CHAPTER – 5

Kinetics Study

Kinetics of NO-SCR

5.1 General

A number of experiments were performed before the kinetics study, in order to know whether physical limitations on the reaction were absent or not. The catalyst bed was diluted to 1 mL with α-alumina in all the experiments purposely to increase in heat transfer area so that the bed temperature remain uniform under kinetic data collection. A blank test with 1 mL α-alumina used as catalyst diluent was performed in place of the catalyst which did not show any activity for NO conversion within the experimental conditions. The investigative tests of external and internal mass transfer limitations were also performed, which showed that the reaction was free from mass transfer restrictions.

Chemical kinetics describes the measured value of reaction rate, used to design a reactor. The apparent rate may be influenced by the physical texture of the catalyst. The porous catalyst particle has a maximum advantage if the active catalyst surface is freely accessible for the reaction, physical resistances at the interface and inside the pores are reduced to the minimum. The significant kinetic data can be obtained from a packed bed reactor, only if the flow pattern within the reactor resembles plug flow. The plug flow behavior provides a simple relationship between ratio of catalyst weight to feed rate and the rate of reaction.

5.2 Experimental

5.2.1 Blank Experiments

Blank runs were made with α-Al_2O_3 only in place of the catalyst. As bed temperature increase up to 300^oC practically no reduction of NO has been observed at different space velocities (Figure 5.1). Thus catalytic effect of the preheater or reactor walls and alumina used as diluent may be neglected below 300^oC.

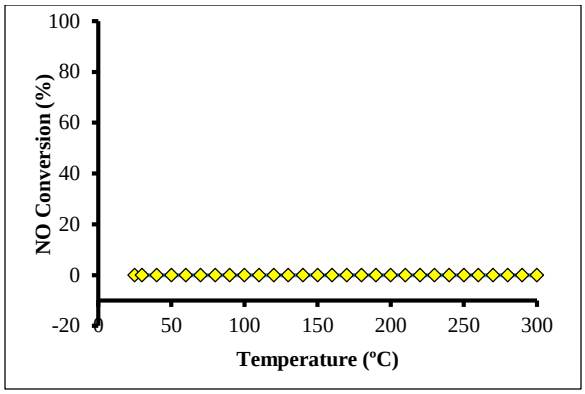

Figure 5.1. Blank test of α-Al_2O_3 over Cat-K

5.2.2 Effect of particle size

To ascertain whether the physical rate processes are interacting significantly with chemical processes, a study of conversion of NO as affected by the particle size of various catalysts and the amount of the catalyst were made under following reaction conditions: temperature: 300K (27°C), feed composition 0.5% NO by volume and W/F_{NO} 27.1 gm-h/gm mol. Figure 5.2 shows the effect of particle size on conversion for different catalysts. It is clear that there was no significant change in the extent of conversion when the particle size was varied between 80-200 mesh no.

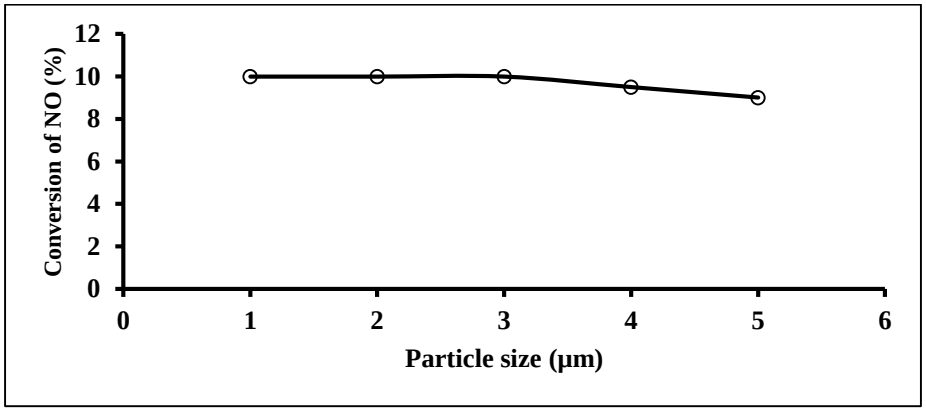

Figure 5.2. Effect of particle size of catalysts on conversion of NO at 300K, feed composition: 0.05% NO by volume, W/F_{NO}: 27.1 gm cat-h/gm mole on Cat-K

But conversion of NO started decreasing for highest particle size than mentioned above. Thus, it is diffusion resistance was not significant in the particle size ranging from 80-200 mesh no. Therefore, particle size 100-150 mesh selected for present study.

