Fly ash Utilization in Preparation of Nickel-Catalyst for CO Oxidation

Manish Agrawal, Ankit Modi, Pranveer S Satvat, Vidya S Batra

Received 20 DEC. 2015, accepted on 13 JUL. 2016

ABSTRACT

Industries especially thermal power plants and steel mills produce fly ash as byproduct in huge quantity on coal combustion. Safe and sustainable disposal of fly ash is still challenge to environmental engineers. Conventionally, it disposes as dump in the open that causes severe menaces like entering heavy metals in food chain through air and water medium. The paradigm shifts in fly ash management since nineties extended its employability in making cement and other construction materials, paving roads and embankments, and ameliorating soils. However, about 40% of total fly ash is still unutilized and disposes as dump in India. Espousing the same concept of effective utilization of fly ash, the present research took over to develop fly ash supported nickel catalyst for oxidation of globally distributed air pollutant- CO (Carbon monoxide). The fly ash is pretreated with acids and is utilized as supportive material for nickel loading from its nitrate salt. The catalytic activities for CO oxidation have been analyzed over Gas Chromatography at three temperatures of 25^{o}C, 250^{o}C, and 500^{o}C. The nitric acid pretreatment resulted in highest increment in surface area fly ash, and higher temperature led to better oxidation of CO gas. On overall basis, it can be deduced that the fly ash supported nickel catalyst is effective in CO oxidation.

Keywords: Fly ash, Nickel, Supportive catalyst, Air pollution, Carbon monoxide

1. **Manish Agrawal,** Department of Civil Engineering, IIT Kanpur, Kanpur, India 208016
   Environmental Engineering Division, SMBS, VIT University, Vellore, Tamil Nadu, India
   E-mail: amanish@iitk.ac.in
2. **Ankit Modi,** Department of Civil Engineering, IIT Kanpur, Kanpur, India
3. **Pranveer S Satvat,** SGT University, Gurgaon.
4. **Vidya S Batra,** Tata Energy Research Institute, Habitat Place, New Delhi, India

1. INTRODUCTION

Prime industrial solid waste i.e. fly ash, constitutes about 13% of total solid waste (960 million tons) generated in India around 130 Mt annually that continually increasing by 2.2% annually [3]. The conventional method for fly ash management i.e. open dumping become very pathetic due to low availability of the dumping area and posing severe environmental threats in terms of heavy metal leaching in groundwater and surface water.

It contains many essential elements like S, B, Ca, Na, Fe, Zn, Mn, and P that can be utilized for making various valuable construction products like cement, concrete and bricks based on emergence of the concept that 'nothing is waste' on which Government of India established 'Fly-Ash Mission' in 1994 to promote the many projects and services through which the fly ash can be utilised eco-sustainably. The major applications for the safe utilization into construction materials such as bricks [5], ceramics [33], road pavements [12], zeolites and geopolymers [13] are possible also. Also, it is used extensively for solving environmental problems *viz.* cost effective adsorbents for pollutants removal from gases and wastewater [17], stabilization of nuclear wastes [21] and for soil amendment [8].

However, about 40% of total fly ash is still unutilized [1]. The utilization of fly ash in the construction sector is about 46% in India [13], and only 25% at worldwide [29]. Thus, more studies are required to explore new valuable applications of fly ash.

The composition of fly ash has oxides of silicon-aluminium, majorly and some minor oxides of alkali metals, alkaline earth metals and some transitional metals, those promote the activity of catalyst during combustion at higher temperature, which shows fly ash can be used as good support for catalyst or as a catalyst [28]. Adopting the same concept, most of researchers used fly ash as base material for various transitional metals like or as a supported catalysts for the oxidation of globally distributed air pollutants like SOx[9] [30], NOx[25] [31], Methane Oxidation[26].

