

Catalysed Decomposition of Hydrazine in Nitric Acid Media on Pt/SiO₂ Catalyst

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Abstract

Decomposition of 0.5 M hydrazine was carried out in 1.5 M nitric acid medium using platinum coated silica (Pt/SiO₂) catalyst of 63 micron particle size in the temperature range of 40-70°C on laboratory scale. The catalytic decomposition of hydrazine in HNO₃ comprises different processes involving disproportionate oxidation of hydrazine at the catalyst surface in nitric acid medium. The overall reaction is described mainly by HNO₃ concentration and temperature. The effect of temperature, amount of catalyst, rate of mixing (RPM) and acidity in terms of nitric acid concentration were also studied at room temperature.

The operating parameters namely temperature, catalyst amount, RPM and acidity have been optimized in the presence of 63micron Pt/SiO₂ catalyst in batch process. The activation energy was 17.494 kJ/mole in the temperature range 312-342K.

Keywords: Pt/SiO₂, hydrazine, decomposition, reprocessing.

Introduction

Hydrazine (salt free reagent) plays an important role in the nuclear reprocessing. The primary and secondary circuits of nuclear power plants are using hydrazine as an anticorrosive protective agent¹. It carries further application as a scavenger for nitrous acid in the PUREX (Plutonium Uranium Reduction EXtraction) process for the separation of uranium and plutonium¹⁻³ e.g. in electrochemical reduction of U(VI) in nitric acid solutions or as a reducing agent for stabilization of actinides in low oxidation states^{4,5}. Presence of hydrazine in final radioactive waste solution is very much undesirable to avoid loss of actinides as well as to reduce the activity of waste.

Hydrazine on reaction with nitrous acid present in nitric acid results in hydrazoic acid which is explosive in nature. The rate of destruction of nitrous acid using hydrazine is very rapid compared to sulfamate reductant. Decomposition of hydrazine in presence of different solid state catalyst is well known. In literature, a large quantity of work on the decomposition of hydrazine in the presence of a number of catalytic materials is reported. The results of these researches have been summarized and reviewed by Schmidt⁶. Presence of Pt/SiO₂ is most promising in nitric acid medium. One of the major advantages of using platinum

as catalyst is non formation of hydrazoic acid (HN₃). This is due to the reason HN₃ adsorbed at the catalyst surface is not desorbed to the solution but is subjected to catalytic decomposition at the platinum surface⁷. The kinetics of the catalytic decomposition of hydrazine in nitric acid was studied by Krot et al⁸. A laboratory scale study was carried out for optimizing the reaction parameters to be implemented in the reprocessing plant. The effect of temperatures between 40°C to 70°C, amount of catalyst, effect of acidity and mixing speed of impeller (RPM) used for homogeneous mixing was studied in batch mode.

Material and Methods

AR grade chemicals with 99.90% purity (Sigma Aldrich and Merck) were used. About 18.50M hydrazine hydrate standard solution was procured from Orion Chem. Pvt. Ltd., Mumbai. Para-(dimethylamino) benzaldehyde (pDMAB) with 98.90% purity used for spectrophotometric analysis of hydrazine was obtained from BDH Prolabo, Chennai. Pt/SiO₂ catalyst in fine powder form was received from Hindustan Platinum Limited, Mumbai.

UV-Vis spectrophotometer supplied by Thermo Scientific India Pvt. Ltd. was used for absorbance measurements. Digital pH-meter model Micro-07 supplied by Chemlabs was used for pH adjustments. Tapson's analytical single pan balance model 200 T with 0.001 gm accuracy was used for weighing. The temperature controller MIC-66A(±0.10C) was obtained from Modern Scientific Instrument Company, Mumbai. Acid-base titrations were carried using PC based automatic titration system from Metrohm.

Two litre stock solution of 0.5M hydrazine nitrate was prepared by dissolving 54.05mL of hydrazine hydrate (18.5M) in 1.5M nitric acid solution. A 500mL stock solution was prepared separately by dissolving 13.51mL of hydrazine hydrate (18.5M) in 2.5M nitric acid. Similarly, this procedure was repeated for 500mL stock solution in 3.0M nitric acid concentration. Sieving was done using Vibrator Sieve Shaker RETSCH Make Model Number AS200 with sieves of different particle size i.e. 63, 38 and 20 micron to separate the fine powder.

