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Synthesis and characterization of Ni/γ -Al₂O₃ nanocatalyst used in catalytic decomposition of hydrazine

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 $Ni/\gamma-Al_2O_3$ nanocatalyst was synthesized by incipient wetness impregnation method for using in the catalytic decomposition of hydrazine. To stabilize the catalyst, $\gamma-Al_2O_3$ support was precalcined which resulting 8% reduction in specific surface area. The catalyst was characterized by XRD, BET and TEM. The results showed that increasing the number of impregnation steps led to a reduction in size of nickel particles. In addition, the number of impregnation steps had a direct effect on strength of catalyst and could reduce the catalyst loss. TPR analysis showed that $Ni/\gamma-Al_2O_3$ nanocatalyst was reduced at about 700 °C.

Key words: Ni/y-Al₂O₃ nanocatalyst, Hydrazine decomposition, Ni particle size, Strength.

Introduction

Hydrazine (N_2H_4) , as a hydrogen-rich substance, has many usages like in PEM fuel cells, gas generators and space thrusters [1,2]. The products of hydrazine decomposition are hydrogen, nitrogen and ammonia. Hydrazine can be decomposed in the presence and/or absence of a catalyst. Usually catalytic decomposition of hydrazine is preferred because of low required initial heat and easy control of reaction progress [2]. Catalytic decomposition of hydrazine may occur in the following reactions:

$$3N_2H_4 \rightarrow N_2 + 4NH_3 \tag{1}$$

$$4NH_3 \rightarrow 2N_2 + 6H_2 \tag{2}$$

This reaction was studied by numerous authors. Metals such as Ir, Ru, Pt, Ag, Fe and Co were proposed for this purpose [2-6]. In 1996, Oyama reported that nitrides and carbides can be used as suitable cases for precious metal catalysts due to their platinum-like performance [7]. In 1997, hydrazine decomposition over molybdenum nitride and tungsten carbide catalysts was reported for the first time [8]. Also Chen et al. studied the hydrazine adsorption and decomposition over Mo_2N/γ -Al₂O₃ catalyst [9]. Application of ternary phosphides (NiCoP) was reported by Ding et al. in the reaction [10].

Shell 405 catalyst containing 30% w/w iridium on alumina represented a milestone to the usage of hydrazine (especially in satellite engines) [2, 11, 12]. However, iridium is very rare and expensive. Hence,

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catalysts. The transition metals of group VIIIB in periodic table (8, 9, and 10) are appropriate for many catalytic

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table (8, 9, and 10) are appropriate for many catalytic processes, especially for reactions involving hydrogen [6]. These metals over various supports can catalyze hydrazine decomposition with a high H₂ selectivity at low temperatures. In addition, some researchers suggested that metallic catalysts like Ni or bimetallic catalysts can be used to avoid using expensive Pt-group metals [13]. In this order, in spite of a great deal of research, there are few reports on the synthesis and use of Ni/γ-Al₂O₃ in catalytic decomposition of hydrazine [14, 15]. In the present study, the impregnation process with repeated steps was used for synthesis of Ni/y-Al₂O₃ catalyst. Results on preparation and characterization of Ni/ã-Al₂O₃ catalyst will be presented. Effects of the number of impregnation steps, pre-calcination of support on catalyst loss, catalyst strength and surface morphology will be studied in before and after reactor tests.

Experimental

Materials

Ni $(NO_3)_2.6H_2O$ (Sigma Aldrich Co.) as the nickel precursor and γ -Al₂O₃ in spherical shape (Sasol Co., South Africa) were purchased for synthesis of Ni/ã-Al₂O₃ nanocatalyst.

Synthesis of Ni/y-Al₂O₃ nanocatalyst

Ni γ -Al₂O₃ nanocatalysts were synthesized by repeated incipient wetness impregnations of γ -Al₂O₃ with aqueous solutions of Ni(NO₃)₂·6H₂O. This aqueous solution was prepared by dissolution of 0.495 g Ni(NO₃)₂·6H₂O in redistilled water at room temperature. The slurry was continuously stirred and evaporated at 70 °C by placing the solution beaker into a vacuum rotary evaporator

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until the water was completely removed. The impregnated solid samples were dried at 110 °C for 16 hrs and then calcinated at 500 °C for 6 h. This process was repeated as many times as necessary (three, six and nine steps) to achieve the value of metallic oxide loadings close to 30 wt%.