Carbon Monoxide is a primary air pollutant and by doing catalytic oxidation of it, we can improve indoor air quality. Various catalysts, like Pd/Fe_3O_4 catalyst [15], Cu–Zr–Ce–O catalyst [34], H_2-selective membrane (defect-free Y-type zeolites, and γ-Al_2O_3) impregnated with noble-metal catalysts[22], $La_{0.8}Sr_{0.2}Co_{0.8}Cu_{0.2}O_3$ (perovskite composition catalyst) [20], Au/CeO_2–TiO_2 catalysts[32], and Nickel Ferrite nano-particles from fly ash[6] have been studied for CO oxidation reaction [24], those have some disadvantages in terms of economy and sustainability and toxicity of metals. The present research is to explorer the utilization of coal fly ash to prepare the cost and environmentally effective catalysts used in CO oxidation.

2. MATERIALS AND METHODS

2.1 Materials

- Fly ash samples from three different power plants.
- 1M HCl Solution
- 2M HCl Solution
- Concentrated Nitric Acid
- Ferric Nitrate
- Nickel Nitrate

2.2 Methods for Preparation and Pre-Treatment

2.2.1 Preparation of fly ash sample

Three fly ash samples are collected from different power plants (F1, F2, and F3). These three samples were sieved through 150 µm sieve for getting uniform sample.

2.2.2 Pre-treatment of fly ash

In this study three methods have been adopted for pretreatment of fly ash samples.

a) Samples were treated with 2M solution of NaOH or 1M solution of HCl (ratio of fly ash 10:1 by weight) after dried at 105°C for 24 h. Then mixture was again dried at 100°C for 24 h and filtered, washed & dried at 105°C for 24 h **(C1)** [16].

b) Samples were treated with 2M HCl solution for 24 h at room temperature and then washed & dried at 110°C overnight **(C2)** [14].

c) Samples were treated with concentrated nitric acid (acid/ash = 5 ml/g) at 700°C for 1 h. Sample were then washed & dried at 300°C for 3 h **(N3)** [31].

2.3 Preparation of Nickel Catalysts

2.3.1 Nickel Loading on Fly Ash Sample (Nickel Catalyst)

2.66 g of Nickel-Nitrate salt were added to 100 ml of distilled water and 10g of fly ash mixed with this solution and kept stirring for 24 h. After this, the samples filtered and dried at 100^{o}C and were calcined at 500^{o}C for 6 h [27].

2.4 LOI determination

ASTM D7348-07 method was used for LOI determination of all fly ash samples. Moisture was first removed by heating in oven at 105^{o}C for overnight. The samples were then heated at 750°C till constant weight. LOI was determined from the % weight loss.

2.5 Catalytic test for carbon monoxide oxidation

For CO oxidation, the catalyst was loaded onto the reactor, sandwiched between thin layers of ceramic wool. After eliminating leaks, the reactor was heated to 100^{o}C. CO was then passed through the inlet and the outlet gases were analyzed using an online GC. The residual gasses from the system were burnt off using an LPG cylinder. Pre-treated fly ash loaded with and 5% Ni was used for CO oxidation and the peak areas for CO and CO_2 at 25^{o}C, 250^{o}C, and 500^{o}C were noted. From this data the rate of catalytic conversion was calculated.

3. RESULTS AND DISCUSSION

The efficiency of developed catalysts governed by amount of metal is possibly loaded, which further depend on the surface area of the supportive base material. Additionally, surface area describes the texture of materials and enables higher dispersion of active phases through which transition metal would precisely load on surface of fly ash particles. Though, fly ash has significant surface area that can be further increased by various pre-treatment, especially with different acids [19] [27]. Therefore, this investigation considered very effective acids namely hydrochloric acids in two different molarities and 16 M nitric acid for pretreatment of fly ash that loaded with the Ni metals and subjected to curbing the carbon monoxides pollution.

3.1 Characterization of Prepared Catalyst

3.1.1 LOI determination

According to ASTM D7348-07 method the LOI % of all treated fly ash samples are determined (ASTM C618-94a, 1994).

Table 3.1: The LOI % of all treated fly ash samples

Type of Acid Treatment	Fly ash Sample	LOI (% by weight)
C1	F3	0.13
	F1	0.30
	F2	0.14
C2	F3	0.06
	F1	0.17
	F2	0.07
N3	F3	0.07
	F1	0.06
	F2	0.16

3.1.2 Surface area of collected fly ash

The fly ash employed as base material in developing transition metal catalyst were collected various thermal power plants and symbolized as F1, F2 and F3. On analysing the surface area, F2 contained highest area followed by F3 and F1 (Figure: 3.1). Therefore, only fly ash type F2 is considered for further experiments.

