

COMPARISON OF THE STRUCTURAL CONFIGURATION OF Co NANOPARTICLES ON TiO₂ AND TNT SUPPORTS

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ABSTRACT

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 TiO₂ 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/TiO₂. The TPR analysis showed that it is much easier to reduce 10%Co/TiO₂, than 10%Co/TNT. This is attributed to be due to the fact that the cobalt particles were adsorbed on the surface of the TiO₂, and formed covalent bonds with TNT. Therefore reduction temperature was higher with TNT than TiO₂. 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 TiO₂ support when the two samples were exposed to carbon environment for the same period of time.

Key words: catalyst, configuration, TNT, TiO₂, support

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

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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].

TiO₂ 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]. TiO₂ 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_x 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 TiO₂ as support for different metal catalysts [6]. It has been known that the Co/TiO₂ 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/TiO₂ catalyst such as cobalt dispersion and reduction behavior [8].

The synthesis of highly dispersed cobalt on a TiO₂ 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/TiO₂ catalyst. It has been known that the dominant surface sites of TiO₂ support consists of two main sites Ti⁴⁺ and Ti³⁺ [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 TiO₂ and TNT supports using the deposition precipitation method for catalyst preparation, coating the supports TiO₂ and TNT with carbon (TiO₂-C and TNT-C) using chemical vapour deposition method and use characterization methods to compare the structural configurations of the two supports and catalysts.

EXPERIMENTAL

A 2.5 g of a hydrated cobalt nitrate (Co(NO₃)₂.6H₂O) 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 TiO₂ support, in an oil bath at 90°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°C in an oven. This catalyst precursor was then calcined at 350°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 TiO_2 and TNT samples with carbon. The description of this reactor has been reported elsewhere [3, 17, 18]. Acetylene was used as a source of carbon for coating 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°C . This was done to ensure an inert atmosphere in order to avoid some side reactions. At 900°C , acetylene was introduced to replace nitrogen gas and the process was done for 60 minutes.

Reducibility behavior 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°C . The temperature was kept at 150°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°C at $5^\circ\text{C}/\text{minute}$. The temperature profiles were collected from a computer.

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

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

RESULTS AND DISCUSSION

Figures 1a, 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.

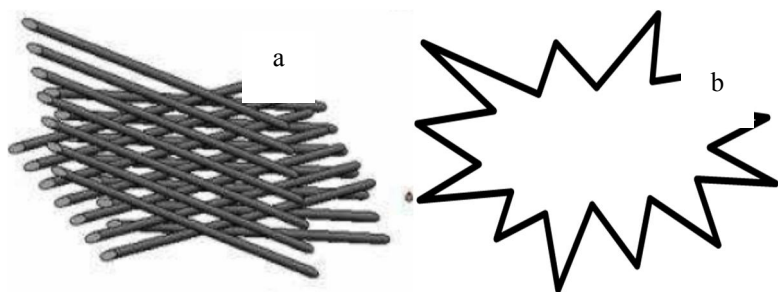


Fig. 1 – Structures of (a) titania nanotubes and (b) titania catalyst supports

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 TiO_2 and the average diameter of the nanotube material is smaller than that of the initial material.

Table 1 – BET analysis of the supports, and 10%Co/TNT & 10%Co/ TiO_2 catalyst samples.

Sample	Average pore diameter (nm)	Pore volume (cm^3/g)	Surface area (m^2/g)
TiO_2	35.5	0.420	47.2
TNT	10.2	0.370	231
10%Co/ TiO_2	28.2	0.379	53.8
10%Co/TNT	12.9	0.484	150

Similar trend is observed in the Co loaded samples of the 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/ TiO_2 sample. This can be attributed to the structural change of TNT support when it was prepared from 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 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°C at the rate of 5°C , and held at 1000°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.

