM SUPPORT IN TITANIUM DIOXIDE AND ZIRCONIUM DIOXIDE

CARLOS H. DELIZ*

School of Science and Technology, Universidad Ana G Mendez, PO Box 3030, Gurabo PR 00778-3030, Puerto Rico

(Received 15 June, 2021; Accepted 30 June, 2021)

Key words: Carbon monoxide, Titanium, Sol-Gel, Zirconium dioxide, Osmium.

ABSTRACT

The use of zirconia as a catalyst or as a support for metal catalysts has lately become increasingly popular. In recent years, studies of the preparation of doped zirconia producing high thermal stability. Doped zirconia in environmental application is significant to reduce carbon monoxides contribute to several environmental hazards to humans, including respiratory illness, and global warming one significant drawback to these materials such as platinum and gold is their high cost. Metallic osmium is proposed as a good candidate because it has been shown to be active for CO oxidation and is less expensive than gold and platinum. The osmium electron configuration (Xe) $4f^{14} 5d^6 6s^2$ is like platinum electron configuration (Xe) $4f^{14} 5d^9 6s^1$. The high orbital d deficiencies cause a stronger interaction with negatively charged molecules. 10% of osmium and platinum were supported on TiO_2 and ZrO_2 prepared by solid by solid, Sol-Gel (SG) and incipient wetness impregnation (IWI) techniques. The catalysts were characterized by surface area analysis, Raman, SEM, X-ray diffraction (XRD), and Fourier transforms infrared spectroscopy. The characterization demonstrated that this noble metal oxide phase is more dominant on the Sol-Gel and solid by solid impregnation support than on wetness impregnation. The complete oxidation of CO to CO_2 could also be observed below $100^\circ C$ for the Sol-Gel and solid by solid impregnation. The studies shown that ZrO_2 Sol-Gel impregnation was more efficient and faster than TiO_2 support.

INTRODUCTION

Research into catalysis is a major field in applied science and involves many areas of chemistry, notably organometallic chemistry, and materials science (Kermagoret, et al., 2014). Catalysis is relevant to many aspects of environmental science, e.g., the catalytic converter in automobiles due high cost and the dynamics of the ozone hole. Catalytic reactions are preferred in environmentally friendly green chemistry due to the reduced amount of waste generated. Many transition metals such as cobalt, platinum and gold were used in heterogeneous catalysis (catalyst differs from the reactants) to reduce pollution emissions, but they are expensive.

Carbon monoxide is a pollutant that is emitted from many sources. There are numerous applications for which a catalyst capable of oxidizing carbon monoxide to carbon dioxide at low temperatures is desirable (Acres, et al., 2013). Carbon monoxide can form because of incomplete combustion of carbon-containing materials. For automotive applications, most of all emissions (80-90%) are released during the "cold-start" period and materials that have high

activity at lower temperatures could help to alleviate pollution from this route (Avgouropoulos, et al., 2008). While the oxidation of carbon monoxide in lean, excess oxygen, conditions have applications for air quality improvement, the preferential oxidation of carbon monoxide in the presence of hydrogen has application for the purification of hydrogen streams for use in fuel cells. Studies showed that an increase in the ratio of CO to O_2 led to higher O_2 selectivity to CO_2 and lower conversion of CO for a given temperature. At a given temperature, the presence of CO_2 or H_2O led to an inhibition of the CO oxidation reaction and a decrease in the CO conversion, as compared to the reactions in which CO_2 or H_2O (Büchel, et al., 2009). Stability studies showed that operating the catalyst in its oxide form was stable while operating around $100^\circ C$, but operation at higher temperatures ($175^\circ C$ - $250^\circ C$) could lead to a loss of activity, likely caused by the partial reduction of catalytic oxide. At higher temperatures, the reduction of catalytic oxide also led to the formation of methane through the $CO+2H_2$ methanation reaction. Stability studies like cobalt and other catalyst supported on various metal oxide

*Corresponding author's email: cdeliz1@uagm.edu

showed that in the test conditions, for example CO/ZrO₂ had the higher activity for the preferential oxidation of carbon monoxide than cobalt on supported on TiO₂, SiO₂, CeO₂, and Al₂O₃ (Castoldi, et al., 2010). Some precious metals such as Pt, Pd and Au are well known oxidation catalysts and have received significant attention in emission control catalysis.

One significant drawback to these materials, however, is their high cost. To address this concern, a search for lower cost, alternative materials like has led to the study of transition metal catalysts like osmium. The osmium tetra oxide was excluded as a catalyst because its oxide is toxic. Mechanistic studies for example on CO oxidation in excess O₂ are carried out and transition metal showed cobalt to be an active metal for the reaction, though carbonate formation could lead to decreased activity at temperatures below 100°C (Chen, et al., 2010; Daniel, et al., 2010). Other studies have shown strong promotional effects of Co and Fe to Pt/Al₂O₃ catalysts, leading to substantial activity. Studies without Pt, using other transition metal catalyst indicate that are active for CO oxidation (Derrouiche, et al., 2006). Data found

that the rate of deactivation could be mitigated or eliminated by operating at elevated temperatures or by increasing the ratio of O₂/CO.

MATERIALS AND METHODS

Catalyst Preparation

The catalysts were synthesized by the incipient wetness impregnation (IWI), Sol-Gel (SG) synthesis and solid by solid impregnation technique. The catalyst loadings were denoted by weight percentages. The incipient wetness impregnation technique involves the addition of a solution containing a dissolved metal to a porous catalyst support (Cant, et al., 2011). All the incipient wetness impregnated catalyst in these studies used distilled water as the solvent to dissolve the ZrO₂ support (Zirconium oxide MP lot: R24968) with the active component, metallic osmium (99.9% Acros lot: A0295616) was added/impregnated onto the support. The solution was added drop wise so that then total volume of the solution added to the support. The same procedure was applied to Pt/ZrO₂. (Metallic platinum black 98.0% Acros lot: A03329875) support on (Zirconium oxide MP lot: R24968). After the impregnation, the catalyst was placed in a drying over at 110°C to evaporate the solvent, leaving the metal on the catalyst support. In some cases, multiple impregnations were used to help reduce possible variations between different particles that could have not been well impregnated.

Following the final impregnation step, the catalysts were calcined in air using a ramp rate of 10°C/hour to 300°C then held at the final calcination temperature for at least 3 hours. The Sol-Gel synthesis method was also employed and can allow additional control of the characteristics of the support and can lead to improved surface area and metal dispersion. Sol-Gel synthesis

employs a controlled hydrolysis reaction of a metal alkoxide precursor (Zirconium (IV) isopropoxide) Acros lot: A0321090 with an aqueous solution containing the catalyst's active metal. The synthesis of Sol-Gel catalyst was based on 5 grams of catalyst (Chupin, et al., 2006). The alkoxide precursor was mixed in a beaker with 50 mL of isopropanol, using a magnetic stir bar. In a separate container, the active metal was dissolved in an aqueous solution and placed in a syringe. To increase the rate of the hydrolysis reaction, the amount of water that was used during the synthesis was greater than the necessary stoichiometric quantity, and a 2:1 ratio of water to metal alkoxide were used (Qu, et al., 2006). The aqueous solution containing the active metal was added to the stirred mixture of isopropanol and the alkoxide precursor at a rate of 0.2 mL/min using a syringe pump. After the aqueous solution had been completed added to the beaker, the gel was left to dry overnight (Gavin Chua, et al., 2014). The dried powder was then mixed/crushed using a mortar and pestle and the powder was subsequently calcined in the same manner that was used from the catalyst prepared by incipient wetness impregnation (Figueroa, et al., 2014; Gates, et al., 2008).

Solid by Solid

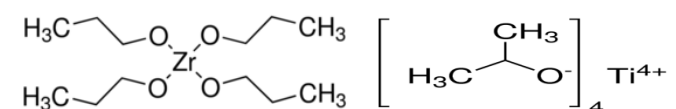
The impregnation solid by solid technique involves the addition of metal (osmium or platinum) 10% mixed with porous catalyst support, ZrO₂. 10%=0.5 grams metal/5 grams ZrO₂. The final impregnation step, the catalysts were calcined for at least 3 hours at 300°C. The dried powder was then mixed/crushed using a mortar and mechanic catalytic mixer (Hamilton, et al., 2014; Haruta, et al., 2001).

Incipient Wetness Impregnation

The impregnation incipient wetness impregnation (IWI) technique involves the addition of osmium or platinum solution 10% (0.5 grams) in water (50 mL) mixed with 5 grams of porous catalyst support such as ZrO₂. The solution was added drop wise in excess (water) to cover all pore volume of the support. Catalyst was placed in a drying over at 110°C to evaporate the water. Catalyst was calcination with ramp rate of 10°C/hour to 300°C.

Sol-Gel Synthesis (SGS)

Sol-Gel synthesis employs a controlled hydrolysis reaction of a metal alkoxide precursor with an aqueous solution containing the catalyst's active metal.