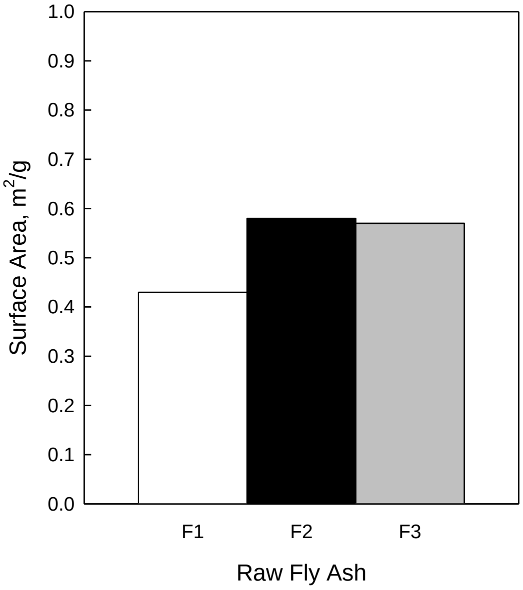


Figure 3.1: Surface Area of Raw Fly ash Samples

3.2 Effect of Various Operations on Surface Area of Different Fly Ash

As surface area of supportive materials regulates efficacy of metal loading and dispersion of active phases, it is necessary to determine the change in surface area of supportive material drawn from different sources and subjected to various acids pre-treatment. Similarly, alteration in surface area after loading of nickel & iron and after oxidation is also considered for the discussion.

3.2.1 Effect of various acids pre-treatment on surface area of fly ash

The effect of different pre-treatments on surface area of raw fly ash is shown in Figure 3.2. The surface area of raw fly ash F2 has 0.58 m^2/g which increased up to 3.17 m^2/g by using 1M HCl. This increment in surface area is about 82.71% but using 2M HCl, gain in surface area is only 2.23 m^2/g (74% higher than raw fly ash). 1M HCl affects the surface area more in comparison to 2M HCl by 29.65%. However, 16M HNO_3 resulted in highest surface area to

6.29 m^2/g that is comparatively higher by 90.78%, 49.60% and 64.54% than that of raw fly ash, 1M and 2M HCl respectively. Xuan (2003) also observes the similar enhancement in surface area of fly ash.

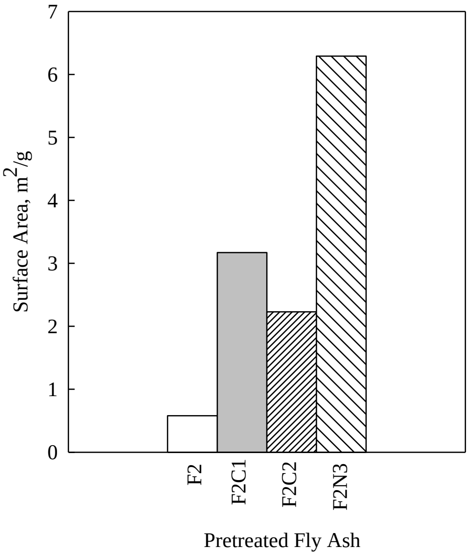


Figure 3.2: Enhancement in Surface Area of Fly ash on Acid Pre-treatment

3.2.2 Effect of type of fly ash on surface area after nitric acid pre-treatment and metal loading

Figure 3.3 compares the all of three fly ash samples treated by HNO_3 with the nickel metal loading. Without metal loading, the surface area of F1N3 is 4.52 m^2/g and in the case of F2N3, this is 6.29 m^2/g which 27.98% increment with respect to F1N3. The surface area of F3N3 is 7.95 m^2/g which increase by 43.14% compare to F1N3 and 20.88% compare to F2N3. Nickel loading reduces the surface area of all fly ash samples. The surface area of F1N3 reduces by 19.24% (3.65 m^2/g) after getting nickel. The reduction in surface area of F2N3 is 26.84% (2.67%) with respect to F1N3. Increment in surface area of F3N3 is 10.54% with compare to F1N3 and 34.56% with respect to F2N3.

