

Green hydrogen from catalytic ammonia decomposition

Oscar A. Anunziata*, Juliana M. Juárez, Marcos B. Gómez Costa
Centro de Investigación en Nanociencia y Nanotecnología (NANOTEC).
Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro
López y Cruz Roja Argentina, 5016, Córdoba, Argentina

Abstract

Ir/ γ -alumina catalysts for decomposition of ammonia were prepared by Iridium ion exchange procedure, onto γ -alumina synthesized by sol-gel method. In order to determine the physical and chemical properties we used X ray diffraction (XRD) analysis, Fourier transformed infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nuclear magnetic resonance (NMR-MAS). The samples displayed the characteristic band at 1620 cm^{-1} corresponds to a N-H bending of ammonia adsorbed on electron-acceptor sites, and the characterization by pyridine adsorption and desorption to determine the presence of Lewis acid sites, with absence of Brønsted sites, showing higher acid strength than commercial sample used as reference. The analysis of particle size and morphology reveal uniformity, with tendency to a spheroid aspect and smaller to $3\text{ }\mu\text{m}$ of diameter. The ^{27}Al NMR-MAS test, allowed determining the tetrahedral and octahedral aluminum presence in both samples, where the higher proportion of octahedral Al in γ -alumina synthesized by us, is correlated toward the greater electron acceptor acid sites. The designed method was effective for Ir/ γ -alumina catalysts synthesis. The surface area was 150 and 260 m^2/g for the commercial sample and the alumina prepared by and us, and after the Ir incorporation (10-18% w/w in both samples), they surfaces were reduced approximately 5.4-8.8% and 4.3-7.2% respectively. XRD analyses show the absence of maximums at 28° and 34.7° 2θ corresponding to iridium oxide, indicating a high efficiency of the reduction treatment, increasing the active sites for the specific reaction of ammonia decomposition. The distribution of the Ir crystallites determined by XRD and TEM indicated that, the samples prepared by ion exchange method produced smaller Iridium clusters than by impregnation procedure of alumina sample, with higher surface area and greater anchorage sites. According to preliminary catalytic tests, the Ir/ γ -alumina catalysts prepared by a novel method showed higher activity to ammonia decomposition to N_2 and green H_2 .

Keywords: Ir/ γ -alumina; Synthesis; Characterization; Ammonia Decomposition, Green H_2

*Corresponding author: +54-351-4690585, oanunziata@frc.utn.edu.ar

1. Introduction

There is a reason that hydrogen is dubbed “the future of energy”. Unlocking the potential of hydrogen as a fuel source is one of the main objectives needed to achieve a low-carbon economy. Green hydrogen (H₂) is produced via electrolysis, utilizing renewable electricity (wind, solar, etc.) and water. The concept of green hydrogen is creating exciting opportunities for the world of energy:

Hydrogen will assist with tackling critical energy challenges by helping to decarbonize the metal, chemical and long haul transportation industries. Hydrogen can help renewable energy have a greater impact by acting as a storage vehicle, providing long-term options for utilizing low cost renewable energy later. Hydrogen is a versatile fuel that can be easily transported through its adsorption stored in porous solids already described (1-5), over long distances, making it applicable and available to multiple industries. A few examples of hydrogen applications are powering fuel cell vehicles (FCEV's), fueling natural gas turbines, heat generation and many more.

Hydrogen carrier candidates, ammonia is unique in that the non-hydrogen part of the ammonia molecule (i.e., the nitrogen) has no carbon and, very importantly, does not need to be directly recovered and recycled after the dehydrogenation step (to release hydrogen). The nitrogen originally comes from the atmosphere (of which it makes up 79%) and is returned to the atmosphere after the hydrogen has been extracted. So, providing the ammonia is generated renewably in the first place (from renewable hydrogen), there is no need for any of the above specified carrier “recycling” processes for ammonia to be a truly zero-carbon hydrogen carrier. Moreover, the process of production of ammonia with nitrogen taken from the atmosphere is highly efficient and far easier than taking carbon from the atmosphere by any route.

Liquid ammonia has several key merits, including its high hydrogen content (18% by mass), ease of liquefaction and similar physical properties to LPG providing an opportunity to use existing storage, transport and terminal equipment. Ammonia also has a long history of large-scale, cost optimized industrial production and its global use as a fertilizer, chemical raw material and refrigerant. As well, liquid ammonia is already transported over large distances with good economics.

Whilst there are many studies devoted to estimating the cost of H₂ (for transport and heat decarbonisation) produced via renewable electrolysis, there has been little work

done on estimating the cost of renewably produced ammonia (via H₂ production by electrolysis) for use as a carbon free “carrier” for storage and for transport of large quantities of hydrogen over large distances. The few recent publications in this area have largely been concerned with the use of said “green ammonia” in sustainable production of basic chemicals and fertilizers.

Considering the above, we report here for the first time, a catalytic process based on mesoporous Alumina containing Ir, with great effectiveness and selectivity to the production of green H₂ and N₂ from Ammonia.