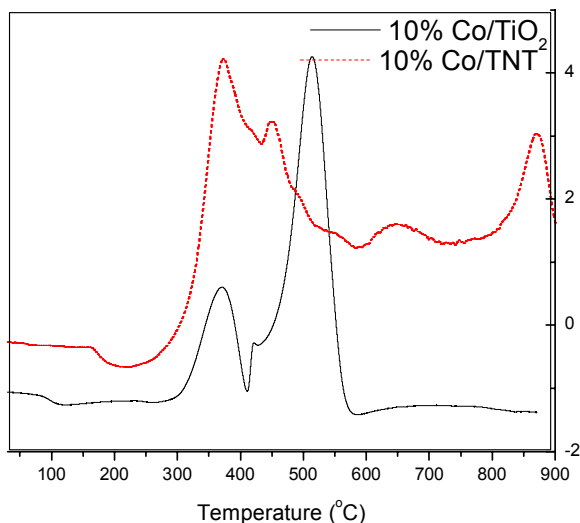


Fig. 2 – TPR profile of 10%Co/ TiO_2 and 10%Co/TNT catalyst samples

The TPR profile shows that the reduction temperature of a 10%Co/TNT occurred at 360°C and 650°C while the reduction temperature of 10%Co/TiO₂ occurred at 360°C and 500°C (*Table 2*). suggests that it is easier to reduce 10%Co/TiO₂ 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 TiO₂ shows that the Co particles adsorbed on the surface of the TiO₂, while the structural configuration of Co loaded on TNT support indicates a bond between the cobalt oxide and the TNT support.

Table 2 – Reduction temperatures of 10%Co/TNT and 10%Co/TiO₂ samples

Sample	Temperature (°C) first peak	Temperature (°C) second peak	Other peaks (°C)
TiO ₂	-	-	500 – 900
TNT	-	-	500 – 900
10%Co/TiO ₂	360	500	-
10%Co/TNT	376	446	-

The height of both peaks was dependent on the consumption of a H₂ that was measured using the TCD detector that was connected to an amplifier. The faster the quantity of H₂ consumed the higher the height of the peak. From the Figure, the peak of the 10%Co/TiO₂ sample is higher than that of 10%Co/TNT catalyst sample which can be due to the distribution of cobalt oxide particles on the TiO₂ support. The reason for the shorter peak of 10%Co/TNT catalyst sample is attributed to the fact the rate of H₂ consumption is slower than that of 10%Co/TiO₂ because the cobalt oxide particles are not close to each other as with 10%Co/TiO₂.

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 *Figure 3a*. The change occurred at 500°C and 900°C, this is the same with a TiO₂ *Figure 3b*.

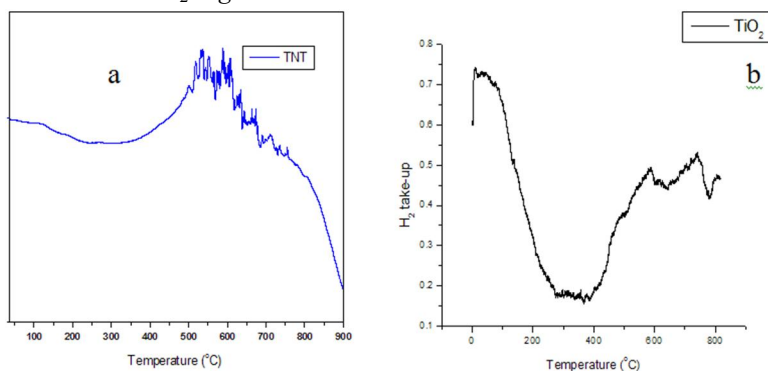


Fig. 3 – TPR profiles of (a) TNT and (b) TiO₂

Table 3 shows the average pore diameters, the pore volumes and the surface areas of a TNT-C_{60minutes} and TiO₂-C_{60minutes} 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-C_{60minutes} sample were higher than that of the TiO₂-C_{60minutes} 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 TiO₂ the carbon particles did not leave some space, as it is believed that the TiO₂ has a spherical structural configuration as previously indicated.

Table 3 – BET analysis of carbon coated TiO₂ and TNT supports

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

CONCLUSIONS

The loading of 10% cobalt particles on TiO₂ 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 TiO₂ which was due to the tubular structure of the nanotubes as compared to the spherical structural configuration of the TiO₂. The surface area of the 10%Co/TNT catalyst sample also is higher than of the 10%Co/TiO₂ catalyst sample. The TPR analysis showed that it is easy to reduce 10%Co/TiO₂, than 10%Co/TNT. This is due to the fact that the cobalt particles were adsorbed on the surface of the TiO₂ and formed covalent bonds with TNT. Therefore reduction temperature was higher in TNT than TiO₂ 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 TiO₂ support when the two samples were exposed to carbon environment for the same period of time.

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