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Experimental methods for activity measurements in environmental catalysis

Paolo Ciambelli*, Diana Sannino, Vincenzo Palma, Paola Russo

Dipartimento di Ingegneria Chimica e Alimentare, Università di Salerno, Via Ponte Don Melillo, 84084 Fisciano (SA), Italy

Abstract

The very specific operating conditions of catalytic processes for the abatement of pollutants from mobile or fixed sources, require an unusual experimental set-up to determine the catalyst performance. Selected examples of environmental catalysis applications such as deNO_x with NH_3 or hydrocarbons, deSO_x with either powder or monolith catalysts, low temperature soot oxidation, are discussed with respect to the experimental methods to be employed for catalytic activity measurements.

Keywords: Experimental methods; Environmental catalysis; deNO_x

1. Introduction

Environmental catalysis has progressively occupied a definite and wide space in the area of catalysis fundamentals and applications [1,2]. In addition to consolidated applications such as automotive catalytic converters, SCR catalysts for NO_x reduction with NH_3 in power plants, VOC catalytic oxidation, numerous other applications are in a more or less developed stage, such as catalytic combustion, clean refinery processes, fuel cells, photocatalytic processes, water treatment, etc. It could be observed that environmental catalysis is substantially catalysis and that is true, but many specific features of this kind of catalytic applications makes it unique in many cases.

Similar to any other catalytic application the development of a catalyst requires the optimisation of its formulation, activity, selectivity, durability, cost. Even in the case of environmental catalysis the ultimate goal of catalysis is to maximise the activity of a catalyst for a desired reaction. Therefore, an accurate characterisation with respect to the catalytic activity is the most significant step in the catalyst development.

The measurement of catalytic activity consists in determining the rate of a given reaction in a catalytic reactor operated at different experimental conditions. The availability of such experimental rate data is essential for either fundamental purposes such as understanding the catalytic reaction mechanism and design purposes, from the screening of candidate catalysts to the scale up towards the industrial application, to the optimisation of the catalytic process.

In order to collect rate data relevant to a given catalyst and reaction, a reactor type and its operating conditions must be selected. Moreover, an analytical section constituted of different analytical techniques based instruments capable of collecting and analysing reactants in the inlet reactor and products in the outlet reactor should be designed. From concentration data obtained with such a section, reaction rate, conversion and selectivity to the various species are calculated and the material balance around the reactor can be

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* Corresponding author. Tel.: +39-89-964151; fax: +39-89-964057.
E-mail address: pciambelli@unisa.it (P. Ciambelli).

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checked. The successive data analysis is the starting point for planning new experiments and/or performing reaction mechanism investigation, reaction kinetics determination, process optimisation.

In addition to these general considerations it is important to take into account the very unusual conditions typical of environmental catalytic processes for the abatement of pollutants from mobile or fixed sources, with respect to the industrial catalytic processes: the very low partial pressure ($<10^{-3}$ atm) of the pollutants to be converted, the very high space velocity (10^4–10^5 h^{-1}) of the catalytic reactor, the wide range of reaction temperature and the changing of all the above conditions during the time like in the case of automotive applications. On the other hand, the very low partial pressure of reactants generally results in low heat generation and consequently reactor temperature profile quite constant.

Concerning the choice of the laboratory catalytic reactor for activity measurements two types of reactors are usually employed: the plug flow reactor (PFR) and the continuous stirred tank reactor (CSTR). However, in the area of environmental applications of catalysis a large percentage of reactors are monolith type. Properties and features of both PFR and CSTR are presented in another paper of this issue; therefore only their advantages and disadvantages will be reminded here. In the case of PFR: (i) the simplicity of construction and (ii) the wideness of conversion range which can be achieved by simply changing the mass of catalyst or the gas flow rate is payed in terms of: (i) limitations for isothermal conditions for highly exothermic reactions, (ii) presence of concentration and temperature gradients at low flow rates and (iii) operation as integral instead of differential reactor at high reactant conversion. The latter disadvantages are absent in the case of CSTR, but it must be remarked that: (i) reaction rates are measured at outlet conditions, and (ii) dead volumes can be present in the reactor.

The assumption of plug flow operation is often made without any verification. Simple rules can be preliminarily applied: for example, in the range of Reynolds number lower than 10 (based on particle diameter) it should be verified that the ratio of the inner reactor diameter and the particle diameter is higher than 10 and the ratio of the length of the catalytic bed and the particle diameter is higher than 50.

Moreover, it must be also reminded that heat and/or mass transport phenomena can be involved in the catalytic process, affecting the accuracy and then the significancy of rate measurements.

Whatever the purpose of the activity measurements, experimental set must be designed planning a statistical number of experimental runs at each fixed set of conditions to assure experimental precision and reproducibility.

Various analytical methods could be employed to measure reactor inlet and outlet composition, but taking into account the specificities of environmental catalysis processes they are limited to:

- gas chromatography,
- high performance liquid chromatography,
- flame ionisation,
- mass spectrometry,
- infrared, ultraviolet, chemiluminescence spectrometry,
- paramagnetism.

In-line methods are very effective in order to continuously monitor reactor outlet composition and detect transient phenomena, or instant concentrations. Off-line methods allow collected samples analysis be repeated.

Typical applications of environmental catalysis to the treatment of emissions from mobile and fixed sources, such as deNO_x with NH_3 or hydrocarbons, deSO_x with either powder or monolith catalysts, low temperature soot oxidation, will be discussed in the following, with the purpose of evidencing the main aspects relevant to the experimental determination of catalytic activity.