A double-jacket glass reactor plugged with temperature controller using Julabo HE circulator was used for kinetic measurements with a vertical stirrer impeller for constant interaction of solid solute and liquid phase as shown in fig.1. The concentration of hydrazine was determined using titrimetry⁹ and spectrophotometric methods¹⁰. Titrimetry method involving acid-base titration was used for higher concentration i.e. in molarity range. However, lower

concentration i.e. in parts per million (ppm) range determination was done spectrophotometrically using pDMAB (p-dimethylaminobenzaldehyde) chromogenic reagent¹⁰. Comparative studies showing the proximity to real value and variation of values among the two methods are reported in table 1.

Batch Experiments: Batch experiments were carried out for optimizing parameters i.e. effect of temperature, amount of catalyst, rate of mixing (RPM) and acidity in terms of nitric acid concentration for the decomposition of hydrazine. Experiments were conducted in a double-jacketed glass reactor with rotor impeller for mixing the solution contents as shown in fig. 1.

The effect of parameters was studied by conducting experiments with 100 mL of 0.5M hydrazine nitrate taken from stock solution in 1.5M nitric acid medium in a double-jacket glass reactor. The solution in the glass reactor was maintained at 60°C temperature. A glass shaft with impeller

attached with RPM controller was then immersed in solution for mixing purpose. The speed of mixing was set to 400 rpm. A known amount of Pt/SiO₂ catalyst 8g was then added to stirring solution with initiation of reaction. Samples were collected at predetermined time interval and analysed using acid–base titrimetry and spectrophotometric method. Similarly, experiments were carried out at different parameters as shown in table 2.

Results and Discussion

The kinetic experiments were carried to study the effect of temperature, acidity, RPM and amount of catalyst on the catalytic decomposition of hydrazine using Pt/SiO₂ catalyst in nitric acid medium. The heterogeneous catalytic decomposition of hydrazine in nitric acid medium in presence of Pt/SiO₂ catalyst¹¹ occurs with the formation of NH₄⁺ ions and of N₂O and N₂:

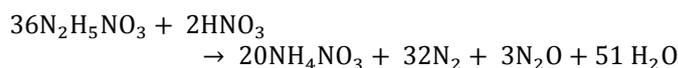


Table 1
Comparison of the hydrazine concentration by titrimetry and spectrophotometry

	Titrimetry		Spectrophotometry	
	[N ₂ H ₄],M	RSD(%)	[N ₂ H ₄],M	RSD (%)
Std 1	0.5255±0.014	0.68	0.527±0.034	2.42
Std 2	0.246±0.023	0.79	0.246±0.023	1.41
Std 3	0.184±0.063	1.48	0.184±0.069	0.89
Std 4	0.107±0.084	2.04	0.109±0.034	0.77
Std 5	0.382±0.014	0.93	0.382±0.014	1.58
Std 6			0.0517 ± 0.021	0.76
Std 7			0.0383 ± 0.0084	0.84

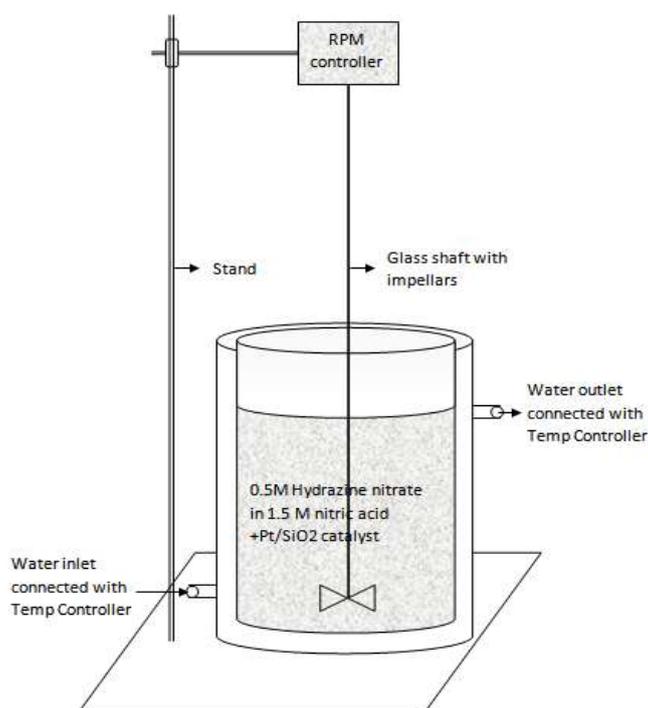


Fig. 1: Jacketed vessel with mechanical agitator

Table 2
Experimental conditions to optimize various parameters on decomposition of hydrazine

