Comparison of Catalytic Behavior of Iridium and Nickel Nanocatalysts for Decomposition of Hydrazine

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Abstract

Hydrazine is a useful material in many industries. In many cases, the applications of hydrazine depending on use a suitable catalyst. In the present study, iridium and nickel nanocatalysts on gamma alumina have been synthesized by the impregnation method. The prepared nanocatalysts have been identified using specific surface measurement (BET) and X-ray diffraction (XRD). The catalytic mechanism was also briefly discussed. The catalytic activity was evaluated for hydrazine decomposition in a designed setup at ambient temperature and the products were detected by gas chromatograph. The main goal of this work is prepare, characterize, and comprise the nanocatalytic behaviour of iridium and nickel supported on gamma alumina in decomposition of hydrazine process. The results of this study show that the mechanisms of hydrazine decomposition on Ir and Ni nanocatalysts are different, while hydrazine decomposition leads to NH₃+N₂ on Ir surfaces at ambient temperature, N₂H₄→N₂+H₂ pathway is more favourable at Ni surface. The results indicate that at low temperature hydrazine decomposition on Ir first yields NH₃ and N₂, whereas on Ni nanocatalyst, H₂ selectivity can reach more than 90% at low temperature. Regarding to our data, we can proposed Ir/γ-Al₂O₃ and Ni/γ-Al₂O₃ nanocatalysts for application in monopropellant systems and fuel cells respectively.

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Keywords: Catalytic behavior, Ir/γ-Al₂O₃ nanocatalyst, Ni/γ-Al₂O₃ nanocatalyst, Decomposition of hydrazine, PEM fuel cell, monopropellant.

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1. Introduction

Hydrazine is a strong reducing agent used as oxygen scavenger for corrosion control in boilers and hot-water heating systems. It is also employed as starting material for many derivatives such as foaming agent for plastics, antioxidants, polymers, pesticides, plant-growth regulators and pharmaceuticals, Schmidt (2001). In many cases, the applications of hydrazine depending on use a suitable catalyst. For example, the applications of hydrazine in monopropellant system of satellites as well as proton exchange membrane (PEM) fuel cells have been achieved with the availability of catalysts that initiate hydrazine decomposition. Hydrazine is used as a monopropellant fuel in liquid rocket systems with the great advantage of elimination of oxidizer. The applications of monopropellant hydrazine in propulsion system of rockets and satellites have been achieved with the availability of catalysts that spontaneously and reproducibly initiate hydrazine decomposition. Hydrazine will decompose with the release of heat and energy in a controlled manner when it comes in contact with catalyst and can be used for operation of altitude control jets for rockets and spacecraft, Janjua et al. (2014). The best specific impulse is attained when little ammonia is allowed to dissociate, Sutton & Biblarz (2001).

In PEM fuel cells is highly desirable to develop a technology for the production of CO-free hydrogen. Since hydrazine is hydrogen-rich and with high energy content and its decomposition is an exothermic reaction and does not need any energy to be provided from outside, so is a good substance to produce CO-free hydrogen, Pakdehi & Rasoolzadeh (2015). The main difference between application of hydrazine in monopropellant systems and PEM fuel cells is the performance of the catalyst. Fuel cells have been required pure hydrogen to work while the specific impulse of monopropellant has been direct relation with reduced amount of produced hydrogen (increased amount of ammonia), Sutton & Biblarz (2001).

Generally, there are two typical reaction routes for hydrazine decomposition:

$$3N_2H_4 (l) \rightarrow 4NH_3 (g) + N_2 (g)$$  \hspace{1cm} (1)

$$N_2H_4 (l) \rightarrow N_2 (g) + 2H_2 (g)$$  \hspace{1cm} (2)

Hydrazine decomposition does not follow the fixed stoichiometry and can be effected by catalyst, temperature, and pressure (S. Pakdehi, Salimi, & Rasoolzadeh, 2014).

The catalyst bed output at any point in time is given by the equation:

$$3N_2H_4 \rightarrow 4(1-x)NH_3 + (1+2x)N_2 + 6xH_2$$  \hspace{1cm} (3)

Where x is the ammonia dissociation fraction. The amount of ammonia remaining in the exit stream of the reactor is used as a measure of the monopropellant efficiency.