2. Catalytic treatment of mobile source emissions

In order to set what performance is required to a catalytic converter operating at the engine exhaust of a vehicle, it can be useful to refer to emissions legislation. Indeed, even if the number of components present in the exhaust gas is very large, todate only the emissions of a limited number of pollutants are regulated with reference to passenger cars (gasoline spark ignition, direct injection diesel, indirect injection diesel engine), light and heavy duty trucks. Emission

Table 1
Main reactions occurring in a three-way catalytic converter

$C_mH_n + \left(m + \frac{1}{4}n\right) O_2 \rightarrow mCO_2 + \frac{1}{2}nH_2O$
$CO + \frac{1}{2}O_2 \rightarrow CO_2$
$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
$C_mH_n + \left(2m + \frac{1}{2}n\right) NO \rightarrow \left(m + \frac{1}{4}n\right) N_2 + mCO_2 + \frac{1}{2}nH_2O$
$CO + NO \rightarrow \frac{1}{2}N_2 + CO_2$
$H_2 + NO \rightarrow \frac{1}{2}N_2 + H_2O$

standards are defined for carbon monoxide (CO), total hydrocarbons (HC), nitrogen oxides (NO_x) and particulate (PM). Therefore, the catalyst must be active enough to reduce the concentration of these pollutants to values lower than the standards.

In the case of spark ignition engine the exhaust pollutants are mainly converted by a three-way catalyst through the reactions listed in Table 1.

Secondary reactions with environmental implications also occur (Table 2). Therefore, it seems important to determine the activity of the catalyst towards these reactions, even if they produce not regulated emissions.

2.1. Experimental determination of catalytic activity

The ultimate determination of the catalyst performance is the result of a vehicle test, in which a vehicle mounted on a chassis dynamometer, after stabilisation in an air conditioned environment ($T = 298\,K$), is driven according to a prescribed velocity pattern and the exhaust gas is collected in one or more plastic bags after appropriate dilution in order to avoid water condensation. At the end of the test the collected gas is analysed with respect to the following components: CO, HC, NO_x, PM, O_2 and CO_2. All emissions but particulate are measured by on-line analysers as described below. The mass of particulate emitted by diesel engine is measured gravimetrically, after collection on a filter paper.

Table 2
Secondary reactions occurring in a three-way catalytic converter

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$
$NO + \frac{1}{2}O_2 \rightarrow NO_2$
$NO + \frac{5}{2}H_2 \rightarrow NH_3 + H_2O$
$2NO + CO \rightarrow N_2O + CO_2$

It must be observed that the actual operating conditions of an automotive catalytic converter are determined by engine speed and load, i.e. by the driving conditions. This results in the fact that the catalyst is requested to work in unsteady-state conditions, and in a wide range of temperatures (typically from 250 to 900 °C) and reactant space times (from 10 to 10,000 $kg\,s\,mol^{-1}$ with respect to the specific pollutant in the exhaust). Therefore, the operating conditions for a catalyst designed for such applications are really much more severe than those typically required to the common heterogeneous catalysts employed in the chemical and petrochemical industrial processes. Moreover, the variability of operating conditions is expected to result in various kinetic regimes occurring during the catalyst operation, from chemical to intraparticle diffusion to interphase diffusion control.

All the above considerations converge to a general question: how to perform a significant experimental test to determine the activity of the catalyst, apart from the vehicle test?

The significance of the vehicle test is really unique, but mainly addressed to verify the catalytic performance with respect to commercial and legislative requirements. For this reason simplified test procedures are employed for research and development purposes, such as: (i) engine test and (ii) synthetic exhaust test.

Typical engine tests are performed by varying independently operation parameters such as engine air-to-fuel feed ratio, catalyst temperature, overall space velocity. The experimental set-up is constituted by an engine mounted on a brake, a catalytic converter, an exhaust cooler or heater located in between them. The analysis of catalytic converter inlet and outlet gas allows to calculate the conversion of regulated pollutants (CO, HC, NO_x) and consequently the catalytic activity. The analysis of not regulated pollutants helps to better understand the catalytic properties of the tested catalyst.

The use of a synthetic exhaust obtained by mixing different streams of pure gas or nitrogen diluted gas mixtures from cylinders (Fig. 1) can be an effective solution to evaluate the catalytic activity of a three-way catalyst.

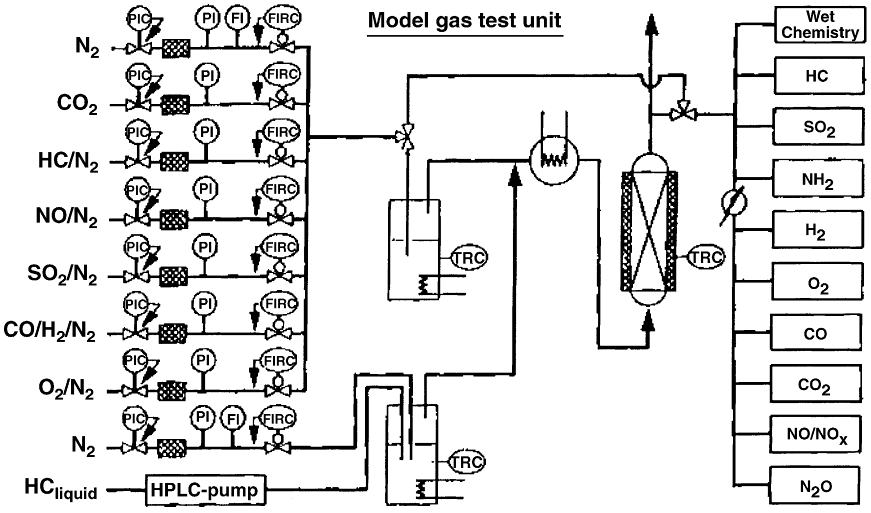

Fig. 1. Model gas reactor to study the activity of automotive emission control catalysts.