Zirconium (IV) propoxide 70% in propanol. Titanium (IV) isopropoxide

The solution containing the active metal with water, 5 mL is added to the stirred mixture the alkoxide precursor at a rate of 0.2 mL/min using a syringe pump. Note:

Additional 5 mL of water to increase the rate of the hydrolysis. 2:1 ratio, 0.500 g metal/5 mL water=0.10 g/mL. Density Titanium (IV) isopropoxide 0.960 g/mL. 5.20 mL (0.96 g/mL)=5 g Titanium (IV) isopropoxide. $(0.10/0.960) \times 100\%=10\%$. $\text{Ti}\{\text{OCH}(\text{CH}_3)_2\}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4(\text{CH}_3)_2\text{CHOH}$. Density Zirconium (IV) propoxide 0.960 g/mL. 5.20 mL (0.96 g/mL)=5 g Zirconium (IV) propoxide. $(0.10/0.960) \times 100\%=10\%$.

Steady-State Reaction System

Laboratory micro scale reaction experiments were performed on the reactor system depicted in Fig. 1. The system was equipped with flow controller (ADM1000 Intelligent Flow meter JW) and allowed a wide range of gas velocities to be introduced to the reactor. The reaction temperature was controlled by Lindberg Blue M Thermo Scientific oven and temperature K-type thermocouple linked model Fluke, designed to run at temperatures up to maximum of 700°C and below. The reactors were constructed from ¼ external diameter stainless steel and copper tubing. The catalyst samples were held in cylindrical reactor of 50 mm high × 4.6 mm diameter (Lindhalm, et al., 2008; Iglesias, et al., 2010). Equilibrium composition of CO oxidation was a highly exothermic reaction and was quite temperature sensitive, So the thermocouple was positioned so it touched the downstream end of the catalyst bed, this ensured an accurate temperature reading that accounts for the heat produced in the reaction (Forzatti, et al., 2008). Screening experiments were compared catalysts based on equal weights as platinum black support on titanium oxide. The temperature range for testing covered the range of 25°C to 200°C. Reactant concentrations were varied. A variety of analytical equipment was used to monitor the feed and product gas stream compositions. A Bacharach Fyrite Tech Infrared Analyzer CO₂ provided simultaneous and continuous monitoring of CO and CO₂ concentrations (Hao, et al., 2009; Hongjuan, et al., 2015). In addition, GC 5890 HP gas chromatograph equipped with a Thermal Conductivity Detector (TCD) and 5A molecular sieve column as well as phenomenex column (Ingelsten, et al., 2005). The catalyst was pre-treated in helium flow at 200°C for a period of 30 min to remove any volatile contaminant and adsorbed gases.

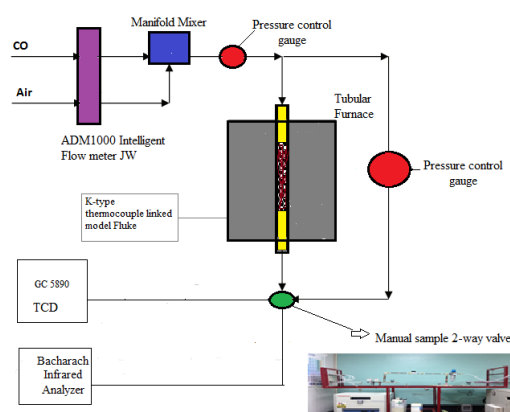


Fig. 1 The experimental oxidation setup.

Material Characterization

Raman spectroscopy

Raman spectra were obtained on powdered samples at room temperature using a Raman Renisaw model 2100 spectrometer with a 10-x microprobe in the back scattering geometry and a 785 nm argon ion laser.

X-ray diffraction (XRD)

X-ray Diffractometer, D8 Advance type (Bruker-AXS). Vertical theta-theta goniometer in powder XRD setting; lowest step size (2-θ), with horizontal sample carrier; nine position multiple stage with automatic sample changer; fixed slit system. One dimensional detector (Lynx Eye type) with collection rate about two orders of magnitude. Copper tart X-ray tube used with nickel filter.

Sem jsm-6010la

SEM with resolution 4 nm at 20 kV. Magnification: 5 X to 300,000 X. Specimen Size: Up to 150 mm diameter and a stage type Eccentric goniometer. On imaging mode with high vacuum: SE (Secondary Electron) and BSE (Back Scatter Electron).

Infrared spectra

The infrared spectra were obtained using FT-IR Nicole Protégé Model 4700 Thermo Electron. The spectrometer lets you collect spectra in the mid-IR, far-IR and near-IR spectral range.

Ultraviolet/Visible scanning spectra

Evolution 201 UV-Visible Spectrophotometer pathway in double-beam with sample and reference cuvette position; Czerny-Turner Monochromator. Spectral Bandwidth (s) 1.0 mm. Operating range 190-1100 nm.

Bet

Micromeritics TriStar II 3020, a fully automated, three-station surface area and porosity analyzer with a Krypton Option can extend surface area measurements to as low as 0.001 m²/g.

FT-IR drift

FT-IR Perkin Elmer model Spectrum Two.

RESULTS AND DISCUSSION

XRD

During the calcinations of the catalysts, in-situ XRD was performed to examine changes and characterization. The diffraction patterns during these experiments for the 10% Os catalysts on TiO₂ and 10% Os catalyst on ZrO₂ prepared via solid by solid, IWI and Sol-Gel, were shown in Figs. 2 and 3 respectively. The 10% Os/TiO₂ showed as anatase and small amount brookite morphology structure of TiO₂ up until 300°C, as indicated by the (101), (103), (004) and (112) diffraction lines at 2-θ values of 25.0°, 39.0°, 44.0°, 47°, 55.0° and 67° respectively (Wachs, et al., 2007).

The 10% Os/ZrO₂ catalyst, showed as cubic crystalline form and small amount tetragonal morphology structure of ZrO₂ up until 300°C, diffraction lines at 2-θ values of 18.0°, 20.0°, 23°, 25.0°, 28.0° and 37.0. The diffraction patterns in Figs. 2 and 3 for 10% Os/ZrO₂ and 10% TiO₂ Sol-Gel shows different transformation behavior than the catalyst prepared by IWI or solid by solid. At 300°C, Sol-Gel reaction low crystalline phases were observed, but broad peaks associated with anatase TiO₂ appeared at, the sharpening of the anatase TiO₂ peaks (Gates, et al., 2008; Hamilton, et al., 2014). The diffraction lines from brookite TiO₂ appear and grow with increasing 2-θ. The diffraction well describes as anatase phase, although it contains a small amount of brookite impurity at 300°C, Sol-Gel reaction low crystalline phases were observed, but broad peaks associated with tetragonal form of the ZrO₂ appeared at, the sharpening of the tetragonal form ZrO₂ peaks (Kohyama, et al., 2015; Haruta, et al., 1993). The diffraction lines from tetragonal ZrO₂ appear and grow with increasing 2-θ. The diffraction well describes as cubic crystalline phase, although it contains a small amount of tetragonal impurity. Crystalline Os or Pt-oxide phases were detected slightly through XRD in either the Sol-Gel or the IWI preparation (Ozbek, et al., 2014).

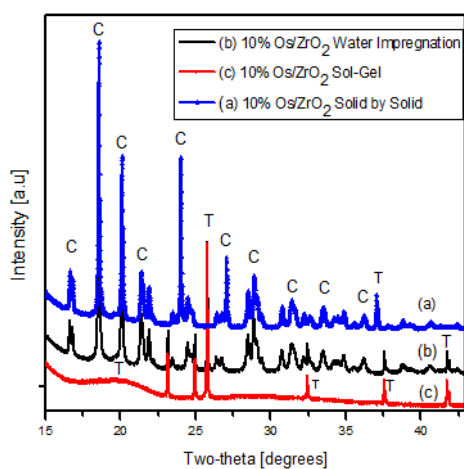


Fig. 2 X-ray diffractogram of Os supported ZrO₂ catalysts synthesized by a) SGI, b) IWI, and c) SSI route.

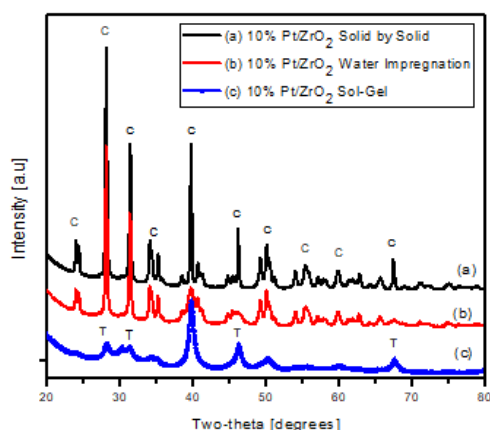


Fig. 3 X-ray diffractogram of Pt supported ZrO₂ catalysts synthesized by a) SGI, b) IWI, and c) SSI route.

