CATALYTIC REDUCTION OF NOx USING LOCALLY PREPARED CATALYST WITH AMMONIA

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ABSTRACT

A preparation of vanadium pentoxide catalyst that was chosen for conducting the catalytic reduction of NO2 in the presence of ammonia was described. Vanadium pentoxide catalyst was prepared from ammonium meta vanadate. And Tested by gradual increase of the concentration of active component from for to 14 wt%. These properties are particle densities, packed bed densities, pore volumes, apparent porosity, surface area, crushing strength. To examine the reliability of the catalyst that prepared from ammonium meta vanadate, catalytic reduction of NO2 were performed in lab-scale unit. Five tests were performed over temperature range from 80 to 200°C at otherwise constant process parameters (i.e., gas hourly space velocity (GHSV) of 240 h–1 and partial pressure of the NO2). It was found the conversion of NO2 increased as the temperature increase and as the concentration of active component increase.

INTRODUCTION

Nitrogen oxide (NOx) is believed to be a key substance responsible for air pollution. Nitric oxide is biochemically less active and less toxic than NO2. The primary health effects of concern for NO2 include acute pulmonary, function responses, acute respiratory infectious disease and chronic lung disease (McKee and Rodriguez, 1993). Acute exposure to NO2 can be quite harmful to human health. The health effects of NO2 vary with the degree of exposure level (e.g., 50-100 ppm of NO2 causes inflammation of lung tissue for a period of 6-8 weeks). Exposure of the subject to 150-200 ppm of NO2 causes bronchiolitis fibrosa. Death generally results within 2-10 days after exposure to 500 ppm or more.

Nitrogen oxides entering the atmosphere are converted to nitric acid which causes acidic precipitation (acid rain) (Manahan, 1995). Control of NOx emission has become an important national and international problem. Not only do nitrogen oxides create a direct health hazard as air pollutants but they also play a key role in smog formation.

The reddish-brown plume of smoke, which traditionally billows out of nitric acid plant may be removed by reduction.

a) Without reducing agent where complete conversion of low concentration of NO was achieved by a composite catalyst support on active carbon without additional reductive gases. Several weight percent of Ni or Co was supported and small amounts of a rare earth oxide and platinum metal was used as Co catalyst. Complete conversion at about 400 C was expected.

$$2NO + C \rightarrow N_2 + CO_2 \qquad (1)$$

b) With reducing agent such as H2, NH3, CH4 and CO. These reactions are favorable than the other processes. Many works have been done on this reduction over various solid catalysts such as noble metals, metal oxide and zeolites. In the presence of oxygen, however most of the reducing gases except ammonia are oxidized, almost the only reducing gas for NO which may be used in practice is NH3.

In general, a catalyst used in commercial plant must posses high activity and selectivity since the flue gas to be treated is extraordinarily large. In addition, low cost catalyst is required to develop an economical process. V2O5 is known as one of the best catalyst for this reaction, because it exhibits high activity and selectivity to form N2 and it is not easily poisoned by reactant gas containing SO2. It is also active even at low temperature so it consumes less fuel, at last it can be used for wide range of NOx (Takagi, 1977), (Tuenter, 1986)

Vanadium pentaoxide catalyst has selected in the present research to study its preparatory procedure from locally available materials (e.g.,

ammonium meta vanadate). The parameter affecting the preparation will be studied (the percentage content of active material, calcination temperature and time of calcination). The investigation will extend to account the physical and mechanical properties of the resulting catalysts besides activity.