Due to the accurate control of the operating conditions, activities of different catalysts can be effectively compared. Activity evaluation and comparison are as much significant as much the gas composition is similar to the real one. In particular, H_2O, SO_2, H_2 should be present in the reactor feed as they can strongly affect the catalytic behaviour. Also the nature of the diluent gas is not subordinate. Nevertheless, He or Ar are commonly used instead of N_2, in order to be able to evidence the conversion of NO_x to N_2. Most of the papers appearing in the literature concerns catalytic studies performed with powder catalyst and simple gas feed containing only a single hydrocarbon, NO, and possibly oxygen when lean burning engine exhaust is simulated. It must be remarked that in these conditions the effect of the other components is completely ignored and, especially in the case of water, the result of experimental test could be strongly deviant.

Catalytic activity evaluation with powder samples has limited validity when extrapolated to that of monolith catalyst. The difficulty of comparing powder and monolith catalytic activities should induce to load the reactor with monolith samples. On the other hand, too small monoliths are not representative for the behaviour of larger monoliths, especially taking into account entrance effects.

Moreover, very often the values of pollutant concentration in the gas feed are at least one order of magnitude higher than the real ones, resulting in inadequate validity of the experiments with respect to the objective of obtaining useful results for application to engine exhaust treatment. Finally, the space velocity values to be investigated should be in the order of several thousands of h^{-1} or higher. In conclusion, activity test performed in these very simplified conditions have only a validity for a preliminary catalytic screening.

The best analytical solution for evaluating the catalytic performance activity with respect to the reactions converting the regulated emissions is to use specific analysers, like in the vehicle test. Specific analysers allow on-line continuous analysis with sufficient sensitivity, precision, response time. Optimal flow rates in the order of 1 l/min allow to load the reactor with large enough catalyst amounts to meet the required space velocity values. This guarantees higher significance of reactor operation with respect to the very low amount of catalyst commonly used for microreactor laboratory test.

2.1.1. Characteristics of specific analysers

Non-dispersive infrared (NDIR) spectrophotometry is the technique on which specific analysers have been developed. Continuous analysis of CO, CO_2, N_2O, CH_4, NH_3 is easily performed. UV absorption is employed for NO analysers, often coupled to a catalytic converter $NO_2 \rightarrow NO$ to get a complete NO_x analysis. Higher sensitivity for NO_x analysis is achieved with chemiluminescence analyser. Paramagnetic or electrochemical analysers for oxygen have been developed. Hydrocarbon analysis is based on a flame ionisation detector (FID).

Infrared analyser module uses a NDIR absorption process, which is based on resonance absorption at the characteristic vibration rotation spectrum bands of non-elemental gases in the middle infrared range between 2 and 12 μm. Because of their bipolar moment, the gas molecules interact with infrared emissions. For selectivity, the receiver is filled with the applicable sample components to establish sensitivity to these components (Fig. 2).

The photometer consists of a thermal emitter, the emissions of which reach a sample cell via a chopper wheel. The sample cell is in the shape of a tube that is divided by a land into sample and reference sides. The measurement effect produced in the receiver is a pressure effect resulting from the chopper frequency, received by a diaphragm capacitor and converted into an electrical signal by an attached preamplifier. The receiver is a two-layer device. The back of the receiver has an optically transparent window so that any residual radiation can reach a second receiver that is sensitive to a second sample component. By adding a second beam path with an emitter, a sample cell and receivers, the photometer can measure one to four sample components simultaneously.

UV analysers as measurement principle use the property of molecules to interact with a beam emitted at a certain wavelength and absorb radiation. Sample component selectivity is achieved using gas filter or interference filter correlation. In Fig. 3 a schematic drawing of the apparatus is reported. The UV beam emitted by an electrodeless discharge lamp is splitted into predetermined wavelengths by a filter wheel fitted with interference filters and/or gas filters.

The splitted beam is then separated by a beam splitter into measurement and reference signals and reaches the reference receiver without passing through an absorption run while reaching the measurement receiver after absorption (sample cell).

Absorption of the emission in the sample cell causes a change in the intensity of the measurement signal. To identify sample component concentration a double-quotient evaluation process is applied to the four time-multiplexed measurement signals thus formed.

