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Low Cost Transition Metals Doping over TiO_2 for NO_x Catalyst Deposited onto Woven Stainless Steel Wire Mesh

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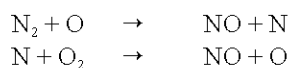
Abstract: The objective of the present study was to develop a high porosity NO_x reduction catalyst using cobalt and multi-component metal from low cost transition element which was deposited onto woven stainless steel wire-mesh monolith honeycomb by sol-gel method. These metals were mixed with titanium (iv) isopropoxide as a metal oxide precursor in sol-gel phase whereby metal titanium also acts as catalyst. The reduction activity of the prepared catalyst was investigated by using Temperature Program Reduction (TPR) instrument. It was found that the synthesized catalyst has shown high porosity in which it was reflected to an amount of single point BET surface area ($100.065 \text{ m}^2 \text{ g}^{-1}$) obtained from TPR data. The morphology of the synthesized catalyst particles was analyzed by using scanning electron, microscope (SEM).

Key words: NO_x reduction, sol-gel coating, low cost transition metal, stainless steel wire mesh

INTRODUCTION

Excessive nitrogen oxide (NO_x) species in the atmosphere can lead to significant environmental problem such as photochemical smog, global warming and stratospheric depletion ozone (Sawyer *et al.*, 2003). Therefore the reduction of NO_x emission has become one of the greatest challenges in environment protection. The most common currently used technology for NO_x reduction is Selective Catalytic Reduction (SCR) using the reducing agent such as ammonia (NH_3), compound containing ammonia such as urea and hydrocarbons (Parvulescu *et al.*, 1998). However this technology has shown several disadvantages where the need of reducing agent during the reaction required temporarily storage and high-cost of the SCR-Ammonia installation (Parvulescu *et al.*, 1998). NO_x formed in combustion process by combination of the N_2 and O_2 present in the air. At temperature above 1500°C , the reaction proceeds at significant rate (Heck *et al.*, 2002). Compounds of NO_x mainly referred to nitric oxide, NO, nitrogen dioxide and NO_2 species. Generally, NO_x can be classified into three categories:

- Thermal NO_x where N_2 and O_2 dissociate and recombine at high temperature. Predominant mechanism involved during this reaction is described by Zeldovich equation:



- Fuel NO_x where nitrogen 'bound' such as pyridine, $\text{C}_5\text{H}_6\text{N}$ or compounds containing nitrogen present in the fuel NO_x forms through oxidation reaction.
- Prompt NO_x , a reaction between hydrogen radicals and N_2 in which nitrogen intermediates are formed which can subsequently be oxidized to NO_x (Bosch and Janssen, 1998).

In recent years, most of the industrial countries in the world such as Europe, Japan and China used incineration technologies as primary treatment method for volume reduction of their Municipal Solid Waste (MSW). However this technology contributes NO_x pollutant from flue gas emission. Nowadays, developing a catalyst for NO_x removal from flue gas system using low cost transition metals has become a great challenge to academia and industries. It is important to study the preparation method and the nature of the interaction between the support material and the catalyst species in gaining a deeper understanding of carrier-containing low cost transition catalysts such as Ag, Cu, Ni and Co (Satterfield, 1980; Zhenlu *et al.*, 2003).

In the present study, titania, TiO_2 catalyst doping with low cost transition metals for NO_x reduction were prepared using sol-gel route to achieve high dispersion of

an active species on a carrier having a homogeneous surface, acceptable mechanical properties and a porous texture which allow the easy diffusion of reactants to those active sites (Lecloux and Pirard, 1998). Woven stainless steel wire-mesh was used as substrate, the so-called monolith honeycomb.

EXPERIMENTAL METHODS

Catalysts preparation: The transition element metals deposition onto TiO₂ samples were prepared by the sol-gel technique from a solution of titanium (IV) isopropoxide in ethyl alcohol as a metal oxide molecular precursor (Su *et al.*, 2004). In order to control the reaction kinetics, diethanolamine was used as chemical additive to moderate the reaction rate. The amount of poly ethylene glycol in sol-gel preparation would influenced the thickness and stability of the final TiO₂ sol (Kajihara and Yao, 1998). All chemicals used were obtained from BDH Chemicals and Merck. Deionized water was gradually added to the mixture followed by continuous stirring to allow hydrolysis process. After 1 hour stirring, the clear sol was obtained.