In order to study the effect of γ -Al₂O₃ pre-calcination on the catalyst loss, the supports were calcinated at 600 °C for 6 hrs. These samples were characterized and used in impregnation process.

Characterization of prepared catalyst

The phase purity and particle size of the samples were determined by powder X-ray diffraction (XRD) using Cu-K α radiation source (0.15432 nm), operating at 40 kV and 30 mA (Philips, model PW 1800). The specific surface area of the samples was measured by the N₂ adsorption apparatus (Covantocrom-model: NOVA 2000, USA).

The reduction of nickel catalyst was analyzed by temperature-programmed reduction (TPR). This analysis was performed in a Micrometric TPD/TPR 2900 instrument (Micromeritiocs, model TPD/TPR 2900) with 0.0752 g of the catalysts from temperature 25 °C to 750 °C, at a rate of 10 °C.min¹ in H₂/Ar gas flow (5 : 95 vol/vol mixture with a total flow rate of 40 Ncc/min). Transmission electron microscopy (TEM) (Philips, model 208 EM) was applied for the detailed microstructure information. The TEM samples were prepared by deposition of a few droplets of nanoparticle suspension over the film grids coated by the amorphous carbon, which were then dried under air atmosphere.

Reactor test

The Ni/ γ -Al₂O₃ catalytic reactor was made of quartz tube with 1 cm internal diameter. Ni/ γ -Al₂O₃ sphericalshaped catalyst was poured into the reactor so that the height of the catalytic bed was 0.5 cm. When the catalyst reached 500 °C, it was reduced by hydrogen gas with a 60 ml/min flow rate. After that, the reactor was allowed to cool down to 100 °C. Then, several drops of liquid hydrazine were passed through the Ni/ γ -Al₂O₃ catalytic reactor. After the test, the catalyst was withdrawn and analyzed.

Results and Discussion

Precalcination of γ -Al₂O₃ support

Hydrazine decomposition is a highly exothermic reaction. In addition, during the synthesis of Ni/ γ -Al₂O₃ catalyst, Ni/ γ -Al₂O₃ reduction needs to be heated and thus, γ -Al₂O₃ may be sintered. To minimize this effect, γ -Al₂O₃ should be stabilized. One way to meet this purpose is pre-calcination of the support.

Calcination of Ni/ γ -Al₂O₃ catalyst is usually carried out about 450 [16]. In our work, this was carried out at 500 °C. To maintain the support in gamma phase,

 Table 1. Textural properties of support with and without precalcination.

Sample			S_{BET} (m ² /g)		
γ-Al ₂ O ₃ (without pre-calcination))	187		
Pre-calcinated support $(\gamma - Al_2O_3)$			172		
2500 2000 1500 1000 500 0	$ \begin{array}{c} N = Nickel Oxide \\ A = \gamma - AI_2O_3 \\ \hline \\ b \\ a \\ 0 \\ 20 \end{array} $	N A A A 40 20 (N N N N N N S0	100

Fig. 1. XRD pattern for Ni/ γ -Al₂O₃ catalyst before the reactor test: a) γ -Al₂O₃; b) Ni/ γ -Al₂O₃ prepared in three steps; c) Ni/ γ -Al₂O₃ prepared in nine steps.

Table 2. Particle size of two different Ni/ γ -Al₂O₃ nanocatalysts.

Sampla	Particle size (nm)			
Sample	Before test	After test		
three steps Ni/γ-Al ₂ O ₃ catalyst	18.19	22.25		
nine steps Ni/ γ-Al ₂ O ₃ catalyst	11.92	15.53		

precalcination of γ -Al₂O₃ was performed at 600 °C. Specific surface areas of the support with and without precalcination are given in Table 1.

It is clear that precalcination of γ -Al₂O₃ at 600 °C reduces the surface area about 8%. Definitely, lower loss of catalysts was observed when pre-calcinated catalysts were used. BET analysis indicates that pre-calcination of support leads to reduction in surface area from 187 m²/g to 172 m²/g. It is due to partial sintering of support exposed to high temperatures. Also, as it will be given later, there is lower catalyst weight loss in precalcinated support than supports without pre-calcination. It seems that the stability in the support morphology and low change in the surface area during the reduction process and reactor test causes low catalyst loss. In similar works, this phenomenon was observed [17-20].