EXPERIMENTAL WORK

Catalyst

It was prepared by impregnating silica gel with vanadyl oxalate (Tsutomu 1981), (Mellor 1960). The following figure show this part.
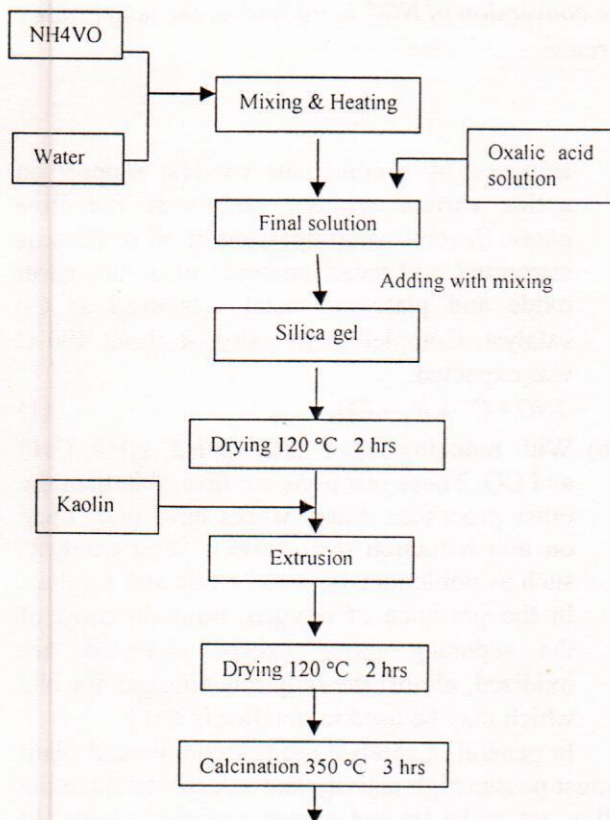

Fig (1) Flow diagram of laboratory manufacturing of vanadium pentoxide V$_2$O$_5$ catalyst.

Through this part of experimental investigation, the influences of weight percent of ammonium meta vanadate and calcination temperature on the physical and mechanical properties of the prepared catalyst were studied.

Characterization of the Prepared Catalyst

Characterization of the catalyst is necessary at every stage of its development. Critical parameters are measured not only to check the effectiveness of each operation but also to provide specification for future product. Preparational procedures can be properly assessed and corrections are made only if guidelines to the properties are available. The properties that were checked are:-

Apparent porosity

Apparent porosity was determined by liquid (water) impregnation method using the following equation (Alfred, 1959)

$$p_a = \frac{w_2 - w_1}{w_2 - w_3} * 100$$

Bulk density

Bulk density is the ratio of the weight of the catalyst particle to the bed volume occupied by the catalyst particle so bulk density is determined as follows (Alfred, 1959).

$$\rho = \frac{w_5 - w_4}{V}$$

Particle density

Particle density is the mass per unit volume here the volume is the sum of solid, closed pores, and accessible pores within the particles. Particle density was determined by liquid impregnation using the following equation (Alfred, 1959).

$$d_p = \frac{w_1 \rho_w}{w_2 - w_3}$$

Pore volume

Total volume of pores was measured by the increase in weight when pores were filled with liquid after impregnation (Satter field et. Al, 1980). The total pore volume was calculated as follows

$$V_p = \frac{w_2 - w_1}{\rho_w}$$

Crushing strength

Radial Cushing strength was measured by a device measure the force required to crush the particle.

BET Surface Area

BET surface area was determined on the basis of physical adsorption of an inert gas at constant temp of liquid nitrogen (Le Page, 1987). The surface area was measured according to this equation:

$$S.A = \frac{V_m}{22400} \times a_m \times N \times 10^{-20}$$

Activity

After catalyst has been prepared, its performance must be checked its reliability towards NO2 reduction. This was performed in a lab-scale apparatus. Activity is a key parameter in design, selection and optimization.