5.2.3 Effect of bed height

No change in the conversion was noticed when the quantity of the catalysts was varied, for Cat-R from 0.1 gm to 0.2 gm with a fixed value of temperature feed composition and W/F_{NO}. The experiment data has been shown in Figure 5.3. This shows that external mass transfer probably does not limit conversion rate for value of W/ F_{NO} <27.1 gm cat-h/ gm mol and temperature < 127^{o}C, which were chosen for kinetics studies.

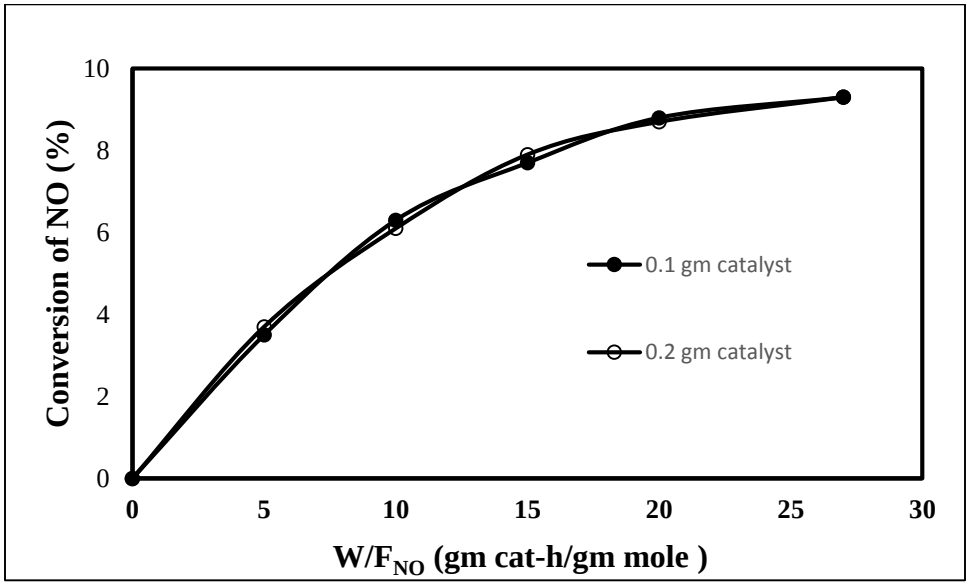

Figure 5.3. Effect of catalyst weight on conversion of NO at 300K, feed composition: 0.05% NO by volume, W/F_{NO}: 27.1 gm cat-h/gm mole on Cat-K

The precautions, taken to avoid a temperature rise of the catalyst bed were sufficient to assure isothermal behavior. Hence, the less severe criteria for the absence of intra-particle heat transfer limitations are automatically satisfied.

The reactor to particle diameter ratio of 20-30 was sufficient to assume a flat velocity profile across the reactor diameter. The catalyst bed length to particle diameter ratio of 50-80 allows one to neglect the axial dispersion in the catalyst bed. In the present study, the latter two conditions are adequately satisfied and which implies that reactor system can be considered an ideal plug flow reactor.

The empirical power law rate expression for the conversion of NO into N_2 was obtained on the catalyst, Cat-K which showed highest activity among the various catalysts tested and has been discussed below:

Meaningful kinetic data can be obtained from a packed bed reactor only if the flow pattern within the reactor resembles plug flow. Plug flow behavior provides a simple relationship between feed rate and the rate of the reaction. The ratio of diameter of reactor to particle should be greater than 15 and ratio of catalyst bed length to its diameter should be 3 - 15 for a flat velocity profile [198]. In the present study, these ratios were 30 and 6, which satisfied the conditions of plug flow in the reactor. Therefore, the following eq. 5.1 can be derived by applying the principle of material balance on NO in the reactor under steady state conditions:

$$-r_{obs} = dX_{NO} / d(W/F_{NO}) \qquad (5.1)$$

A series of runs in a packed bed was made using varying reciprocal weight hourly space velocity (W/F_{NO}). The mass of the catalyst, 0.2 gm, was kept constant throughout the steady state experimental program. Variation of W/F_{NO} was achieved by adjustment of feed rate of NO. To minimize heat and mass transfer effects and to appropriate differential reactor, conversion for each run was kept <10%. The rate at any conversion can be obtained by taking the slope of X_{NO} versus W/F_{NO} plot.