Parameter	Temp (°C)	Catalyst(g)	Mixing(rpm)	HNO ₃ (mol/m ⁻³)
Effect of temperature	40	8	400	1.5
	50			
	60			
	70			
Effect of amount of catalyst	60	0	400	1.5
		4		
		6		
		8		
		10		
Effect of mixing speed	60	8	200	1.5
			300	
			400	
			500	
Effect of acidity	60	8	400	1.5
				2.0
				2.5

Effect of temperature: The catalytic decomposition of hydrazine using Pt/SiO₂ catalyst in nitric acid medium was studied at different temperatures. The plot of hydrazine concentration vs. time is shown in fig. 2. It is observed from the graph that time involved in complete decomposition of hydrazine at 60°C temperature is less compared to 40°C and 50°C. This is due to the reason that with increase in temperature decomposition, rate becomes higher and that is highest at 60° C which follows the Arrhenius equation.

Experiments carried out at 70°C result in even faster decomposition but sample collection was not feasible and analysis also not reproducible. Hence, temperature was set at 60°C for hydrazine decomposition studies. The values of activation energy were calculated from the slope of ln (r) vs. 1/T plot (Fig. 6) and were found to be 17.494 kJ/mol in the temperature range 312-342 K.

$$k = Ae^{-\frac{E_a}{RT}}$$

where k is the rate constant, A is pre exponential factor, T is absolute temperature, E_a is activation energy and R is universal gas constant.

Amount of catalyst: The effect of amount of catalyst on the catalytic decomposition of hydrazine in nitric acid medium was studied. From fig. 3, it is observed that in the absence of catalyst, the decomposition of hydrazine took more time compared to its presence showing the importance of catalyst. With 4 and 6g catalyst, decomposition of hydrazine is not as effective i.e. in terms of rapid reaction compared to 8g. Experiments were also carried using 10g catalyst showing much difference from decomposition occurring with 8g catalyst. Sample collection with 10g was difficult as it contains a major amount of catalyst in sample and interferes in the analysis. Moreover, the high cost of noble metal

catalyst consequently, reduces the economic feasibility of a large scale system and the catalyst replacement or regeneration is easy. Hence, the amount of catalyst under desired conditions was optimized as 8g.

Rate of mixing: The effect of rate of mixing on the catalytic decomposition of hydrazine in nitric acid medium was carried out. Experiments were consisting of mixing i.e. interaction of two phases i.e. catalyst as solid and hydrazine solution as liquid phase. The effect of rate of mixing i.e. rpm on hydrazine decomposition is shown in fig. 4. It was found that at 500rpm, the decomposition of hydrazine was more rapid compared to the one carried out at 400rpm. At higher RPM, solute-solid (catalyst) interaction is more due to easier penetration of solute through the solvent film before the reaction with catalyst and easier disappearance of reaction products over the catalyst surface.

At lower rate of stirring i.e. at 200 and 300rpm, it took more time for same amount of hydrazine decomposition. Experiments carried out at 500rpm prove to be more effective in comparison to 400rpm. Glass reactor constraint in term of hold up solution volume at 500rpm with ease is not possible resulting in over spillage of reaction contents. Hence, the rate of mixing was optimized to 400rpm for studies.

Effect of acidity: The effect of acidity in terms of nitric acid concentration with constant hydrazine concentration of 0.5M was studied. Here, 100mL of stock solution of 0.5M hydrazine in 2.5M nitric acid was taken in glass reactor. Experiments were carried out with optimised parameters i.e. reaction temperature set at 60°C, amount of catalyst taken equal to 8g, rate of stirring two phases at 400rpm. Samples were collected at pre-determined intervals and analysed. The effect of acidity in terms of hydrazine conc. vs. time is shown in fig. 5.

Similarly, experiment was carried out 3.0M nitric acid concentration. It was observed that decomposition of hydrazine was more rapid at 3.0M compare to 1.5 and 2.5M nitric acid medium. Since the plant conditions carrying

nuclear fuel reprocessing in terms of hydrazine are restricted to 1.5M nitric acid, so the studies reported here are in 1.5M nitric acid medium.

