

CATALYTIC ENGINEERING FOR AUTOMOBILE EMISSION CONTROL

ENGENHARIA DA CATÁLISE NO CONTROLE DOS ESCAPES DE AUTOMÓVEIS

1. INTRODUCTION

Three excellent reviews have recently been published on the problem of Catalysts for Automobile Emission Control: one by Wei, in *Advances in Catalysis* (1), one by Shelef in *Catalysis Review* (2), and one by Hightower at the *Congress on Catalysts Preparation* in Brussels (3).

Although borrowing, of course, much information from these papers, I shall try to give specific insight by looking to see how Catalytic Engineering can help solve this applied catalytic problem. On addition, some new data since the last of these three publications are furnished.

The term Catalytic Engineering must be considered in its more general meaning which can be illustrated from the description of the Figure 1. The final objective concerns the promotion of all desirable

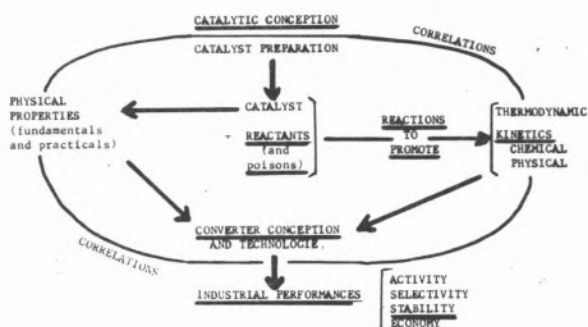


Fig. 1

Different aspects of the Catalytic Engineering

reactions. For such a purpose present knowledge in Catalytic Engineering gives some precise ideas for the choice of efficient catalyst formulas. For the next step, catalyst preparation, Catalytic Engineering today gives very useful laws or working principles. The catalyst obtained has then to be used under optimum conditions in the presence of reactants, and unfortunately of poisons. Catalytic Engineering provides kinetic laws or the method of their determination to achieve such optimization. Such studies include the utilization of the concept of Simulation as will be seen later on. Besides, knowledge of the physical properties of the catalytic solid by itself brings, very useful informations both for fundamental comprehension and for the technology of utilization, and this, constitutes another aspect of Catalytic Engineering. All these properties lead, to the reactor conception taking also into account the other element of the Catalytic Unit, which here is the car itself. The final step, may be the most important, has to do with the economic optimization of the whole catalytic process on the basis of the industrial needed performances, of Activity, Stability, and Stability. All these previous elements of the catalytic process are connected by correlations, here represented by the circular line which, through a better comprehension of phenomena, provides a tool for practical optimization.

The truth obliges us to say that reality is not so idyllic as what can be imagined from this schematic description. Firstly, present practical achievements have not exactly been obtained by simple deduction

from this schema on the basis of Catalytic Engineering laws. It is indeed a mixture between rationality and hard experimental research lasting for fifteen years, which has led to the present achievements. But such effort now makes it possible to try to describe the situation rationally. Secondly, numerous problems remain to day unsolved, and cannot be solved by the only aid of deductive methods. We will encounter some examples of these remaining unanswered questions. Due to the breadth of the subject, my talk will be limited to the points underlined in figure 1 :

- reactions to be promoted ;
- choice of catalytic formulas and performances deduced from simple catalytic tests, or more complete kinetic experiments ;
- converter conception ;
- industrial performances with special accent on the problem of their stability, i.e. the problem of aging.

2. REACTIONS TO BE PROMATED AND CATALYTIC FORMULAS

Exhaust gases composition depends on the air /fuel ratio, fed to the engine. In the absence of NO production, the stoichiometric ratio enabling complete combustion of hydrocarbons is $\rho = 14.5$ for conventional gasoline.

For fuel rich conditions with, for example, $\rho \approx 14$, exhaust gas composition can have the following value: 3% CO, 1% H₂, hydrocarbons much smaller, O₂ around 1%, CO₂ and H₂O around 10%, and compounds with lead, sulfur, phosphorus and halogens. When the air/fuel ratio goes from rich conditions (hydrocarbon excess) to lean conditions (O₂ excess), the composition varies as shown by figure 2. Unburned decrease, while O₂ increases, and NO

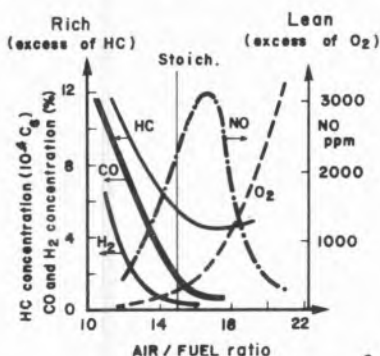


Fig. 2

Pollutant concentrations as a function of A/F ratio

goes through a maximum after the stoichiometric ratio value. The total elimination of pollution would consist in reducing to zero the percentage of unburned and NO. Of course, this is not possible and some realistic norms for elimination have to be defined. These norms have been and will be again subject to numerous modifications in time and in space.

So I shall just give here, as an illustration, the standards stipulated by the Federal Clean Air Act (1970) in the United States.

