Summary

This PhD Thesis is devoted to experimental study of the catalytic converters used for the aftertreatment of exhaust gas from Diesel and lean-burn gasoline engines, namely Diesel oxidation catalyst (DOC) and NO\textsubscript{x} storage and reduction catalyst (NSRC). Diesel oxidation catalyst is used primarily for the oxidation of CO and unburned hydrocarbons, but partial reduction of NO\textsubscript{x} by hydrocarbons takes place as well. The NO\textsubscript{x} storage and reduction catalyst is used to abate NO\textsubscript{x} emissions in alternating lean (low CO and HC concentration, excess of O\textsubscript{2}) and rich (high CO and HC concentrations) conditions. Depending on the reaction conditions, several N-products (N\textsubscript{2}, NO, NH\textsubscript{3} and N\textsubscript{2}O) can be formed during the NO\textsubscript{x} reduction. The NO\textsubscript{x} reduction selectivity is studied experimentally with samples of the industrial DOC and NSRC converters. The attention is focused mainly on the kinetics of N\textsubscript{2}O formation during the regeneration of the NO\textsubscript{x} storage and reduction catalyst. The N\textsubscript{2}O is emitted in two peaks — the first peak appears after the switch from the lean to rich conditions as a product of the incomplete NO\textsubscript{x} reduction. The second N\textsubscript{2}O peak is formed at the transition back from the rich to lean conditions.

This Thesis is divided into three main parts. The first part (Chapter 1) is devoted to a review of the automotive emissions and possible methods of their treatment. The main types of catalytic converters used for the emission abatement are described along with the principles of their operation and key catalytic reactions. The NO\textsubscript{x} storage and reduction catalyst (NSRC) is discussed in more detail, especially the mechanisms and selectivity of the stored NO\textsubscript{x} reduction in the dependency on the local reaction conditions during the regeneration period.

The apparatus used for experiments are described in Chapter 2. The first part of experimental work was performed using the bench flow reactor at the Department of Chemical Engineering, Institute of Chemical Technology, Prague. This involves steady-state measurements of reactions light-off for the DOC sample as well as lean/rich cycling experiments with the NSRC sample, focused mainly on the N\textsubscript{2}O formation kinetics. The second part of the experimental work was performed at the Fuels, Engines and Emissions Research Center, Oak Ridge National Laboratory. These experiments were dedicated to
the identification of the reaction mechanisms for the secondary $\text{N}_2\text{O}$ peak formation in the NO$_x$ storage and reduction catalyst. Two laboratory reactors were employed with different methods for analysis of gas components and reaction intermediates in the catalyst: SpaciMS (Spatially Resolved Capillary Inlet Mass Spectrometry) and DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy).

The obtained experimental results are described and discussed in the third part of the Thesis (Chapter 3). In the Section 3.1, dependence of the light-off temperatures of individual reactions on the DOC inlet mixture composition is discussed in detail, and the self- and cross-inhibition effects of CO, C$_3$H$_6$, NO and NO$_2$ are quantified. Very high selectivity of the lean NO$_x$ reduction by hydrocarbons to $\text{N}_2\text{O}$ is observed with all tested gas compositions.

The Section 3.2 summarizes the results obtained with the NO$_x$ storage and reduction catalyst in Prague. After the initial screening of the catalyst activity (lean and rich light-off experiments, isothermal NO$_x$ adsorption and lean/rich cycling at different temperatures in the range 150–550°C), the additional experiments were dedicated to the kinetics and selectivity of NH$_3$ reactions in the NSRC (NH$_3$ oxidation with O$_2$ and NO$_x$ in a gas phase, interactions of NH$_3$ with the stored O$_2$ and NO$_x$, and the influence of CO$_2$ and H$_2$O presence in the feed).

The results obtained from the SpaciMS and DRIFTS measurements at Oak-Ridge National Laboratory are presented in the Section 3.3. These experiments were focused primarily on the elucidation of the $\text{N}_2\text{O}$ formation dynamics under various regeneration conditions. The formation of reduction intermediates and their possible effect on the secondary $\text{N}_2\text{O}$ formation as well as their inhibition effect on the regeneration process are discussed in detail. A reaction mechanism proposed for the secondary $\text{N}_2\text{O}$ formation at the rich/lean transient involves reactions of the residual stored NO$_x$ (remaining on the catalyst surface after an incomplete regeneration) with the adsorbed reductants under increasingly lean conditions.