The oxidation of NO to NO$_2$ ($\text{NO} + \frac{1}{2} \text{O}_2 = \text{NO}_2$) over a supported noble metal component is an important step involved in NOx abatement techniques, e.g., selective catalytic reduction (SCR) and NOx storage/reduction (NSR) processes being developed for lean-burn diesel engines to limit their NOx emission. In fact, NO to NO$_2$ oxidation is the first step that occurs in the cyclic NSR process. Pt has been the oxidation catalyst of choice due to its high red-ox activity and its presence as a major component in the current automobile exhaust (or three-way) catalysts.

We demonstrate here the kinetics of NO oxidation reaction on a Pt/Al$_2$O$_3$ catalyst. The kinetics measurements were randomized and their design was based on a modified full factorial approach. The experiments were thus performed at all combinations of selected temperature and species concentration levels which were varied simultaneously to account for the possible interactions between the kinetic parameters. The rate equation for the reaction was determined to be:

$$r = k [\text{NO}]^{1.05 \pm 0.08} [\text{O}_2]^{1.03 \pm 0.08} [\text{NO}_2]^{-0.92 \pm 0.07}$$

where $k$ is the rate constant with an apparent activation energy of 82 kJ mol$^{-1}$ ± 9 kJ mol$^{-1}$. Thus, the product NO$_2$ inhibits the forward rate. Based on our experimental results, we have proposed a reaction mechanism consisting of the following elementary steps:

1. $\text{NO} + * \leftrightarrow \text{NO}^* \quad \text{(quasi eqbm., } K_1\text{)}$
2. $\text{NO}_2 + 2 * \leftrightarrow \text{NO}^* + \text{O}^* \quad \text{(quasi eqbm., } K_2\text{)}$
3. $\text{O}_2 + * \rightarrow \text{O}_2^* \quad \text{(rate determining step, } k_3\text{)}$
4. $\text{O}_2^* + * \rightarrow 2\text{O}^* \quad \text{(O}^*\text{ = most abundant surface species)}$

where * denotes a Pt site and $K_i$ and $k_i$ the equilibrium constant and rate constant of the $i^{th}$ step respectively.

We will also discuss the effects of Pt particle size/metal size and other exhaust gas species like water on this reaction. Our experimental results indicate that an increase in the Pt particle size from ca. 2.5 nm to ca. 7.0 nm caused the turnover rate (TOR) to increase 4 times, showing that larger Pt particles can turnover faster. Water vapor was found to have an irreversible effect on this reaction in that it decreased the surface area of the catalyst but did not alter the activation energy and reaction orders.

Deactivation of the catalyst was observed. Flow experiments and XPS measurements suggest that the deactivation is due to over-oxidation of Pt by the reaction mixture. It takes a two-monolayer equivalent of oxygen to completely deactivate the catalyst. Moreover, two catalyst samples with Pt particle sizes of ca. 2.5 nm and 7.0 nm were found to get oxidized to the same extent after NO oxidation reaction and also after their complete deactivation, suggesting that Pt oxidation is independent of its particle size.