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Automotive Emission
Control

Edited by

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PREFACE

Automotive Emission Control

Automotive emission control is certainly one of the success stories of our profession. Faced with both acute and chronic environmental problems such as smog and acid rain, in the seventies of the last century industry in general and car manufacturers in particular engaged in a major research and development effort. Since then, environmental regulations have become more stringent with so-called zero emission vehicles as ultimate goal. To meet this challenge it was not sufficient to limit progress to the internal combustion engine front alone. It soon appeared that catalytic oxidation of the non-combusted hydrocarbons (function 1) and carbon monoxide (function 2) as well as the reduction of nitrogen oxides (function 3) was required. The three-way catalytic converter was born. It can be safely stated that today this is the most abundant catalytic reactor in the world. From it a lot of other technologies evolved, the most common being NO_x storage and reduction catalysts and selective catalytic reduction (SCR) catalysts both for lean NO_x removal, diesel oxidation catalysts for lean CO and hydrocarbon removal and (coated) diesel particulate filters for soot removal, or combinations of those. Moreover the range of conditions at which these devices are operating is much broader than that of any chemical reactor in the process industry.

Of course, a key to this success has been the design of catalysts combining different functions and resistant to the harsh reaction conditions. That is why the first contribution of this issue, the most “chemical” one, illustrates the present approach with respect to so-called three-way catalysts and NO_x storage practised by the largest car manufacturer in the world. Issues related to oxygen storage and release, to the sintering of the precious metals group catalyst components as well as to the details of the NO_x storage and reduction are discussed. The present level of understanding is impressive and the expectation is for further progress.

This volume, however, emphasises the role of chemical engineering in automotive emission control. Clearly the development of mathematical models describing the different functions of the converter(s), as well as their interaction, has been and still is crucial. Each of the contributions advocates the implementation of the latter, combined with experimental validation, rather than engaging into elaborate experimental programs. The developed reactor models are capable of covering the wide range of operating conditions. Even more challenging, they cover quite a spectrum of time and length scales. They

are, e.g. accounting for the transient operation connected to both the cold start-up of the engine and the periodic changes of the composition of the engine outlet induced by the interaction between the engine and the converter. Needless to say, in view of the computational costs, any implemented feature of the models has been carefully assessed as to its benefits. This has, e.g. lead to the choice of Langmuir–Hinshelwood–Hougen–Watson rate equations rather than of microkinetics, i.e. of kinetics accounting implicitly rather than explicitly for every significant elementary reaction. Still, these models have empowered the involved research themes in their efforts aimed at catalyst and/or reactor development and optimization. In doing so, it was and is important to realize that the emissions control system does not function in isolation, but in combination with the engine. Combining computational fluid dynamics with chemical kinetics, e.g. to investigate the effect of flow maldistributions at the diesel particulate filter, is emerging.

The second contribution comes from a major catalyst manufacturer and illustrates how insight in the reaction paths involved in three-way conversion leads to a fundamental, i.e. based on first principles, model. The emphasis in this contribution is on the chemistry rather than on the reactor model, i.e. on the description of the physical phenomena occurring in the monolith reactor. In this sense, this contribution is the bridge from the first to the third contribution.

The latter elaborates further on the monolith reactor model. It is the result of a long collaboration between a major car manufacturer and two academic groups indicating the degree of effort required to reach the present state-of-the-art. It elaborates further on the monolith reactor model and is the result of a long collaboration between a major car manufacturer and two academic groups indicating the degree of effort required to reach the present state-of-the-art. It is in this section that the reader will find the detailed description and modelling of different lean exhaust aftertreatment technologies. The reactions taking place in the diesel oxidation catalyst and the different steps involved in the removal of NO_x from the lean engine exhaust are covered. The NO_x storage and reduction catalyst as well as SCR technology is discussed in depth.

The last contribution illustrates the progress concerning the removal of particulate matter. It is the most “physical” of the four. In contrast to the first three it comes exclusively from an academic group. Its very strong collaboration with the automotive industry is clearly apparent, among other things from the long list of Society of Automotive Engineers (SAE) technical papers. I am convinced that the present volume will help to position this work in the archival literature. The combination of state-of-the-art computational techniques with heuristics is an example for the chemical engineering community.

Before concluding, let me remind you that the aim of *Advances in Chemical Engineering* is to provide the reader with *personal* views of authorities in the field. These should allow assessment of the state-of-the-art in a particular domain and to develop a feeling of its further evolution without claiming to be exhaustive. This is particularly true for the present volume. I was very happy

that major players in the field have accepted to contribute and to allow us to have a look into their “kitchen”. For the involved companies this is not obvious and I am very grateful to them.