A difficulty in their definition comes from the eminently transient nature of the driving mode of engines, which causes variations in the air/fuel ratio during the cycle. So an integrated process had to be defined, which was called: (CVS - CH). It concerns :

- a standard typical mode of driving, which includes a cold and a hot start (CH), with a shut down of 10 min during a total cycle of 40 min ;
- a constant volume sampling (CVS), all during the cycle.

The integrated requirements, not yet in force, are given in table 1. They correspond roughly to 90% conversion relative to car emissions around 1970.

Table 1
Permitted emissions of pollutants during 50.000 miles of utilization (Federal Clean Air Act, 1970, U. S. A.)

Pollutants	HC	CO	NO
g/mile	0,41	3.4	0.4

So, the catalytic species must belong roughly to two categories : catalysts for hydrocarbons and CO oxydation; catalysts for NO reduction. The determination of their basic (or potential) performances brings up the problem of simulation. Indeed, the complexity of real experimentation, which concerns a running car, with complex gas collection and analysis, requires simplified tests simulating reel ones to be developed. Such simulation is an usual notion in Catalytic Engineering. But it represents here a quite special problem, due to the large scale of simulation, which ranges from quite simple laboratory tests concerning oxidation of CO and one hydrocarbon, and NO reduction by H₂ and CO; to almost real tests on an engine dynamometer. Between these extremes cases, there is plenty of room for the utilization of various charges, which can be obtained by synthetic mixtures or by the use of a burner of gasoline, containing more or less typical additives. This simulation also concerns, of course, as seen further on, the aging of catalysts. We must note that the term simulation can designate, besides, the mathematical computer modeling of the kinetic evolution in the converter, which can provide precious informations.

3. OXIDATION CATALYSTS

Historically, research and achievements first concerned CO and hydrocarbon oxidation. The efficient catalysts are well known and figure 3 presents the specific activity (per m²) of some species for CO or ethylene oxidation. We can see the enormous superiority of some precious metals such as Pt and mainly Pd. Some simple oxides, such as cobalt or copper oxides, or some mixed oxides (of spinel or perovskite structures) are also quite efficient. From the point of view of practical activity, per g. of catalyst, some oxides can support the comparison with precious metals if we consider :

- that precious metals, not very abundant and very expensive, must (and can) be used in quite low percentages on the carrier (0.1 to 1%);
- that base metal oxides can be used in bulk form or with a high percentage on the carrier.

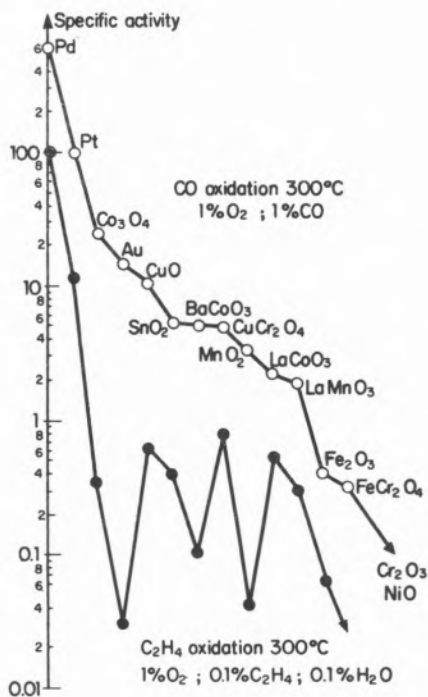


Fig. 3

Specific activity (by m^2) of different elements for CO and C_2H_4 oxidation (4)

For defining activity, the turnover number would be a more fundamental characteristic, but the site number can be difficult to define, particularly for oxides. Beyond, classification by activity is not the only basis for selection. The variation of activity with temperature – the apparent activation energy – can be a more important property if we consider cold starting and the transitory period of heating. It should be also emphasized that resistance to aging may be a more important property than fresh activity. Higher resistance of Pt than Pd to lead poisoning, for example, improves the practical interest of Pt.

Moreover, the classification by activity depends on experimental conditions due to the different kinetic expressions for each catalyst. The classification can then be quite different for different pressure or temperature. Considering the importance of kinetic differentiation, figure 4 schematically represents different types of kinetics

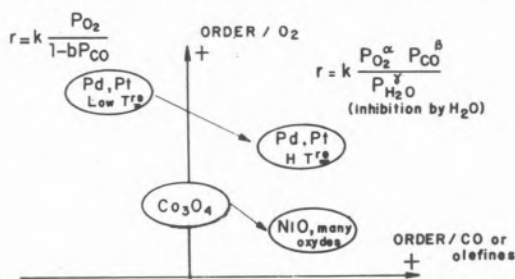


Fig. 4

Domain of variation of formal kinetics order as a function of active species and experimental conditions (4) (5) (6) (7)

observed for standard oxidation catalysts. For Pd or Pt, at low temperature, we observe a positive order for O_2 , but a negative order for CO or olefin; in other terms, an inhibition by CO or olefins. But this inhibition disappears at high temperature. For oxides, we often observe kinetic laws with positive fractional orders for O_2 , CO and olefins, and inhibition by H_2O . Formally, these results lead to the following rate equations :

– for Pt or Pd at low temperature,

$$r = k \frac{P_{O_2}}{1 + bP_{CO}}$$

with $bP_{CO} \gg 1$, at low temperature, and $bP_{CO} < 1$ at high temperature, due to the decrease of b , the CO chemisorption coefficient.

$$\text{For oxides } r = k \frac{P_{O_2}^\alpha P_{CO}^\beta}{P_{H_2O}^\gamma}$$

From a fundamental point of view, these different kinetic equations reveal different mechanisms. From a practical point of view, they explain the quite different evolution of conversion, as a function of temperature, as illustrated by figure 5.