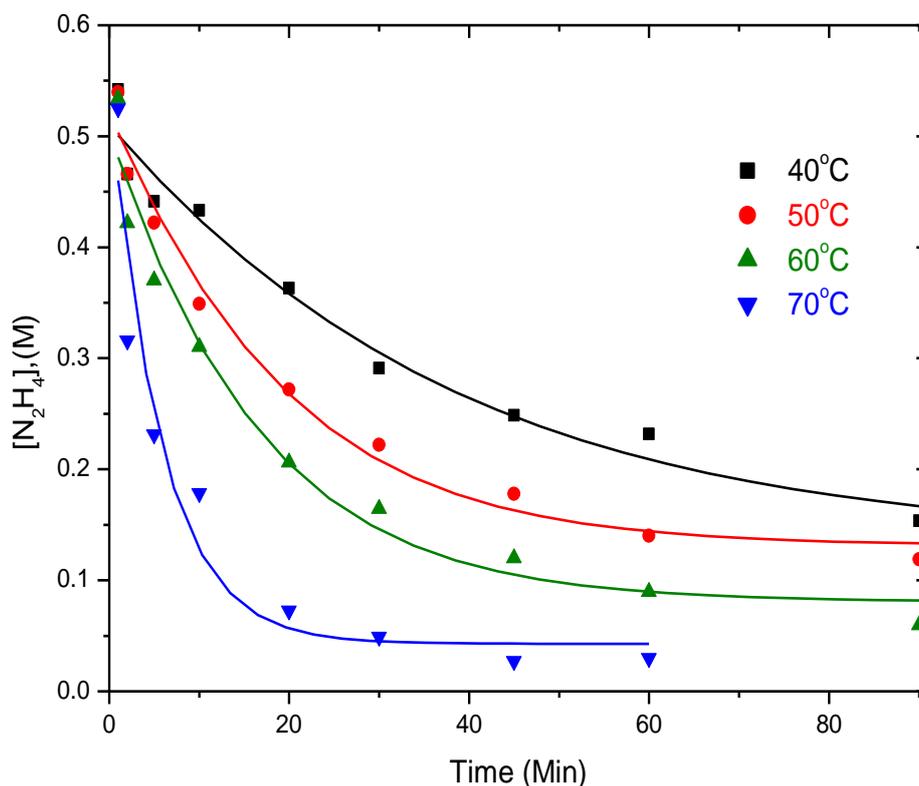


Fig. 2: Effect of temperature on hydrazine decomposition.

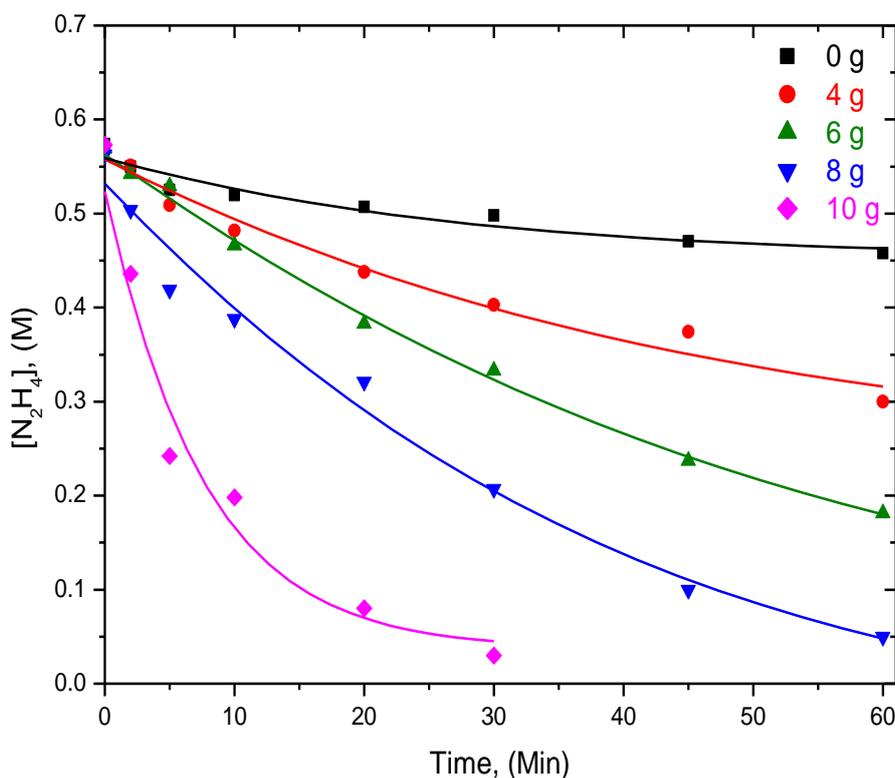


Fig. 3: Effect of amount of catalyst on hydrazine decomposition.