Figure (2) shows the reaction apparatus. The reactant gases (NO2) were supplied from the reaction of Cu with HNO3 while ammonia was supplied from its cylinder. The reactor is made of stainless steel of type 316 with inside diameter of 6.25cm and depth of 10cm. the volume of catalyst used was 200cm3. The reactor was heated with electrical heating tape controlled by an electronic thermo setter. Reaction conditions were as follows.:- 10000ppm NO2, excess ammonia with 240h-1 GHSV.
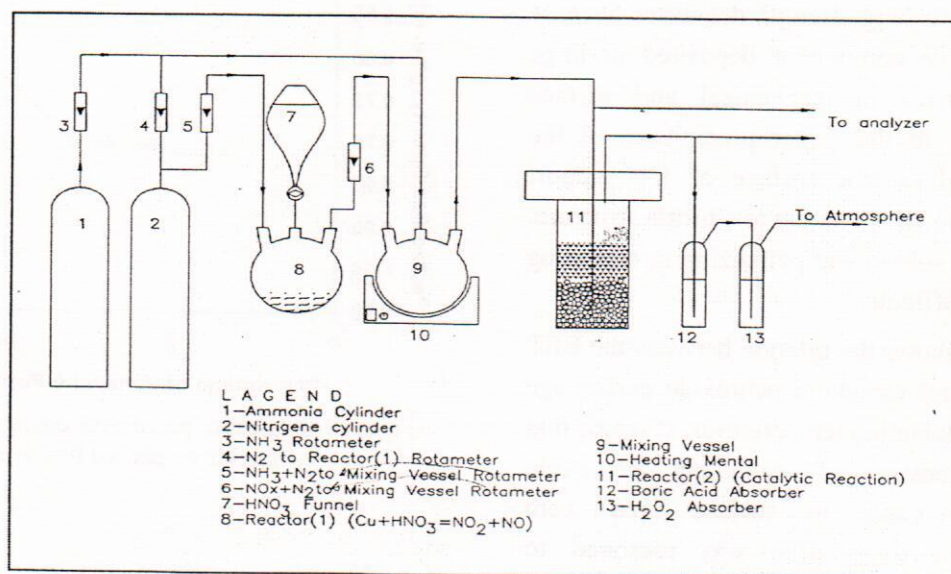

To analyzer

To Atmosphere

LAGEND
1—Ammonia Cylinder
2—Nitrigene cylinder
3—NH$_3$ Rotameter
4—N$_2$ to Reactor(1) Rotameter
5—NH$_3$+N$_2$ to Mixing Vessel Rotameter
6—NOx+N$_2$ to Mixing Vessel Rotameter
7—HNO$_3$ Funnel
8—Reactor(1) (Cu+HNO$_3$=NO$_2$+NO)
9—Mixing Vessel
10—Heating Mental
11—Reactor(2) (Catalytic Reaction)
12—Boric Acid Absorber
13—H$_2$O$_2$ Absorber

Fig. (2) Schematic diagram of the apparatus

RESULTS AND DISCUSSION

Affecting Parameters on Catalyst Characterizations

The effects of the content of active material on physical and mechanical properties were studied with respect to particle density, packed bed density, pore volume, crushing strength, loss on attrition and BET surface area. The effect of calcination temperature on BET surface area was also studied.

Figure (3) shows the effect of increasing the percentage of vanadium pentoxide on catalyst particle density, it shows an increasing attitude that as the percentage of vanadium pentoxide rises, the particle density of the catalyst rises.

The effect of increasing the percentage content of vanadium pentoxide of the resulting catalyst on packed bed density was also represented in Fig (4). It is clear that since the percentage of vanadium pentoxide increases, packed bed density increases due to the increase in particle density.

In Fig (5), the particle pore volume was related to the percentage content of vanadium pentoxide. It shows that as the percentage of vanadium pentoxide increases, the pore volume decreases. This was attributed to larger precipitates of the active component inside the pores of the resulted

catalyst and consequently smaller pore volume will ensue.