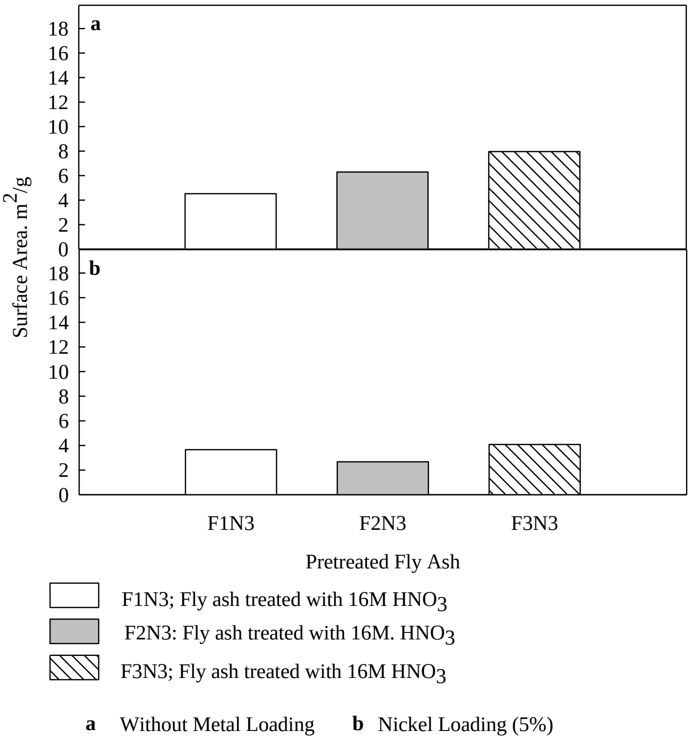


Figure 3.3: Effect of Type of Fly ash on Surface Area after Pretreatment with Nitric Acid and Metal Loading

3.2.3 Effect of pre-treatment on catalyst surface area

Figure 3.4 describes the effect of transition metal (Ni) loading on the raw fly ash (F2).