XRD analysis

XRD patterns for Ni/ γ -Al₂O₃ catalysts before and after the reactor tests are given in Fig. 1 and Fig. 2, respectively. The nickel appears at angles of 37.33 °, 43.25 °, 62.94 °, 75.35 ° and 79.37 °. The sign peak for Ni is 43.25 °. The average size of nanoparticles was

calculated using Debye-Scherrer's formula. The particle size of different Ni/ γ -Al₂O₃catalysts is given in Table 2. In XRD patterns, the sharper pick means the larger particle size. It is clear that more steps in impregnation of nickel catalyst cause more reduction in particle size. Comparative study of the results indicated that nine steps Ni/ γ -Al₂O₃ catalyst showed more successful activity than three steps Ni/ γ -Al₂O₃ catalyst.

TEM analysis

TEM image of the Ni/ γ -Al₂O₃ nanocatalyst (Fig. 3) reveals the presence of irregularly shaped nanoparticles with partial aggregation of nanoparticles. Mean particle size of nickel was calculated by microstructure measurement software. In this catalyst, it is about 8.54 nm. Also Fig. 4 shows the TEM image of nine steps Ni/ γ -Al₂O₃ catalyst before the reactor test. In this catalyst, the mean particle size of nickel is about 3.86 nm. There is a clear difference between mean particle size of three- and nine- steps Ni/ γ -Al₂O₃ catalysts. More impregnation steps cause smaller particle size of Ni on the support surface.



Fig. 2. XRD pattern of Ni/ γ -Al₂O₃ after the reactor test: a) γ -Al₂O₃; b) Ni/ γ -Al₂O₃ prepared in three steps; c) Ni/ γ -Al₂O₃ prepared in nine steps.



Fig. 3. TEM image of three steps $Ni/\gamma\text{-}Al_2O_3$ catalyst before reactor test.



Fig. 4. TEM image of nine steps Ni/γ -Al₂O₃ catalyst before reactor test.



Fig. 5. Three steps Ni/γ -Al₂O₃ catalyst. A: before reactor test; B: After reactor test.



Fig. 6. Six steps Ni/γ -Al₂O₃ catalyst. A: before reactor test; B: After reactor test.



Fig. 7. Nine steps Ni/γ -Al₂O₃ catalyst. A: before reactor test; B: After reactor test.

It may happen because of a reduction in nickel concentration [21].

By comparing Fig. 3 and Fig. 4, it is observed a better dispersion for particles in nine steps catalyst than three- steps catalyst. TEM analysis validates the relationship between the number of impregnation steps and crystal size of Ni obtained in XRD analysis.



Fig. 8. TPR profile for Ni/γ-Al₂O₃ catalyst with 30 wt% loading.

Catalyst strength

The effect of the number of impregnation steps on strength of the different catalysts is presented in figures 5-7. It is shown that nine- step catalysts have the highest strength in hydrazine decomposition reaction and subsequently represent lower loss. Approximately, all of the three- step catalysts were crushed and loosed during reactor test. Around 67.5% loss was observed in six -step catalysts. This loss was about 25% in nine-step catalyst. More impregnation steps and therefore more reduction in particle size led to more catalyst strength. It may be that the smaller Ni particles were located inside the pores or channels of the support and the strong nickel-support interaction. This phenomenon was observed in a similar work by Wang et al. [22].

TPR profile

The reduction process for Ni/ γ -Al₂O₃was performed during about 80 minutes. The TPR profile for the Ni/ γ -Al₂O₃ catalyst is shown in . A pick at about 580 °C and a valley at 697 °C in TPR profile may be related to two different phases on the account of physical and chemical bonds between Ni and γ -Al₂O₃, respectively. The chemical bond is stronger than the physical bond. Therefore, the reduction of the physical bond is easier than the chemical bond. Based on the consumed hydrogen in TPR process, it seems that NiO₂ is converted to NiO and subsequently to Ni.

Conclusions

 Ni/γ -Al₂O₃, as a cheaper and proper catalyst in decomposition of hydrazine in some applications, was synthesized by the several steps incipient wetness impregnation method. To stabilize the support, γ -Al₂O₃ was precalcinated at 600 °C in which 8% reduction in

BET area was observed. Increasing the number of impregnation steps led to a more reduction in Ni particle size and strength of catalyst. TPR diagram demonstrated that Ni/ γ -Al₂O₃ was finally reduced at about 700 °C to become ready for hydrazine decomposition.

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