Laser Raman Spectroscopy

Raman spectra were obtained on powdered samples at room temperature using a Raman Renisaw model 2100 spectrometer with a 10-x microprobe in the back scattering geometry and a 785 nm argon ion laser (Wang, et al., 2011). Figs. 4 and 5 show the laser Raman spectra taken over the impregnated solid by solid, Sol-Gel and IWI of the 10% Os/TiO₂ and 10% Os/ZrO₂ catalysts at 300°C (Wachs, et al., 2007). The cubic and tetragonal (Pérez, et al., 2005). The TiO₂ bands at 145, 197, 396, 520, and 639 cm⁻¹ are typical of anatase TiO₂. For the 10% Os/TiO₂ catalysts, the TiO₂ bands were visible. The broadening of the TiO₂ bands may be attributed to interactions with Os species and disorder in the oxygen sub-lattice. The lack of metallic osmium raman bands at lower calcinations temperatures on the TiO₂ supported samples suggests that Os does not form as readily on the surface as compared to the TiO₂ support (Rivallan, et al., 2009). This difference in surface Os is likely related to the differences in CO oxidation activity observed over the TiO₂ catalysts. The ZrO₂ bands at 182, 388, 545, 715 cm⁻¹ are typical tetragonal form and 1516, 1607, 1535, 1610 cm⁻¹ are typical of cubic form of the ZrO₂. For 10% Os/ZrO₂ catalysts, the ZrO₂ bands were visible. The broadening of the ZrO₂ bands may be attributed to interactions with Os species and disorder in the oxygen sub-lattice (Rivera, et al., 1993). The lack of metallic osmium raman bands at lower calcinations temperatures on the ZrO₂ supported samples suggests that Os does not form as readily on the surface as compared to the ZrO₂ support. This difference in surface Os is likely related to the differences in CO oxidation activity observed over the ZrO₂ catalysts. These results indicate that osmium was presents in the 10% Os/TiO₂ and 10% Os/ZrO₂ catalyst (Rodriguez, et al., 2013). The lack of clearly visible vibrational bands from the TiO₂ support in the sample 10% Os/TiO₂ can was explained by the smaller Raman cross-section of rutile and anatase tetragonal forms of TiO₂. Also, visible vibrational bands from the ZrO₂ support in the sample 10% Os/ZrO₂ can was explained by the smaller Raman cross-section of cubic and tetragonal forms of ZrO₂.

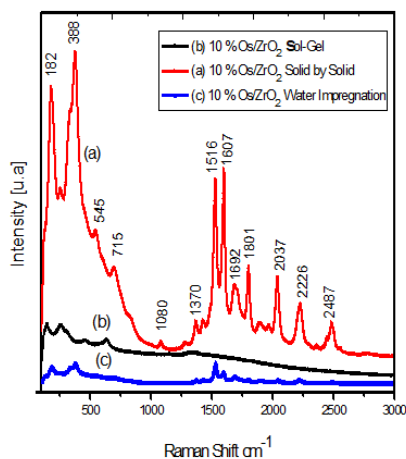


Fig. 4 Laser raman spectroscopy taken over the impregnated solid by solid, Sol-Gel and IWI of 10%Os/ZrO₂.

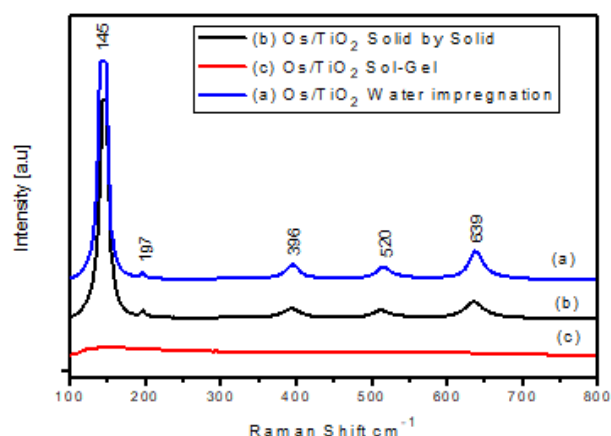


Fig. 5 Laser raman spectroscopy taken over the impregnated solid by solid, Sol-Gel and IWI of 10% Os/TiO₂.

FT-IR

The adsorption spectra of the 10% Os/ZrO₂ and 10% Pt/ZrO₂ were obtained to examine the types of surface species using a FT-IR Nicole Protégé Model 470. For 10% Os/ZrO₂ Sol-Gel impregnation, the high wave number region in Fig. 6 exhibits bands at 3500 cm⁻¹ that correspond to terminal, bi-bridged, and tri-bridged OH groups, typical of the OH vibration of physically adsorbed H₂O. For Sol-Gel, IWI and solid by solid were observed by a combination band at 2900 cm⁻¹ and the C-H stretch at 2800 cm⁻¹. In the low wave number region, Figs. 6 and 7 were observed from the band at 1484 cm⁻¹ as well as the C-H bending and symmetric C-O stretching modes at 1379 cm⁻¹ at 1358 cm⁻¹, respectively (Wade, et al., 2006; Zou, et al., 2010). Other bands in the 1000-500 cm⁻¹ have been assigned to ionic carbonate at 1484 cm⁻¹ which shifts to 1440 cm⁻¹ and carbonate species at 1300 cm⁻¹ and 700 cm⁻¹ (Daniel, et al., 2010).

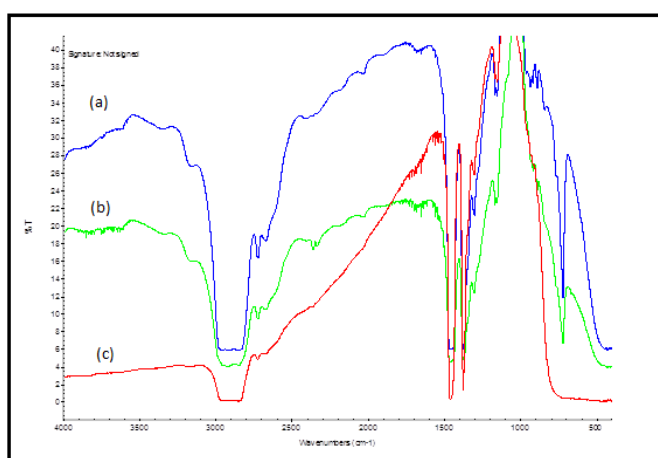


Fig. 6 The adsorption spectra of the 10%Os/ZrO₂.
 (a) Os/ZrO₂, Sol-Gel Impregnation
 (b) Os/ZrO₂, Incipient wetness impregnation
 (c) Os/ZrO₂, Solid by Solid Impregnation

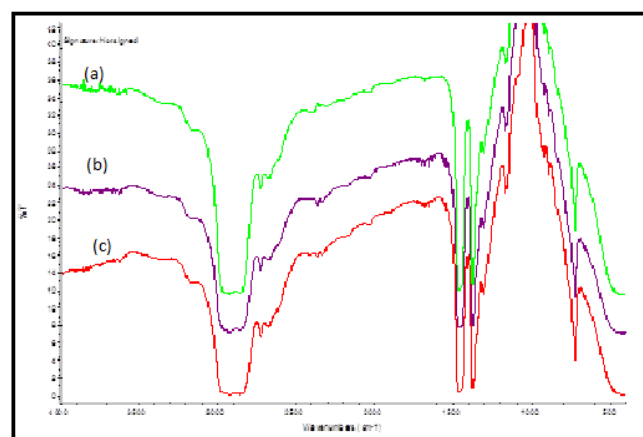


Fig. 7 The adsorption spectra of the 10% Os/TiO₂.
 (a) Pt/ZrO₂, Sol-Gel Impregnation
 (b) Pt/ZrO₂, Incipient wetness impregnation
 (c) Pt/ZrO₂, Solid by Solid Impregnation

Ultraviolet/Visible Scanning Spectra

Ultraviolet/Visible scanning spectra were obtained on powdered samples at room temperature using a Spectrophotometer Evolution 201 Thermo Scientific. The reading was 600 nm to 200 nm see Figs. 8 and 9 show the spectra taken over the impregnated solid by solid, Sol-Gel and IWI of the 10% Os/ZrO₂ and 10% Pt/ZrO₂ catalysts at 300°C, respectively, along with reference spectra taken over unloaded (Xianyong, et al., 2010). The fundamental absorption of ZrO₂ appeared in the UV region about 333, 347 nm for Os/ZrO₂ and 382 nm for 10% Pt/ZrO₂ (Wonyong, et al., 2014). This indicated that UV-Vis absorption was closely related to doping metal ion (Wachs, et al., 2017). The cubic and tetragonal forms were present with high activity in 333 and 382 nm, but we notice that transformation factor in the three different preparation (Yasuo, et al., 2009; Young, et al., 2007). The dopant element was significant in solid by solid and sol gel preparations with mayor absorbencies. These results show that was concurrent with high catalyst activities.

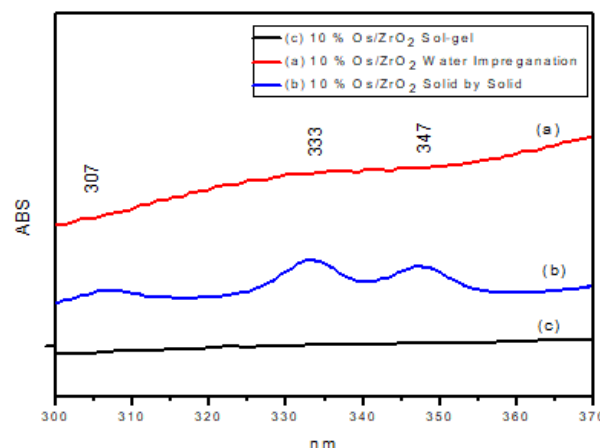


Fig. 8 The spectra taken over the impregnated solid by solid, Sol-Gel and IWI of the 10%Os/ZrO₂.