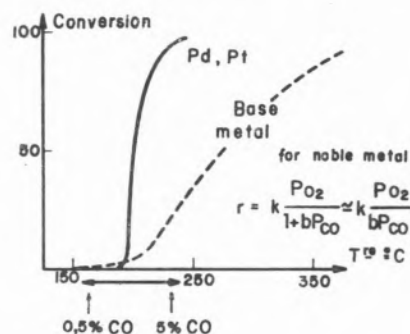


Fig. 5

Activity comparison of base metal and noble metal oxidation catalysts

For precious metals, the drastic increase in conversion corresponds to the elimination of inhibition by CO, by a decrease in the CO chemisorption coefficient, b . Such a property is particularly important for attaining the required rapid increase in performances during a cold start. The intervention of inhibition by CO appears clearly if we consider the influence of the CO percentage on the threshold temperature for the appearance of CO conversion, as illustrated by figure 5. When going from 0.5 to 5% CO, this temperature increases by 100°C(8). For base metal oxides, the variation in conversion with temperature is smoother, and overall performances are weaker.

For saturated hydrocarbons, the oxidation rate is generally weaker than for CO or olefins. With saturated hydrocarbons and H_2 , inhibition is not observed, for these molecules are not so strongly chemisorbed on precious metals.

Moreover, the real case corresponds, of course, to the mixture of different hydrocarbons and CO, and leads to competition phenomena in their chemisorption, which can decrease the overall performances. The oxidation of SO₂ also has to be considered, due to the noxiousness of SO₂ for health and to the promotion of catalyst aging by the formation of sulfates as seen further on. Fortunately, at high temperature, this oxidation is thermodynamically limited, except, of course, for high concentrations of O₂.

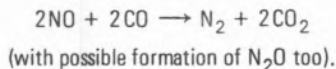
Finally, industrial applications generally including Pd and Pt, exist today and give excellent initial performances and sufficient resistance to aging.

4. REDUCTION CATALYSTS

The NO reduction problem is much more complex and difficult than oxidation of unburned gases. An important factor of complexity comes from the complexity of the exhaust gases themselves, in which several reduction types of molecules exists. Catalytic Engineering principles lead to proceed by an analysis of each possible different elementary reactions, before describing the overall performances and the reactor conception: so, going by growing order of complexity, we shall describe :

- NO reduction by CO alone.
- NO reduction by H₂ alone.
- NO reduction by CO in the presence of H₂O.
- NO reduction by hydrocarbons.
- NO reduction by CO + H₂.
- Influence of O₂ on NO reduction.
- NO reduction by NH₃
- NO reduction in the real atmosphere of exhaust gases.

4.1. NO REDUCTION BY CO ALONE



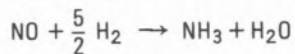
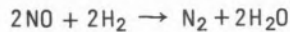
Many catalysts have been tested, and some classifications according to their activity have been proposed as shown below.

- Fe₂O₃ > Cu Cr₂O₄ > UO > Cu₂O > Cr₂O₃ > NiO > Pt > Co₃O₄ > Al₂O₃ > MnO > V₂O₅ (9)
- Co₃O₄ > CeO₂-Co₃O₄ > La_{0.85}Ba_{0.15}CoO₃ > CuO₂O₄ > LaCoO₃ (10)

A redox mechanism has been proposed to interpret the experimental results.

4.2. NO REDUCTION BY H₂ ALONE

Two possible ways of evolution, both thermodynamically complete, are to be considered.



Due to the possible reoxidation of NH₃ into NO on an oxidation converter coming after the reduction converter, the best catalysts are those performing selective reduction of NO into N₂. They will be called «selective catalysts».

