

## Comparison of the Structural Configuration of Cobalt Nanoparticles on Titania and Titania Nanotube Supports

A.S. Afolabi<sup>1,\*</sup>, A.S. Abdulkareem<sup>1</sup>, E. Muzenda<sup>2</sup>

<sup>1</sup> Department of Civil and Chemical Engineering, College of Science, Engineering and Technology University of South Africa, P/Bag X6, Florida 1710 Johannesburg, South Africa

<sup>2</sup> Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, Johannesburg South Africa

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In this study, two cobalt based catalyst samples were prepared on titania and titania nanotubes supports using the deposition precipitation method. Their structural configurations were characterized and compared using BET, and TRP analyses. The BET analysis showed that the surface area of TiO<sub>2</sub> is much higher than that of TNT which was due to their structural differences. Analyses of the results obtained revealed that the surface area of the 10 % Co/TNT catalyst sample is higher than that of the 10 % Co/TiO<sub>2</sub>. The TPR analysis showed that it is much easier to reduce 10 % Co/TiO<sub>2</sub>, than 10 % Co/TNT. This is attributed to be due to the fact that the cobalt particles were adsorbed on the surface of the TiO<sub>2</sub>, and formed covalent bonds with TNT. Therefore reduction temperature was higher with TNT than TiO<sub>2</sub>. The investigation of structural changes of these catalysts when they were coated with carbon, using chemical vapour deposition method was also conducted. The catalyst prepared on TNT support showed better properties in terms of average pore diameter, pore volume and surface area than the catalyst sample prepared on TiO<sub>2</sub> support when the two samples were exposed to carbon environment for the same period of time.

**Keywords:** Catalyst, Configuration, TNT, TiO<sub>2</sub>, Support.

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### 1. INTRODUCTION

A catalyst can either be heterogeneous or homogeneous, depending on whether it exists in the same phase as the substrate. Most heterogeneous catalysts are solids that act on substrate in a liquid or gaseous reaction mixture, and the total surface area of solid has an important effect on the reaction rate. Thus the smaller the catalyst particle size the larger the surface area for a given mass of particles and the higher the reaction rate [1]. Supports provide a platform from which heterogeneous catalysts, can act to change the rate of a reaction without being consumed during the reaction. The support material may or may not take part in the catalytic reaction. The support is usually a surface such as a metal oxide or carbon material. The support and catalyst may bond together in such a way to enhance the reactivity of the catalyst. In other cases, the support may be inactive and provide a high surface area substrate to increase the collisions of the reactants with the catalysts. For example, in catalytic converters, a ceramic honeycomb acts as a high surface area support for a catalyst such as platinum, rhodium, or palladium for changing pollution gases from the engine to environmentally friendly products. In fuel cells, platinum catalysts are located on a carbon support, which provides a means for conduction of the electrons for the electrocatalytic reactions [2-3].

TiO<sub>2</sub> is used in heterogeneous catalysis as a photo catalyst, in solar cells for the production of hydrogen and electric energy, as gas sensor, as white pigment, as a corrosion-protective coating, as an optical coating, in ceramics, and in electric devices such as varistors [4]. TiO<sub>2</sub> is not suitable as a structural support material, but small additions of titania can modify metal-base

catalysts in a profound way. A strong-metal support interaction is in part due to encapsulation of the metal particles by a reduced TiO<sub>x</sub> over layer [5]. The support provides a high surface area substrate to increase the collisions of the reactants with the catalysts which increase the reaction rate; it also gives a good dispersion of a catalyst which results in an optimal surface area. Previous studies have shown the performances of TiO<sub>2</sub> as support for different metal catalysts [6]. It has been known that the Co/TiO<sub>2</sub> catalyst is considered to have a strong metal support interaction (SMSI) and shows a high activity in CO hydrogenation reactions [6-7]. This interaction is an important factor used for determining the properties of a Co/TiO<sub>2</sub> catalyst such as cobalt dispersion and reduction behavior [8].

The synthesis of highly dispersed cobalt on a TiO<sub>2</sub> support requires the strong interaction between cobalt and support. However a too strong interaction can produce a Co-support compound as a suboxide at an interface that is highly resistant to reduction [9-11]. It has been reported that Co-support compound formation (Co-SCF) during standard reduction resulted in a lower reducibility of a Co/TiO<sub>2</sub> catalyst. It has been known that the dominant surface sites of TiO<sub>2</sub> support consists of two main sites Ti<sup>4+</sup> and Ti<sup>3+</sup> [6, 12-16]. The effect of surface sites on the formation of Co-SCF has not yet been investigated.