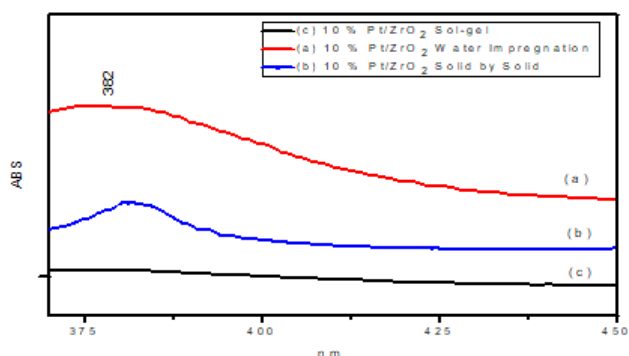


Fig. 9 The spectra taken over the impregnated solid by solid, Sol-Gel and IWI of the 10% Os/TiO₂.

BET Surface Area for Catalysts

Surface area analysis was performed over supported metallic osmium catalysts 10% Os/ZrO₂ using BET method with a Micromeritics TriStar II 3020 instrument. N₂ was selected as the adsorbent, and analysis was performed at liquid nitrogen temperature (77 K). The samples were degassed before surface area measurement (Liu, et al., 2014). The results from these experiments were shown Table 1 (Cheng, et al., 2014; Zhang, et al., 2014). The 10% Os/ZrO₂ catalyst had a significantly lower surface area than the other literature supports. Generally, surface area decreases because of pore blocking/clogging due metallic bond formation (Collins, et al., 2014). If there are not have such effect, either because your pores are too wide or because they are only a low amount of them, then the addition of a new phase at the surface of a substrate should logically create heterogeneity, roughness, and therefore a higher surface area, provided that very small particles were deposited (Yang, et al., 2014; Widmann, et al., 2014; He, et al., 2014; Zhao, et al., 2009; Petoud, et al., 2011). The high catalyst active due to significantly lower micropore volume (Kermagoret, et al., 2014). The catalyst process in gas states were influenced by physiochemical variable such as particular size. The influence of particle size of zirconium on catalytic activities has been demonstrated. Rivera reported increasing rate of catalyst for zirconium particle in the range of 4-50 nm, photocatalytic and gas catalytic activity increased with decreasing size. The micropore size permitted mayor radio material interaction in adsorption phenomenon versus macropores with minor radio interaction in gas catalyst (Kohyama, et al., 2015). The micropores exhibit outstanding CO capture

and conversion performance at atmospheric pressure and room temperature. As pressure increases, the gas condenses first in the pores with the smallest dimensions. By extending this process so that the gas could condense in the pores, the sample's fine pore structure (Yasuo, et al., 2009; Young, et al., 2007; Liu, et al., 2014). The pressure was increased until saturation was reached, at which time all pores are filled with liquid. The adsorptive gas pressure then was reduced incrementally, evaporating the condensed gas from the system. Evaluation of the adsorption and desorption branches of these isotherms and the hysteresis between them reveals information about the size, volume, and area (Rivera, et al., 2015). Chemisorption interaction of an active gas and a solid surface, involving the sharing of electrons between the adsorptive molecule and the solid surface (Wang, et al., 2011). It was generally assumed that a chemisorbed layer will not exceed a single molecule in thickness. The efficiency of a catalyst in promoting a chemical reaction was related directly to the density of active sites on its surface. In addition, hydrogen reduction of platinum group metal black at elevated temperature can result in a substantial loss of surface area (Hafizovic, et al., 2007). Thus, an osmium or platinum black heated at 300°C in hydrogen a decline in surface area due to sintering. The reduction on dispersion explains that actives hydrogen proton gain electron particles. This is explaining the possibility that osmium in zirconium oxide could work to generate hydrogen (Kermagoret, et al., 2014).

SEM

Figs. 10-15 shows the cross sectional image was obtained on powdered samples at room temperature using a JOEL (JSM-6010LA SEM). The 10% Os/TiO₂ and 10% Os/ZrO₂ calcined at 300°C. These micrographs show different particle size distribution with grain size 2 μm to 5 μm (Tsao, et al., 2007; White, et al., 2009). The films were nanoparticles structures that have a microporo size area and help to enhance its sensitivity (Liu, et al., 2015). The particles exhibit a highly ordered morphology. The Energy Dispersive Spectrometer (EDS) was employed to test the average estimation composition of osmium and platinum in zirconium dioxide impregnation, where the main elements were the following results showed Table 2. The 10% of the precious metal (osmium and platinum) were proportional to 3-10 grams of this metal in automobile catalytic converter (Ning, et al., 2017; Lonergan, et al., 2011).

Table 1. The samples were degassed before surface area measurement.

	Synthesis technique	Surface area (m ² /g)	Micropore volume (cm ³ /g)	Micropore area (m ² /g)
10% Os/ZrO ₂	Water Imp	2.1615	0.000015	0.0821
10% Os/ZrO ₂	Sol-Gel	12.8839	0.002338	5.0029
10% Os/ZrO ₂	Solid by Solid	2.2638	0.000010	0.1046

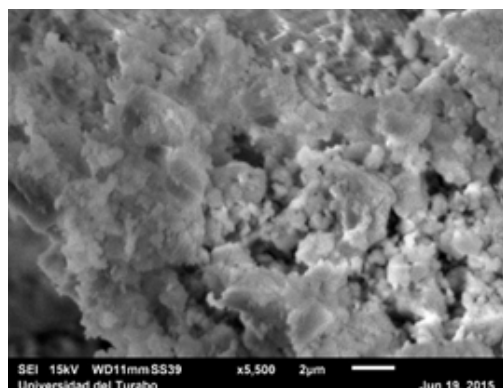


Fig. 10 Morphology of the synthesized samples, incipient wetness impregnation of 10%Os/ZrO₂.

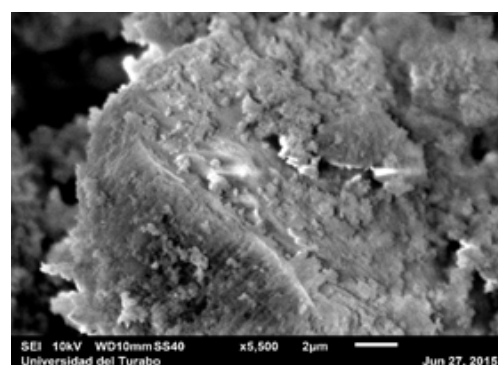


Fig. 13 Morphology of the synthesized samples, Sol-Gel of 10% Os/TiO₂.

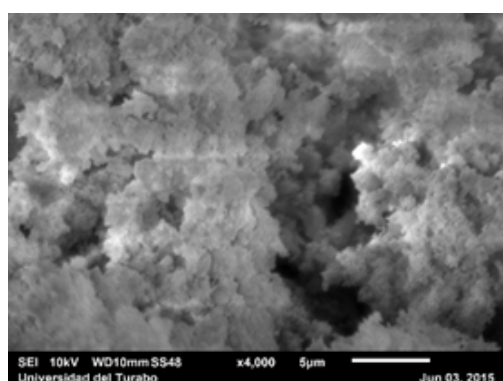


Fig. 11 Morphology of the synthesized samples, incipient wetness impregnation of 10% Os/TiO₂.

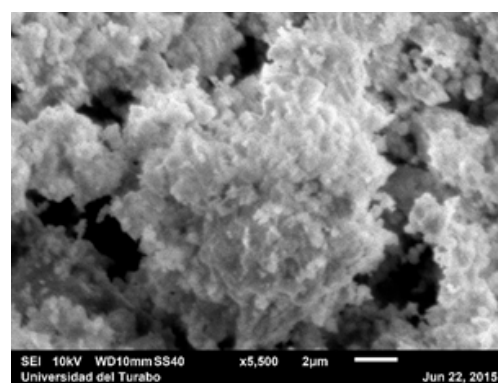


Fig. 14 Morphology of the synthesized samples, solid by solid of 10%Os/ZrO₂.

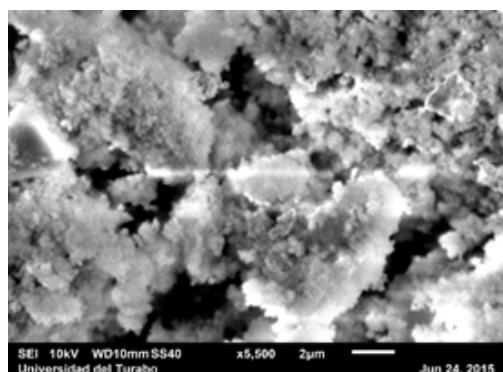


Fig. 12 Morphology of the synthesized samples, Sol-Gel of 10%Os/ZrO₂.

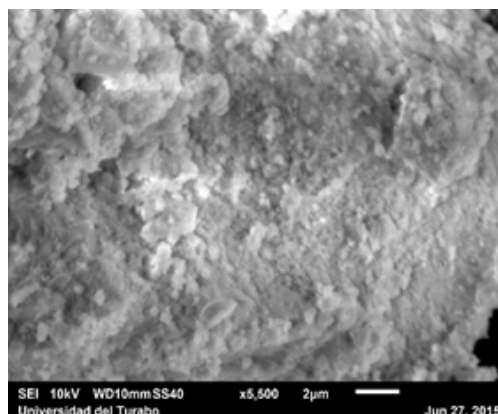


Fig. 15 Morphology of the synthesized samples, solid by solid of 10% Os/TiO₂.