The majority of the catalysts used for hydrazine decomposition are supported catalysts. The supported metal catalysts have many advantages: (1) depositing a very small amount of active metal on inert support; (2) uniform distribution of active metal without any problem of sintering; (3) penetration of fuel deep inside the pores; (4) continuation of catalytic reaction even after the heavy metal erode off from exterior surface on successive firings; (5) easy recovery of precious metal and recycling of catalysts, Armstrong et al. (1978 and 1980), Jang et al. (2012). For this purpose, active metal nanoparticles are deposited on the surface of solid support (e.g., alumina, clays, polymers and zeolites) to form heterogeneous catalysts, Zhong (2007). Al₂O₃ is the most commonly used catalytic support because of its high surface area to volume ratio, great porosity and uniform pore size distribution besides the thermal, chemical, and mechanical stability, Karim et al. (2011).

Mostly, impregnation method is adopted for preparation of supported nanocatalysts during which the support is immersed into an aqueous or non-aqueous solution of a metal salt followed by solvent evaporation and metal reduction in hydrogen atmosphere, Janjua et al. (2014). The impregnation is repeated several times to obtain the desired metal content.

The selection of active metals for hydrazine decomposition catalysts has been jokingly described as a "black art." This is very appropriate since most of the catalysts are black in appearance. The entire periodic table of elements has been scanned in search of the optimum active metal. In this paper, we have been synthesis and investigate some catalysts to decompose hydrazine and with attention of products choose the application.

This paper describes the program of laboratory tests which have been carried out to investigate suitable catalysts for decomposition of hydrazine.

In surveying various metals that catalyze hydrazine decomposition Eberstein and Glassman noted that transition metals having incomplete d sub shells act as strong catalysts for hydrazine decomposition, whereas metals having no...
d sub shells or completely filled d shells are not catalytic. With this description, almost the Group VIII nanomaterials are catalytically active in hydrazine decomposition. Although all the Group VIII nanomaterials are catalytically active in various reactions, Literature reviews of the paper show that Iridium combines reasonable activity and high thermal stability. On the other hand, nickel is the favored nanocatalyst for many reactions by virtue of its life, high activity, and it's comparatively low cost.

2. Experimental

2.1. Catalyst preparation

Nanocatalyst samples were in the form of 1/8 inch pellets. Metal nanocatalysts Ni/Al₂O₃ (15.0 wt %) and Ir/Al₂O₃ (15.0 wt %), were prepared and tested in this work. The nanocatalysts were prepared by repeated impregnations of the Al₂O₃ support with aqueous solutions of Ni(NO₃)₂•6H₂O and H₂IrCl₆•6H₂O. After drying at 393 K for 12 h, the Ni/Al₂O₃ and Ir/Al₂O₃ were calcined in air at 823 K and 723 K for 2 h respectively, followed by reduction in pure H₂ for 2 h. The reduction temperatures were 723 K for Ir/Al₂O₃ and 823 K for Ni/Al₂O₃.

2.2. Catalyst characterization

The measurement of solids specific surface area was determined by N₂ adsorption at 77.3K and 1 atm, preceding the adsorption measurements, the catalysts were degassed at 673 K for 2 h, under vacuum. BET analyses of the prepared samples were recorded using Nova Station A instrument.

XRD measurements were performed with 2θ values between 10 and 85° by using a Riguku D/Max-RB diffractometer employing the graphite filtered Cu Kα radiation.

2.3. Test of catalytic activity

The experimental device used for the evaluation of the catalyst performance in the reaction of hydrazine decomposition, is illustrated in Fig. 1.

In our work the hydrazine decomposition reaction was performed in a fixed-bed continuous-flow reactor at atmospheric pressure. 1 gram of catalysts (20–40 meshes) was placed in reactor. The products N₂, H₂, and NH₃, as well as any remaining N₂H₄, were detected by an off-line gas chromatograph (Agilent 6890A with 13X and Chromossorb 103 columns) equipped with a TCD detector. The setup has been employed for hydrazine decomposition is shown in Fig. 1.

![Fig. 1. Set up for testing.](image-url)
3. Result and discussion

3.1. Characterization of the supports and catalysts

Table 1 presents composition of catalysts, their BET specific surface area, and particle size measured by XRD. Fig. 2 and 3 show the XRD of the $\gamma$-Al$_2$O$_3$ support, Ir, and Ni nanocatalysts. The average crystallite sizes ($d_{\text{XRD}}$) of Ir and Ni nanocatalysts were calculated using Debye Scherrer formula and results are presented in Table 1.