Finally, I would like to dedicate this issue to Jozef Hoebink, my former colleague at Eindhoven University of Technology. Jozef has been active in the field of automotive emission control for more than fifteen years before he left us too soon. Those who have met him will not forget his warm personality and his enthusiasm for our profession.

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Ghent, Belgium,
July 2007

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DYNAMIC BEHAVIOR AND CHARACTERIZATION OF AUTOMOBILE CATALYSTS

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Abstract

Automotive catalyst technology is now faced with very difficult problems. The recent progress of research on the dynamic behavior and characterization of automobile catalysts, and their development to solve these problems are reviewed in this chapter. The oxygen storage and release phenomena under the non-steady atmosphere are investigated in terms of the oxygen storage capacity, the oxygen mobility and the local structure of oxygen storage materials. These parameters are in good correlation with each other. The sintering and re-dispersion phenomena of Platinum Group Metals (PGM) on metal oxides are studied by X-ray absorption analysis. The sintering of Pt is suppressed by making a bond between Pt and surface oxygen of oxides such as CeO_2 under the oxygen rich atmosphere, and sintered Pt particles on CeO_2 are re-dispersed under appropriate conditions. The NO_x storage-reduction (NSR) catalyst, which was developed for automotive lean-burn engines, can reduce NO_x under the oxygen-rich atmosphere. The NO_x reduction phenomena are investigated by four steps. NO is oxidized on Pt under the oxygen-rich atmosphere. NO_2 reacts with basic materials and then is stored in the NSR as nitrate. The stored NO_x is released after the decomposition of nitrate under the oxygen deficient atmosphere. The released NO_x is reduced into N_2 on PGM by the reaction with a reducing component such as HC , CO and H_2 . The main cause of deterioration for the NSR is sulfur poisoning. The sulfur-poisoning mechanism and the way for an NSR with high tolerance to sulfur poisoning is studied in storage materials, support materials, substrate structures and the arrangement of catalysts.

I. Introduction

Nowadays automobile prevails across the globe as the most popular and important mode of transportation in our daily life. About 50 million cars are produced each year, and totally over 700 million cars are being used worldwide. Thus, the application of automotive catalysts for detoxifying the pollutants, such as carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM) in the exhaust gases is absolutely indispensable in every vehicle.

The composition, temperature and flow amount of automotive exhaust gases vary continuously with driving conditions. The circumstance of the exhaust catalysts exposed is far more different from that in chemical factories. The automotive catalysts are requested to purify infinitesimally small amount of the

toxic gases in the exhaust perfectly under the unsteady condition, and also have a long-term durability during an automobile life. It is very important to manage and control the exhaust gas transient, in particular the fluctuation of atmosphere. The technology of automotive catalysts had already developed for the practical application, while it still needs to be paid more efforts for reaching the final goal of zero-emission.

In this chapter, following a general illustration on the automotive exhaust catalyst, we tried to discuss the recent progress and catalyst development for controlling the atmosphere fluctuation in the exhaust gases based on our research results.

II. Automotive Exhaust Catalyst and its Specific Features

A. INTRODUCTION OF EXHAUST CATALYST

In early 1970s, the serious photochemical smog in California brought the strict regulations of automotive exhaust emissions to both USA and Japan. Through lots of trials including engine modifications, the catalytic system for exhaust gases had been recognized as the only efficient method to meet the regulations. The oxidation catalyst for CO and HC was first adopted in 1974, and then in 1977, the 3-way catalyst (TWC) with the oxygen sensor was introduced for simultaneously detoxifying the three pollutant gases, CO, HC and NO_x. The catalytic methods for exhaust gases have established and most of automobiles have equipped the catalysts for emission control from then on.

The composition, temperature and flow amount of the exhaust gases from automobiles are very variable with the driving conditions. Figure 1 exemplifies an exhaust gas composition emitted from a gasoline engine as a function of air to fuel ratio (A/F) (Kummer, 1980). Much CO and HC are emitted under the rich condition, and there appears a NO_x emission peak around A/F = 16. The temperature of the catalyst ranges from sub-zero to more than 1,000°C, and the flow rate varies at different order of magnitude. The exhaust catalyst is requested to purify these toxic gases over such a wide range of these gas conditions as earlier.

Figure 2 illustrates a conventional monolith-type catalyst. Exhaust catalysts are composed of several components, including noble metals, Pt, Rh and Pd as active site, alumina-based supports with a high surface area even at high temperature, and metal oxides as promoter materials. Cerium oxides as oxygen storage material and basic materials for NO_x storage are typical promoter materials in the catalysts. The catalysts component is some hundreds micrometers thick and loaded on the substrate, usually made from cordielite ($2\text{MgO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$).

