CHAPTER 9

Isothermal Kinetics of Diesel Soot Oxidation over $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$ Perovskite Catalysts

9.1 Introduction

During the last decade, diesel engines have increased in popularity compared to gasoline engines all around the world, due to better fuel efficiency, lower operating cost, higher durability, and reliability, simultaneously associated with a favourable fuel tax situation in several countries. They are energy efficient, durable, and drivable but their emissions of particulate matter (PM) or soot and NOx are responsible of severe environmental and health problems. Specifically, diesel PM has led the legislation to adopt stringent emission standards. Diesel particulate filters (DPF) are becoming widespread as an effective measure to reduce soot emissions from diesel vehicles as they have filtration efficiencies of almost 100%. As the filters accumulate PM, it builds up back pressure that has many negative effects such as decreased fuel economy and possible engine and/or filter failure [Mishra and Prasad 2014]. To prevent these negative effects, the DPF has to be regenerated periodically, i.e. the combustion of the accumulated soot. It is therefore, vital to understand the regeneration process in order to optimize the application and operation of DPF both for lifetime durability and fuel economy purposes. However, diesel soot elimination is known to be a hard task, since

this material burns at around $600^{\circ}C$ with air, while diesel exhaust gases temperature most of the time lies between $150-450^{\circ}C$. Therefore, some artifice is needed to promote soot oxidation. Very often this is carried out by the use of an oxidation catalyst based DPF [Fino et al. 2007] in order to lower the required combustion temperatures.

Despite the significant progress in soot oxidation studies and the extended literature, there is still high uncertainty concerning the corresponding kinetic equations. Great scatter is observed regarding the reported activation energy (E), the order of reaction with respect to both the oxidants and the running soot mass [Dernaika and Uner 2003] in the oxidation reaction. The basic reasons, which lead to those discrepancies, are related with the soot samples, type of catalysts, soot catalyst contacts and experimental setup characteristics. The reported activation energy (E) of the various soot-catalyst mixtures is given in Table 9.1. Different experimental approaches have been used in the literature including thermo-gravimetric analysis (TG) [Illekova and Csomorova 2005], flow reactor [Lopez-Fonseca et al. 2005], semi-batch fixed bed reactor [Dernaika and Uner 2003]. Several studies [Ahlstrom and Odenbrand 1989, Du et al., 1991] on the kinetics of non-catalytic and catalytic soot oxidation have been reported in the literature. It is concluded that more detailed insight in the kinetics of soot oxidation might help in developing more active and selective soot oxidation catalysts and in modelling of catalytic DPF [Dernaika and Uner 2003].