2. Experimental

-Preparation of Ir/ γ -Al₂O₃ catalysts

-Iridium hexachloride was used as Iridium source. The Ir-sample was prepared using alumina (sample AT), by wetness impregnation with the Iridium source in water, mixing and aging for 12 h. The Ir content in the sample was 10 and 18% w/w (denoted as sample SATCl1 and SATCl2) respectively.

- γ -Al₂O₃ developed in our laboratory using Iridium Acetylacetonate (99.9% Ir(Acac)₃) as source of Ir. The ion exchange procedure was repeated three and five times to reach 10.1% and 18.2% w/w (samples SASUAc1 and SASUAc2) of Ir content, similar to the sample prepared by wetness impregnation.

- γ -Al₂O₃ prepared by us (sample ASU) with incorporation of Ir by the same procedure using for the ASU but employing Iridium hexachloride . The Ir content in this sample was 18.3% w/w, and was denoted as SASUAc2.

- Commercial γ -Al₂O₃ (sample AT), obtained by ion exchange with acetylacetonate as Ir source. The Ir content in this sample was 18.3% w/w, and was denoted as SATAc2.

-Post-treatments

Samples SATCl1, SATCl2 and SASUAc2: Thermal programmed desorption in inert atmosphere: under 20 ml/min N₂ flow, the temperature was increased from 25 °C to 200 °C at 10°C/min, maintaining this temperature for 5h. Then the temperature was increased for a second time, at 10 °C/min from 200 to 470 °C, maintaining this temperature for 5-7 h. Hydrogen temperature programmed reduction: due to iridium is active for the reaction in its metallic state; it was reduced in H₂ flow of 20 ml/min,

using the same temperature program describe when we applied TPD under inert atmosphere.

Samples SASUAc1, SASUAc2 and SATAc2:

Thermal programmed desorption under inert atmosphere: the temperature increased from 25 to 200 °C with a ramp of 10°C/min, and then temperature was increased again at 10 °C/min from 200 °C to 500 °C, maintaining this temperature by 5 h under 20 ml/min N₂ flow. Calcination: with the objective to remove a few coke formed in the last step, the sample was heat up in air at 500 °C during 2 h.

Hydrogen temperature programmed reduction: the same procedure employed for samples prepared by impregnation was fitting.

SATAc22H: A second thermal programmed reduction with H₂ was made to Sample B, applying the same procedure in order to determine the efficiency of the reduction of Ir in the catalyst.

Catalytic ammonia decomposition was performed in a continuous-flow quartz reactor with pure ammonia gas (purity >99.9%), under atmospheric pressure (gas flow rate=50 ml/min, GHSVNH₃: 15L. g⁻¹. h⁻¹), in the temperature range of 200-900 °C. Product analyses were performed on a gas chromatograph (Hewlett Packard), using Ar as carrier gas and Poropak Q column, equipped with TCD detector. NH₃ conversion in a blank reactor was <0.5% at 500°C.

3. Results and Discussion

A. Characterization

Considering that the results presented here are being protected, we report only the critical results to understand their catalytic activity.

The support has a high crystallinity and a size and shape of particles similar to a reference commercial sample. The synthesis method allowed increasing to the proportion of octahedral aluminum respect to the commercial catalyst and having greater superficial area to obtain higher metal loading with better dispersion. Respect to the acidity, it has not terminal OH groups, agreeing with the study of pyridine adsorption, where we have not found the characteristic bands of Brønsted acid sites.

On the other hand, the obtained sample has a slightly higher amount of Lewis acid sites, with superior acid strength than the reference sample. This feature can be ascribed to the greater proportion of AlVI determined in γ -alumina sample ASU. The partial charge analysis obtained by Sanderson method, confirmed the location of the bands to AlVI and AlIV, indicating that the greater positive loading density on the AlVI constitutes in a Lewis site with superior acid strength.

Thus, alumina was synthesized with excellent textural properties, and nature and amount of sites for anchoring metallic Iridium.

The smaller dimensions of NH₃ molecules, allow accessing to smaller pores than it were inaccessible for pyridine molecule. The sites found through FTIR with NH₃ are Brønsted and Lewis sites, represented by the bands at 1470 cm⁻¹ and 1620 cm⁻¹, respectively.

The NH₃ adsorption is weaker than the pyridine adsorption on Lewis acid sites, of γ -alumina, because the NH₃ desorbs completely at 250 °C whereas the pyridine is retained up 400 °C, although the maximum of desorption temperature is verified at 250 °C. The support has not adsorbed Ammonia irreversibly at analyzed temperatures; this topic is very important because it increments the free active sites, increasing the activity of the support to anchor the metal.

The ion exchange method to incorporate Iridium onto γ -Al₂O₃ support is considered efficient. This simple and effective nanoparticle loading method, permit a highly dispersed incorporation of the metal nanoparticles in alumina synthesized by us, as were demonstrated by XRD and TEM studies. Compared to the more conventional impregnation method, it produces a higher metal dispersion allowing for high metal contents, and the loading is not limited to the external surface of the support due to its smaller crystal size.