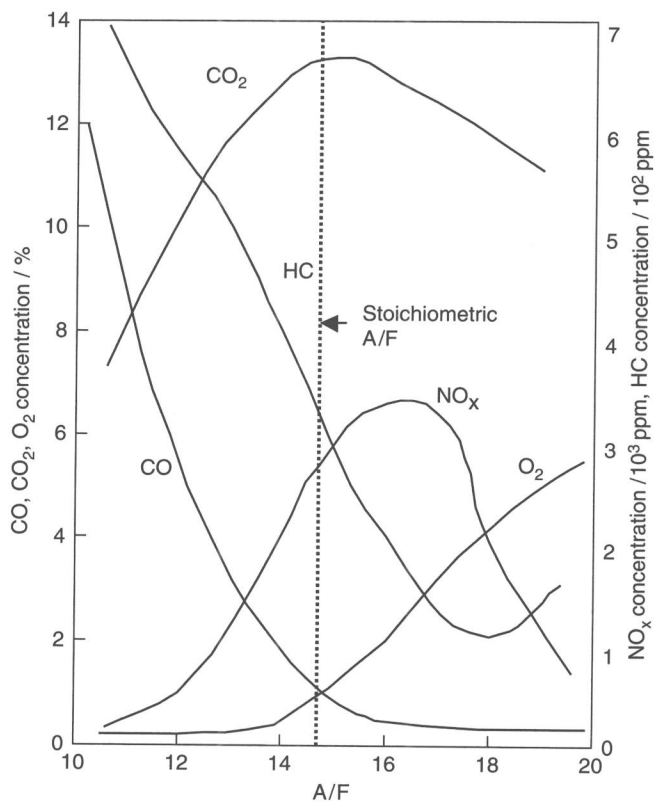


FIG. 1. Concentrations of CO, NO_x, HC (as hexane), O₂ and CO₂ emitted by spark-ignited engine as a function of the intake A/F.

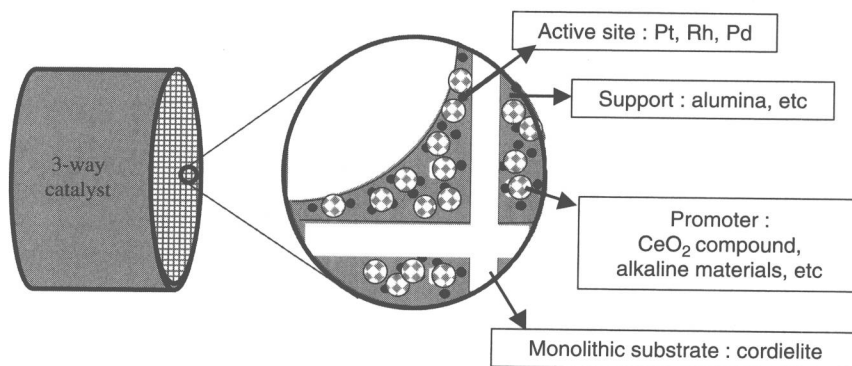


FIG. 2. Outline of 3-way catalyst.

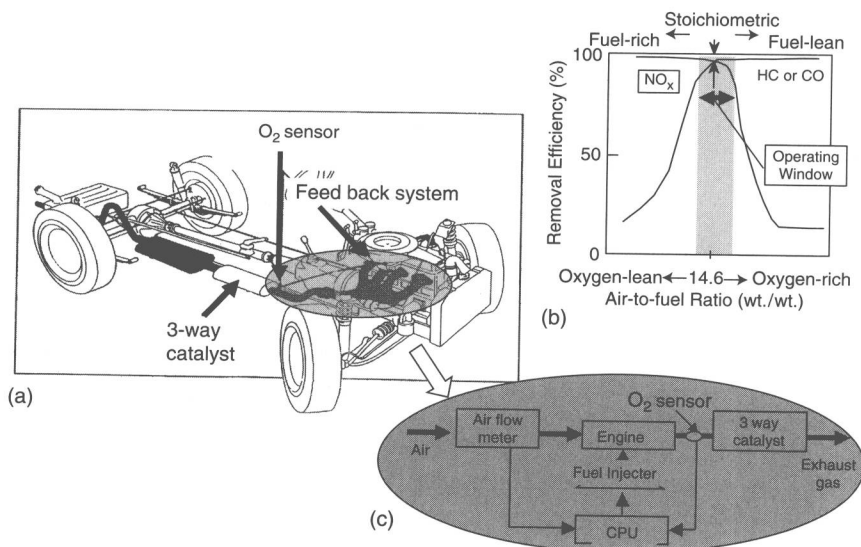


FIG. 3. 3-way catalyst system. (a) Diagram; (b) performance and (c) feedback system.