Table 2. Average estimation composition of osmium and platinum in zirconium dioxide impregnation.

Catalytic	Synthesis technique	ZrO ₂ and TiO ₂ wt%	Oxygen wt%	Metal wt%
10% Os/TiO ₂	Water Imp	65.26%	25.93%	8.81%
10% Os/TiO ₂	Sol-Gel	53.11%	32.12%	13.77%
10% Os/TiO ₂	Solid by Solid	45.52%	42.15%	12.33%
10% OsZrO ₂	Water Imp	71.89%	19.40%	8.71%
10% Os/ZrO ₂	Sol-Gel	54.70%	25.37%	19.93%
10% Os/ZrO ₂	Solid by Solid	72.60%	18.88%	8.52%

Activation Energy

The Arrhenius plot shown in Figs. 16 and 17, and the activation energy for oxidation of CO to CO₂ over 10% Os/TiO₂, 10% Os/ZrO₂ and Pt as referent standard were calculated Table 3. The Sol-Gel technique in TiO₂ and ZrO₂ preparations required less activation energy, so the reactions occur faster. The Arrhenius plot was obtained by plotting the logarithm of the rate constant, k, versus the inverse temperature, 1/T (Pérez, et al., 2005). $k=Ae^{-E_a/RT}$ where k represents the rate constant, E_a is the activation energy, r is the gas constant (8.3145 J/K), and T is the temperature expressed in Kelvin (Munir, et al., 2018). A is known as the frequency factor, having units

of L/mol.s. We can graphically determine the activation energy by manipulating the Arrhenius equations to put it into the form of a straight line (Wonyong, et al., 2014; Young, et al., 2007). Taking the natural logarithm of both sides give us; $\ln k = -E_a/RT + \ln A$. A slight rearrangement of this equation then gives us a straight line plot for $\ln k$ versus 1/T, where the slope is $-E_a/R$. $\ln k$ (rate constant) data were obtained knowing gas flow velocities (45 mL/minutes) and reactor volume 831 mm³. The value obtained was multiplied by the percentage obtained at the temperature required to complete the entire conversion of CO to CO₂.

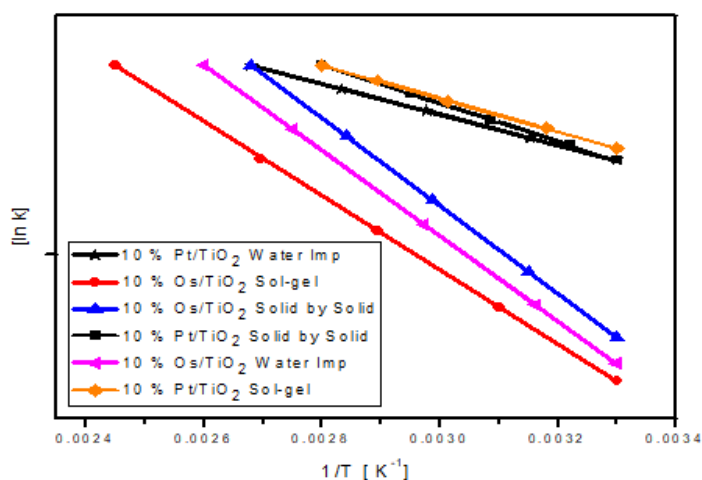


Fig. 16 Arrhenius plot of 10% Os/TiO₂.

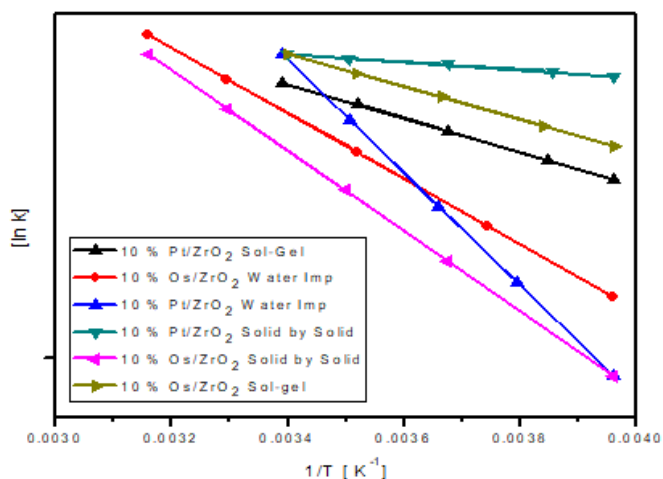


Fig. 17 Arrhenius plot of 10% Os/ZrO₂.

Table 3. The activation energy for oxidation of CO to CO₂ over 10% Os/ZrO and 10% Pt/ZrO₂.

Catalytic			
10% Os/TiO ₂	21 kJ/mol Sol-Gel	50 kJ/mol Water Imp	59 kJ/mol Solid by Solid
10% Pt/TiO ₂	25 kJ/mol Sol-Gel	57 kJ/mol Water Imp	22 kJ/mol Solid by Solid
10% Os/ZrO ₂	19 kJ/mol Sol-Gel	37 kJ/mol Water Imp	46 kJ/mol Solid by Solid
10% Pt/ZrO ₂	18 kJ/mol Sol-Gel	64 kJ/mol Water Imp	11 kJ/mol Solid by Solid

CO to CO₂% Conversion

Activity measurements

The catalytic activity was in terms of % conversion. (X) of CO gas to CO₂ according to the following equation: $X_{CO} = (\text{ppm CO in} - \text{ppm CO}_2 \text{ out}) / \text{ppm CO in} \times 100$. Time on stream studies at room temperature (25°C) were conducted on the 10% Os/ZrO₂ catalyst using feed streams containing 300 ppm CO (Industrial Scientific) lot # 1500206 in balance with air. Fig. 20 shows the concentrations of CO and CO₂ during the experiment using a feed stream of 45 mL/min. Complete conversion of CO to CO₂ was obtained and no decline in conversion was observed over the course of this experiment. To further study the catalyst's activity, an additional experiment was conducted using Pt/ZrO₂ standard catalyst under same conditions (Gao, et al., 2017). During this experiment, the temperature was increased by temperature increments of 25°C (Yang, et al., 2014; Widmann, et al., 2014). To 10% Os/TiO₂ Sol-Gel and solid by solid impregnation the complete conversion was obtained at 100°C. The IWI in both cases, the completed conversion to 10% Os/TiO₂ about 130°C. The other way with 10% Os/ZrO₂ Sol-Gel was obtained at 75°C. The IWI, the completed conversion to 10% Os/ZrO₂ was 100°C. The experiment was run over the course of several days and the catalyst was shown to be stable during the experiment, with no decline in activity at any of their ported temperatures. It can be observed in Sol-Gel impregnation to both catalysts that the decrease in CO concentration was accompanied by the simultaneous and fast increase in CO₂ concentration (Rodriguez, et al., 2013; Wade, et al., 2006). However, water impregnation to both catalysts, there appeared to be some inhibition effect, with temperature required for complete CO conversion shifting by about 50°C (Cheng, et al., 2014). Water impregnation in Figs. 18 and 19 shows that complete conversion of CO was not obtained until about 135°C to 10% Os/TiO₂ and 100°C to Os/ZrO₂, possibly

due to a competitive adsorption effect. Osmium-based catalysts have been synthesized and studied both for the low temperature oxidation of CO in low oxygen as well as for the preferential oxidation of CO were found that high activity could be achieved even at room temperature (Hao, et al., 2009; Hongjuan, et al., 2015; Ingelsten, et al., 2005; Wachs, et al., 2007; Kohyama, et al., 2015; Haruta, et al., 1993). The reaction studies examined the effect of water, which was found to have an inhibitory effect on CO oxidation.

Effect of Water on Dual-Catalyst Performance

In addition to evaluating the effects of the exhaust components that have been previously discussed, the effect of water vapor was also be examined. In addition to a certain level of H₂O due to atmospheric humidity, the combustion of hydrocarbons to form water and CO₂ leads to exhaust streams that contain a substantial level of water vapor (Zhang, et al., 2014; Collins, et al., 2014). Although the actual water concentration that would be expected in an exhaust stream could vary significantly and depends on several factors, a concentration of 10 wt% H₂O would be in the realm of realistic operating conditions. To examine the influence that water has on the reaction performance over catalyst bed containing 10% Os/ZrO₂ and 10% Os/TiO₂, steady-state reaction experiments were conducted at various water concentrations (0%, 5%, and 10% H₂O) and the results are shown in Fig. 20. On a dry basis the gas phase composition was 300 ppm CO was observed at 100°C. Fig. 20 shows that increases in the water concentration led to significantly lower CO conversion to CO₂ yields over the entire temperature range. When 5% water was present, a maximum of 88% of CO₂ was obtained with 10% Os/ZrO₂ Sol-Gel and 85% with 10% Os/TiO₂ Sol-Gel. To 10% H₂O was present, a maximum of 82% of CO₂ was obtained versus 10% Os/ZrO₂ Sol-Gel and 76% were observed at 100°C for each of the experiments at the varying water concentration (Pérez, et al., 2005; Rivallan, et al., 2009).