This study is therefore aimed at loading cobalt particles on both TiO<sub>2</sub> and TNT supports using the deposition precipitation method for catalyst preparation, coating the supports TiO<sub>2</sub> and TNT with carbon (TiO<sub>2</sub>-C and TNT-C) using chemical vapour deposition method and use characterization methods to compare the structural configurations of the two supports and catalysts.

\* [afolaas@unisa.ac.za](mailto:afolaas@unisa.ac.za)

## 2. EXPERIMENTAL

A 2.5 g of a hydrated cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) sample was mixed with 0.76 g of urea respectively and 5 ml of deionised water was added to dissolve the solid mixture. A few drops of deionised water were added in a beaker with 5 g of the  $\text{TiO}_2$  support, in an oil bath at  $90^\circ\text{C}$  while stirring. A solution of urea and ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) was added drop-wise into the support using a burette, while stirring until the mixture was dry. The sample was then dried overnight at  $120^\circ\text{C}$  in an oven. This catalyst precursor was then calcined at  $350^\circ\text{C}$  for 6 hours in air. The same procedure was adopted to impregnated Co particles on TNT.

A chemical vapour deposition (CVD) reactor was used to coat the  $\text{TiO}_2$  and TNT samples with carbon. The description of this reactor has been reported elsewhere [2, 17-18]. Acetylene was used as a source of carbon for coating  $\text{TiO}_2$  and TNT. About 0.2 g of each sample was placed in a small ceramic boat placed at the middle of the quartz tube that is about 80 cm in length. The tube was then passed through the ceramic tube of the horizontal furnace. Nitrogen gas (Afrox, 99.99 %) was introduced while heating the sample at a rate of  $10^\circ\text{C}/\text{min}$  to  $900^\circ\text{C}$ . This was done to ensure an inert atmosphere in order to avoid some side reactions. At  $900^\circ\text{C}$ , acetylene was introduced to replace nitrogen gas and the process was done for 60 minutes.

### 2.1 Characterization

#### 2.1.1 Temperature programmed reduction (TPR)

The reducibility behaviour of all the calcined catalysts were studied using an in-house designed TPR. A 0.2 g catalyst sample was placed in a U shaped quartz reactor on top of quartz wool which is used as a catalyst bed. Pure nitrogen gas (for degassing) was first passed through the quartz reactor while heating the reactor at the rate of  $10^\circ\text{C}/\text{minute}$  from room temperature to  $150^\circ\text{C}$ . The temperature was kept at  $150^\circ\text{C}$  for thirty minutes to ensure that all the moisture content was driven off. The reactor was then cooled to room temperature after degassing the sample, 5% hydrogen in argon gas was introduced at the rate of 30 ml/minute and nitrogen gas was then turned off. Temperature was adjusted from room temperature to  $900^\circ\text{C}$  at  $5^\circ\text{C}/\text{minute}$ . The temperature profiles were collected from a computer.

#### 2.1.2 Thermal gravimetry analysis (TGA)

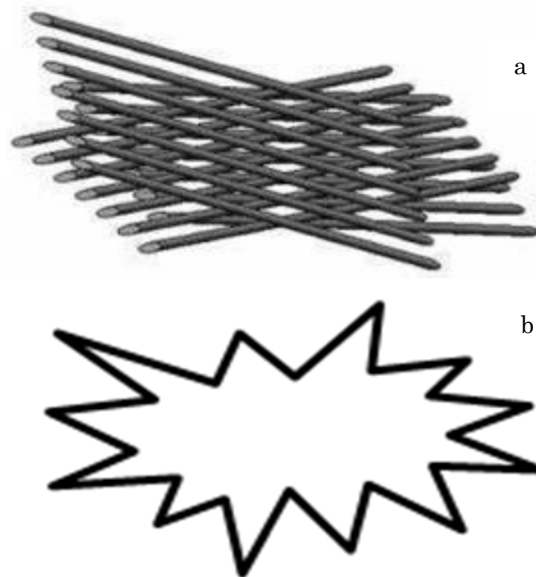
TGA analyses were conducted on a Perkin Elmer TGA 4000. After placing  $\sim 20$  mg sample in a ceramic pot it was heated at  $10^\circ\text{C}/\text{minute}$  from room temperature to  $900^\circ\text{C}$  under a constant flow of air (20 ml/minute). The weight loss as a function of temperature was monitored on a computer.

#### 2.1.3 BET and pore size distribution measurement

Nitrogen adsorption measurements were performed at  $-196^\circ\text{C}$  using a Micrometrics Tristar adsorption analyzer. The samples (mass  $\sim 0.2$  g) were loaded in the Micrometrics tubes and degassed at  $150^\circ\text{C}$  for overnight in nitrogen (99.99 % purity). The tubes were then attached to the Tristars analysis and run overnight.