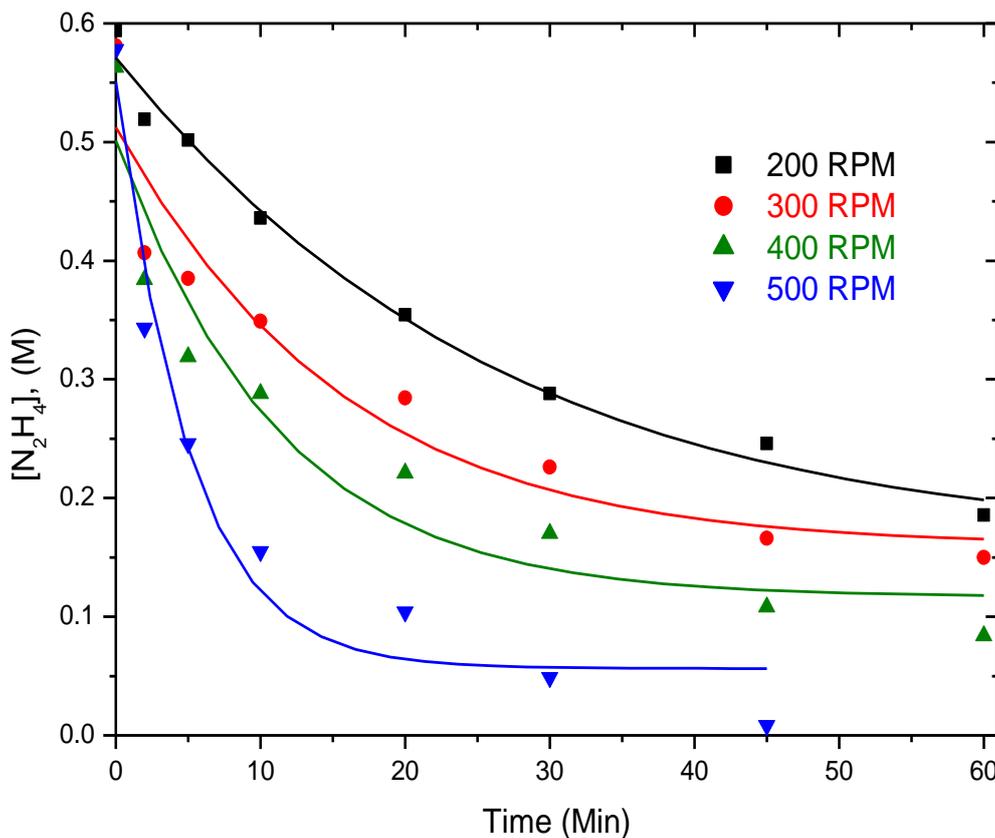


Fig. 4: Effect of rate of mixing on hydrazine decomposition.