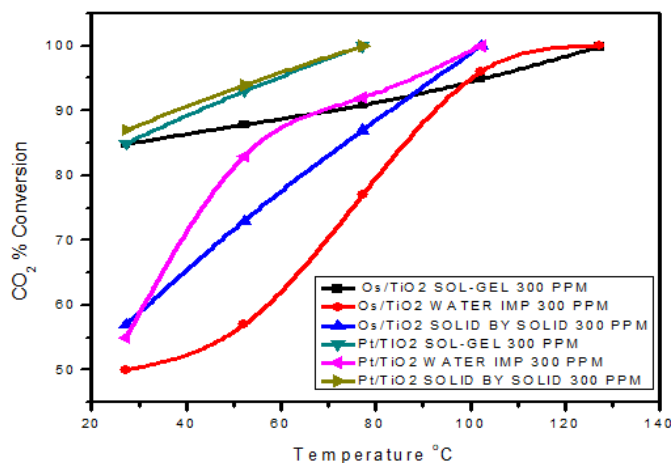


Fig. 18 The concentrations of CO and CO₂ of 10% Os/TiO₂.

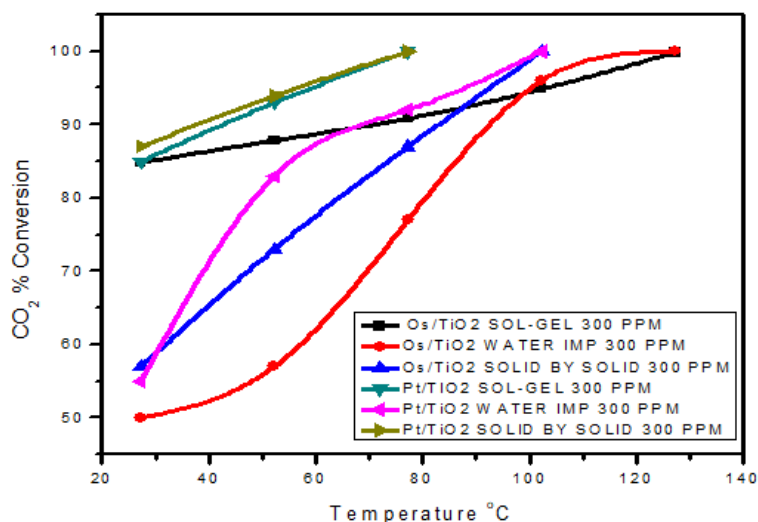


Fig. 19 The concentrations of CO and CO₂ of 10% Os/ZrO₂.

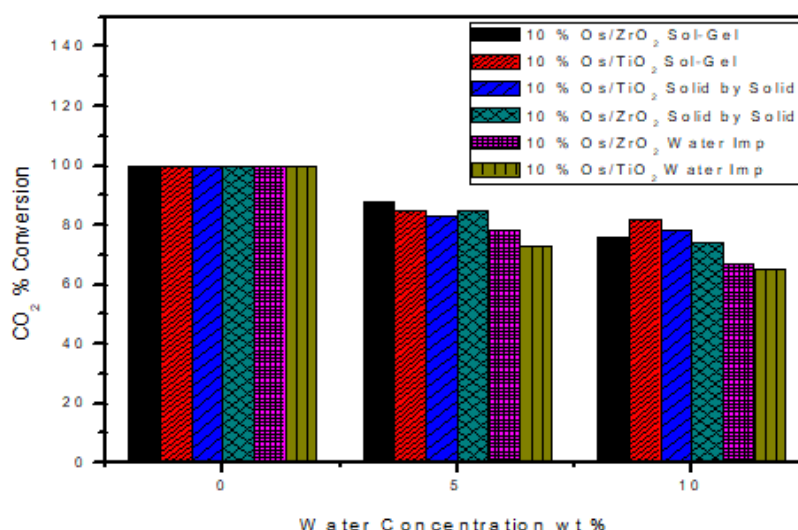


Fig. 20 Shows that increases in the water concentration led to significantly lower CO conversion to CO₂ yields over the entire temperature range.

Sol-Gel Impregnation TiO₂ Anatase and ZrO₂ Cubic structure

Activity measurements

Time-on-stream study of CO oxidation over 10% Os/ZrO₂ and 10% Os/TiO₂ Sol-Gel impregnation at 700°C calcined with cubic and anatase structures Figs. 21 and 22, respectively. Reaction conditions: 300 ppm CO at 25°C and 200 mg catalyst. Fig. 23 shows the concentrations of CO to CO₂ during the experiment using a feed stream of 45 mL/min, zirconium cubic structure was more efficiency with 15 minutes to complete conversion of CO to CO₂ versus titanium anatase structure with 20 minutes. Both structures do not decline in conversion was observed over the course of this experiment (Ning,

et al., 2017).

Temperature Programmed Reduction of 10% Os/ZrO₂ and 10% Os/TiO₂ Sol-Gel at 700°C Calcined. Hydrogen Consumption at 4% Balance with Air

Temperature-Programmed Reduction (TPR) reduction experiments were carried out on the oxidation catalysts on micro reactor Fig. 1. TPR is a bulk technique and allows for the determination of the strength of the metal-support interaction, the average metal oxidation state, quantification of metal sites in various oxidation states, and the number of different types of metal sites. The hydrogen 4% in nitrogen that is consumed in reducing the metal species was measured using a Thermal Conductivity Detector (TCD) (Cheng, et al., 2018).

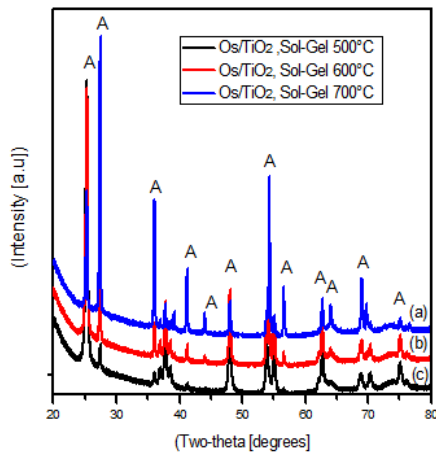


Fig. 21 Study of CO oxidation over 10 % Os/TiO₂.

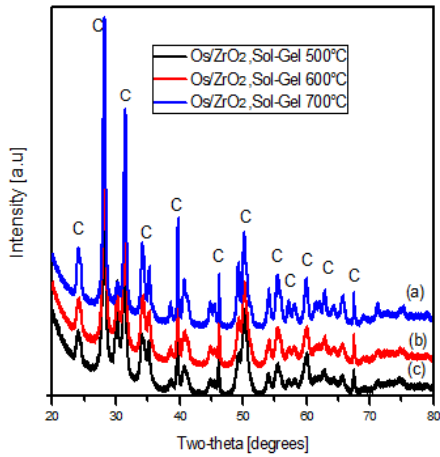


Fig. 22 Study of CO oxidation over 10 % Os/ZrO₂.

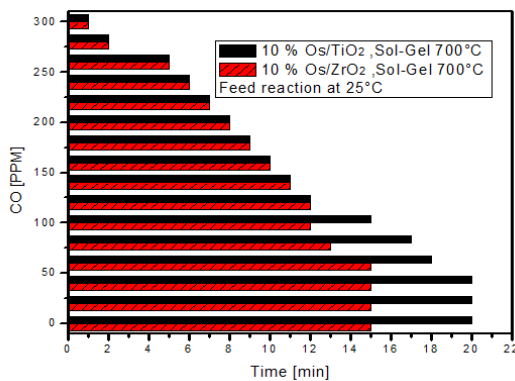


Fig. 23 Shows the concentrations of CO to CO₂ during the experiment using a feed stream of 45 mL/min, zirconium cubic structure was more efficiency with 15 minutes to complete conversion of CO to CO₂ versus titanium anatase structure with 20 minutes.

TPR was performed on the 10% Os/TiO₂ Sol-Gel and 10% Os/ZrO₂ Sol-Gel at 700°C, catalyst series to compare the effect of calcination temperature and support choice on the reducibility of the supported Os. Fig. 24 shows TPR for the 10% Os/ZrO₂ and 10% Os/TiO₂ samples showed broad reduction peaks beginning between 375°C and 400°C. The broad reduction features indicate heterogeneity in the oxidation states and sites where the Os species are located (Kasipandi, et al., 2019; Chung, et al., 2019). The Sol-Gel preparation which provides

linkages between TiO₂, ZrO₂ and Os species could partially account for this behavior. This heterogeneity was more pronounced in the 10% Os/ZrO₂ sample. The 10% Os/ZrO₂ Sol-Gel catalysts calcined at 700°C a showed better-defined reduction peak at 400°C. The high reduction temperatures indicate strong interaction with TiO₂ and ZrO₂ support.