## 3. RESULTS AND DISCUSSION

Figs. 1(a) and (b) show the typical structures of the titania nanotubes and titania supports respectively. It can be seen that the titania nanotubes have tubular structure while the titania has a spherical structural configuration. The titania nanotubes also show a well-ordered structure with relatively simple compositions are formed by titania materials [19]. The tubular structure of the titania nanotubes is similar to those of carbon nanotubes and it is expected that they will possess exceptional physical, mechanical and electrical properties such as the latter.



**Fig. 1** – Structures of (a) titania nanotubes and (b) titania catalyst supports

The surface area property is very important in the preparation of catalyst because it is responsible for the distribution of the catalyst particles on the support. The larger the surface area of the support, the better it is for good distribution of the catalyst particles and the better the activity of the resulting catalyst. The tubular structure of the titania nanotubes gives it a larger surface area than their titania counterpart. This is confirmed by the comparative surface areas results of the two structures as shown in Table 1.

Table 1 shows the BET analysis of the two supports and their respective catalyst samples which reveals the pore volume, pore diameter and the surface area of the samples. The average diameters of the supports and the Co-loaded catalysts exist within the nano-range of the 10.2 and 35.5, which shows that the particles are fine enough to give even distribution and subsequent good catalytic activity for hydrogen oxidation and oxygen reduction reactions [20]. The preparation method is also a crucial method in the size of the particles; TNT was prepared from the  $\text{TiO}_2$  and the average diameter of the nanotube material is smaller than that of the initial material. Similar trend is observed in the Co loaded samples of the  $\text{TiO}_2$  and TNT in which the latter has a smaller size compared to the former. It can also be observed that the surface area and the pore volume of a 10 % Co/TNT sample were much higher than that of a 10 % Co/ $\text{TiO}_2$  sample. This can be attributed to the

structural change of TNT support when it was prepared from  $\text{TiO}_2$  of surface area  $47.2 \text{ m}^2/\text{g}$  that resulted in a very high surface area of  $231.1 \text{ m}^2/\text{g}$ .

The temperature programmed reduction (TPR) profile (Figure 2) indicates the behaviour of a cobalt oxide loaded on  $\text{TiO}_2$  and TNT supports. These catalysts were both prepared using the deposition precipitation method. Urea is used as a cobalt particles precipitator and is believed to be favourable for the production of small metal particles as well as acted as a reducing agent during the catalyst preparation. The prepared catalyst samples were heated to  $1000 \text{ }^\circ\text{C}$  at the rate of  $5 \text{ }^\circ\text{C}$ , and held at  $1000 \text{ }^\circ\text{C}$  for two hours followed by slow

cooling in static air. The form of heat treatment is an important and necessary step in the preparation of the catalysts because it has a significant impact on the Co metal particle size and distribution, particle surface morphology, and Co particle distribution on the supports [21]. The calcination or thermal treatment, removed the volatile compounds contained in the catalysts and removed the undesirable impurities resulting from the early preparation stages, to allow a uniform dispersion and stable distribution of the Co particles on the supports, and therefore improves the electrocatalytic activity of the synthesized catalysts.

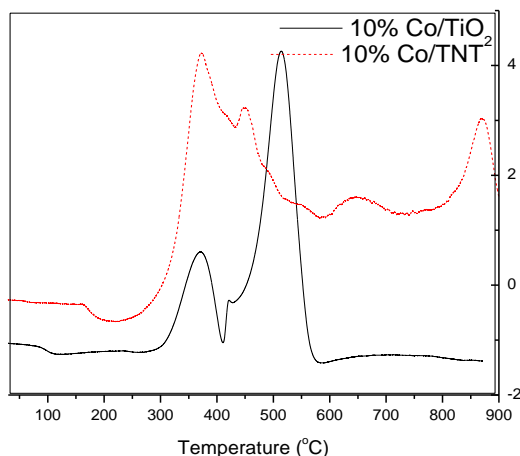
**Table 1** – BET analysis of the supports, and 10 % Co/TNT & 10 % Co/ $\text{TiO}_2$  catalyst samples

Sample	Average pore diameter (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )	Surface area ( $\text{m}^2/\text{g}$ )
$\text{TiO}_2$	35.5	0.420	47.2
TNT	10.2	0.370	231
10 % Co/ $\text{TiO}_2$	28.2	0.379	53.8
10 % Co/TNT	12.9	0.484	150