Figure (6) shows the relation between percentage content of vanadium pentoxide in regard to the crushing strength of the resulted catalyst. It seems that increasing the percentage content of the active material in the resulted catalyst will lead to higher crushing strength. Once again this was resulted from low pore volume of the generated catalyst that resulted from increasing the content of the active material. Furthermore, some may contribute to the higher interactions that might concur between the support material and the active material in the course of increasing the percentage content of ammonium meta vanadate. This currency of characterization was endured till percentage content of 8%. Beyond this, crushing strength decreases because when the active component deposited in large amounts, changes in mechanical and surface properties due to the larger precipitates of the active material on the surface of the support material may occur which led to a brittle structure. Consequently, subsequent pelletizing or extruding may become difficult.

Figure (7) shows the relation between the BET surface area and vanadium pentoxide percentage at different calcinating temperatures. It seems that as the percentage of vanadium pentoxide increases, decreases in surface area were expected. This expectation was reasoned to plugging the micro-pores of the support material by active material deposits. Same characterization was also examined through studying the effect of percentage content of the active material on pore volume of the prepared catalyst. Also wherein the temperature of calcination increases, the BET surface area decreases especially above 300°C where a series of phase changes may occur. But still at 350°C the magnitude of BET surface area is high even small amount of sintering may expected to occur.

From the above characteristic examination, a justification had been taken about where the suitable percentage content of vanadium pentoxide was well occurred at 8%.
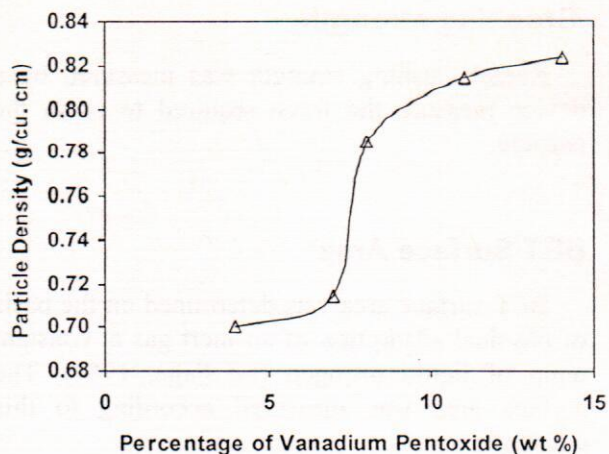
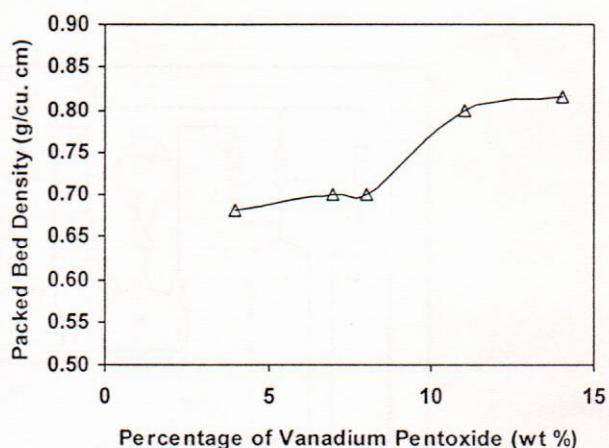Fig (3) The effect of percentage content of vanadium pentoxide on particle density.

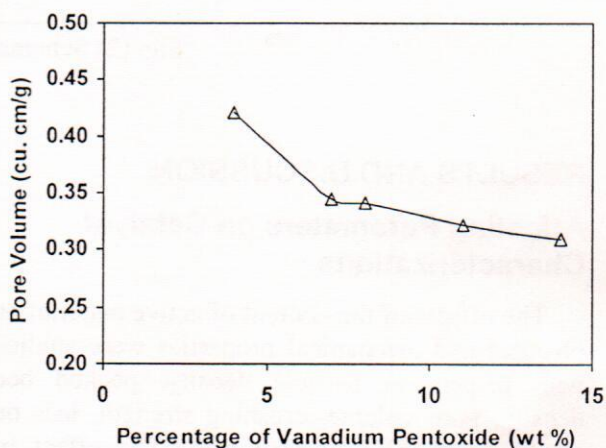Fig (4) The effect of percentage content of vanadium pentoxide on packed bed density.