FID analysers are used for monitoring total hydrocarbons. The analyser typically consists of the following equipments: air injector, vacuum regulator, combustion air regulator, combustion gas regulator, detector and sample gas inlet. The air injector causes a pressure reduction that drives the sample gas, the combustion gas (H_2) and combustion air into the combustion chamber. A constant volume of gas sample is

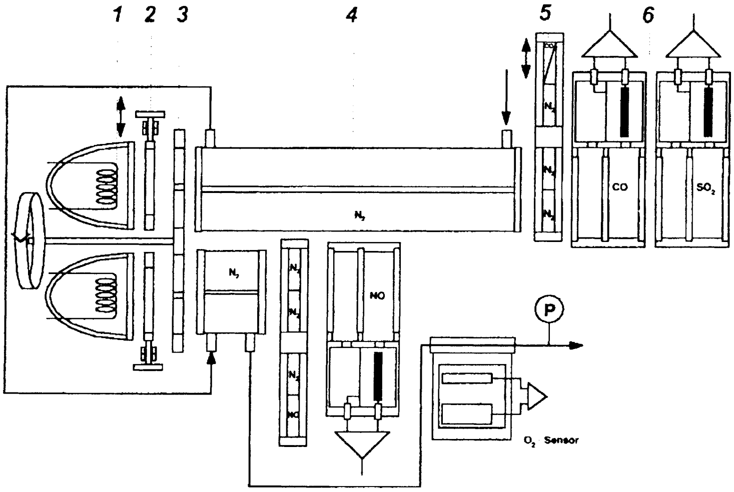

Fig. 2. Scheme of an NDIR analyser: (1) emitter, (2) aperture, (3) chopper wheel, (4) sample cell, (5) adjusting unit/calibration cell and (6) receiver (reprinted on permission of ABB Instruments).

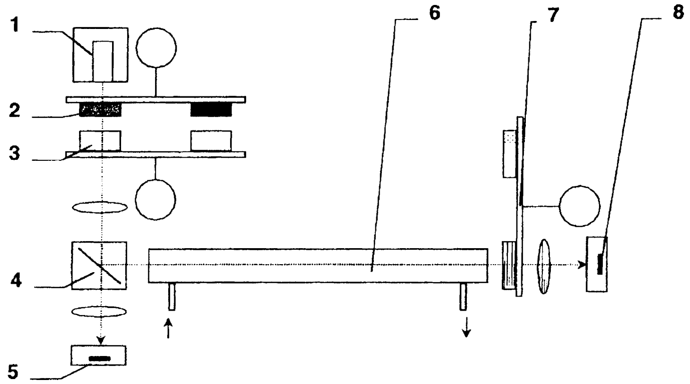

Fig. 3. ND-UV measuring principle: (1) UV lamp, (2) filter wheel with interference filter, (3) filter wheel with gas filter, (4) beam splitter, (5) reference receiver, (6) sample cell, (7) calibration wheel with calibration cells and (8) measurement receiver (reprinted on permission of ABB Instruments).

mixed with the combustion gas and sent to the burner nozzle placed between two electrodes. This mixture is burned and, due to the presence of hydrocarbons in the sample gas, ionised particles are formed causing an ions flow between the electrode shells. The ions flow is directly proportional to the amount of hydrocarbons in the sample gas. Hydrocarbons concentration is easily determined after detector calibration.

For the analysis of O_2 continuous analysers employ the paramagnetic principle. The sample gas to be analysed flows through the two-chambers system. Both chambers have temperature-sensitive annular resistors. On the sample side, oxygen molecules are drawn into the non-homogeneous magnetic field of the permanent magnet. The “magnetic wind” thus generated cools the heated temperature-sensitive measuring resistors. The change in temperature is proportional to oxygen content and can be converted into an electrical signal. The measurement unit is located in a thermostat chamber so that measured values are extensively free from variations of ambient temperature. Calibration is effected with oxygen-free process gas, with a known oxygen concentration or with a substitute gas.

An alternative analytical technique is mass spectrometry. A quadrupole detector in-line gives a continuous monitoring of the emission, following the concentrations of given m/z ratios related to the exhaust components. In the same way as for the specific analysers, from the comparison of reactor inlet and outlet concentrations the reaction rate can be calculated. Due to signal interferences and equality of m/z ratio for different compounds a software treatment of data is necessary. The mass spectrometry based technique is becoming more and more popular in research laboratories.

One more alternative, less diffuse todate but very promising is the use of specific sensors. They are mainly based on electrochemical reactions for detecting typical emissions such as CO, H_2, SO_2, etc. The sensors work with an electrochemical cell. For example, oxygen is electrochemically converted at the cathode/electrolyte boundary layer in similar manner as a fuel cell. The resultant current at resistor R is proportional to the oxygen concentration.

The following reactions occur between the anode and cathode:

$$\text{Cathode}: \quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

$$\text{Anode}: \quad 2Pb + 2H_2O \rightarrow 2PbO + 4H^+ + 4e^-$$

$$\text{Total}: \quad O_2 + 2Pb \rightarrow 2PbO$$

The sensor’s temperature is maintained constant by electrical compensation to correct the temperature sensitivity. The specific sensors are very small devices with respect to the instruments above discussed and are low cost. Limitation of durability, operating conditions such as highly humid atmosphere and constant temperature are disadvantages, but their properties will be certainly improved since they will be more and more employed in the vehicles.