Figure 3 shows a TWC system and a typical performance of the TWC. The three components are highly purified over the catalyst around the stoichiometric point. The oxidizing and reducing components have almost the same chemical equivalent in the narrow shadowed region, and CO , HC and NO_x are converted into H_2O , CO_2 and N_2 (Fig. 3b). The atmosphere of the TWC is automatically controlled around the stoichiometric point by the TWC system. The flow rate of air is monitored and the fuel injection is controlled by a computerized system to obtain a suitable A/F ratio (Fig. 3c). The signal from oxygen sensor is used as a feedback for the fuel and air injection control loop. Therefore, the exhaust gases are fluctuating streams between oxidizing and reducing periodically and alternatively.

B. CATALYTIC PERFORMANCE IN FLUCTUATING CONDITION

The oscillations of atmosphere fluctuation occur with a frequency in the order of 1 Hz, and the catalytic activities are greatly affected by the species of noble metals and exhaust gas conditions. Figure 4 shows the NO_x conversion efficiency on a Pd catalyst as a function of oscillating periods and amplitudes in an engine test (Yokota *et al.*, 1985). This figure indicates that there are suitable cycling conditions, which the catalytic activities are superior to that under the static condition, and the catalyst performance depends on the cycling

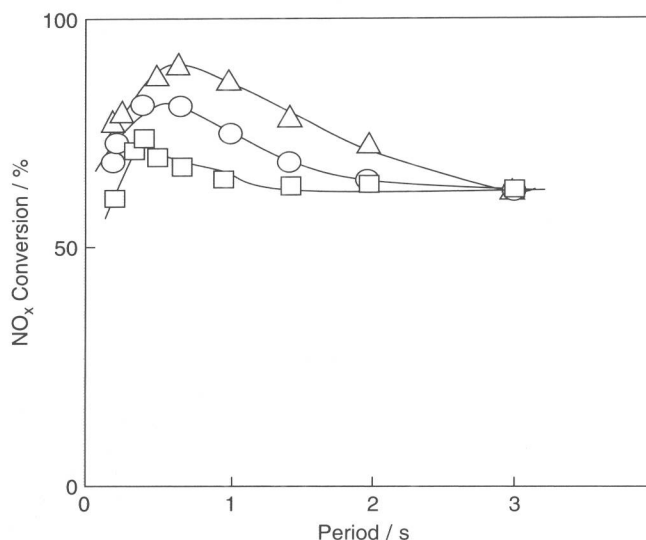


FIG. 4. NO_x reduction behavior on Pd/alumina catalyst as a function of oscillation periods and amplitudes in an engine test. Engine: 2 L, 1,600 rpm and -440 Torr; catalyst: Pd 0.05 g/L. A/F amplitude of oscillation: 0.4(Δ), 0.7(○) and 1.0(□).

conditions. These behaviors also found in the simulated exhaust gases and even in the simple binary reaction gas system such as CO-O₂, and Pd and Pt catalysts are particularly improved by controlling the cycling characteristics. Figure 5 illustrates an example of the periodic operation effect on simple binary gas systems (Muraki *et al.*, 1985). This figure shows the periodic operation effect for Pt catalyst in C₃H₆ oxidation (Shinjo *et al.*, 1989). The maximum conversions are observed for any temperature, and the optimum period for maximum conversion decreases with increasing temperature. From the results of kinetics and evolution pattern analysis, the periodic operation effects arise from a difference of adsorption capability between the two reactants on the catalyst surface, that is, the self-poisoning reactant is the one more strongly adsorbed on the catalyst surface (Shinjo *et al.*, 1987). Accordingly, the catalyst surface under static conditions is almost covered by the stronger ad-species, and the desired reactions are suppressed. Conversely, under optimum cycling conditions, these ad-species are eliminated and surface compositions are suitable for reaction to take place. Under these circumstances, the reaction rate reaches the maximum value. These periodic operation effects can be applied to improve the reactivity of TWCs by a selection of suitable cycling condition. Figure 6 shows CO oxidation reaction with various oscillation periods. The dashed line indicates the best operation for high CO conversion, that is, the oscillation period should be longer at low temperature (20 s at 50°C), and turns shorter