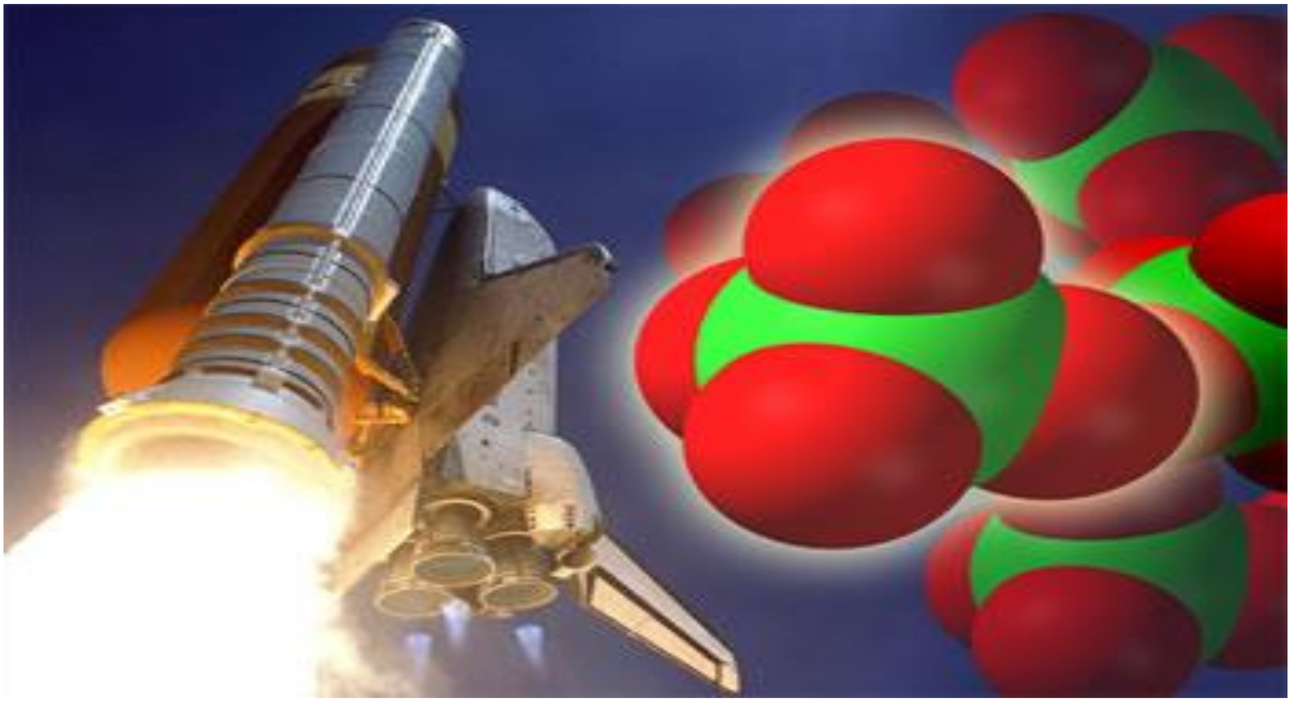
Burning Constituents for Rocket Launch – Ammonium Perchlorate



The atomic structure of ammonium perchlorate and rockets, on the left is a rocket blasting off using ammonium perchlorate as fuel and on the right is a molecule of ammonium perchlorate.

Transition metal nanoparticles consisting of Copper, Cobalt, Nickel, and Iron were used as catalysts to speed up the thermal decomposition of ammonium perchlorate. The amount of activity in these four catalysts increased in order from Fe, Ni, Cu, and Co; and their respective activation energies were found to be proportional to the amount of activity.

Gurdip Singh and collaborators from the Chemistry Department at D. D. U Gorakhpur University in Gorakhpur, India have recently published the paper, “Nanoparticles of Transition Metals as Accelerants in the Thermal Decomposition of Ammonium Perchlorate”. The team worked on Transition Metal Nanoparticles – also known as TMNs – by testing several catalysts that speed up thermal decomposition of ammonium perchlorate. The catalysts help the reaction by lowering the activation energy and thus requiring less energy for reaction.

Rocket propellant research is becoming increasingly important because it is an important oxidizer for composite solid rocket propellants. Ammonium perchlorate (AP) is known for its fueling abilities as an oxidizer. An oxidizer is a type of chemical required for a fuel to burn; an example would be oxygen is used as an oxidizer for wood to burn. For decades, AP has been an important oxidizer used as fuel for space launch, military, amateur, and hobby, high-powered rockets. If one can determine the most efficient way to use its burning efficiency, the amount required could potentially decrease. Take for example space launch, AP is used frequently in space shuttle solid rocket boosters as fuel. When the fuel combusts, it gives the rocket energy that pushes the rocket in the opposite direction; in this case, against gravity. The energy produced must be powerful enough to overcome the gravitational well faced by the rocket. Rocketry is very crucial to help push forth the knowledge of the planet we live on.