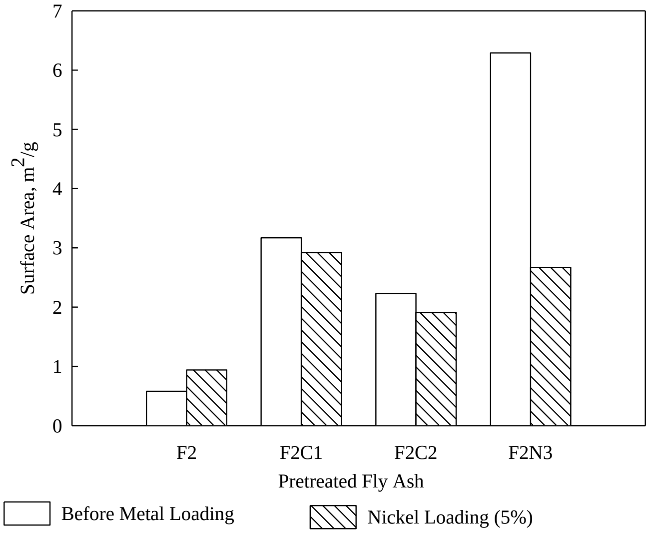


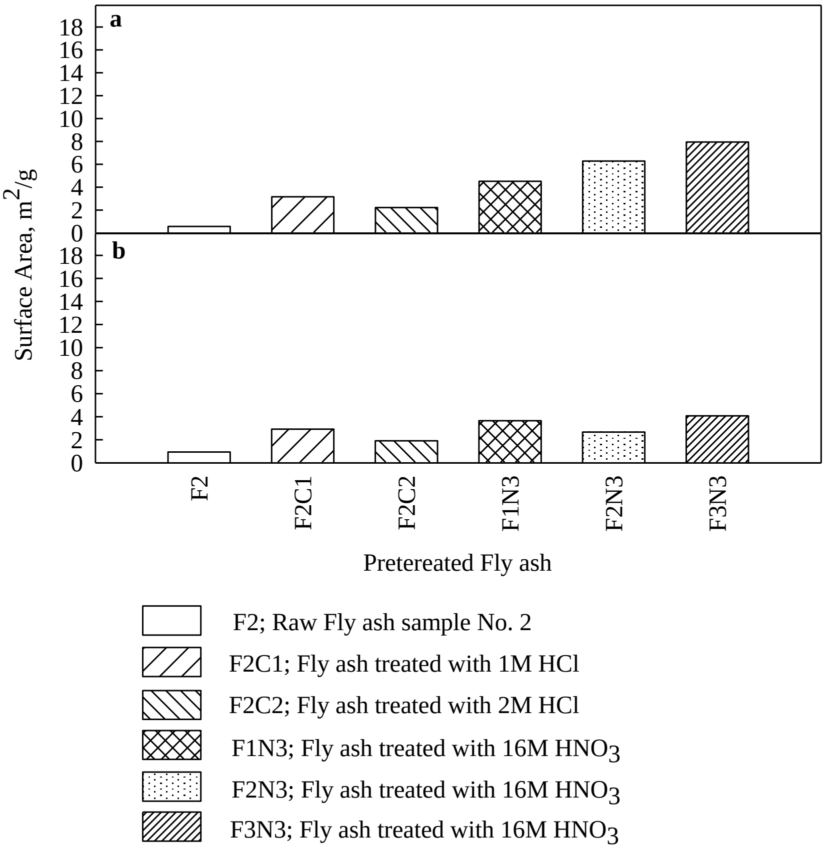
Figure 3.4: Effect of Different Acids Pretreatment and Metal Loading on Surface Area of the Synthesized Catalysts

The surface area of nickel loaded raw fly ash is 0.94 m^2/g, which is increase by 93.53% after getting nickel loading, the increment is 38.30%, which is due to pore blockage by NiO as the temperature goes high, at which $Ni(NO_3)_2$ break down to NiO. The surface area of treated fly ash using 1M HCl is 3.17 m^2/g which reduces in surface area by 8.56% (2.92 m^2/g) after nickel loading and for 2M HCl it reduces by 16.75% (1.91 m^2/g). The surface area of treated fly ash using 16M HNO_3 is 6.29 m^2/g which reduces by 57.55% (2.67 m^2/g) getting nickel.

3.2.4 Effect of transition metal loading on surface area

Figure 3.5 shows the effect of catalysts on surface area of fly ash samples. After getting nickel metal, surface area of all the catalysts increases.

Increment in surface area of F2 catalyst has higher 39.29% after soaking up of nickel comparison to raw. Surface area of F2C1 catalyst without metal loading is 3.71 m^2/g in which diminution occur when nickel metal absorbs on raw F2C1 catalyst by 7.88% (2.92 m^2/g). F2C2 catalyst has surface area of 2.23 m^2/g without absorption of any metal but it reduces by 14.34% due to nickel loading on F2C2 catalyst. The surface area of F1N3 without contact of any metal is 4.52 m^2/g, but it comes down to 19.24% (3.65 m^2/g). F2N3 catalyst has surface area 6.29 m^2/g which reduces after nickel loading by 57.55% (2.67m^2/g). Surface area of F3N3 catalyst is 7.95 m^2/g which decreases upto 48.67% (4.08 m^2/g) after assimilation of nickel on the F3N3 catalyst.



a Without Metal Loading **b** Nickel Loading (5%)

Figure 3.5: Effect of Metal Loading on Surface Area of the Catalyst

3.3 Performance Evaluation of Synthesized Catalysts in CO Oxidation

The fly ash catalysts supported by transition metal have been used for oxidation of CO using online GC. These oxidation reactions have been examined on 25°C, 250°C, and 500°C. These catalysts showed better catalytic activity at 500°C than 250°C.