Table 9.1 Reported activation energy for catalytic soot oxidation at a glance

Reference	Cat.preparation method	Experimental	Operating Parameter	E(KJ/mol)
[Dernaika and Uner 2003]	0.4% Pt/Ce-ZrO$_2$ impregnation	TPO, 700 mg soot/catal = 1:20, loose contact	Heated 5 ^{o}C/min, air flow 300 ml/min, isothermal	161
[Darcy et al. 2007]	1% Pt/Al$_2$O$_3$ impregnation	TPO, 500 mg soot/catal = 1:9, loose contact	Heated 2 ^{o}C/min, air flow 50 ml/min, non-isothermal	161
[Darcy et al. 2007]	1% Pt/CeO$_2$ impregnation	TPO, 500 mg soot/catal = 1:9, loose contact	Heated 2 ^{o}C/min in air flow 50 ml/min, non-isothermal	154
[Darcy et al. 2007]	1% Pt/La$_2$O$_3$ impregnation	TPO, 500 mg soot/catal = 1:9, loose contact	Heated 2 ^{o}C/min in air flow 50 ml/min, non-isothermal	147
[Darcy et al. 2007]	1% Pt/SiO$_2$ impregnation	TPO, 500 mg soot/catal = 1:9, loose contact	Heated 2 ^{o}C/min in air flow 50 ml/min, non-isothermal	159
[Darcy et al. 2007]	1% Pt/ZrO$_2$ impregnation	TPO, 500 mg soot/catal = 1:9, loose contact	Heated 2 oC/min in air flow 50 ml/min, non- isothermal	158
[Lopez-Fonseca et al.2005]	Mn$_2$O$_3$	TGA, Soot/Mn = 9:1 Soot doped with Mn-acetate	Heated 1.5-7.5 ^{o}C/min in air flow 50 ml/min, non-isothermal	107
[Hernandez et al. 2012]	LaCrO$_3$, La$_{0.9}$CrO$_3$, La$_{0.8}$CrO$_3$, La$_{0.9}$Rb$_{0.1}$CrO$_3$, La$_{0.9}$Na$_{0.1}$CrO$_3$, La$_{0.9}$K$_{0.1}$CrO$_3$, La$_{0.8}$Cr$_{0.9}$Li$_{0.1}$O$_3$ Soln. combustion	TGA, Soot/catal = 1/2 tight contact	Different heating rates (Φ = 5, 10, 20, 30, and 40 ^{o}C/min) air flow of 100 ml/min	142 128 123 119 129 114 115
Present Study	La$_{0.9}$Sr$_{0.1}$Co$_{0.5}$Fe$_{0.5}$O$_3$ Sol gel	Semi batch, 110 mg soot/catal = 1/10 tight contact	Isothermal, 320-350 ^{o}C, air flow 150 ml/min	101.08

A platinum group metals (PGM) coated DPF has been presented as an efficient after-treatment system. But in recent years, considering the high cost, limited availability of the noble metals and their instability with impurities, more attention has been focused on the metal oxide perovskite structure and mixed metal oxide catalysts [Mishra and Prasad 2014]. Vast literature is available for the oxidation of soot over various catalysts. Thus, this study deals with the kinetics of catalyzed oxidation of diesel soot in a laboratory set-up, using a very sturdy and selective, $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$ perovskite catalyst prepared by citric acid sol gel method. The soot oxidation was investigated under isothermal conditions at ambient pressure in a specially designed mini semi-batch reactor.

9.2 Experimental

9.2.1 Catalyst Preparation and Characterization

The double substituted perovskite catalyst was prepared by citric acid sol-gel method using nitrate precursors of the constituent element as described in the section 6.2.1 of this thesis. All AR-grade chemicals were used in the preparation of the catalyst.

The textural characterization of the catalysts was carried out by low temperature N_2-sorption method using a Micromeritics ASAP 2020 analyzer. Phase identification of the catalysts was carried out by X-ray diffraction (XRD) patterns on a powder X-ray diffractometer (Rigaku Ultima IV) using $CuK\alpha 1$ ($\lambda = 1.5405$ Å) radiation with a nickel filter operating at 40mA and 40kV. FTIR spectra of the catalysts were recorded in the range of 400-4000 cm^{-1} on Shimadzu 8400 FTIR spectrometer with KBr pellets at room temperature. The surface morphology was studied with FEI Quanta 200 scanning electron microscope (SEM) instrument. An accelerating voltage of 30kV and magnification of 10000 and 100000x were applied.

9.2.2 Bench Scale Reactor

Experimental set-up for collecting kinetic data under isothermal air oxidation of soot is shown in Figure 9.1. It was consisted of a tubular furnace with a microprocessor based temperature controller, a specially designed quartz reactor and a condenser for condensing water vapour and cooling the product gas to room temperature. The reactor has a sample tube (Figure 9.1) attached to it by B-14 socket joint and a thermocouple well for measuring the temperature of the soot-catalyst bed. The bends of the sample tube and the tube connecting the sample tube to the reactor are such that when the sample tube is at position Y, the solid sample falls into the reactor. The outlet of the reactor is connected to a cooler cum condenser as shown in the figure 9.1. The furnace temperature can be controlled to ± 0.5 ^{o}C and the temperature of the bed is measured by a thermocouple connected to a separate temperature indicator (T). There is a hole in the lower part of the outer tube of the reactor, to take care of breakage due to the expansion or contraction of air in between co-axial tubes as the unit is subjected to the variation of temperature from ambient to the reaction temperature.