B- Catalytic testing

NH₃ decomposition activity over γ -Al₂O₃ (AT and ASU) and Ir/ γ -Al₂O₃, indicating the reaction temperature needs for initial ammonia decomposition (>2% w/w), middle conversion level (50%) and highest conversion level (100% for Ir-samples and 80% for Alumina), as a function of the mean crystals size of metallic iridium in different samples. In the figure, we also show the effect of Ir content and the nature of the support.

The initial reaction temperature of ammonia thermal decomposition is 680 °C and NH₃ cannot decompose entirely even at 900 °C, (not showed). However, the initial decomposition temperature of ammonia over Al₂O₃ has not been changed as compared to thermal decomposition, slightly higher NH₃ conversion exists over γ -Al₂O₃ at the reaction temperature region. This implies that γ -Al₂O₃ exhibits certain ammonia decomposition activity. According to the data, the sample that has higher surface area, reaches to higher conversion levels at same reaction temperature. It is worthwhile to note that the initial decomposition temperature of NH₃ is decreased greatly and NH₃ conversions are increased significantly when iridium is introduced into Al₂O₃. These results imply that iridium sites are active center for NH₃ decomposition reaction. Furthermore, NH₃ conversions on Ir/Al₂O₃ samples, is slightly higher at lower temperature for the sample with higher Ir content (even just by a little greater size of metallic iridium crystal, sample SASUAc2), sustaining that better iridium loadings and higher content, on better support is beneficial to the NH₃ decomposition. From the results indicated above, one can see that higher surface areas of catalysts are beneficial to mass transfer of reactants and products in the gas reaction. The metal dispersion of heterogeneous catalysts is an important factor influencing the catalytic performance of catalysts (figure 1).

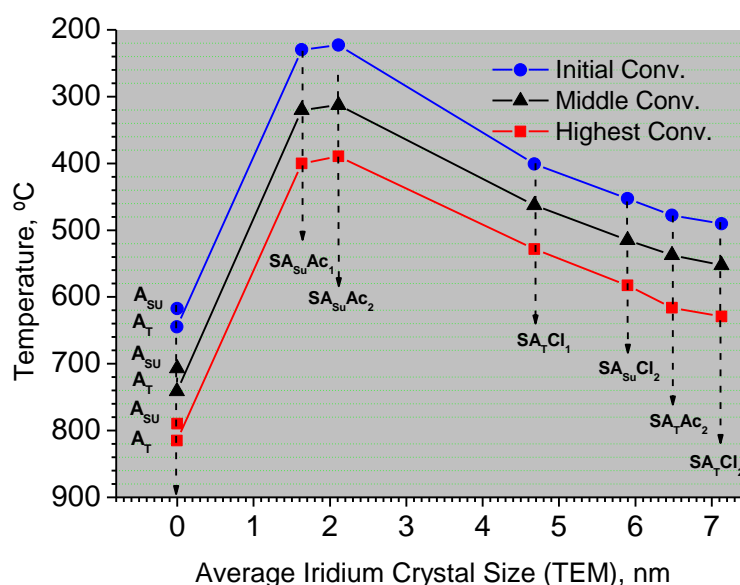


Fig. 1- Catalytic activity of the samples for ammonia decomposition to N₂ and H₂

4. Conclusions

It has been found that catalytic activity of supported Ir catalyst, Ir/ γ -Al₂O₃ for ammonia decomposition producing green H₂, depends on support properties, high concentration of electron-deficient groups, high thermal stability, and high surface area (for good dispersion of Iridium). From the data of catalytic activity, the smaller crystal size of Ir in nanometer scales, with higher dispersion, favors the catalytic activity of ammonia decomposition. The metal dispersion of heterogeneous catalysts is an important factor influencing the catalytic performance of catalysts.

Let us briefly compare the two preparation methods described in experimental section. First, an Ir salt solution was added to the support by impregnation. Ir was incorporated onto the alumina leads to big Ir clusters. The samples show a narrow crystal size distribution by TEM characterization methods.

In the second one, Ir as organic source was employed and incorporated to alumina by ion exchange, given a well-distributed metallic Ir with smaller clusters size.

Both observations were regarded as proof of the effect of the Ir nature source and Oc/Th Al ratio in the alumina samples. One could say that there was, as a fairly suggestion, two synergic effects, the Alumina type and the source and procedure of Iridium loading.

Finally, the present study leads on Alumina samples with relatively higher Ir content (10-18%). Our initially results are very encouraging to produce green H₂ from Ammonia decomposition.

Acknowledgments

O.A.A, J.M.J, M.B.G.C., Conicet Researcher. The authors are grateful to FONCYT (Project PICT 1740) and the Universidad Tecnológica Nacional (Córdoba, Argentina).

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