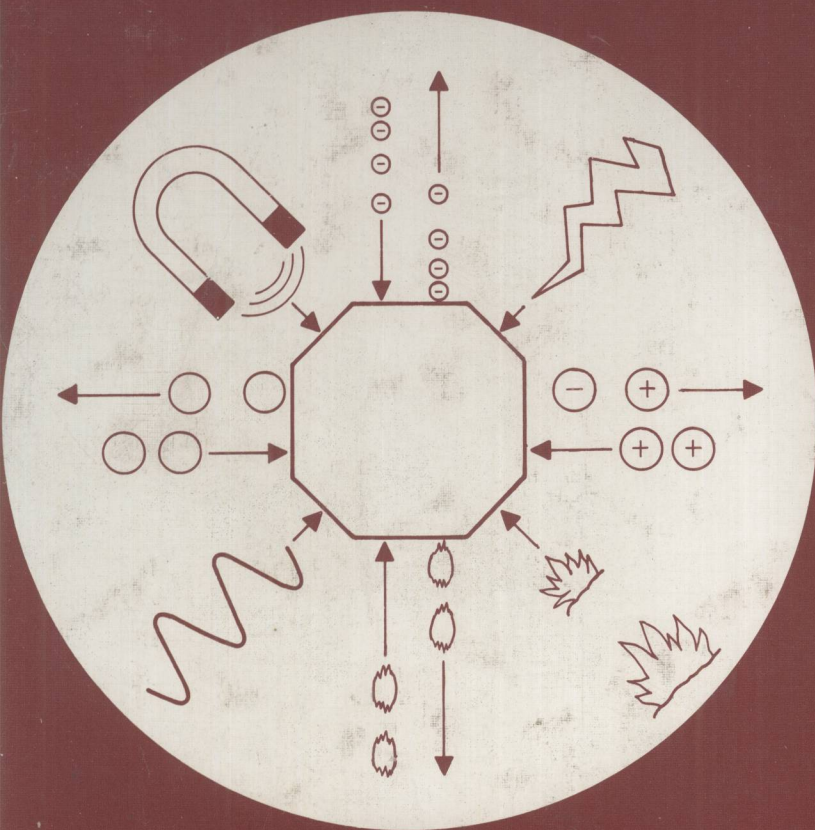


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CATALYST DEACTIVATION 1987

B. Delmon and G.F. Froment
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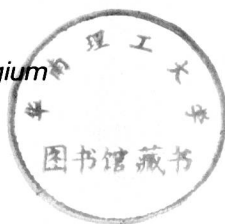
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CATALYST DEACTIVATION 1987

PREFACE

This Symposium on Catalyst Deactivation came after those organized in different styles successively in Berkeley (1978), Antwerp (1980) and Berkeley again (1985).

For the present symposium, the emphasis was laid on three topics: the techniques used in deactivation studies, the mechanisms of catalyst deactivation, and modelling. With respect to the first, it became apparent that the study of deactivation faces even more difficulties than the characterization of fresh catalysts and the measurement of activity or selectivity. This is due to the multiplicity of interacting processes occurring during deactivation. It was hoped that these points would be clarified in the course of the symposium. Quite substantial progress has been made recently in the understanding of the mechanisms of various processes, particularly coking. It was therefore desirable to accord more time to these topics during the symposium. The third topic corresponds to a problem which is very central to development studies and to the chemical engineering aspect of catalysis: it deals with the representativity of accelerated tests and the modelling of the deactivation phenomena.

We are very grateful to the members of the Scientific Committee whose names appear below, for their help in the difficult task of selecting, from the many submitted contributions, the papers which are assembled in this volume.

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COKING OF REFORMING CATALYSTS

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ABSTRACT

The purpose of this review is to link experimental working conditions of reforming catalysts to the quantity, the chemical nature, the location and the toxicity of deposited coke. A discussion of the effect of the metallic and acidic functions brings out that coking is a balanced reaction between production and destruction of coke precursors, nucleation, growth and gasification of more ordered carbon deposits.