9.2.3 Experimental Procedure

A known weight of the soot-catalyst mixture was taken in the sample tube and it was connected to the system (position X). Before the oxidation reaction, the soot-catalyst mixture, in a 1/10 weight ratio, were milled in an agate mortar for ''tight contact''. 110 mg of this catalyst-soot mixture was placed in the sample tube. The heating of the furnace was started and the dry and the CO_2 free air was fed at a flow rate of 150 ml/min. When the reactor attained the required temperature shown by the temperature indicator (T) the sample was dropped in the reactor by turning the sample tube by 180° (i.e. position Y) and the Gaseous products were analyzed by a gas chromatograph as a

function of time. The isothermal catalytic soot oxidation data were collected in the temperature range of 325-355 $^{\circ}$C.
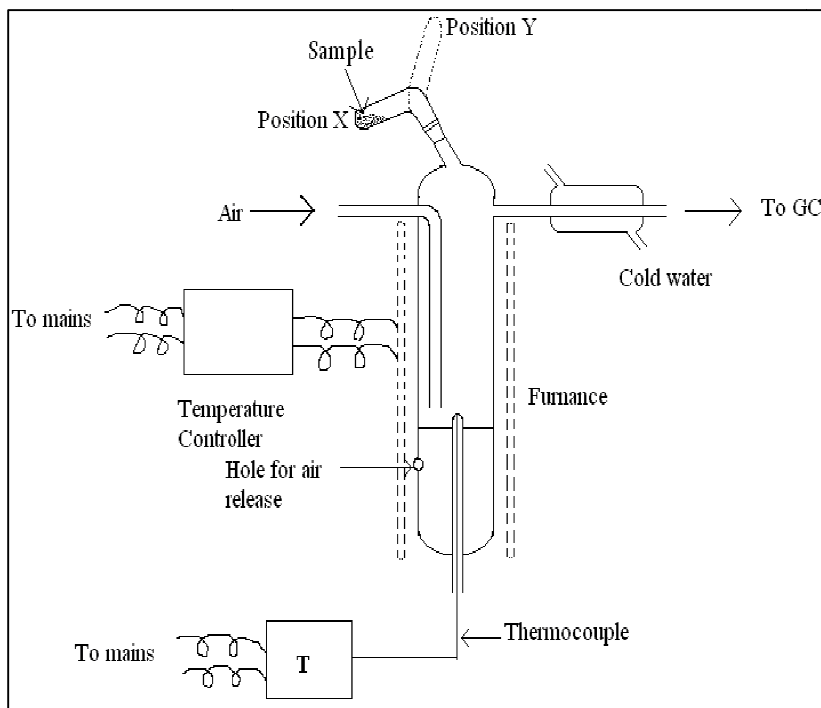

Figure 9.1 Schematic diagram of the semi-batch reactor

9.3 Results and Discussion

9.3.1 Characterization of Catalyst by XRD

The powder XRD pattern of catalyst sample is shown in Figure 9.2. The XRD peaks were found to be very sharp indicating that the ABO_3 perovskite structure is well maintained after substitution. Since the standard XRD data for substituted catalyst sample is not available in the literature, the obtained XRD data were compared with the XRD data of the standard JCPDS pattern for $LaCoO_3$ (JCPDS card No. 25-1060). The Fe-substitution in Catalyst increased the intensity of the main diffraction peaks, which indicates that Fe-substitution increases the degree of crystallization. The crystallite size of the catalyst was estimated using the Scherrer Equation 3.9, 18.42 nm.
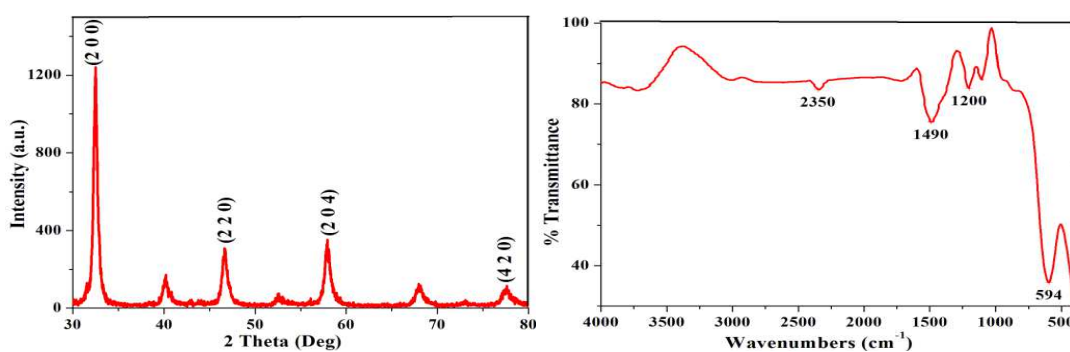
Figure 9. 2 XRD pattern and FTIR spectra of the Perovskite Catalyst