A portion of prepared TiO₂ sol was retained for further analysis and comparison purpose. The solution of metal catalysts at 1 wt % was then carefully added to the sol and continuously stirred for another 5 h. Then the wire-mesh was immersed into the solution at a speed of 7cm min⁻¹ by using dip-coater. The samples were then dried in the oven by slowly raising the temperature to 100°C for 24 h. Then the samples were calcined at 550°C at a rate of 4°C min⁻¹.

Catalyst characterization: Temperature Programmed Reduction (TPR) profiles of Cobalt/TiO₂ was analyzed by using Thermo Finnigan TPDRO 1100 instrument. The sample was first pretreated with pure nitrogen gas at flow rate 20 mL min⁻¹. TPR profiles were obtained in the temperature range 50°C to 700°C at a rate of 50°C min⁻¹. 5% hydrogen in nitrogen mixture at flow rate 20 mL min⁻¹ was used as reducing gas.

The particle distribution of synthesized catalysts on wire mesh substrate was analyzed by using Scanning Electron Microscope (SEM) model Hitachi S2500. The

Table 1: List of samples

No	Sample Code	Magnification
1	Cobalt /TiO ₂	30x
2	Cobalt /TiO ₂	1000x
3	Mixture K* /TiO ₂	30x
4	Mixture K* /TiO ₂	1000x
5	Uncoating wire mesh	30x
6	Uncoating wire mesh	1000x

Where mixture K* is a multi-component of low cost transition metals

samples were cut about 2 cm diameter and mounted on the stub using aluminum tape, they were then coated with platinum using Ion Sputter. The SEM operating condition was conducted at 15 KV high vacuum. Table 1 shows the samples which have been prepared for SEM investigation.

RESULTS AND DISCUSSIONS

Temperature-programmed reduction analysis: All the data obtained from the analysis is shown in Table 2. First peak that appeared in the profile of Co/TiO₂ reduction as shown in Fig. 1 was occurred at maximum temperature of 369°C which suggested that TiO₂ anatase phase exists in the synthesized catalyst. Furthermore, the single point BET surface area (100.0 m² g⁻¹) is higher than that of TiO₂ (50-80 m² g⁻¹) (Kajihara and Yao, 1998). This is expected because the pores in each support are partially filled by cobalt particles (Santo *et al.*, 2001). It has also been shown that higher surface area can be obtained by the sol-gel route. The analysis also revealed the amount of hydrogen gas as reducing agent which is reflected to the number of active sites of the synthesized catalyst that available for reduction process to occur.

Particle distribution by SEM analysis: Figure 2 and 3 showed the particles of Co/TiO₂ randomly distributed on the wire mesh surface with an irregular shapes and sizes. From the observation, it can be seen that the presence of small and large individual Co/TiO₂ particles as shown in

Table 2: List of data obtained from the TPR analysis of cobalt/TiO₂

Type of data	Description
Amount H ₂ gas adsorbed	1121.30 μmol g ⁻¹
Amount of catalyst reacted	2242.40 μmol g ⁻¹
Total Single point BET surface area	100.0 m ² g ⁻¹
TiO ₂ Phase	Anatase
Mean particles diameter	0.131 nm
Temperature at Max. Peak	369°C
Reduction duration	8 min

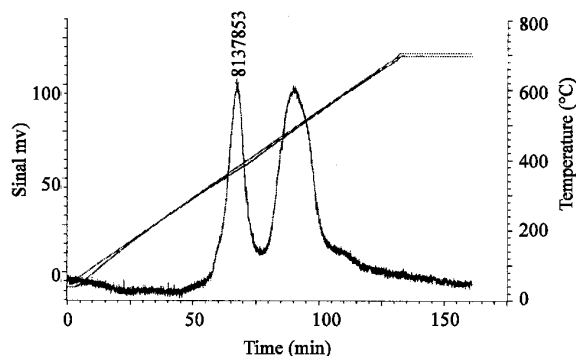


Fig. 1: Profile of temperature program reduction for cobalt /TiO₂.