INTRODUCTION

Metal based catalysts are used to promote a variety of reactions involving carbon-bearing feedstocks, and coke is deposited on most catalysts. The coking of catalysts containing noble metals has long been of interest, primarily as a result of the industrial importance of reforming process. Most studies have been carried out using a Pt/Al₂O₃ reforming catalyst. In such catalysts, it is well established that total deactivation, as a result of coking, takes many thousands of hours of operation. As a matter of fact the selectivity of reforming catalysts for coking reaction is low, since only one atom of carbon out of 200.000 activated by the catalyst is transformed into a non desorbable deposit of coke under the operating conditions used (1).

The thermodynamics of the reforming reactions are such that it is desirable to work at high temperatures and low pressures (1), but these are the conditions that favor coke formation. In recent years it has been found possible to use multimetallic catalysts supported on alumina to promote reforming. Combination of Pt-Re, Pt-Ir, Pt-Sn and Pt-Ge have been reported and are now used widely in industry (3)(4). The essential contribution of such catalysts has been greater stability in time. It nevertheless can be seen that the stabilizing effect of additives has not yet received a simple or general explanation. The additives used, however, can at least be grouped into two types (5):

i) additives such as rhenium and iridium which really diminish coke deposit rate

ii) additives such as germanium and tin, for which the coking rate seems at least equivalent, if no higher, than that observed with platinum alone.

It stands to reason that producing less coke under the reaction conditions is not enough to counteract the effects of coking. Indeed the location of this coke and its nature play an important role on its inhibiting effects in various catalytic reactions.

The purpose of this paper is to study the modification of the quantity, the location, the nature and the toxicity of coke induced by a change of the experimental conditions (temperature, pressure), or by a change of the nature of the catalyst (support and metallic phase (dispersion, alloying)). Finally the effect of these different parameters on the coking reaction will be discussed in relation to a described coke build up mechanism.

I) Location, composition and structure of carbon deposits on bifunctional catalysts :

I-1) Location

Coke may be removed by gasification with oxygen. The temperature programmed combustion (TPC) of coked catalysts shows two oxidations, one at around 300°C and the other at around 450°C. These two peaks are particularly well resolved when platinum is supported on non acidic and non microporous alumina. Nevertheless if such is the case, a low oxygen pressure during the TPC analysis, allows a good resolution of the two peaks (figure 1).

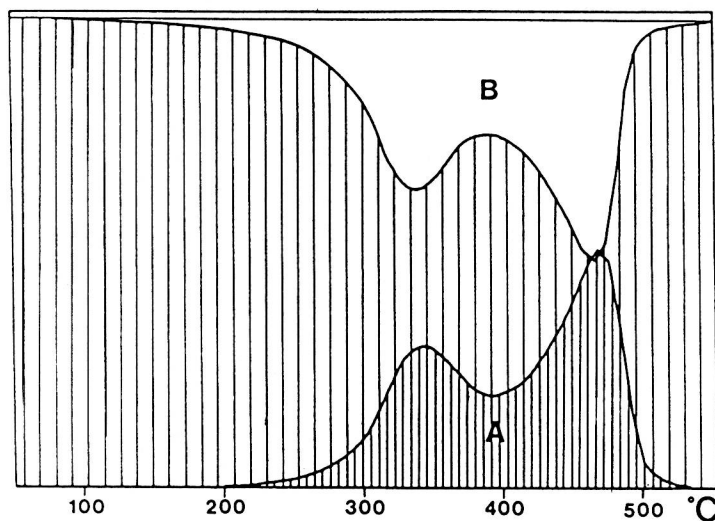


Figure 1 : Temperature programmed oxidation of coked Pt/Al₂O₃ catalyst

(A) CO₂ production (B) O₂ consumption.

A study of these peaks shifting with an increasing temperature shows that the activation energy of coke combustion is equal to 10 kcal for the first peak and 15 kcal for the second one.

Many materials are known to catalyse the gasification of coke, and these include several metals. So it has been found that the low temperature combustion is due to the presence of coke on the metallic phase (6) (7) (8). As a proof, when Pt/SiO₂ catalyst and pure alumina are coked as a mixture and analysed apart by TPC experiments, coke deposited on Pt can be oxidized at 260°C when coke deposited on alumina is oxidized at 550°C (figure 2). Such a difference can be explained by assuming either that platinum catalyses the oxidation of carbon or that coke deposited on the metal is different than coke deposited on the alumina.