9.3.2. Characterization of Catalyst by FTIR

Figure 9.2 depicts the FTIR spectra of the catalyst calcined at $750^{o}C$ in stagnant air. The broader peak appeared at 594 cm-1 is characteristic of the MO6 octahedra commonly found in perovskite oxide powder and is observed in this system, too (Ramesh et al., 1995). The peaks found near to 2350 cm^{-1} in the samples are due to the presence of atmospheric moisture as reported earlier [Mandelovici et al. 1994]. The absorption band at 1490 is corresponded to nitrate ion. In addition, the band at 1200 cm-1 is corresponded to Co-OH bending which is confirmed with the reported value that MOH bending mode appears below 1200 cm^{-1} [Nakamoto1997].

9.3.3. Characterization of Catalyst by SEM

The SEM micrographs of perovskite catalyst at different magnifications are shown in Figure 9.3. It can be seen that the morphologies of particles are of irregular shape and within the nanoscale (>100 nm). Morphological microscopy of the explored samples also demonstrated agglomerates that involved mostly thin, smooth flakes and perforated cracked layers having large number of pores.
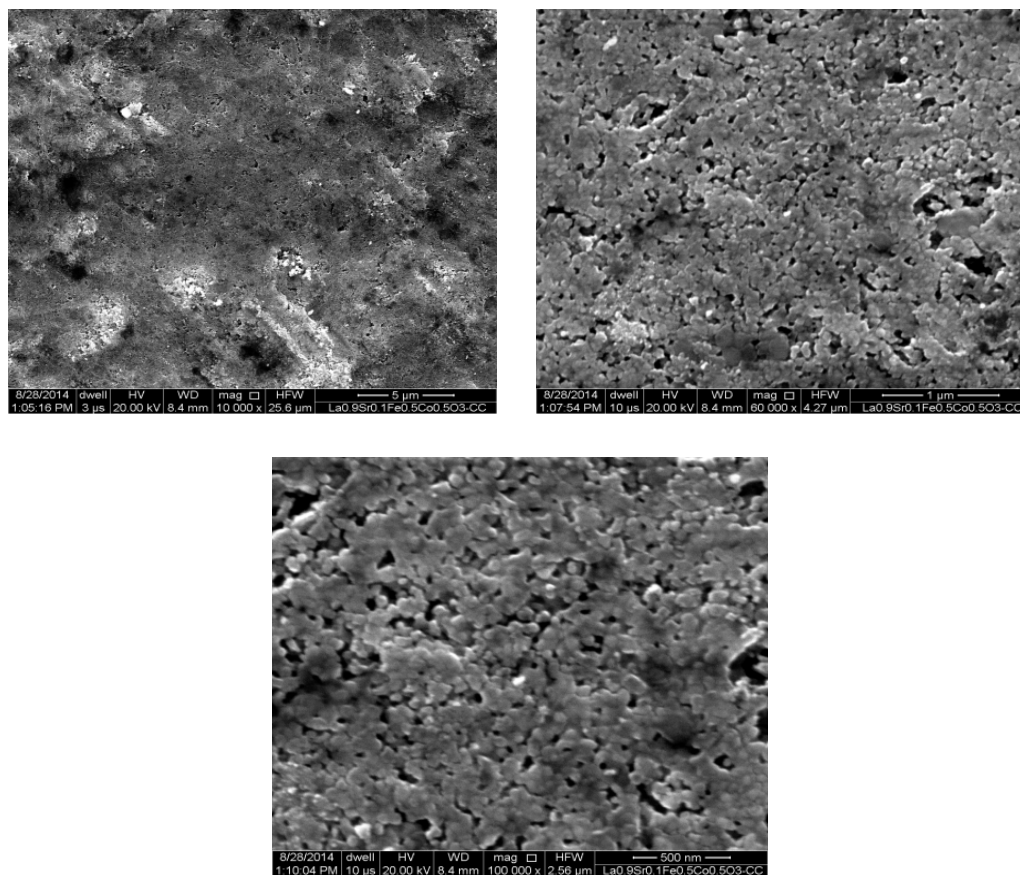
Figure 9. 3 SEM images of the perovskite Catalyst at different magnifications