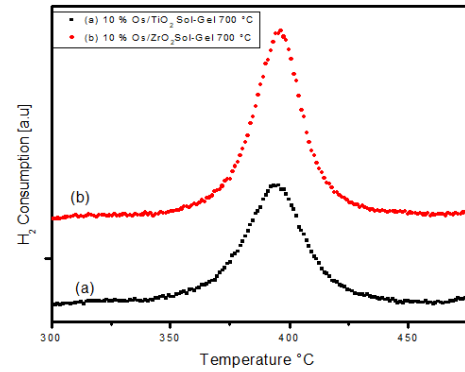


Fig. 24 Shows TPR for the 10 % Os/ZrO₂ and 10 % Os/TiO₂. A Comparative Study of Thermal Oxidation Reaction of Os/TiO₂ and Os/ZrO₂ at Room Temperature

Fig. 25. The formed species on all of catalysts after the catalyst were exposed to a flow of 45 mL/min of CO₂ using FT-IR Drift technic with a spectrophotometer Perkin Elmer Spectrum Two. In ZrO₂ preparation, the formed species were dominate surface at 1450 and 1377 cm⁻¹ on the Os/ZrO₂ solid by solid and Sol-Gel preparation (Oenema, et al., 2020). In TiO₂ preparation catalysts dominate, species were Os/TiO₂ solid by solid and Sol-Gel preparation. In overall comparison, the most dominant were species were Os/ZrO₂ solid by solid and Sol-Gel. The activities of catalysts for the formation of surface species are in the order of Os/ZrO₂ solid by solid>Os/ZrO₂ Sol-Gel>Os/ZrO₂ water impregnation>Os/TiO₂ solid by solid>Os/TiO₂ Sol-Gel>Os/TiO₂ water impregnation. In this test, the most significant formed species was detected on Os/ZrO₂ solid by solid with a mayor absorbance and strong

bands (Sautel, et al., 2000; Gao, et al., 2017).

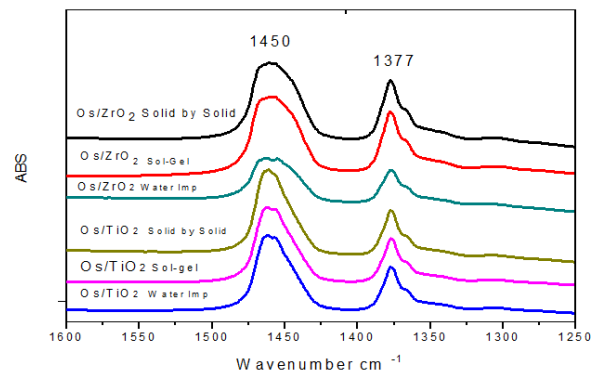


Fig. 25 The formed species on all of catalysts after the catalyst were exposed to a flow of 45 mL/min of CO₂ using FT-IR Drift technic with a spectrophotometer Perkin Elmer Spectrum Two.

CONCLUSION

High increasing demand of catalysts for industrial and environmental applications, it is of prime importance to search for improved supports for a variety of reactions. The high activity of catalyst is also of prime importance, which effectively reduces the amount of expensive catalyst. Considering the increasing cost of noble metal based catalysts for environmental applications, as well as their limited availability, it is of most importance to develop new catalysts with improved catalytic activity under the conditions of practical relevance. 100% CO conversion was observed in a temperature range 50–140°C, on space velocity 3250 h⁻¹ and initial CO concentrations at 300 ppm CO. This is of interest for industrial CO control, where the off gas temperature was often low, because of the use of dry scrubber or catalytic converter to remove the poisonous gases. For the oxidation catalysts, osmium supported on ZrO₂ was outstanding shown to have high activity versus TiO₂. Sol-Gel and solid by solid synthesis techniques were examined; with overall higher activity, but the Sol-Gel technique in ZrO₂ preparation require less activation energy, so the reactions occur faster. In addition, the maximum CO₂ yields was with Sol-Gel preparation in water vapor exposition. Sol-Gel at 700°C calcined using a feed stream of 45 mL/min and 25°C, zirconium cubic structure was more efficiency with 15 minutes to complete conversion of CO to CO₂ versus titanium anatase structure with 20 minutes. In TPR, the heterogeneity was more pronounced in the 10% Os/ZrO₂ sample. The 10% Os/ZrO₂ Sol-Gel catalysts calcined at 700°C showed better-defined reduction peaks at 400°C. The high reduction temperatures indicate strong interaction with TiO₂ and ZrO₂ support. Studies using SEM, XRD, FT-IR, UV, BET and Raman spectroscopy were consistent with this observation and its characterization. Osmium could be alternative material; osmium was proposed as a good candidate because it has been shown to be active for CO oxidation and is less expensive than gold and platinum. Concluded that the presence of osmium and the support's ability to promote the formation of CO₂. The oxidation of CO was complete over most of the temperature range, indicating that the osmium mixed catalyst bed can work to eliminate CO.

REFERENCES

- Kermagoret A, Nathaniel KR, Matthew PC and Emmanuel C. 2014. Chlorodiethylaluminum supported on silica: A dinuclear aluminum surface species with bridging M₂-Cl-ligand as a highly efficient co-catalyst for the Ni-catalyzed dimerization of ethene. *J Catal.* 313:46.
- Acres K and Swart K. 2013. Gmelin handbook of inorganic and organometallic chemistry. 8th Edition. 132-140.
- Avgouropoulos G, Manzoli M, Boccuzzi F, Tabakova T, Papavasiliou J, Ioannides T and Idakiev V. 2008. Catalytic performance and characterization of Au/doped-ceria catalysts for the preferential CO oxidation reaction. *J Catal.* 256:237-247.
- Büchel R, Strobel R, Krumeich F, Baikerb A and Pratsinis SE. 2009. Influence of Pt location on BaCO₃ or Al₂O₃ during NOx storage reduction. *J Catal.* 261:201-207.
- Castoldi L, Lietti L, Forzatti P, Morandi S, Ghiotti G and Vindigni F. 2010. The NOx storage-reduction on PtK/Al₂O₃ lean NOx trap catalyst. *J Catal.* 276:335.
- Chen Z, Yang Q, Li H, Li X, Wang L and Tsang SC. 2010. Cr-MnOx mixed-oxide catalysts for selective catalytic reduction of NOx with NH₃ at low temperature. *J Catal.* 276:56.
- Daniel C, Clarté M, Teh S, Thion O, Provendier H, Van Veen A, Beccard B, Schuurman Y, and Mirodatos C. 2010. Spatially resolved catalysis in microstructured reactors by IR spectroscopy: CO oxidation over mono- and bifunctional Pt catalysts. *J Catal.* 272:55-64.
- Derrouiche S and Bianchi D. 2006. Modifications of the elementary steps involved in the O₂-oxidation of the adsorbed CO species over Pt/Al₂O₃ by co-adsorbed NO species. *J Catal.* 242:172.
- Cant NW, Chambers DC and Liu I. 2011. The reduction of 15N14NO by CO and by H₂ over Rh/SiO₂: A test of a mechanistic proposal. *J Catal.* 278:162.
- Chupin C, Van Veen AC, Konduru M, Després J and Mirodatos C. 2006. Identity and location of active species for NO reduction by CH₄ over Co-ZSM-5. *J Catal.* 241:103.
- Qu Z, Zhang X, Yu , Liu X and Fu Q. 2015. Role of the Al chemical environment in the formation of silver species and its CO oxidation activity. *J Catal.* 321:113-122.
- Gavin Chua YP, Kasun Kalhara Gunasooriya GT, Saeys M and Seebauer E. 2014. Controlling the CO oxidation rate over Pt/TiO₂ catalysts by defect engineering of the TiO₂ support. *J Catal.* 311:306-313.
- Figuerola S and Newton M. 2014. What drives spontaneous oscillations during CO oxidation using O₂ over supported Rh/Al₂O₃ catalysts?. *J Catal.* 312:69-77.
- Gates B, and Guilar V. 2008. Kinetics of CO oxidation catalyzed by highly dispersed CeO₂-supported gold. *J Catal.* 260:351-357.
- Hamilton N, Warringham R, Silverwood I, Kapitán J, Hecht L, Webb P, Tooze R, Wuzong W, Frost C, Parker S and Lennon D. 2014. The application of inelastic neutron scattering to investigate CO hydrogenation over an iron fischer-tropsch synthesis catalyst. *J Catal.* 314:221-231.
- M. Haruta and Daté M. 2001. Advances in the catalysis of Au nanoparticles. *Appl Catal.* 222:427-437.
- Lindholm A, Currier NW, Li J, Yezerets A and Olsson L. 2008. Detailed kinetic modeling of storage and reduction with hydrogen as the reducing agent and in the presence of CO₂ and H₂O over a Pt/Ba/Al catalyst. *J Catal.* 258: 273-288.