Precious metals are quite active, but some of them, such as Pd and Pt, are not selective, while Ru, for example, is quite selective. In reality, the problem is much more complex, and it appears necessary to present, as is done in figures 6 to 10, the characteristics of

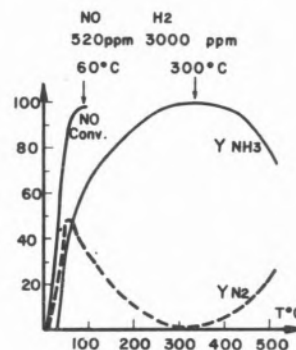


Fig. 6
NO reduction by H₂; Pt (or Pd) type catalyst.
Total conversion of NO, and yields of NH₃ and N₂ (2) (11)
(Total conversion = Y_{NH₃} + Y_{N₂})

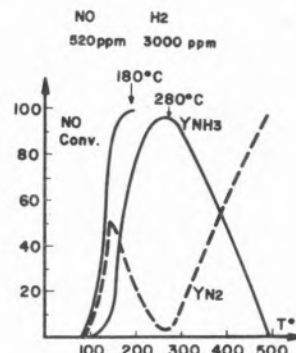


Fig. 7
NO reduction by H₂.
Rh type catalyst (2) (11)

different types of catalysts, according to NO conversion and separate yield of N₂ and NH₃, as a function of temperature. Figure 6 shows the quite good activity of Pt (or Pd); but the yield of NH₃ is quite high, and N₂ appears selectively only above 600 °C. Figure 7 shows that Rh is also very active and that N₂ already appears selectively at the lower temperature of 400 °C. In figure 8, Ru appears like a rather «magic» catalyst, since activity and selectivity are quite good even at low temperature. Unfortunately, we shall see that the

volatility of its oxide severely hampers its use. Figure 9 shows that some base metals such as Ni, Ni-Cu or their oxides (nickel chromites for example) are in an intermediate position, rather similar to Rh. Numerous types of other base metal oxides have been investigated, as presented in figure 10. According to the only criterion of activity, the first four appear good, but selectivity criteria lead to the selection of only the first two.

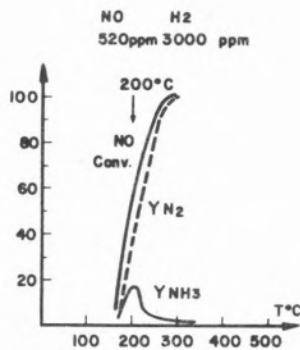


Fig. 8
NO reduction by H₂.
Ru type catalyst (2) (11).

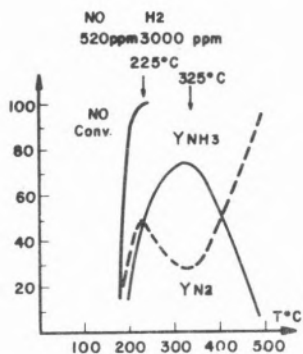


Fig. 9
NO reduction by H₂
Ni Cr type catalyst
Ni or
Ni Cu (Monel) (2) (11)

The mechanism of the formation of both products, N₂ and NH₃, can be understood from figure 11 showing, from already formulated interpretation (13) (14), and in a simplified form, the evolutions in the chemisorbed phase. On these basis, NO can be chemisorbed associatively or dissociatively; H₂ is chemisorbed dissociatively. The first reaction occurs between chemisorbed NO and H₂, to form chemisorbed nitrogen, σ_N, and σ_{OH}. Two σ_{OH} give water and σ_N is able to disappear in two different ways. One by reaction with another σ_N, to produce molecular nitrogen :



according to a kinetic law such as :

$$r_1 = k_1 \sigma_N^2$$

Ni Cu Ni Cr	MOD	Cu Cr	Cu O	Ni O	Cr ₂ O ₃	Fe oxide
ACTIVITY Temperature for 90% Conversion						
200	225	275	280	425	480	480
← Active						
SELECTIVITY Temperature for high N ₂ selectivity						
450	480	700	630	500	400	700
← Selective						
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Fig. 10
Activity and selectivity in NO reduction by H₂, for oxide catalysts (2) (11) (12).

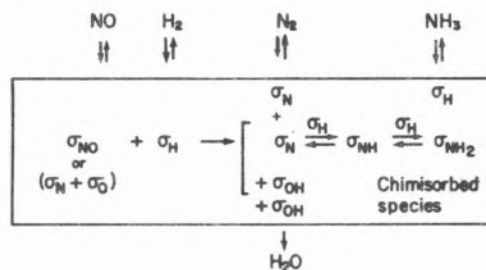
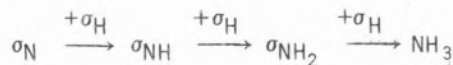


Fig. 11
NO reduction by H₂ (evolution of adsorbed species)
- Towards N₂ : r₁ = k₁ σ_N · σ_N
- Towards NH₃ : r₂ = k₂ σ_N · σ_H

The other, by reaction with σ_H, to produce NH₃ :



according to a kinetic law such as :

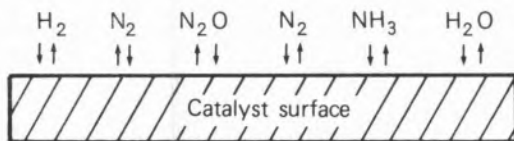
$$r_2 = k_1 \sigma_N \sigma_H$$

or even, may be, with a higher order with regard to σ_H. This mechanism explains the influence of partial pressure of NO or H₂ on the nitrogen selectivity. An increase in NO partial pressure, more or less increases selectivity towards N₂. This, results from the increase in chemisorbed NO concentration, and therefore in σ_N, so as to increase selectively r₁ (the second order reaction in σ_N) with regard to r₂ (the first order reaction in σ_N) (15) (16). The reverse effect is of course observed for a hydrogen pressure increase, and results only in enhancing r₂ = σ_N σ_H. According to these interpretations, the best catalysts for nitrogen selectivity are those that chemisorb NO most strongly. Ru is known to strongly chemisorb NO (16), and may even, do so dissociatively to produce σ_N and σ_O, as opposed to Pt. Beyond, considering the high thermodynamic constant of the decomposition of NH₃ at

temperatures higher than 250°C, all catalysts active for this decomposition must have good selectivity towards N₂ above 250 °C. Effectively, the best catalysts for NH₃ decomposition (Ni, Ru) are selective catalysts for NO reduction by H₂ (14).