9. 3.4. Catalytic Combustion of Soot over La$_{0.9}$Sr$_{0.1}$Co$_{0.5}$Fe$_{0.5}$O$_{3-\delta}$ Catalyst

The activity of the catalyst for soot oxidation was evaluated on the basis of light off temperature characteristics T$_i$, T$_{50}$ and T$_f$, i.e. the temperature corresponding to the start of soot ignition, the 50% conversion of soot and complete combustion of soot respectively. All the catalysts were selective for CO$_2$ as no CO was detected in the flue stream and showed total combustion of soot within the diesel exhaust range of 150-450°C (figure 9.4). To verify the reproducibility of the experimental data each experiment was performed at least twice repeatedly for the soot oxidation and the data were found to be reproducible within ± 1% of deviation.
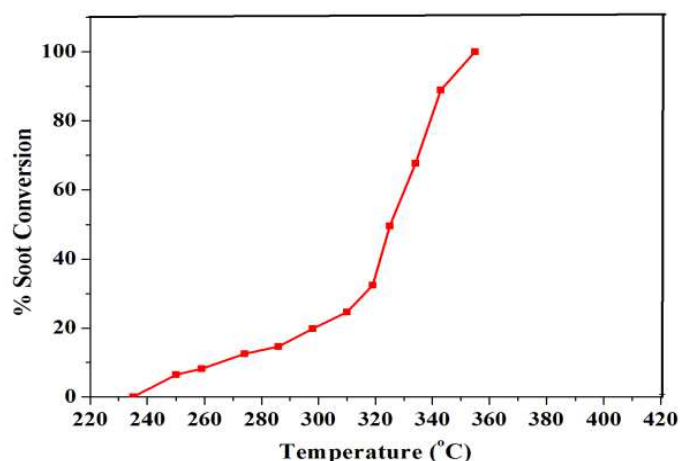
Figure 9.4 Soot conversion over $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$, calcination at 750^oC, catalyst/soot: 10/1, tight contact, air flow rate: 150 ml/min

Table 9.2 Characteristic light off temperature for soot oxidation over perovskite catalysts

| Catalyst	$T_i(^oC)$	$T_{50}(^oC)$	$T_f(^oC)$
$La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$	238	330	355

3.6. Kinetics Study

The kinetics of catalyzed soot oxidation with air was studied under isothermal conditions as described above. Temperature range chosen for performing kinetic study is predicted from below mentioned light off temperatures of $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$ catalyst (Table 9.2). The screening of the prepared catalysts showed that $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$ was the most active for soot oxidation under the experimental conditions studied [Mishra and Prasad 2015]. Therefore, $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$ catalyst in tight contact with soot was chosen to determine the kinetic model, activation energy and Arrhenius constant of the oxidation reaction as discussed below.