- Iglesias E and Weiss B. 2010. Mechanism and site requirements for NO oxidation on Pd Catalysts. *J Catal.* 272:74-81.
- Forzatti P, Lietti L, Nova I, Morandi S, Prinetto F and Ghiotti G. 2010. Reaction pathway of the reduction by CO under dry conditions of NO_x species stored onto PtBa/Al₂O₃ lean NO_x trap catalysts. *J Catal.* 274:163-175.
- Hao Y, Mihaylov M, Ivanova E, Hadjiivanov K, Knözinger H and Gates B. 2009. CO oxidation catalyzed by gold supported on MgO: Spectroscopic identification of carbonate-like species bonded to gold during catalyst deactivation. *J Catal.* 261:137-149.
- Hongjuan W, Hao Y, Feng P and Xiaomei N. 2015. Pt nanoparticles interacting with graphitic nitrogen of N-doped carbon nanotubes: Effect of electronic properties on activity for aerobic oxidation of glycerol and electro-oxidation of CO. *J Catal.* 325:136-144.
- Ingelsten H, Zhao D, Palmqvist A and Skoglundh M. 2005. Mechanistic study of the influence of surface acidity on lean NO₂ reduction by propane in HZSM-5. *J Catal.* 232:68-79.
- Wachs IE, Kim T, Burrows A, and Kiely CJ. 2007. Molecular/electronic structure-surface acidity relationships of model-supported tungsten oxide catalysts. *J Catal.* 246:370-381.
- Kohyama M, Tomoki A and Yasushi M. 2015. Low-temperature CO oxidation properties and TEM/STEM observation of Au/Γ-Fe₂O₃ catalysts. *J Catal.* 324:127-132.
- Haruta M, Tsubota S, Kobayashi T, Kageyama H, Genet MJ and Delmon B. 1993. Low-temperature oxidation of CO over gold supported on TiO₂, Al-Fe₂O₃, and CO₃O₄. *J Catal.* 144:175-192.
- NIST standard reference database 69: NIST chemistry webbook.
- Ozbek MO and Niemantsverdriet JW. 2014. Elementary reactions of CO and H₂ on C-terminated X-Fe₅C₂₀ 0 1 surfaces. *J Catal.* 317:158-166.
- Wang Y, Ma X, Wu Y, Lu Y, Xu J and Zhu Y. 2011. Effect of compensated codoping on the photoelectrochemical properties of anatase TiO₂ photocatalyst. *J Phys Chem.* 115 16963-16969.
- Pérez J, Kondratenko E and Debbagh M. 2005. Transient studies on the mechanism of N₂O activation and reaction with CO and C₃H₈ over Fe-silicalite. *J Catal.* 233:442-452.
- Rivallan M, Ricchiardi G, Bordiga S and Zecchina A. 2009. Adsorption and reactivity of nitrogen oxides NO₂, NO, N₂O on Fe-zeolites. *J Catal.* 264:104-116.
- Rivera AP, Tanaka K and Hinsanaga T. 1993. Photocatalytic degradation of pollutant over TiO₂ in different crystal structures. *Appl Catal B: Environ.* 3:37-44.
- Rodriguez J, Evans J, Feria L, Vidal A, Liu P and Nakamura K. 2013. CO₂ hydrogenation on Au/TiC, Cu/TiC, and Ni/TiC catalysts: Production of CO, methanol, and methane. *J Catal.* 307:162-169.
- Wade LG. 2006. Organic chemistry. 6th Edition. 6:139-142.
- Zou X, Qi S, Xu J, Suo Z, An L and Li F. 2010. Study on Au/Al₂O₃ catalysts for low-temperature CO oxidation in Situ FT-IR. *J Nat Chem.* 19:307-312.
- Xianyong S, Mueller S, Shi H, Haller G, Sanchez-Sanchez M, Van Veen A and Lercher J. 2014. On the Impact of co-feeding aromatics and olefins for the methanol-to-olefins reaction on HZSM-5. *J Catal.* 314:21-31.
- Wonyong C, Sang-Hyup L, Palanichamy M, Narayanan L, Jae Y, Jae S and Jonghun L. 2014. Synergic photocatalytic effects of nitrogen and niobium codoping in TiO₂ for the redox conversion of aquatic pollutants under visible light. *J Catal.* 310:91-99.
- Yasuo I, Tomonobu M, Takumi M, Mitsutaka O, Masakazu D and Masatake H. 2009. A kinetic study on the low temperature oxidation of CO over Ag-contaminated Au fine powder. *J Catal.* 62:280-286.
- Young Y, Meijun L, Wolfgang MS and Weitz E. 2007. Low-temperature Nox reduction with ethanol over Ag/Y: A comparison with Ag/γ-Al₂O₃ and BaNa/Y. *J Catal.* 246:413-427.
- Liu J, Z. Guo, D. Childers, N. Schweitzer, C. L. Marshall, R. F. Klie, J.T. Miller and R.J. Meyer. 2014. Selective adsorption of manganese onto rhodium for optimized Mn/Rh/SiO₂ alcohol synthesis catalysts. *J Catal.* 313:149.
- Cheng D, Xu H and Fortunelli A. 2014. Tuning the catalytic activity of Au-Pd nanoalloys in CO oxidation via composition. *J Catal.* 314:47-55.
- Zhang H, Dai B, Li W, Wang X, Zhang J, Zhu M and Gu J. 2014. Non-mercury catalytic acetylene hydrochlorination over spherical activated-carbon-supported Au-Coiii-CuII catalysts. *J Catal.* 316:141-148.
- Collins SE, Aguirre A, Chen X, Delgado J, Calvino JJ and Berna S. 2014. Reversible deactivation of a Au/Ce_{0.62}Zr_{0.38}O₂ catalyst in CO oxidation: A systematic study of CO₂-triggered carbonate inhibition. *J Catal.* 316:210-218.
- Yang K, Liu J, Si R, Chen X, Dai W and Fu X. 2014. Comparative study of Au/TiO₂ and Au/Al₂O₃ for oxidizing CO in the presence of H₂ under visible light irradiation. *J Catal.* 317:229-239.
- Widmann D, Hocking E and Behm RJ. 2014. On the origin of the selectivity in the preferential CO oxidation on Au/TiO₂ - nature of the active oxygen species for H₂ oxidation. *J Catal.* 317:272-276.

- He J, An Z, Dai Y, Li B and Yu C. 2014. Enhanced heterogeneous asymmetric catalysis via the acid-base cooperation between achiral silanols of mesoporous supports and immobilized chiral amines. *J Catal.* 317:105-113.
- Zhao Z, Li Z and Lin YS. 2009. Adsorption and diffusion of carbon dioxide on metal-organic framework MOF-5. *Chem Res.* 48:10015-10020.
- Petoud S, An J, Shade CM, Chengelis-Czegana DA, and Rosi NL. 2011. Zinc-adeninate metal-organic framework for aqueous encapsulation and sensitization of near-infrared and visible emitting lanthanide cations. *J Am Chem Soc.* 133:1220-1223.
- Hafizovic J, Bjørgen M, Olsbye U, Dietzel PDC, Bordiga S, Prestipino C, Lamberti C and Lillerud KP. 2007. The inconsistency in adsorption properties and powder xrd data of mof-5 is rationalized by framework interpenetration and the presence of organic and inorganic species in the nanocavities. *J Am Chem Soc.* 129 3612-3620.
- Tsao CS, Yu MS, Chung TY, Wu HC, Yu Wang C, Chang KS and Chen HL. 2007. Characterization of pore structure in metal-organic framework by small-angle x-ray scattering. *J Am Chem Soc.* 129 15997-16004.
- White KA, Chengelis DA, Gogick KA, Stehman J, Rosi NL, and Petoud S. 2009. Near-infrared luminescent lanthanide MOF barcodes. *J Am Chem Soc.* 131:18069-180671.
- Liu Q, Gao J, Gu F, Lu X, Liu Y, Li H, Zhong Z, Liu B, Xu G and Su F. 2015. One-pot synthesis of ordered mesoporous Ni-V-Al catalysts for CO methanation. *J Catal.* 326:127-138.
- Ning X, Yu H, Peng F and Wang H. 2017. Electron transfer dependent catalysis of Pt on N-doped carbon nanotubes: Effects of synthesis method on metal-support interaction. *J Catal.* 348:100-109.
- Lonergan WW, Wang T, Vlachos DG and Chen JG. 2011. Effect of oxide support surface area on hydrogenation activity: Pt/Ni bimetallic catalysts supported on low and high surface area Al₂O₃ and ZrO₂. *Applied Catal.* 408:87-95.
- Munir D, Irfan MF and Usman MR. 2018. Hydrocracking of virgin and waste plastics: A detailed review. *Renew. Sustain. Energy Rev.* 90:490-515.
- Gao P, Li S, Bu X, Dang S, Liu Z, Wang H, Zhong L, Qiu M, Yang C, Cai J, Wei W and Sun Nat Y. 2017. Direct conversion of CO₂ into liquid fuels with high selectivity over a bifunctional catalyst. *Chem.* 9:1019-1024.
- Cheng K, Zohu W, Kang J, Wen W, Pan Y and Wang Y. 2018. Bifunctional catalysis for the conversion of synthesis gas to olefins and aromatics. *Chem.* 10:1107-1112.
- Kasipandi S and Bae JW. 2019. Spatially confined cobalt nanoparticles on zirconium phosphate-modified KIT-6 for an enhanced stability of CO hydrogenation to hydrocarbons. *Fuel.* 239:547-558.
- Chung SH, Stosic D, Chowdhury AD, Van Der Wal LI, Fu D, Zecevic J, Travert A, Houben K, Baldus M and Weckhuys BM. 2019. Multiscale mechanistic insights of shaped catalyst body formulations and their impact on catalytic properties. *ACS Catal.* 9: 4792-4803.
- Oenema J, Hofmann JP, Hensen EJM, Zečević J and Jong KP. 2020. Assessment of the location of Pt nanoparticles in Pt/zeolite Y/ γ -Al₂O₃ composite catalysts. *ChemCatChem.* 12:615-622.
- Sautel M, Elmaleh H and Leveiller F. 2000. Comparison of specific surface areas of a micronized drug substance as determined by different technique. *Stud Surf Sci Catal.* 128:633-642.
- Gao M, Zou K, Deng Y, Zhao Z, Li Y and Chen G. 2017. An unprecedented case: A low specific surface area anatase/N-doped carbon nanocomposite derived from a new single source precursor affords fast and stable lithium storage. *ACS Appl Mater Interfaces.* 34:28527-28536.