In conclusion, the mechanism described here, can altogether take into account the effect of NO chemisorption and the intervention of activity for ammonia decomposition.

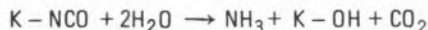
An important point is that such interpretation has led to the designing of dual catalysts, by associating one active and one selective component, such as in Pt-Ni, which seems to be a good catalyst. We can remark that the mechanism can also take into account the possible formation of N₂O. This product appears as an intermediate between NO and N₂, in a sort of «rake-like» scheme (17) as illustrated hereunder :



4.3. NO REDUCTION BY CO IN THE PRESENCE OF H₂O

The introduction of H₂O decreases the desired selectivity for N₂, i.e. increases the parasite selectivity for NH₃. Two explanations have been proposed :

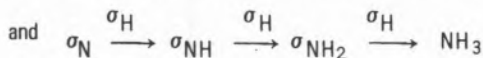
- 1) One involving the so-called isocyanate mechanism. Hydrolysis of the chemisorbed isocyanate formed from CO + NO leads to NH₃ (18) :



- 2) One involving the formation of chemisorbed hydrogen, σ_H , by the water gas-shift reaction, (W.G.S.R.) and the reaction of this highly reactive form of hydrogen to form NH₃ :



with H₂ appearing as σ_H in the chemisorbed phase :



An argument in favour of this last mechanism seems to be the increase toward NH₃ selectivity, by H₂O addition on active catalysts for W.G.S.R. (2) (19).

4.4. NO REDUCTION BY HYDROCARBONS

Within the limit of the simple ideas imposed by such a general review, hydrocarbons can be considered as being weakly active for NO reduction. This can be explained by their highly difficult dissociative chemisorption, giving small concentrations of chemisorbed hydrogen. Indirect action, by means of steam reforming, giving chemisorbed or molecular hydrogen, also seems to be of little importance.

4.5. NO REDUCTION BY H₂ + CO

The addition of CO to H₂ would seem to be a way to improve the selectivity towards N₂, compared with the selectivity observed with H₂ alone, due to the sole production of N₂ for NO reduction by CO. Such an improvement is not observed, and moreover the complex influence of CO depends on the catalytic species.

Firstly, figure 12 shows that CO brings on a strong kinetic inhibition

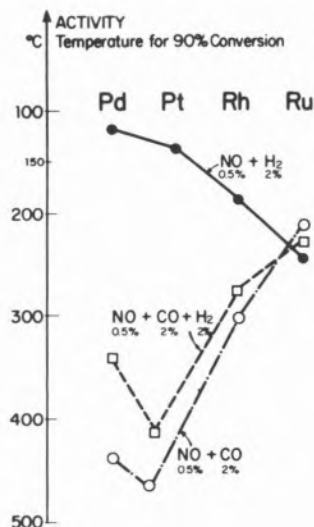


Fig. 12

Activity of precious metals in NO reduction : by H₂, CO and CO + H₂

in the NO reduction rate with Pd and Pt (16). On the contrary, no inhibition appears with Ru and inhibition is weak with Rh. Such phenomena would result from the characteristics of the competition in the chemisorption between CO and NO. On Pd and Pt, NO is displaced by strongly chemisorbed CO; on Ru, more strongly chemisorbed NO is only weakly removed. Secondly, authors have observed that CO introduction reduces the selectivity towards N₂ on Ru, and can enhance it on Pd and Pt (15). The explanation would be that on Ru an even small (due to strong chemisorption of NO) removing of σ_N by σ_{CO} , would decrease N₂ formation

$$(r_1 = k_1 \sigma_N^2)$$

compared with NH₃ formation

$$(r_2 = k_2 \sigma_N \sigma_H),$$

while NO conversion hardly remains affected. On Pd or Pt, the removing of σ_N should also produce reducing effect on selectivity toward N₂. But even in the absence of CO this selectivity is quite low, and so not able to be decreased by the strong CO competitive chemisorption. On the contrary the strong chemisorption of CO would be responsible for some direct NO reduction by CO, giving only N₂. This discussion essentially concerns selectivity in a certain range of relatively low temperatures.

At temperatures higher than 500°, selectivity towards N₂ is also governed by the catalytic decomposition of NH₃, which may depend weakly (or differently) on CO chemisorption.

Although all the above described results cannot be extended to other catalytic formulas, they clearly show the intervention of competition of chemisorption between CO and H₂. May be also they give some arguments to attribute an essential role to molecular or chemisorbed hydrogen, in the NO reduction by the mixture of all exhaust gases.