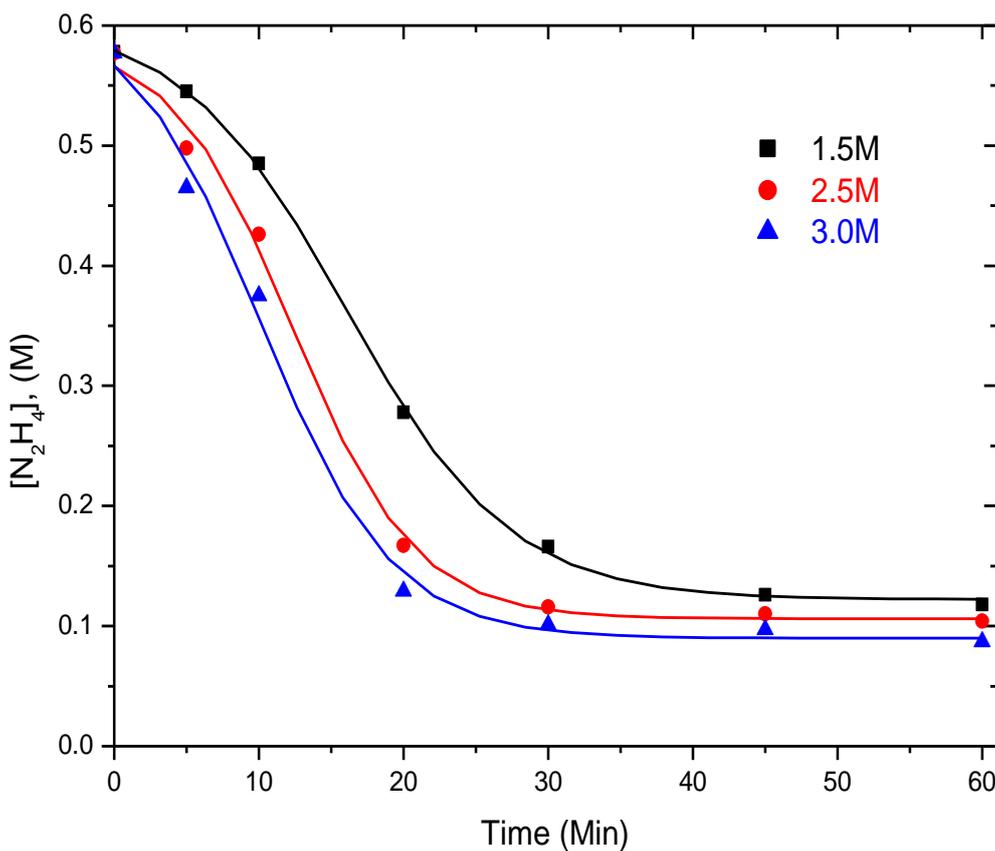


Fig. 5: Effect of acidity on hydrazine decomposition.

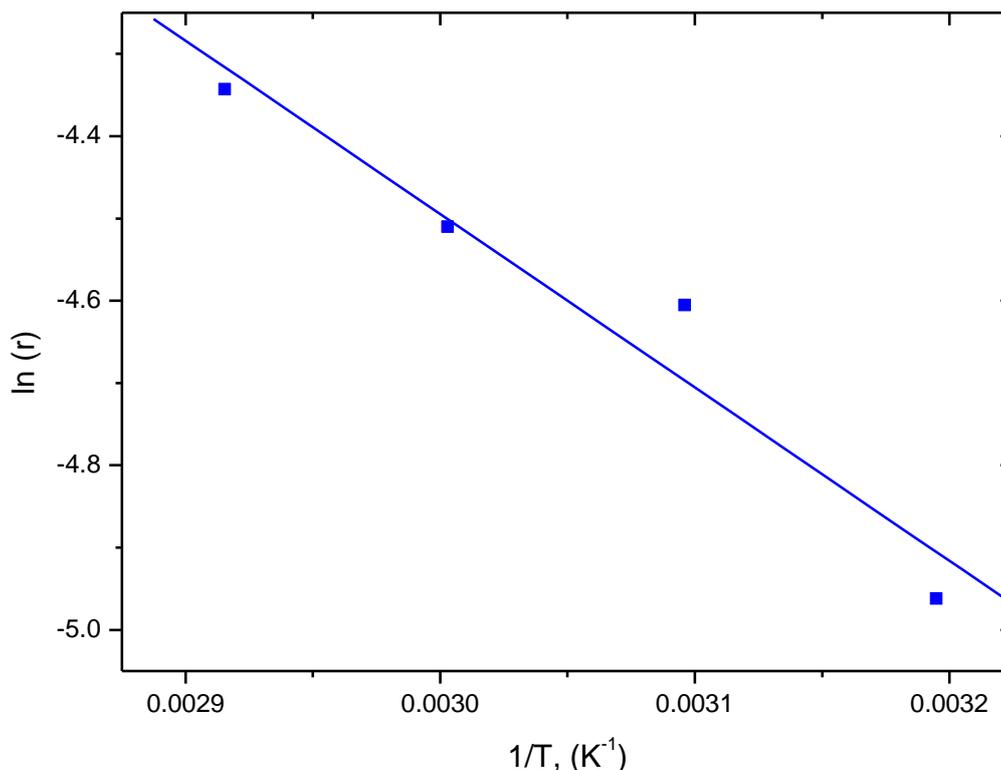


Fig. 6: Arrhenius plot of initial rate of destruction of hydrazine

Conclusion

The effect of temperature, amount of catalyst, RPM and acidity in terms of nitric acid on the decomposition of hydrazine was optimized. The presence of Pt/SiO₂ catalyst speeds up the decomposition of hydrazine showing the importance of catalyst. It was found that decomposition was rapid at 60° C temperature using 8 g catalyst in 1.5M nitric acid medium at 400 RPM for 100 ml solution in batch method. This method is applicable for destruction of hydrazine in plant scale.

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