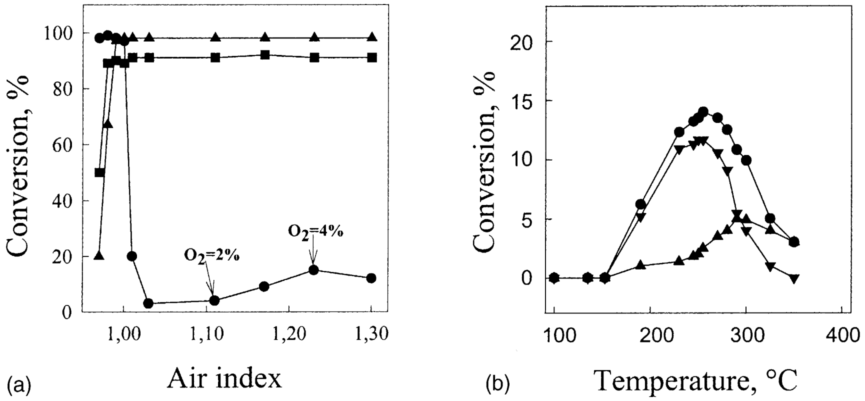

Fig. 4. Performance of a commercial "three-way" converter at the exhaust of a lean burn engine: (a) conversion of NO_x (●), HC (■) and CO (▲) versus air index (air on fuel ratio in the test/stoichiometric ratio), $T = 270$–300 °C. (b) NO_x overall conversion (●) and NO_x conversion to N_2 (▲) and N_2O (▼) at air index = 1.23. For (a) and (b) space velocity = 30,000 h^{-1}.

2.2. High efficiency engines

High efficiency engines such as lean burn spark ignition, diesel, natural gas engines are characterised by overstoichiometric air to fuel ratio and consequently by the presence of oxygen in the exhaust. In these conditions the three-way catalysts are not active for NO_x reduction as shown by engine test experimental set-up (Fig. 4). In this test a N_2O specific analyser has also been used in order to evidence the activity of three-way catalyst to N_2O [3]. Obviously, engine test and model exhaust test are similar to those for three-way catalysts, but one major difference of the catalytic system has also experimental implications. In fact, at variance of three-way catalysts, the candidate materials for lean burn exhaust treatment allow NO_x reduction by hydrocarbons and not by carbon monoxide. Since only part of hydrocarbons present at the exhaust are selective for NO_x reduction, it would be very useful try to determine the deNO_x catalytic activity of each hydrocarbon, or at least of those present in highest concentration.

We have arranged an improved engine test (lean-burn S.I. engine, 1350 cm^3 displacement, air/fuel mass ratio $A/F = 18$, 2000 rpm, 17 kW) to determine the three-way activity of Cu-ZSM5 catalysts operating in lean burn conditions. The exhaust gas average volume composition was the following: $O_2 = 4\%$, $CO_2 = 11\%$, $H_2O = 12\%$, HC (as propane) = 410 ppm, $NO_x = 1220$ ppm, CO = 1310 ppm, N_2 = balance. The experiments were performed at space velocity of 30,000 h^{-1}. Together with typical on-line analysers, such as chemiluminescence for NO_x, flame ionisation for total HC, infrared for CO and N_2O, and electrochemical for O_2, we included in the set of analytical instruments a gas-chromatographic automatic system, with a FID detector and on-line sampling valve, to analyse the individual hydrocarbon concentrations every 30 min about [4].

Comparing the reactor inlet and outlet concentrations of these hydrocarbons it is possible to determine single hydrocarbon reaction rates and try to find correlations to deNO_x activity. Some results are shown in Fig. 5.

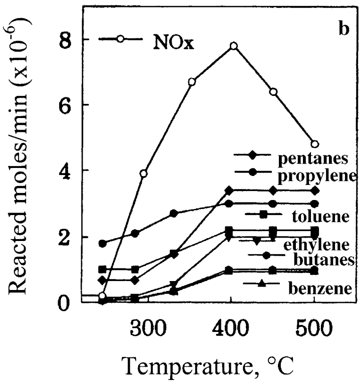

Fig. 5. Reactivity of the most selective hydrocarbons as evaluated during temperature programmed tests at space velocity = 30,000 h^{-1} on Cu-ZSM5.

In the case of natural gas driven engines the problem is simplified by the fact that methane is practically the only hydrocarbon present in the exhaust. NDIR CH_4 specific analysers allow the catalytic activity of methane conversion to be easily determined.

2.3. Diesel engines

Because of differences in the air/fuel mixing and ignition, nature of fuel and operating conditions, diesel engine emissions are characterised by the presence of specific components such as SO_x, oxygenated compounds, and especially particulate. Only the latter emission is regulated by legislation together with CO, HC and NO_x. The diesel oxidation catalysts are active for the oxidation of CO, HC, aldehydes. Catalytic oxidation of hydrocarbons adsorbed on the particulate results in the reduction of the mass of particulate emitted at the exhaust, without affecting the mass of soot, main constituent of particulate.

Therefore, catalyst testing is similar to that for gasoline S.I. engine, but the catalytic activity for particulate must be also determined. This is generally accomplished by particulate filtering and gravimetric analysis. Less precise but on-line determination of particulate concentration is obtained by optical devices (smokemeters), commonly used for engine test, based on gas opacity measurement.

More complex activity tests take into account that a diesel oxidation catalyst must exhibit oxidation activity to CO_2 and H_2O, whereas oxidation activity of NO to NO_2 and SO_2 to SO_3 must be suppressed. Moreover, the oxidation to SO_3 results in sulphuric acid and sulphate formation, increasing the mass of particulate. Therefore, diesel catalyst investigation should be addressed to these features, too. Again, the best solution for activities determination is the use of monolith catalyst and specific analysers for SO_2 and NO_x. SO_x analysis will be discussed with reference to the emissions from fixed sources.