**Table 2** – Reduction temperatures of 10 % Co/TNT and 10 % Co/ $\text{TiO}_2$  samples

Sample name	Temperature ( $^\circ\text{C}$ ) first peak	Temperature ( $^\circ\text{C}$ ) second peak	Other peaks ( $^\circ\text{C}$ )
$\text{TiO}_2$	–	–	500-900
TNT	–	–	500-900
10 % Co/ $\text{TiO}_2$	360	500	–
10 % Co/TNT	376	446	–

The TPR profile shows that the reduction temperature of a 10 % Co/TNT occurred at  $360 \text{ }^\circ\text{C}$  and  $650 \text{ }^\circ\text{C}$  while the reduction temperature of 10%Co/ $\text{TiO}_2$  occurred at  $360 \text{ }^\circ\text{C}$  and  $500 \text{ }^\circ\text{C}$  (Table 2). Suggests that it is easier to reduce 10%Co/ $\text{TiO}_2$  catalyst sample than 10%Co/TNT catalyst sample. This could be due structural metal surface interface (SMSI), because the structural configuration of Co when loaded on  $\text{TiO}_2$  shows that the Co particles adsorbed on the surface of the  $\text{TiO}_2$ , while the structural configuration of Co loaded on TNT support indicates a bond between the cobalt oxide and the TNT support.



**Fig. 2** – TPR profile of 10%Co/ $\text{TiO}_2$  and 10%Co/TNT catalyst samples

On 10 % Co/TNT graph two more peaks appears on the far end of the graph, which was due to the structural change of the TNT support, this is further emphasized in Fig. 3(a). The change occurred at  $500 \text{ }^\circ\text{C}$  and  $900 \text{ }^\circ\text{C}$ , this is the same with a  $\text{TiO}_2$  Figure 3(b).

Table 3 shows the average pore diameters, the pore volumes and the surface areas of a TNT- $\text{C}_{60\text{minutes}}$  and  $\text{TiO}_2\text{-C}_{60\text{minutes}}$  samples coated with carbon for 60 minutes. The two samples both spent the same period of time (60 minutes) in the furnace to obtain carbon coating from acetylene. It can be observed that the surface area and the pore volume of TNT- $\text{C}_{60\text{minutes}}$  sample were higher than that of the  $\text{TiO}_2\text{-C}_{60\text{minutes}}$  sample. This can be attributed to the difference in the configurations of the TNT structure the distribution of carbon on the TNT support left some space in between as the structure has a certain value of length, and when it was distributed on  $\text{TiO}_2$  the carbon particles did not leave some space, as it is believed that the  $\text{TiO}_2$  has a spherical structural configuration as previously indicated.

**Table 3** – BET analysis of carbon coated  $\text{TiO}_2$  and TNT supports

Sample	Average pore diameter (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )	Surface area ( $\text{m}^2/\text{g}$ )
$\text{TiO}_2\text{-C}_{60\text{minutes}}$	30.4	0.019	2.4
TNT- $\text{C}_{60\text{minutes}}$	12.2	0.026	3.9