3.3.1 Nickel catalysts

In Figure 3.6, the nickel supported F1N3 showed only 3.22% conversion of CO at 250°C which is 62.86% less catalytic active than iron supported catalyst and it converts the CO 13.76% at 500°C which is 74.85% less catalytic active than iron supported catalyst. Similarly, the nickel loaded F2N3 exhibited catalytic activity about 4.55% at 250°C which is 94.11% less catalytic active than iron supported catalyst and 12.61% at 500°C which is 87.39% less catalytic active than iron supported catalyst. The nickel absorbed F3N3 indicate only 1.31% at 250°C which is 53.04% less catalytic active than iron supported catalyst and only 8.27% at 500°C which is 86.90% less catalytic active than iron supported catalyst. The F2C1 nickel supported catalyst catalyzed the CO by 1.26% at 250°C which is 96.13% less catalytic active than iron supported catalyst and 8.15% at 500°C which is 91.85% less catalytic active than iron supported catalyst. The nickel deposited F2C2 catalyst showed the catalytic conversion 11.94% at 250°C which is 22.56% less catalytic active than iron supported catalyst but it shows highest catalytic activity among all nickel supported catalysts by 100% at 500°C. Nickel loaded F2 showed catalytic activity at 250°C which is 15.28% which is 91.81% more catalytic active than iron supported catalyst and similarly it exhibited the rate of catalytic activity at 500°C by 100%.

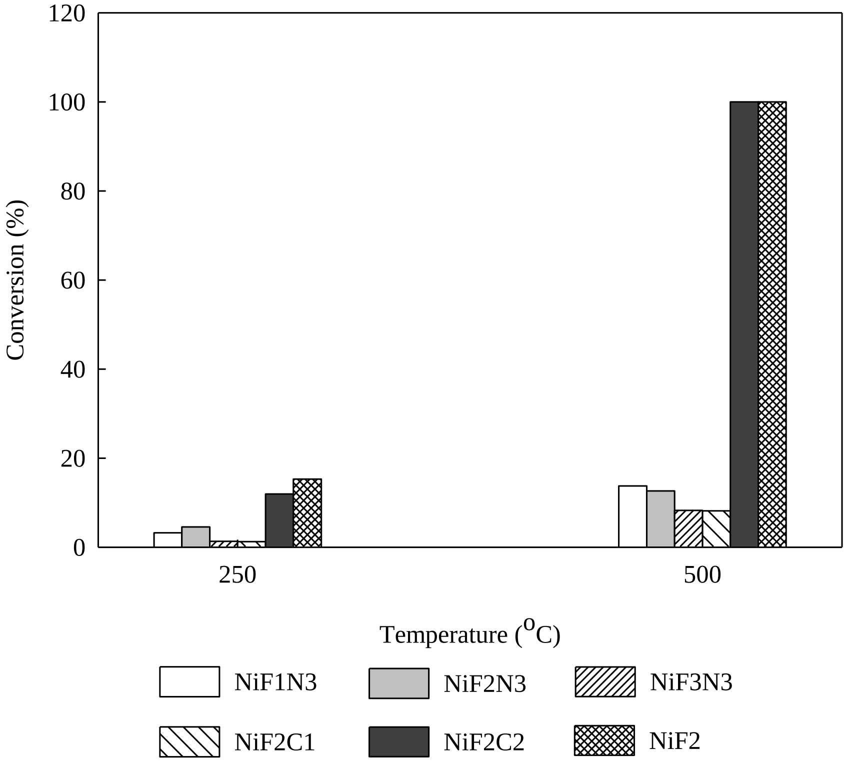


Figure 3.6: Oxidation of CO using Nickel Catalysts

3.4 Effect of Oxidation:

Oxidation of catalysts reduce the surface area due to deposition some particles so it is essential to examine the change in surface area of due to oxidation. Oxidation of different pretreated fly ash catalysts with the loading of nickel and iron, and before oxidation is also considered for the discussion.

3.4.1 Change in surface area of the catalyst during CO oxidation

The surface area of catalysts is going to be affected due to oxidation analysed in figure 3.7. Before oxidation, the surface area is high compare to after oxidation, so metal loading helps to get high surface area. The surface area of F2 catalyst is 0.94 m^2/g before oxidation which reduces up to 12.76% (0.82 m^2/g) after oxidation. Nickel loaded F2C1 catalyst has surface 2.92 m^2/g before oxidation which lesser by 26.36% (2.15 m^2/g) after oxidation. Before oxidation of F2C2 catalyst has the surface area of 1.91 m^2/g after absorption of nickel which going to decrease after oxidation by 10.99% (1.70 m^2/g). Nickel absorption on F2N3 before oxidation help to get the surface area of 2.67 m^2/g which decrease by 38.95% (1.63 m^2/g) after oxidation.