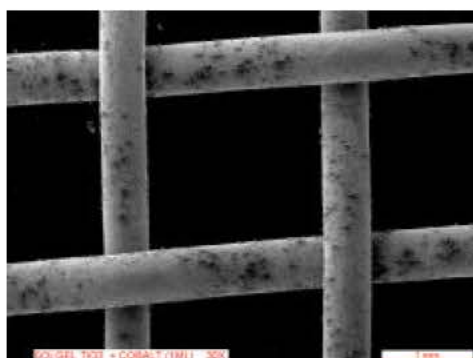


Fig. 2: Micrograph of Co/TiO₂ particle distribution on wire mesh substrate at 30x magnification.

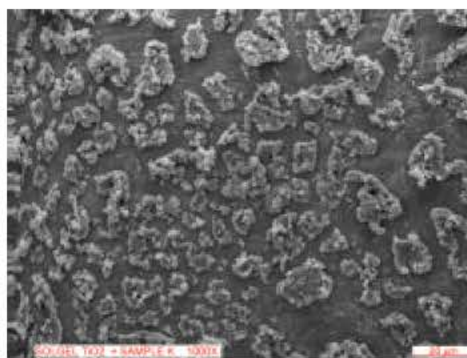


Fig. 5: Micrograph of mixture K/TiO₂ particle distribution on wire mesh substrate at 1000x magnification

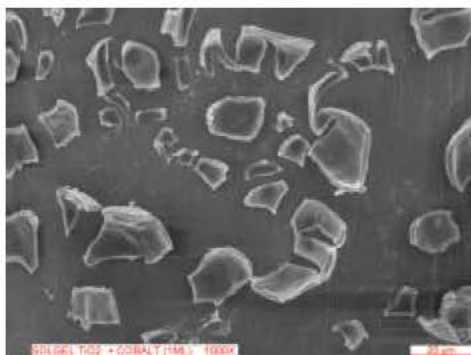


Fig. 3: Micrograph of Co/TiO₂ particle distribution on wire mesh substrate at 1000x magnification.

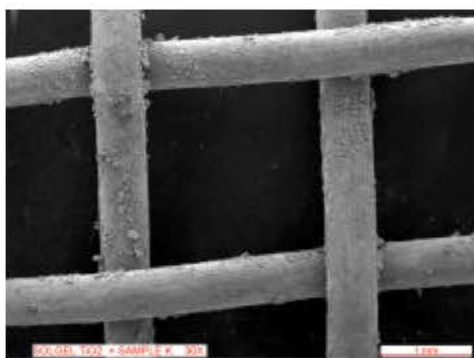


Fig. 4: Micrograph of mixture K/TiO₂ particle distribution on wire mesh substrate at 30x magnification.

Fig. 3 in which most of them were cracked. Consequently, these cracked particles would provide higher surface area as found by TPR result. These are explained by the fact that the particles experienced stresses during heat

treatment. Santo *et al.* (2001) and Sonawane *et al.* (2002) investigated that through sol-gel preparation, aging time and calcinations conditions determine the amount of the surface area, therefore it increases the porosity of the prepared catalyst.

Nevertheless, Figure 4 and 5 show the distribution of multi-component metal catalyst with higher surface coverage and consist of small and large clusters due to high concentration of sol and withdrawing time. Some of the clusters indicated the existing of pores with diameter size of 20 μm, hence the increase in thickness of the sol has greatly increased the porosity of the synthesized catalyst as investigated (Kajihara *et al.*, 1998). However, it has been revealed that the adhesion of the particles to the metal was not so good, therefore it could affect a durability of the catalyst. Most of the clusters especially at crosslink area depicted re-bonding phenomena, where these particles and clusters having a tendency to pull out from the surface as explained by Santo *et al.*, 2001.

CONCLUSIONS

Synthesized catalyst Co/TiO₂ by sol-gel technique exhibited higher surface area of 100.0 m² g⁻¹ and consequently reflected to a high porosity of the catalyst deposited onto woven stainless steel wire mesh. However based on the SEM micrograph, it was found that the catalyst particles were not homogenously dispersed on the wire mesh substrate. Furthermore, the adhesion of the particles was not so strong as it was found from the surface structure by SEM images.

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