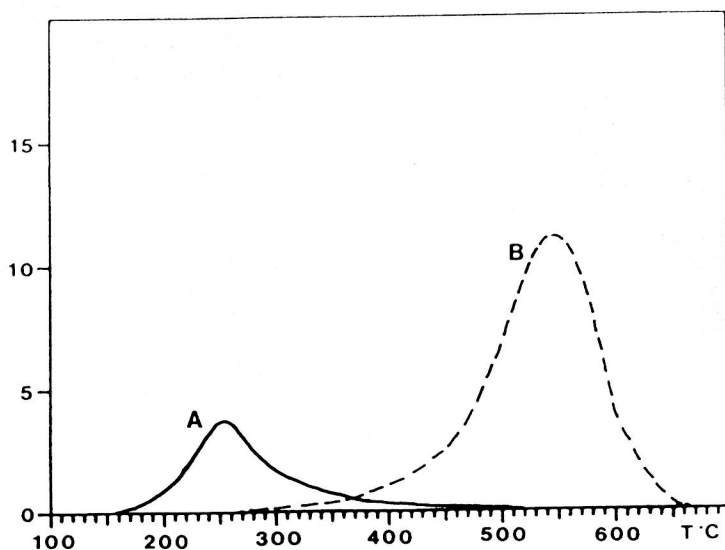


Figure 2 : Temperature programmed oxidation of coke :

(A) deposited on Pt

(B) deposited on Al₂O₃.

The oxidation of coronene deposited on a Pt/Al₂O₃ catalyst proves the catalytic part played by the metal (figure 3).

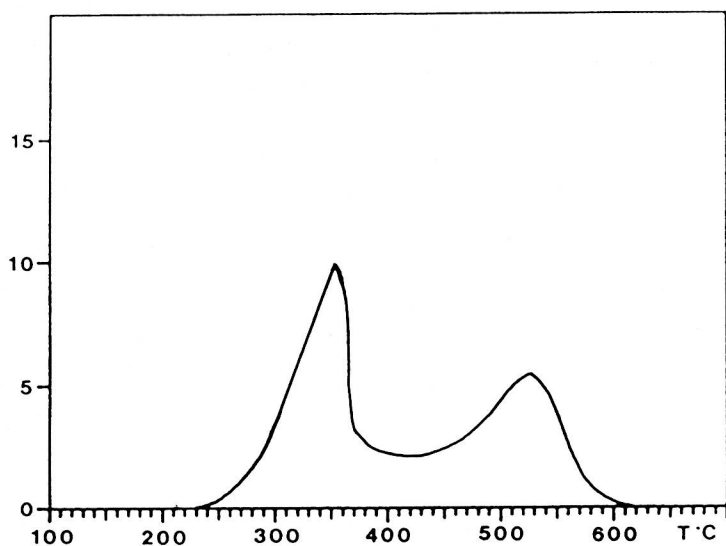


Figure 3 : Temperature programmed oxidation of coronene deposited on $\text{Pt}/\text{Al}_2\text{O}_3$.

In conclusion, distinction between coke deposited on the metallic surface and on the support can be carried out by temperature programmed combustion. The amount of coke deposited on the metallic phase of a bifunctional catalyst can be determined by combustion at moderate temperature (300°C).

1-2) Composition

Measuring the oxygen consumed and the amount of carbon dioxide produced during temperature-programmed combustion indicates that the coke deposited on $\text{Pt}/\text{Al}_2\text{O}_3$ corresponds to the formula CH_x . Table 1 shows that coke accumulated on the metal is less dehydrogenated than coke deposited on the support.

catalyst	coking conditions	H/C
Platinum black	cyclopentane + 10% of cyclopentene (400°C)	1.05
Chlorinated Al_2O_3	cyclopentane + 10% of cyclopentene (400°C)	0,5

Table 1 : Comparison of the H/C ratio of coke deposited on pure Pt and pure Al_2O_3 catalysts.