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>BET surface area ($\text{m}^2 \text{ g}^{-1}$)</th>
<th>Particle size measured by XRD (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$</td>
<td>172</td>
<td>5.9</td>
</tr>
<tr>
<td>Ir/ $\gamma$-Al$_2$O$_3$</td>
<td>152</td>
<td>6.8</td>
</tr>
<tr>
<td>Ni/ $\gamma$-Al$_2$O$_3$</td>
<td>163</td>
<td>6</td>
</tr>
</tbody>
</table>

Figures 2 show the XRD diffractograms of the $\gamma$-alumina support, Ni, and Ir nanocatalysts. The significant peaks at 37°, 46° and an intense peak at 67° clearly indicated the formation of single phase crystalline $\gamma$-Al$_2$O$_3$ nanoparticles as depicted in Fig. 2(I).

![Fig. 2. (A) XRD patterns of I) $\gamma$-Al$_2$O$_3$ support and II) Ni/ $\gamma$-Al$_2$O$_3$ nanocatalyst](image)

![Fig. 2. (B) XRD patterns of I) $\gamma$-Al$_2$O$_3$ support and II) Ir/ $\gamma$-Al$_2$O$_3$ nanocatalyst.](image)

3.2. Catalytic activity test

The decomposition of hydrazine on Ir/ $\gamma$-Al$_2$O$_3$ nanocatalyst at 373K result in almost 100% nitrogen as the permanent gas product and for each molecule of hydrazine decomposed 1.33 molecules of ammonia are produced. These results indicate that the overall reaction may be represented by reaction 1 above, reaction 2 occur to a small extent to produce the trace of hydrazine found.

Regarding to these results, following scheme is proposed for the decomposition on Ir/ $\gamma$-Al$_2$O$_3$ nanocatalyst.

The hydrazine molecule exists in the gauche form and as such may be adsorbed on the surface through the two lone pairs of electrons. Hydrazine molecule in solution may then approach the adsorbed molecule and abstract two hydrogen atoms to form two ammonia molecules and leave diimide on the surface, Ping-Xia Zhang et al. (2011), Schmidt and Gordon (2013). From stereochemistry considerations it seems likely that the adsorbed diimide exists in the cis form due to the abstraction of two cis hydrogen atoms by the solution hydrazine molecule. The cis- diimide
may then decompose by either of the mechanisms, one involves an adjacent diimide molecule which rearrange with bonds breaking and reforming to produce nitrogen, which is desorbed and one molecule of hydrazine which remains adsorbed on the surface. The desorption of nitrogen leaves a vacancy to be filled by another hydrazine molecule on adsorption the second mechanism for the decomposition of diimide involves diimide adsorbed on the surface, in a position, such as at a dislocation on the edge of a metal crystallite, where it has no adjacent diimide molecule to react with, and in this case the diimide molecule decomposed directly to nitrogen and hydrogen.

The change from iridium to nickel as the active component results in hydrogen being formed as major product while the nitrogen molecule is still formed having both atoms derived from one hydrazine molecule.

The decomposition of hydrazine on Ni/γ-Al₂O₃ nanocatalyst at 373K results in a permanent gas of approximately equal parts of hydrogen and nitrogen and not ammonia is produced. These results show that N₂H₄→N₂ +H₂ pathway is more favorable at Ni surface. It is worth mentioning that while hydrazine decomposition leads to NH₃+N₂ on Ir surfaces, N₂H₄→N₂ +H₂ pathway is more favorable at Ni surface. Our data show that the H₂ selectivity can reach more than 90% at 323 K on Ni/γ-Al₂O₃ catalyst for hydrazine decomposition.

4. conclusion

All of the results we have discussed so far lead us to conclude that at low temperature hydrazine decomposition on Ir first yields NH₃ and N₂, while at higher temperature H₂ is also formed. For the whole process of hydrazine decomposition on Ir, the most favorable mechanism is that NH₂ radicals firstly interact with the hydrogen atoms of the adsorbed N₂H₄ molecule and subsequent fragments N₂Hₓ (x = 1-3), leading to formation of NH₃ and N₂. As temperature elevating, the produced NH₂ will further decompose to produce H₂. When the temperature is high enough, all NH₃ is decomposed, leading to N₂ and H₂ as the only products.

Regarding to these results, although that some conditions such as temperature and pressure is important in decomposition of hydrazine, but Ni/γ-Al₂O₃ is proportionate nanocatalyst for PEM fuel cells to produce pure hydrogen at low temperature, while that Ir/γ-Al₂O₃ nanocatalyst is suitable for monopropellant to attain high specific impulse.

References