As an oxidizer, the AP works very well as a fuel. AP is stored as a salt composed of ammonium – nitrogen and ammonia – and perchlorate – chlorine and oxygen. Since it is 55% oxygen by weight as opposed to air which is only 21% oxygen it is richer in oxygen and it promotes combustion of most fuels more intensely (Freudiger, 2007). When used as engine fuel it requires an elastromer binder (such as hydroxyl-terminated polybutadiene), small amounts of metal (such as aluminum, magnesium, or zinc – most rockets use aluminum because it has the highest performance), and oxidizing catalysts. The elastromer binder holds the oxidizing agent and the fuel, – which in this case was aluminum – into a small volume. The authors tested the efficiency of several oxidizing catalysts by testing these catalysts and determining which lowered the activation energy the most for AP to decompose.

Experimentally, the authors worked to synthesize several nanoparticles. These nanoparticles consist of Copper, Cobalt, Nickel, and Iron. These nanoparticles have strong research promise due to their unique optical, electrical, catalytic, and magnetic properties. These TMNs were prepared by hydrazine reduction of metal chloride in ethylene glycol without the use of a protective agent. The sizes of particles were characterized using x-ray diffraction. The metal nanoparticles began to form after an hour at 60^{O}C and constant stirring.

All TMNs were found to reduce the time it took for decomposition of AP. They performed in two different ways. The model fitting method is used to describe the kinetics of thermally induced reactions in solid compounds, written:

$$d\alpha/dt = k(T)(\alpha)$$

Where α is the degree of conversion, t is time, T is absolute temperature, k(T) is temperature-dependent rate constant and follows the Arrhenius equation shown below, and f(α)is a function known as the reaction model:

$$k(T) = Aexp\left(-\frac{E}{RT}\right)$$

Where A is the pre-exponential Arrhenius factor, E denotes the activation energy, and R is the gas constant. The integrated form of the model fitting method and using it, one can estimate the corresponding rate constant from the slope of the integral vs. time plots. The other method is the isoconversional method which allows evaluation without assumptions and allows one to explore multistep kinetics.

$$-\ln t_{\alpha,i} = \ln[A/g(\alpha)] - E_\alpha/RT_i$$

Where E_α is the activation energy at a particular α.

Out of the oxidizing catalysts Cobalt was the most active catalyst and Iron was the least active. Another important part of the comparison of the catalysts is that the catalysts with a higher accelerant activity also require less energy to thermally decompose. It was clear that increasing the amount of TMNs in AP sped up accelerant activity. Cobalt has a smaller E_a than the rest, thus showing that Co requires the least energy to perform the reaction.

Nanopowders are very useful because of the properties of their crystal lattice. Crystal lattices of metal nanopowders contain defects in which atoms located at the defect are unsaturated but can become saturated with the help of electrons. Unsaturated, meaning that the atoms where the defects are do not have a full valence; as oppose to saturated where the atoms do have a full valence. Luckily, the nitrogen atom within AP contains additional electrons, thus making the nitrogen's bonds weak and its electrons can be absorbed from. All energy gained from the breakdown of this reaction can be absorbed by the TMNs and thus accelerate the reactions, and in the process can transform the metal nanoparticles into metal oxides, which can also serve as accelerants in this form as well.

From this research, many positives can come from this. This research could lead to future developments in air quality enhancement. This research could aid in the goal of reducing emissions from space launches and thus would be less harmful to environment. This could be done by successfully finding a catalyst that lowers the activation energy enough so less would be required for take-off. This could possibly lead to improvement in climatology research, military applications, telecommunications such as GPS, etc. therefore minimizing costs and environmental impact.

Interview

Jordan: Was there anyone else that you worked on this experiment with, besides the authors of the article?
Dr. Singh: No

Jordan: What were you expecting to happen with this experiment? If the results were not what you had expected, was the outcome beneficial for this experiment?
Dr. Singh: We were expecting similar type of results. The results are always beneficial.

Jordan: Did the experiment go as planned? If not, explain.
Dr. Singh: Yes.

Jordan: When and where did this experiment take place?
Dr. Singh: During the year 2010. DDU Gorakhpur University, Gorakhpur, India

Jordan: Is there a specific type of chemistry that you prefer to work with?
Dr. Singh: No.

Jordan: Why did you perform this experiment?
Dr. Singh: Transition metal oxides are very good catalyst for the thermal decomposition of AP.

Jordan: In your article you mentioned that Ni and cobalt were prepared using a hydrogen plasma method. What is this method?
Dr. Singh: It is hydrazine reduction method and not hydrogen plasma method. The method has been described in the above cited paper.

Jordan: Other than rocket fuel, does the burning of AP have any other applications that may be looked at in the future (e.g. rocket size? air pollutants? Fireworks?)?
Dr. Singh: Most of these compounds are oxidation catalyst and hence we did work on these compounds.

Jordan: What are your next steps in research?
Dr. Singh: We are still doing research in this field taking metal oxides other than transition metal series.

Works Cited

Freudiger, M. (2007, March 15). *Ammonium Perchlorate Blast*. Retrieved from http://www.youtube.com: http://www.youtube.com/watch?v=oc_nnnBmMbM

Singh, G., Sengupta, S., Kapoor, I., Dubrey, S., Dubey, R., & Singh, a. S. (2012). Nanoparticles of Transition Metals as Accelerants in the Thermal Decomposition of Ammonium Perchlorate, Part 62. *Journal of Energetic Materials*, 165-177 (12).