Fig (5) The effect of percentage content of vanadium pentoxide on pore volume.
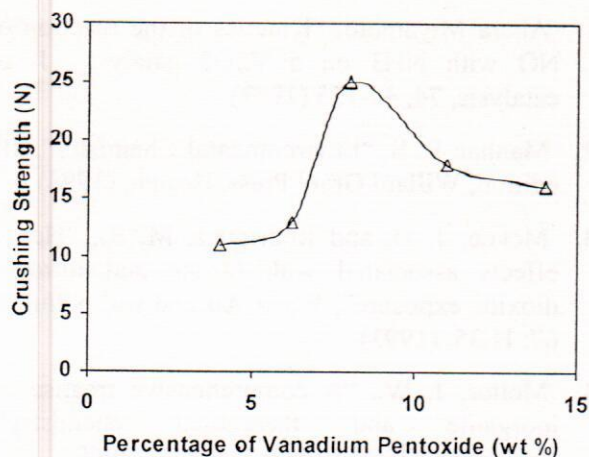
Fig (6) The effect of percentage content of vanadium pentoxide and calcination temperature on crushing strength.
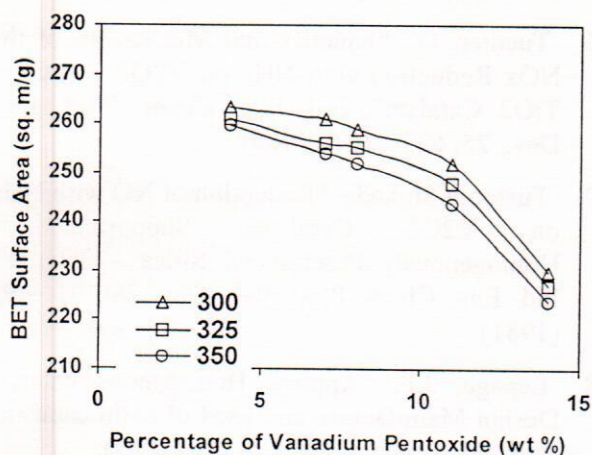

Fig (7) The effect of percentage content of vanadium pentoxide and calcination temperature on BET surface area.
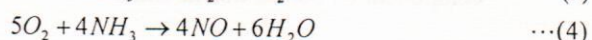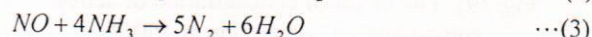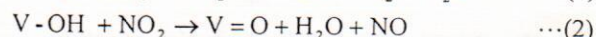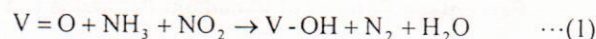
Activity test

Nitrogen dioxide NO_2 was chosen because of its majority among other oxides that emitted from nitric acid plant. The validity and reliability of the prepared catalyst was investigated through temperature range between 80 to 200°C, furthermore the examination was extended to consider the visibility of catalyst of the same type but with different active component contents.

Temperature dependence of the catalytic conversion of NO_2 over the prepared type catalysts in the presence of NH3 at different reaction temperatures between 80 and 200 °C was presented graphically in Fig (8). It can be seen that conversion of NO2 increases with increasing temperature. Lower reaction temperature of NO2

in comparison with reaction temperature for the reduction of NO only means that the activation energy of NO2 reduction is lower than that of NO reduction.

The catalyst was prepared with different concentration of active component. The activities of the prepared catalysts were compared at constant temperatures 150°C as shown in Fig (9).