3.6.1. Determination of Kinetic Model

Figure 9.5 shows the chromatogram area at varying time obtained during experiment at four different constant temperatures (325, 335, 345 and 355 ^{o}C). Here as temperature increases the time required for complete oxidation of soot decreases due to higher rate of oxidation at higher temperature.

The fractional conversion of soot, (α) is defined as:

$$\alpha = (m_o\text{-}m_i)/m_o \qquad\qquad (9.1)$$
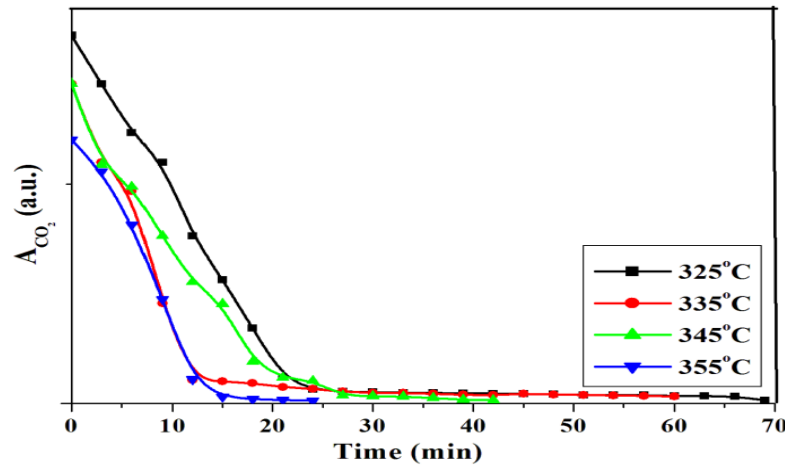
Figure 9.5 Plot of chromatogram area of CO_2 (ACO$_2$) vs time at four constant temperatures over $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$

Where, m and m_o are the running and the initial sample mass respectively. The value of α at various extent of reaction is calculated using the following formula:

$$\alpha = \frac{\sum_0^t (\bar{A}_{co2})_i \, \Delta t_i}{\sum_0^\infty (\bar{A}_{co2})_i \, \Delta t_i} \qquad\qquad (9.2)$$

where, Δt is the time differences. The empirical rate law equations as favoured by Levenspiel (1999), have been used to derive the kinetic parameters of diesel soot oxidation. The most general rate equation of solid-state reaction as given by Equation (9.3).

$$d\alpha/dt = k\ f(\alpha) \qquad (9.3)$$

Where α is fractional conversion, k is the reaction rate constant at any temperature and $f(\alpha)$ is any function of conversion. The assumption often made in the literature (Neeft et al. 1997) is that the global soot oxidation rate in large excess oxygen can be described by a first order kinetic equation with respect to fraction conversion of soot, (α). In the present study flowing oxygen was in large excess, therefore Equation (9.3) becomes pseudo first order:

$$d\alpha/dt = k\ \alpha \qquad (9.4)$$

Integrating Equation (9.4) we get:

$$\ln \alpha = kt \qquad (9.5)$$

Calculating α from Equation (9.1) and plotting Equation (9.5) as ln α vs. t, one should get a straight line passing through the origin. Figure 9.6 shows such plot for the first order kinetics of soot oxidation.

These results obtained are best fit models having a high regression coefficient. Slope of the straight lines gives the values of reaction rate constants, 'k' at different temperatures.
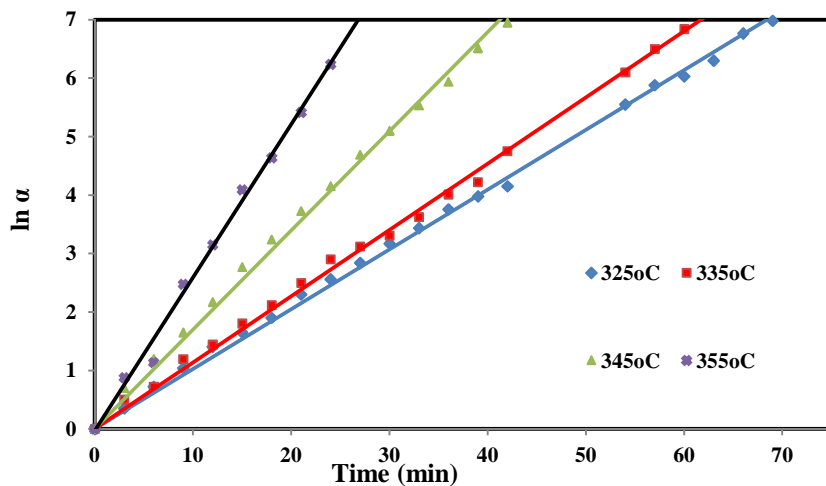
Figure 9.6 First order kinetics model for catalytic oxidation of soot at different temperature

