Catalysts for Automotive Exhaust Cleaning
-Aspects on TWC Deactivation and Lean NO_x Reduction

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Abstract

From both environmental and human health perspectives, it is desirable to reduce the air pollution from road traffic. One successful technology which has been used for several decades is based on the so called three-way catalytic converter (TWC). TWC's simultaneously reduce the main pollutants CO, hydrocarbons (HCs) and NO from conventional gasoline engine vehicles. Recently, the environmental threat of global warming calls for a reduction of fossil carbon dioxide emissions and an improved fuel economy in the transportation sector. A step towards this is substituting conventional Otto engines by the more fuel-efficient diesel and lean burn gasoline engines. However, the lean oxygen-rich environment makes the conventional TWC no longer efficient in removing NO_x from such engines. One objective of this thesis was to study zeolite materials for selective catalytic reduction (SCR) of NO_x with hydrocarbons (HC-SCR) at lean conditions. Another objective was to obtain information on the state of in-use TWCs in Swedish car fleet, their performance and possible deactivation factors.

48 full scale commercial TWCs were investigated by using a test rig. Their performances were investigated in terms of light-off temperature, steady state, as well as transient conversion for CO, HC and NO at lean and stoichiometric conditions. The results show that there was no significant impact of aging up to about 120 000 km. The steady state conversion for CO and HC were not significantly affected by aging. However, the steady state conversion of NO was reduced with increased mileage at the conditions studied. The results of high HC transient conversion showed a considerable difference between individuals. A trend of decreased transient conversion was noted above 120 000 km. The surface characterization shows that the main cause of deactivation was loss of specific surface, both of washcoat and precious metals. Poisoning elements, typically phosphorus, lead, sulphur and calcium, were found on the catalysts surface. The investigation indicates that NO_x conversion is the property most sensitive to aging in the studied material.

The activity for lean NO_x reduction by propane, isobutane, n-pentane and n-octane was investigated in flow reactor experiments over acidic zeolite, with or without the presence of water vapor. The NO_x reduction and N_2 formation is strongly dependent on the hydrocarbon. Isobutane was efficiently activated by the catalyst at low temperature, and, the NO_2 reduction was sustained over a wide temperature range. Octane was activated at low temperature; however at the same time it was probably cracked into small active species which were also reacting with oxygen, thus the NO_x to N_2 reduction was low. The influence of zeolite acidity on the SCR reaction, and the reaction mechanism was studied by step-response experiments with in-situ Fourier Transform Infrared (FTIR) Spectroscopy over acidic zeolites. The activity correlated well with zeolite acidity and the reaction seems to proceed via Brønsted acid sites. It is likely that hydrocarbons were activated over the Brønsted acid sites forming carbenium ion-like species, and the resulting derivatives react with adsorbed NO^+ species to form isocyanates. The latter compounds appear to be hydrolyzed to amine species. Rapid reaction of isopropylamine with NO_2 over Brønsted acid sites was observed by FTIR in diffusive reflectance mode (DRFITS). It is thus conceivable that amine species are reaction intermediates in the SCR reaction under the conditions of the present work. The hydrocarbon activation and the formation of NO^+ species are indispensable initiating steps for the reaction to occur.

Key words: Three way catalytic converters, deactivation, lean NO_x reduction, saturated hydrocarbons, HZSM-5, acidic mordenite, in-situ FTIR, Brønsted acid sites