Selective reaction of NO2 by NH3 on V2O5 catalyst may involve four reactions competing for the NH3 as shown below:

$$V = O + NH_3 + NO_2 \rightarrow V\text{-}OH + N_2 + H_2O \quad \cdots(1)$$
$$V\text{-}OH + NO_2 \rightarrow V = O + H_2O + NO \quad \cdots(2)$$
$$NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad \cdots(3)$$
$$5O_2 + 4NH_3 \rightarrow 4NO + 6H_2O \quad \cdots(4)$$

Reaction (1) and reaction (3) provides the desired conversion of NO_2 to N_2. Reaction (4) is undesirable, not only because it produces NO but also because it consumes NH_3. The results had also shown that the rate of NO_2-NH_3 reaction on V_2O_5 was markedly accelerated with increasing the temperature of the reaction. This acceleration has been found to be due to the mechanism shown in above equations. According to this mechanism, first, NO_2 and NH_3 react at the surface V=O site to form N_2, H_2O, and V-OH species. This will followed by reaction between the V-OH species and NO_2 to form V=O, H_2O and NO. Then, NO-NH_3 react at the surface V=O site to form N_2 and H_2O this in return followed by undesirable oxidation of NH_3 to form NO and H_2O. The significance of catalytic activity towards temperature had justified the significance of chemical reaction in comparison to the significance of pore diffusion control model. (Akera 1982).
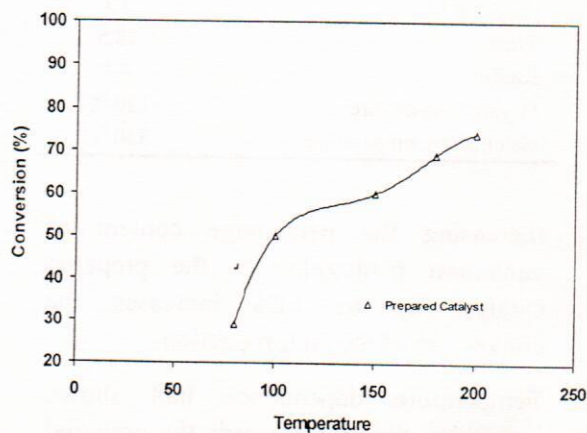

Fig (8) The effect of temperature on conversion of NO_2 over prepared catalyst
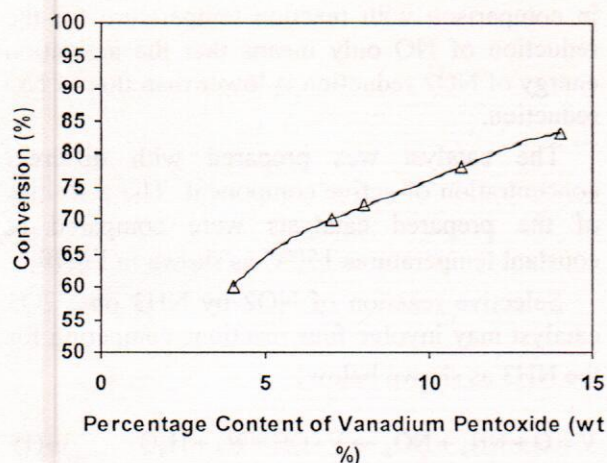
Fig. (9): The effect of concentration of active component on conversion at 150C°

CONCLUSIONS

1. The prepared catalyst with the percentage of active component (i.e., vanadium pentoxide) not more than 8% shows good mechanical and physical properties.

2. Vanadium pentoxide catalyst shows high reliability for the reduction of NO$_x$ even at high concentration (not less than 10000 ppm).

3. The recommended composition and preparatory conditions for ammonium meta vanadate catalyst type are:

Table (1) recommended composition

Composition and other preparatory conditions	Wt%
Silica gel	48
Ammonium meta vanadate	5.8
Oxalic acid	3.3
Water	38.5
Kaolin	4.4
Drying temperature	120 °C
Calcination temperature	350 °C

4. Increasing the percentage content of vanadium pentoxide for the prepared catalyst up to 14% increases the conversion of the NO$_x$ reduction.

5. Temperature dependence had shown increasing function towards the prepared catalyst.

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