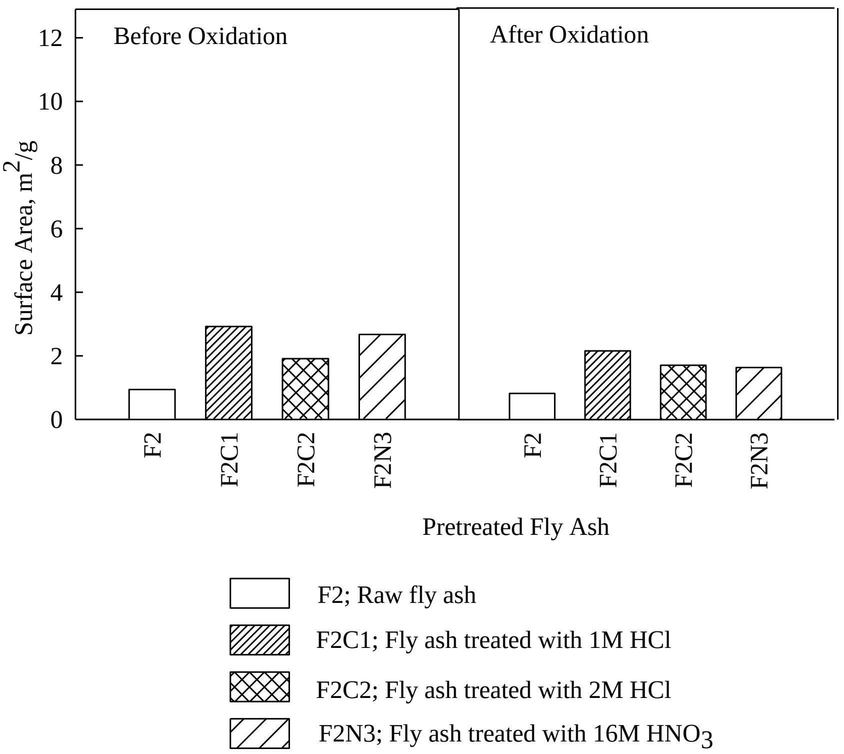


Figure 3.7: Variation in Surface Area during CO Oxidation

3.4.2 Effect of various fly ash on catalysts surface area

In figure 3.8, nickel loaded F1N3 catalyst has the surface area of 3.65 m^2/g which decreased by 47.39% (1.92 m^2/g) after oxidation. F2N3 catalyst before oxidation has surface area of 2.67 m^2/g after soaking up of nickel but after oxidation, this surface area decreased by 38.95% (1.63 m^2/g). F3N3 nickel loaded catalyst has the surface area of 4.08 m^2/g which reduced by 12.50% (3.57 m^2/g).

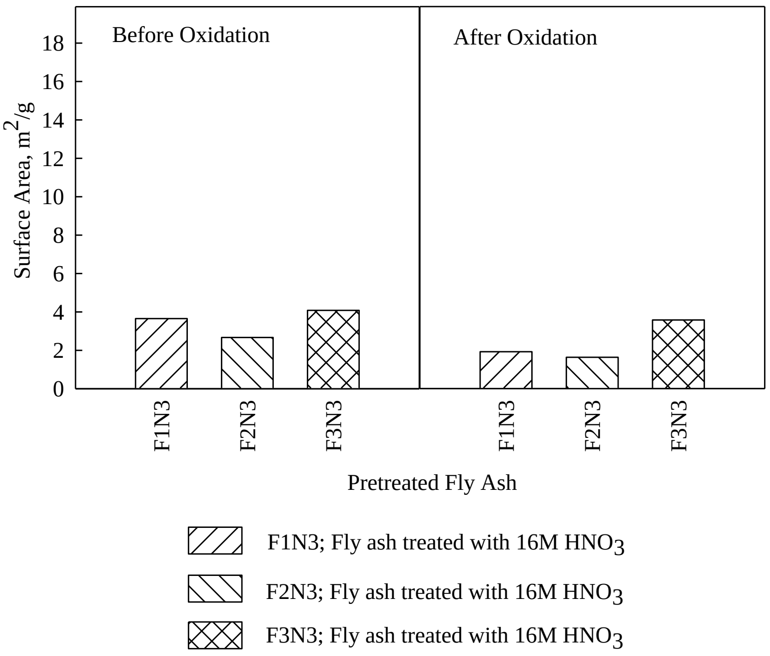


Figure 3.8: Type of Fly Ash Effect on Oxidation

3.5 Effect of experimental conditions on surface area of catalysts

In Figure 3.9, nickel absorbed F2 has surface area of 0.94 m^2/g which decrease after oxidation by 12.76% (0.82 m^2/g).