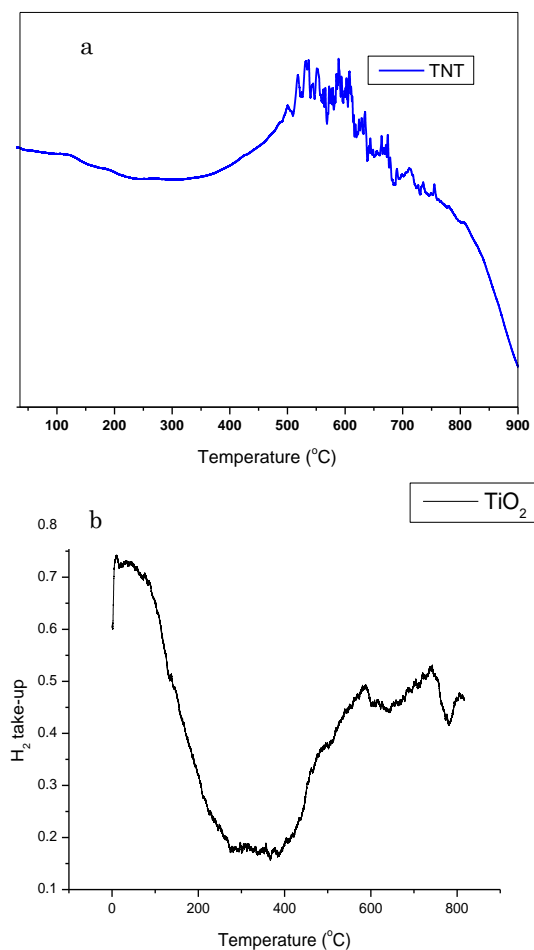


Fig. 3 – TPR profiles of (a) TNT and (b) TiO<sub>2</sub>

## REFERENCES

1. P. Sabatier and J.B. Senderens, *C.R. Acad. Sci. Paris* **134**, 514, (1962).
2. U. Diebold, *Appl. Phys. A-Matter* **76**, 1 (2002).
3. A.S. Afolabi, *PhD thesis, University of the Witwatersrand, Johannesburg South Africa*, (2009).
4. G.L. Haller, D.E. Resasco, *Adv. Catal.* **36**, 173 (1989).
5. L.S. Dubrovinsky, N.A. Dubrovinskaia, V. Swamy, J. Muscat, N.M. Harrison, R. Ahuja, B. Holm., B. Johansson, *Nature* **410**, 653 (2001).
6. J. Li, N.J. Coville, *Appl. Catal. A-Gen.* **181**, 201 (1999).
7. N.J. Coville, J. Li, *Catal. Today* **71**, 403 (2002).
8. S. Sun, N. Tsubaki, K. Fujimoto, *Appl. Catal. A-Gen.* **202**, 121 (2000).
9. G. Lu, A. Linsebigler, J.T. Yates, *J. Phys. Chem.* **98**, 11733 (2000).
10. Y. Zhang, D.D. Wei, S. Hammache, G.J. Goodwin, Jr. *J. Catal.* **188**, 281 (1999).
11. B. Jongsomjit, C. Sakdamnusun, J.G. Goodwin, P. Prasterthdam, *Catal. Lett.* **94**, 209 (2004).
12. V. Hendrich, R.L. Kurtz, *Phys. Rev. B* **23**, 6280 (1981).
13. H.W. Kroto, J.R. Heath, S.C. O'Brien, R.F. Curl, R.E. Smalley, *Nature* **318**, 162 (1985).
14. J.-M. Pan, B.L. Maschhoff, U. Diebold, T.E. Madey, *J. Vac. Sci. Technol. A* **10**, 2470 (1992).
15. I. Nakamura, N. Negishi, S. Kutsuna, T. Ihara, S. Sugihara, K. Takeuchi, *J. Mol. Catal. A* **161**, 205 (2000).
16. S. Mezheny, P. Maksymovych, T.L. Thomson, O. Diwaald, D. Stahl, S.D. Walck, J.T. Yates, *Chem. Phys. Lett.* **369**, 152 (2003).
17. A.S. Afolabi, A.S. Abdulkareem, S.D. Mhlanga, N.J. Coville, S.E. Iyuke, *J. Exp. Nanosci.* **6**, 248 (2011).
18. S.D. Mhlanga, S.E. Iyuke, A.S. Afolabi, S.A. Abdulkareem, N. Kunjuzwa, N.J. Coville, *J. Exp. Nanosci.* **5**, 40 (2010).
19. H. Peng, G. Li, Z. Zhang, *Mat. Lett.* **59**, 1142 (2005).
20. M.-C. Tsai, T.-K. Yeh, C.-H. Tsai, *Electrochem. Comm.* **8**, 1445 (2006).
21. K.S. Han, Y.-S. Moon, O.H. Han, K.J. Hwang, I. Kim, H. Kim, *Electrochem. Comm.* **9**, 317 (2007).

## 4. CONCLUSIONS

The loading of 10 % cobalt particles on TiO<sub>2</sub> and TNT supports using the deposition precipitation method was carried out in this investigation. The structural configurations of the resulting catalyst samples were characterized and compared using TGA, BET, and TRP analyses. BET analysis showed that the surface area of TNT is much higher than that of TiO<sub>2</sub> which was due to the tubular structure of the nanotubes as compared to the spherical structural configuration of the TiO<sub>2</sub>. The surface area of the 10 % Co/TNT catalyst sample also is higher than of the 10 % Co/TiO<sub>2</sub> catalyst sample. The TPR analysis showed that it is easy to reduce 10 % Co/TiO<sub>2</sub>, than 10 % Co/TNT. This is due to the fact that the cobalt particles were adsorbed on the surface of the TiO<sub>2</sub> and formed covalent bonds with TNT. Therefore reduction temperature was higher in TNT than TiO<sub>2</sub> support. The investigation of structural changes of these catalysts when they were coated with carbon, using chemical vapour deposition method was also conducted. The catalyst prepared on TNT support showed better properties in terms of average pore diameter, pore volume and surface area than the catalyst sample prepared on TiO<sub>2</sub> support when the two samples were exposed to carbon environment for the same period of time.

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