An effective way for soot removal from diesel exhausts consists in the use of ceramic traps suitable for collection and subsequent combustion of trapped carbon particulate at diesel exhaust temperatures. Since diesel soot spontaneously burns at 800–900 K and such temperatures are far from typical values occurring at the exhaust of commercial diesel engines, there is a need for developing suitable oxidation catalysts. Active catalysts should reduce the soot combustion temperature allowing more frequent trap regeneration at lower temperatures and avoiding filter failure by melting or breaking [5].

A simple test of catalytic activity for soot oxidation can be performed with temperature programmed oxidation (TPO) [6]. A microreactor loaded with soot/catalyst mixture and connected in-line to a

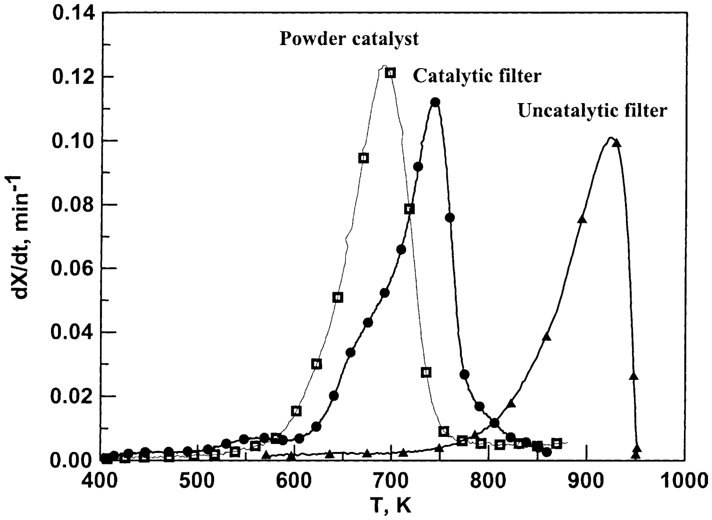

Fig. 6. Reactivity–temperature profiles of catalytic and uncatalytic soot combustion (feeding gas, 10 vol.% O_2 in N_2; gas flow rate = 500 N cm^3/min; heating rate = 10 K/min).

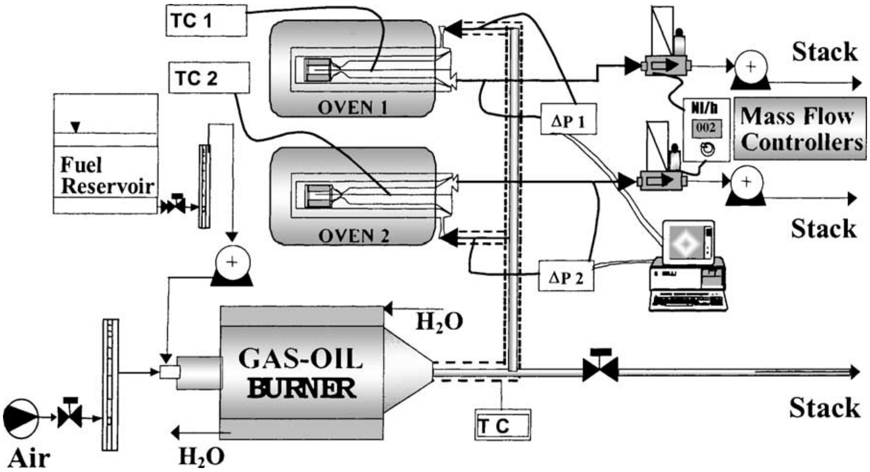

Fig. 7. Experimental apparatus for soot generation and deposition on catalytic and uncatalytic filters.

CO/CO_2 specific continuous analyser allows the reaction rates to CO and CO_2 be calculated. Typical results of TPO are shown in Fig. 6.

Further stage of development of catalyst for soot oxidation is a larger scale apparatus for particulate abatement. Carbon oxides produced by soot oxidation cannot be distinguished from those formed by fuel combustion, therefore, indirect ways must be employed to give evidence of the catalyst activity. Pressure drop through TC catalytic and uncatalytic filters are measured by pressure transducers (Fig. 7).

3. Catalytic treatment of fixed sources emissions

The development of catalysts for stationary sources involves coal-, oil-, gas-fired power plants, gas turbines, waste incinerators, gasifiers. Selective catalytic reduction (SCR) of NO_x with NH_3 is widely applied and is a mature technology todate.

Several geometries have been used for SCR monolith catalysts, the most typical being a honeycomb geometry. Single elements assembled together to obtain the designed catalyst volume are 150 mm × 150 mm × (700–1000) mm in size. Channel diameter ranges from 3 to 10 mm, wall thickness from 0.5 to 1.5 mm.

SCR catalysts are tested at laboratory and bench scale. In laboratory testing powdered or micromonolith samples (typically, 3 × 3 channels, 200–300 mm length) are tested. Powder samples can also originate from monolith crushing. In bench scale larger monolith (20 × 20 channels, 1000 mm length) are tested. The structure of the testing apparatus is the same as for powder catalyst, consisting of a feeding section for gas feed preparation, a reaction section with the catalyst and the heating system, an analytical section with the relevant analytical equipment.

The main reactions occurring in the system are listed in Table 3. Selective catalysts favour the reactions leading to nitrogen formation. Moreover, their activity toward the oxidation of SO_2 to SO_3 must be very low, in order to limit reaction with ammonia forming ammonium sulphate.