3.6.2. Determination of Activation Energy

The kinetic rate constant 'k' in the model Equation (9.4) is temperature dependent and expressed by Arrhenius equation (Equation 9.6):

$$k = Ae^{-(E|RT)} \tag{9.6}$$

Where A is the frequency factor, E is activation energy, T is absolute temperature, R is the gas constant. On taking log of equation (9.6), it can be written as
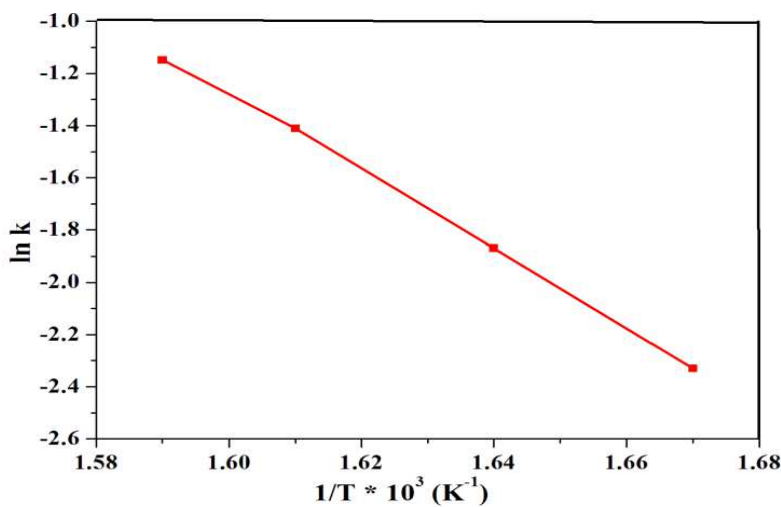
$$lnk = lnA - \frac{E}{RT} \tag{9.7}$$

And at two different temperatures this equation modifies to

$$\frac{k1}{k2} = e^{-\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \qquad where \ T_2 > T_1 \tag{9.8}$$

The obtained value of k when fitted in equation (9.7) gives straight line also known as Arrhenius plot as shown in the Figure 9.7. The slope of the straight line 'S' is related to activation energy which can be given as follows

$$S \quad = -\frac{E}{R} \tag{9.9}$$

Figure 9.7 Arrhenius plot for catalytic oxidation of soot

With the help of Arrhenius plot obtained value of activation energy, E = 101.08 kJ/mol. The value of the activation energy obtained is lower than that reported by various previous authors. Again using equation (9.9) for two different temperatures frequency factor 'A' was calculated which is equal to $6.46*10^{10}$. Thus the rate of catalytic oxidation of soot can be written as follows:

Rate = $6.46*10^{10}$exp (-101.08 kJ/RT)(α) g soot/(g cat. min).

9.4 Conclusions

Soot oxidation was studied in a specially designed mini semi-batch reactor under isothermal conditions. Intrinsic reaction rate of air oxidation of diesel soot over $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_{3-\delta}$ catalyst was determined as a function of temperature and fractional conversion in the temperature range of 325-355°C, given by

Rate = $6.46*10^{10}$exp (-101.08 kJ/RT) (α) g soot/ (g cat. min).

The value of activation energy is found to be 101.08 kJ/mol which is the least compared with the reported activation energy for different catalysts in the literature.