4.6. INFLUENCE OF OXYGEN ON NO REDUCTION

At first view, one might think that O₂ would decrease the reducing power of the medium and, as such, decrease the performances. Figures 13 and 14 present results obtained on different catalysts,

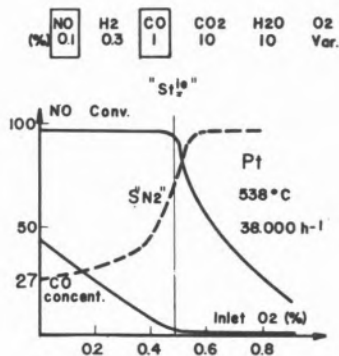


Fig. 13

Effect of O₂ in NO reduction on Pt (20)

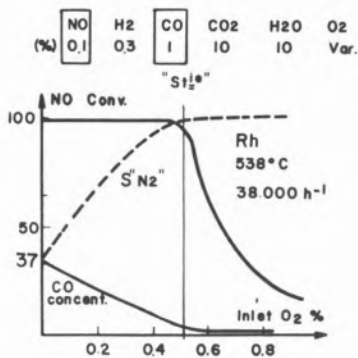


Fig. 14

Effect of O₂ in NO reduction on Rh (20)

with simulated feeds containing increasing percentages of O₂. Figure 13 shows that with Pt, O₂ does not decrease the NO conversion until a stoichiometric percentage is attained (20). Beyond this value, a decrease in conversion is observed. The interesting point is that selectivity towards N₂ increases regularly. Figure 14 shows that with Rh the same results are observed concerning the activity and also qualitatively concerning the selectivity towards N₂. But, here, N₂ selectivity starts from a higher value, and is much more enhanced

than for Pt, when the O₂ percentage increases. Similar results are also observed for Ir, Ni-Cu and Cu.

These quite interesting results can be interpreted on the basis of the previously described mechanism, as shown in figure 15. The

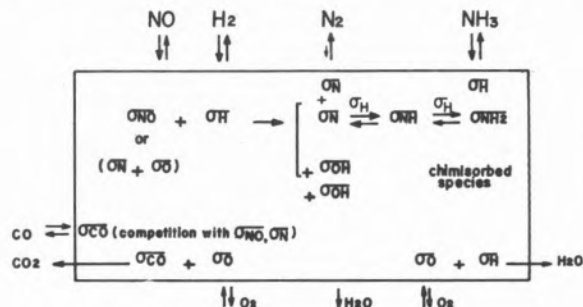
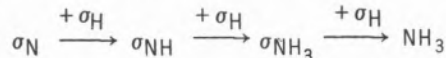


Fig. 15

Influence of O₂ (and CO) in NO reduction

- CO : σ_{CO} reduces N₂ selectivity.
- O₂ : a) Under stoichiometrie : σ_O enhances N₂ selectivity by decreasing σ_H and σ_{CO} .
- b) Excess of O₂ : σ_O reduces, then cancels NO conversion.

chemisorption of molecular oxygen creates σ_O entities, and σ_O reacts with σ_H to produce σ_{OH} , then water. It is understandable that the resulting decrease in σ_H would preferentially affect the overall rate of successive reactions leading to NH₃



rather than the rate of NO conversion



As long as σ_H remains at a sufficiently high level, the NO conversion may be practically unaffected, while NH₃ formation could be appreciably reduced. This corresponds to the situation observed with Pt or Rh, for low oxygen partial pressure. Of course, when the oxygen pressure, and consequently σ_O , became too high, the drastic decrease in σ_H decreases NO conversion, while selectivity remains excellent toward N₂. We must note that beyond this effect on σ_H reduction, the chemisorbed oxygen, σ_O , can also eliminate σ_{CO} , whose possible inhibiting power on nitrogen formation has been pointed out above.

4.7. NO REDUCTION BY NH₃

This reaction can be explained by the previously invoked mechanism. Moreover, ammonia oxidation leads not only to NO, but also to N₂ or N₂O by possible selective oxidation.

4.8. NO REDUCTION BY EXHAUST GASES

In spite of the complexity of the reactive medium, it seems possible to find again some of the properties described above with elementary reactions. The selective catalysts toward N₂ are those

selective with H_2 alone. The catalysts active for W.G.S.R. appear to make NH_3 formation, possible, perhaps by way of CO conversion to chemisorbed hydrogen. Sufficiently weak oxygen concentrations improve selectivity toward N_2 , without much decreasing the activity.

Finally this fundamental knowledge enables a choice to be made of the best catalytic formulas, of the best operating conditions, and of converter conception as will now be presented.

5. APPLICATION TO CONVERTER CONCEPTION

The fundamental performances described above lead, as an application of catalytic engineering principles, to different converter conceptions.

I want, first of all, to mention the two most common geometric forms of industrial catalysts: i) pellet form, which is used, for example, by General Motors with Rhone Poulenc alumina pellets; ii) monolithic form, which is used, for example, by Ford with an Engelhard catalyst (PTX catalyst).