Once the rate of reactor is known as a function of concentration of limiting reactant, an empirical power law type of the equation can be fitted:

$$-r_{obs} = k(C_{NO})^n \qquad (5.2)$$

Table 5.1: Fractional conversion of NO (X_{NO}) vs W/F_{NO} at different temperatures

W/F_{NO} gm-cat-h/ gm mol	Conversion at temperature (^oC)			
	27	37	47	57
10.1	0.013	0.026	0.040	0.060
13.7	0.016	0.035	0.052	0.074
18.3	0.020	0.040	0.062	0.088
27.1	0.024	0.050	0.075	0.100

The rate constant, k is a function of temperature and can be represented by Arrhenius equation:

$$k = A \exp(-E/RT) \qquad (5.3)$$

If the power law functionality is successful and r versus C_{NO} data are known at constant temperature n and k at that temperature can be determined from log-log plot of r_{obs} versus C_{NO}. The activation energy of the reaction, E can be evaluated from the slope of a plot of ln k versus 1/T.

A plot of conversion of NO to N_2 (X_{NO}), when the catalyst showed steady performance, versus W/F_{NO} at four different temperatures is shown in Figure 5.4.

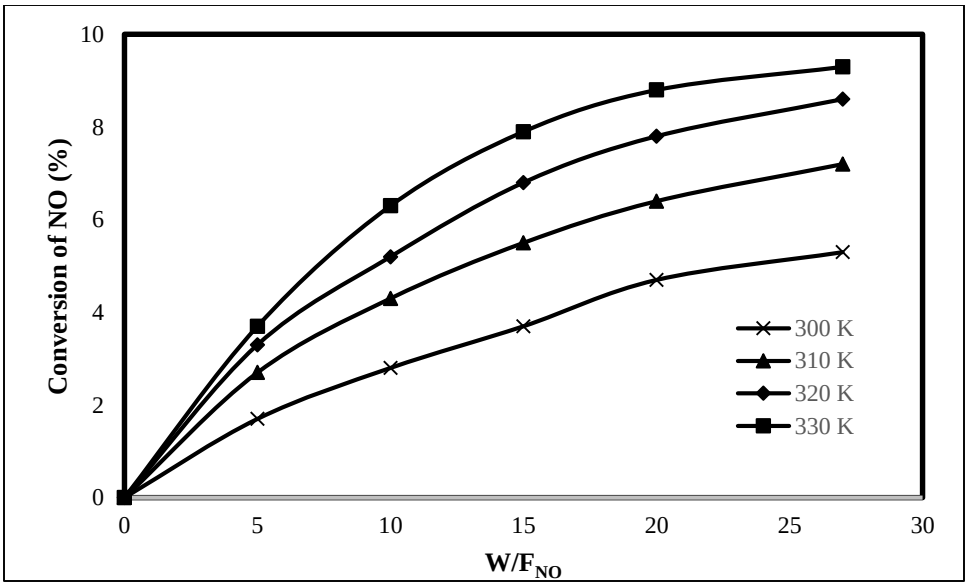

Figure 5.4. Conversion of NO (%) Vs W/ F_{NO} at 300, 310, 320, 330K

Rates of reaction (r_{obs}) at different conversion levels for each temperature were calculated by measuring the slopes of the curve (differential method of analysis of rate data). The calculated rates at different conversion are given in Table 5.2.

Table 5.2. Rate of reaction, r_{obs} (gm mol NO/ gm Cat-h) and concentration, C_{NO} (gm mole/ ml) at different conversion (X_{NO})

Temperature (^oC)	X_{NO}	C_{NO} x 10^7	r_{obs}
27	0.015	10.82	0.0063
	0.017	10.56	0.0059
	0.020	10.29	0.0056
	0.022	10.02	0.0052
37	0.030	10.67	0.0202
	0.036	10.42	0.0183
	0.042	10.15	0.0172
	0.048	9.91	0.0165
47	0.045	10.29	0.0498
	0.055	10.01	0.0464
	0.064	9.78	0.0428
	0.072	9.54	0.0399
57	0.065	10.01	0.1023
	0.078	9.78	0.0963
	0.086	9.54	0.0907
	0.096	9.30	0.0863