The high activity to SO_2 oxidation is one of the reasons for modifying the formulation of commercial catalysts from V_2O_5/TiO_2 to $V_2O_5/WO_3/TiO_2$ and $V_2O_5/MoO_3/TiO_2$ containing less than 1 wt.% V_2O_5. For this reason the test of activity of SCR catalysts should combine deNO_x and deSO_x activity. The

Table 3
Main reactions involved in SCR process

$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$

$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2O + 6H_2O$

$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O$

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

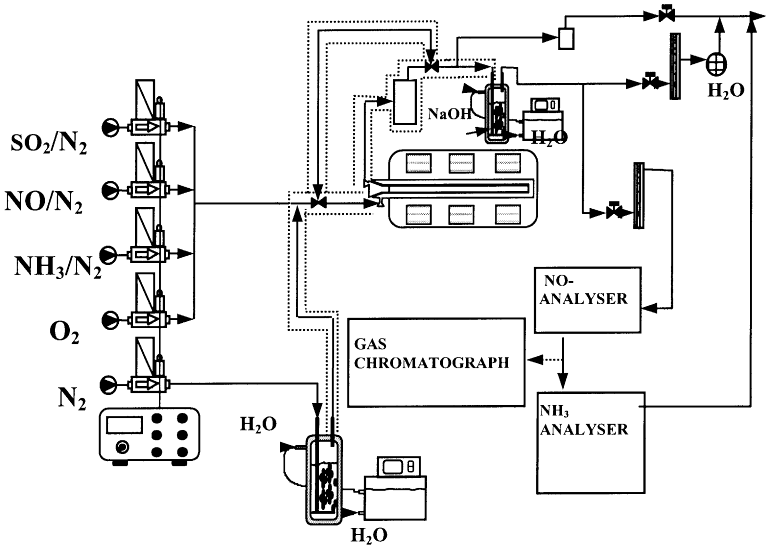

Fig. 8. Experimental apparatus for deNO$_x$ monolith catalyst testing.

most significant data should be obtained with monolith samples.

3.1. *deNO$_x$ testing apparatus*

An experimental apparatus designed to these purposes is sketched in Fig. 8. The gas feeding stream is prepared by mixing single gas streams from cylinders. The single flow rates are measured and controlled by mass flow meters (MFC). The feeding gas contains NO$_x$, NH_3, SO_2, H_2O, O_2 and N_2.

Feeding systems for water vapour can be performed by different ways such as inert gas component saturation upon gas bubbling in a water containing saturator whose temperature is controlled at ±0.1 °C by a water circulating system. An alternative is vaporisation of a water stream fed by a pump at controlled rate. The presence of water and/or low vapour pressure components in the feeding gas requires line heating at controlled temperature, measured by a thermocouple.

A valve system allows to feed directly or by-pass the reactor to analyse the outlet or the feeding gas. Reactor heating by an electrical oven with independently heat driven zones allow isothermal longitudinal profile along several centimetres. This feature is especially significant for activity measurement of monolith reactors whose length cannot be too small. The experimental temperature profile along the reactor is shown in Fig. 9.

A monolith catalyst (3 × 3 channels, 150 mm length) was placed in a Pyrex tube (ID = 23 mm). The whole space between monolith and tube was filled in order to suppress any reactor by-pass flow. A K thermocouple monitored the longitudinal monolith temperature. A larger axial Pyrex tube (ID = 35 mm) allows feeding gas preheating.

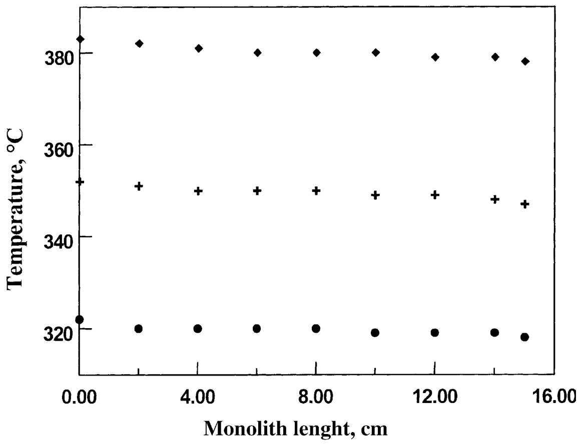

Fig. 9. Temperature profiles along a monolith sample.

At the reactor outlet an expansion chamber was placed to collect the ammonium sulphate possibly formed and thus to protect the reactor by-pass line.

The gas analysis was performed very carefully as:

- NH_3 is highly soluble in water even at low partial pressure.
- H_2O can produce interference with NH_3 and NO analysers.

Reactor inlet and outlet gas were analysed by:

- A specific NH_3 continuous analyser.
- A non-dispersive UV continuous analyser giving NO concentration. This instrument was coupled to a $NO_2 \rightarrow NO$ catalytic converter for complete NO_x analysis.
- A specific N_2O continuous analyser.
- A gas-chromatograph with a multi-way valve, pneumatically driven for automatic gas sampling at inlet and outlet reactor. N_2 and O_2 are analysed. A thermal conductivity detector is commonly employed, optimised with respect to the analytical sensitivity by setting suitable current intensity values, in order to detect the very low outlet concentration of O_2 and N_2 relevant to low NO_x conversion. In order to limit the interference of water on N_2 analysis a P_2O_5 trap is inserted before the gas chromatograph.
- A relative humidity analyser for water concentration in the gas.

An analog–digital board was employed for computer acquisition of concentration data from the analysers.