In this latter case, the non-porous honey-comb structure is generally covered by what is called a wash-coat, i.e. a porous material, acting as the carrier of the active species. The diffusion path along the pores is longer through pellets, than through the wash-coat, but this is balanced, or overbalanced, by the higher surface area of pellets. Many other problems are involved in making a comparison between these two solutions, but they would need more time for discussion.

5.1. OXIDATION CONVERTER

For such a simple converter, the existing industrial solutions give satisfying results, except maybe, for SO_3 formation, in the presence of excess oxygen.

5.2. DUAL-CATALYST CONVERTER

Figure 16 presents its conception, based on the separation of the two functions desired.

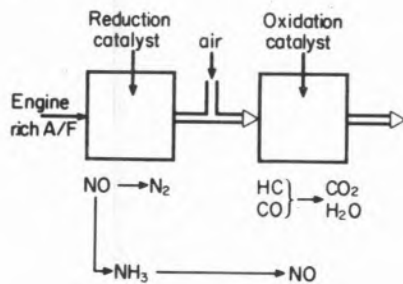


Fig. 16

Dual-catalyst converter (ammonia problem)

- 1) The first converter is designed to selectively reduce NO into N_2 , for an engine working with rich conditions. This leads to using the previously described selective catalysts.
- 2) The second converter is designed to achieve the complete

oxidation of unburned gases, by the aid of secondary air injection.

For steady-state conditions, each converter assumes its own function. But for cold engine starting, the first converter is not able to start the catalytic reduction and even slackens the heating rate and the starting of the oxidizing converter.

Consequently, the secondary air is switched towards the first converter during the beginning of such a driving cycle, to achieve the oxidation in the first converter. Of course, the catalyst of this converter must be active for oxidation as well as for reduction.

The advantage of a dual converter comes from the relative separation of the two functions, which allows a specific optimization for each of them. But several drawbacks are introduced which concern :

- a) The high total quantity of catalyst and high pressure drop.
- b) The economic penalty for rich feeding.
- c) The need for alternating working conditions for the first converter. This would be peculiarly harmful with Ru catalyst, due to the volatility of Ru oxides. But, for any catalyst, alternating oxidizing and reducing conditions can induce detrimental structural strains.
- d) The difficulty to avoid in the first converter, the formation of NH_3 , which is converted back into NO in the oxidizing converter.
- e) SO_3 formation in the oxidizing converter.

5.3. THREE WAY CATALYTIC CONVERTER

To avoid the drawbacks of the dual converter, the idea soon arose to bring about, in a single converter, by means of one efficient catalyst, the complete transformation of exhaust gases into CO_2 , H_2O and N_2 . This is, of course, possible with an infinitely active catalyst and by feeding the engine at the stoichiometric value ($A/F \approx 14.5$). Such a catalyst would have to promote three reactions: NO reduction, CO oxidation and hydrocarbon oxidation in the complex atmosphere of exhaust gases (hence the name three-way catalyst).

Figure 17 shows what performances can be observed for NO and CO

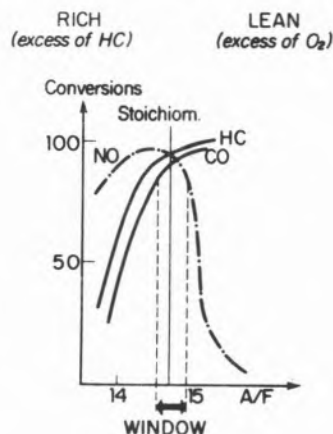


Fig. 17

Performances of a 3 way catalyst, as a function of A/F ratio

conversion, as a function of A/F for a real catalyst having mean performances.

For A/F under the stoichiometric value, NO reduction is high, but CO oxidation becomes limited by the lack of O₂ in this reductive medium. When A/F increases towards excess of O₂, the CO conversion increases and NO reduction decreases.

A «window» can be defined as the A/F interval allowing 80% conversion for all transformations, as presented in figure 17. The quality of the catalyst will be characterized by the window width, by considering, of course, not only CO, but hydrocarbon oxidation. With a simple catalyst, this width can have the excessively low value of 0.1 to 0.3 A/F units. But the window can be enlarged by the association of several different catalytic elements. On the rich side, highly active elements for oxidation, such as Pt and Pd, are desirable, with the risk of inducing NH₃ formation by NO reduction. On this side, besides, the difficult CO elimination can be improved by active elements for the water-gas shift reaction, again with the risk of inducing NH₃ formation from NO :



On the lean side, highly active elements for NO reduction in the presence of oxygen, are desirable. We have shown with some detail (figure 14) that Rh can be considered as one of them. On the lean side, besides, NO reduction produces mainly N₂.

To maintain the engine inside the window, the motor feed must be regulated. This is done by means of a sensor, detecting O₂ concentration in the exhaust gases, and acting by a feedback signal on the motor injection (figure 18). Electronic injectors are more efficient than carburetors for such calibrated injection.