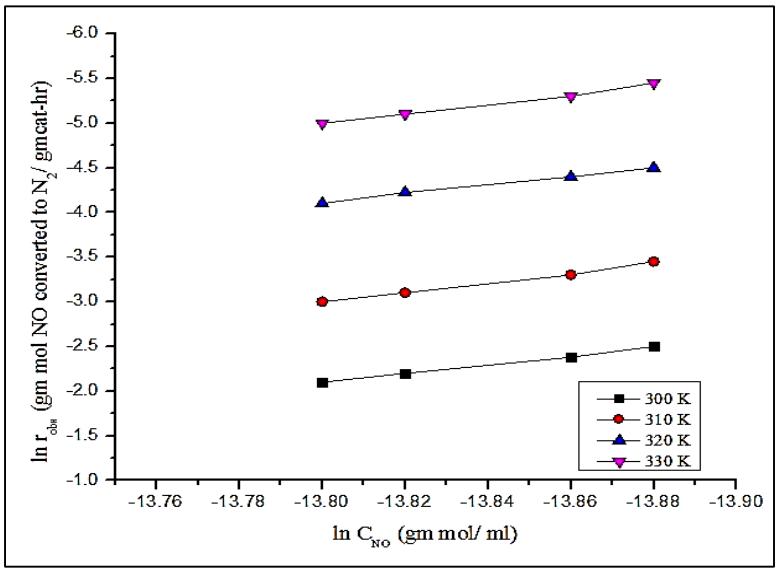

Figure 5.5. Plot of ln r_{obs} vs. ln C_{NO} at 300, 310, 320, 330K

Plots of r_{obs} versus C_{NO} is shown in Figure 5.5 for four different temperatures at which data were recorded. The plots are linear. It must be pointed out that the reactant (NO) was a lean mixture (0.05%), and conversion was less than 10% therefore the change in volume in the course of reaction was negligible and the following expression was valid.

Table 5.3. Order of reaction (n) and rate constant, k (gm mol/gm cat-h) at different temperature (ºC)

Temperature (ºC)	n	k
27	0.70	0.0067
37	0.70	0.0178
47	0.71	0.0387
57	0.70	0.0820

$$C_{NO} = C_{NO\,(inlet)}\,(1-X_{NO}) \qquad (5.4)$$

Slope and intercept of the lines give order of reaction (n) and ln k respectively, which are reported in table 5.3. Order of the reaction was found to be 0.70**.** The activation energy (E) and pre-exponential factor (A) of Arrhenius equation were calculated by measuring the slope and intercept respectively of the plot of ln k versus 1/T as shown in Figure 5.6.

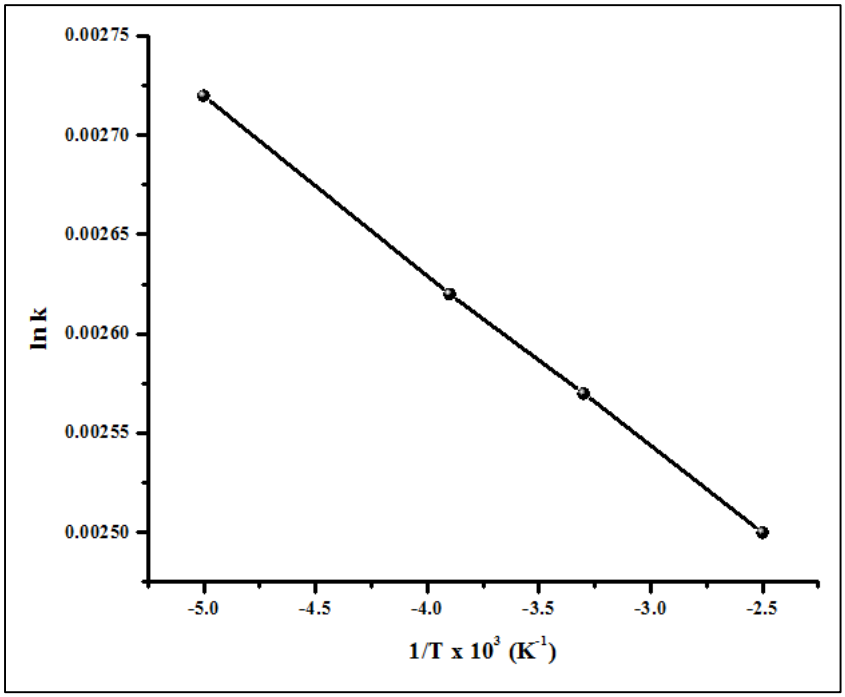

Figure 5.6. Arrhenius Plot

The values thus obtained are: Activation energy (E) = 93.82 kJ/ gm mol; Pre-exponential factor = 14.78×10^{10} gm mol/ gm cat-h

The value of activation energy obtained is lower among the values of activation energy reported in literature by different workers. This confirms the higher activity of the best catalyst, Cat-K than the commercial catalyst for NO-SCR.

On the basis of the experimental findings and the above discussions the observed rate of reaction in the temperature range of 27-57^{o}C on the supported catalyst, Cat-K can be expressed as: 14.78×10^{10} exp (93820 / RT) $C_{NO}^{0.7}$ gm mol/gm cat-h.