3.2. deSO$_x$ testing apparatus

The deSO$_x$ test apparatus (Fig. 10) is the same as for deNO$_x$ test with respect to the feeding and the reaction sections. The feeding stream contains SO_2, O_2, H_2O and N_2.

Many aspects must be taken into account in designing the analytical section for deSO$_x$ activity characterisation. A major problem comes from the very low SO_2 conversion values to be determined, since the very small change of SO_2 inlet concentration cannot be determined by SO_2 specific analyser with sufficient precision. We have employed an SO_2 sensor, constituted by a membrane semipermeable to SO_2 and by three electrodes. SO_2 diffuses to the surface of a specific electrode where it reacts as follows:

$$SO_2 + 2H_2O \Rightarrow H_2SO_4 + 2H^+ + 2e^-$$

The current intensity signal generated (4–20 mA) is proportional to the SO_2 concentration. For better precision the sensor was kept at constant temperature (20 °C) and relative humidity and a flow rate of 30 l/h was fed. The intensity signal was converted to a tension signal fed to a multichannel analog to digital conversion card. A Labwindows code has been developed

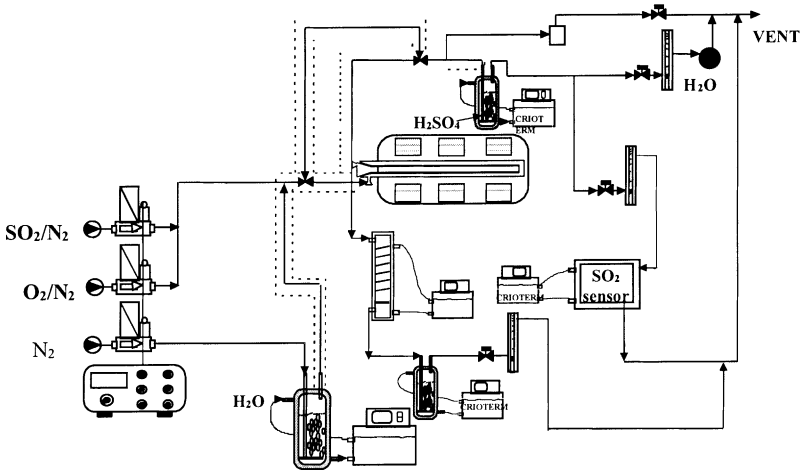

Fig. 10. Experimental apparatus for deSO$_x$ monolith catalysts test.

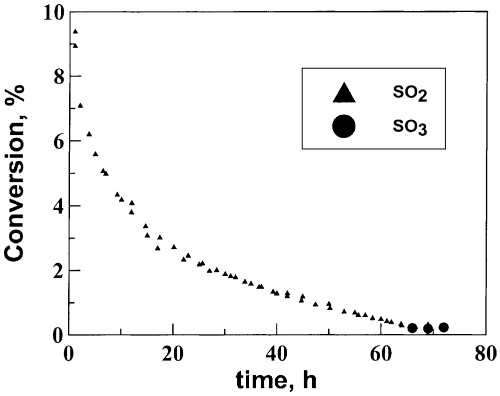

Fig. 11. SO_2 apparatus conversion against time on stream on a V_2O_5/TiO_2 monolith sample at 320 °C.

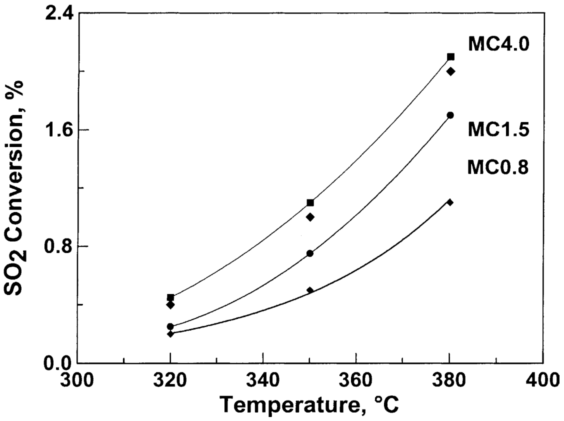

Fig. 12. SO_2 steady-state conversion as function of temperature on different V_2O_5/TiO_2 monolith.

for data acquisition and control. In these conditions the error on the SO_2 concentration was only 1–2 ppm.

On the other hand, due to the high solubility of SO_2 the presence of water can strongly affect the measurements. To overcome this difficulty the gas stream has been fed to a 60% w/w sulphuric acid solution, kept at 20 °C. By this way SO_2 is not solubilized and water content is reduced but maintained at optimal humidity values for sensor operation.

The water content in the gas stream has been analysed as described above for the deNO$_x$ measurements. The determination of SO_3 concentration has been performed by SO_3 selective condensation as sulphuric acid on sintered glass filter (5–15 μm) in a glass condenser kept at 75 °C. The condensed sulphuric acid was titrated with 10^{-3} N NaOH solution.

With this apparatus transient apparent conversion of SO_2 was evidenced due to catalyst progressive sulphation to steady-state conversion (Fig. 11). Steady-state values obtained with different monolith catalysts at various temperatures are shown in Fig. 12.

4. Conclusions

Many experimental complications are encountered when catalytic activity determination has to be performed in "realistic" conditions. The right choice of catalyst geometry, reactor type, analytical instrumentation allows to obtain reaction rate data useful for evaluating catalytic performance in environmental processes application.

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