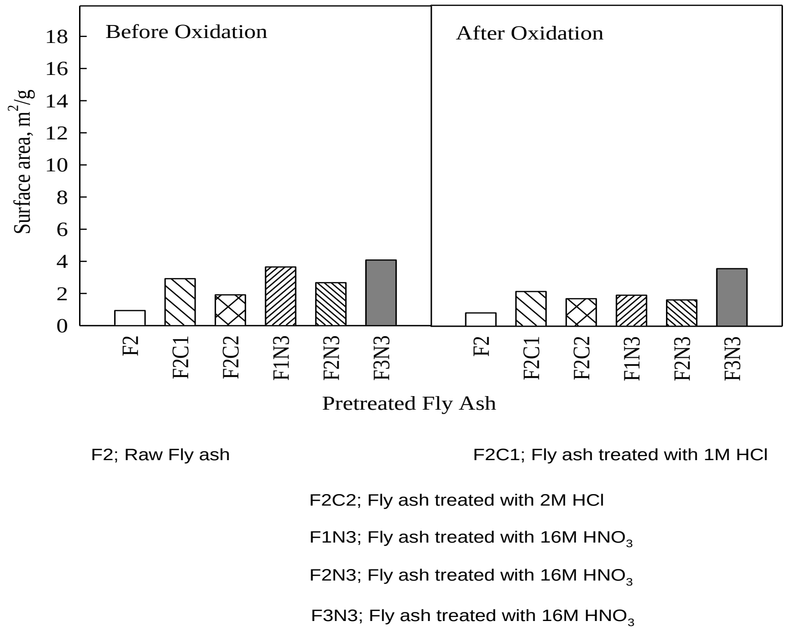


Figure 3.9: Variation in Surface Area of the Catalysts during Different Experimental Conditions

F2C1 catalyst has the surface area is 2.92 m^2/g after absorption of nickel before oxidation which comes down by 26.36% (2.15 m^2/g) after oxidation. Nickel loaded F2C2 catalyst has the surface area of 1.91 m^2/g before oxidation which is going to be little decrease by 11% (1.70 m^2/g) after oxidation. Nickel loaded F1N3 catalyst has the surface area of 3.65 m^2/g which is going to be decrease by 47.39% (1.92 m^2/g) after oxidation. F2N3 catalyst before oxidation has surface area of 2.67 m^2/g after soaking up of nickel but after oxidation, this surface area decreases by 38.95% (1.63 m^2/g). F3N3 nickel loaded catalyst has the surface area of 4.08 m^2/g which is going to be comes down by 12.50% (3.57 m^2/g).

4. CONCLUSIONS

The fly ash supported transition metal catalysts have been synthesized for the abatement of CO pollution through its oxidation. Some of prepared catalysts show complete oxidation of CO passed through them, especially at 500°C. Though the coal constituents and burning parameters may determine the surface area of generated fly ash, pre-treatments, especially with acids, significantly enhance its surface area facilitating effective metal loading and dispersion of metal's active phase.

Loading of transition metals also significantly increases the surface area of fly ash. However, iron loaded catalysts show larger surface area as compared to that of nickel loaded in all kinds of fly ash treated with different acids considered. The synthesized fly ash supportive transition metal catalysts are effective in oxidation of carbon monoxide except raw fly ash F3.

ACKNOWLEDGEMENT

The authors acknowledge the assistance of Mr. Prahlad K Tewari, Mr. Ravi K Singh, and Mr. Bhagwat S Bisht in experimental works. The authors also thank Dr. R. K. Pachauri, Director General, TERI, Delhi, India for support in carrying out this work.

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