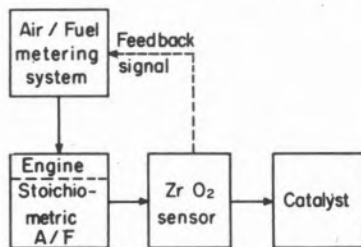


Fig. 18

Three-way catalyst closed-loop

Compared with dual converters, three-way catalyst converters have several advantages :

- a smaller quantity of catalyst for the same efficiency, and hence a smaller pressure drop,
- a much better elimination of NH₃ formation and of its reoxydation into NO,
- an elimination of SO₃ formation.

But, of course, some difficulties remain, which are :

- the obligation to work inside a narrow window of A/F variation, which needs a rather complex regulation of the feed,

- the possible intensive aging and loss of performances, which are understandable if we consider the high level of performances required for the fresh catalyst.

5.4. COMPLEX THREE-WAY CATALYST

To improve the performances of a three-way catalyst and particularly to enlarge the A/F window, the idea arose of adding a metal capable of storing excess oxygen under lean conditions and to give this oxygen back under rich conditions.

Such a metal does not act like a catalyst but by via the following stoichiometric gas-solid reaction :

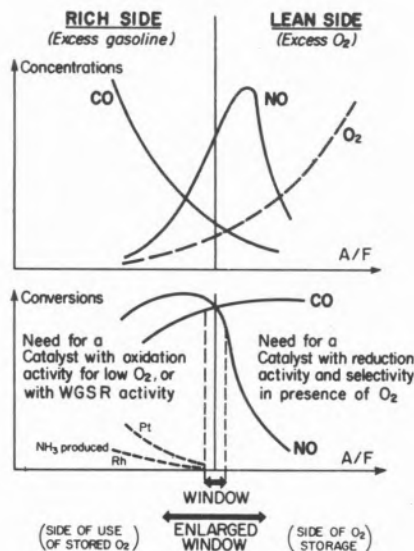
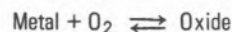


Fig. 19

Simple window for a three-way catalyst. Enlarged window by addition of a metal capable of storing and giving back oxygen

Figure 19 gives an illustration of possible window enlarging. Of course, the quality of the performance depends both :

- On the capacity of O₂ storage,
- on the rate of the two reverse gas-solid reactions,

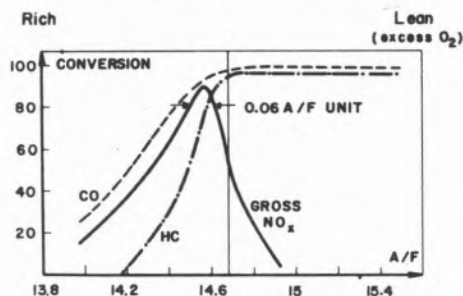


Fig. 20. A

3 way-complex catalyst. Performances without modulation. 538 °C GHSV 50.000 h⁻¹.

— and on the structural resistance of the metal (and oxide) to the strains induced by such alternating transformations.

As an illustration, figure 20 presents an example, borrowed from the

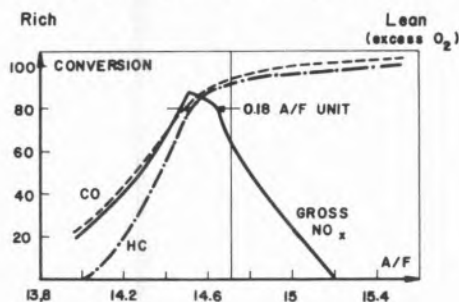


Fig. 20. B

3 way-complex catalyst. Performances with sawtooth modulation of 1.0 Hz and 1 A/F amplitude

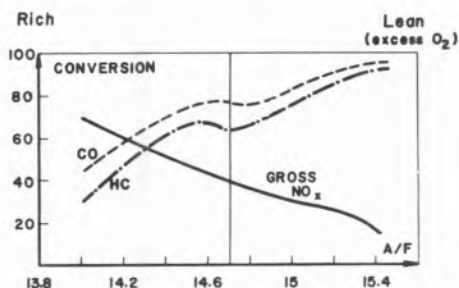


Fig. 20. C

3 way-complex catalyst. Performances with sawtooth modulation of 0.1 Hz and 1 A/F amplitude

literature, of performances obtained with such catalysts (21). The three cases correspond respectively to steady-state conditions and to two types of modulation, simulating temporary ventures into the lean or rich side.

6. AGING

Catalytic performances must, of course, be maintained for a sufficiently long time. The Federal Clean Air Act, for example, fixes at 50,000 miles the distance along which the norms are to be obeyed. Studying this problem of stability, or of aging, leads to a one degree rise in the level complexity. Why? Because in addition to the complexity encountered for activity and selectivity problems, there are several ways of aging that, moreover, are often difficult to disentangle.

- 1) Aging by mechanical breaking, whose importance is easily understandable for cars.
- 2) Aging by thermal sintering, due to the high temperature attained in converters. Sintering can concern the different elements of the catalyst:
 - a) The carrier, although thermally stable carriers exist to day,

such as special aluminas of relatively high surface area (50 to 100 m²/g) (22).

- b) The deposited metal, whose crystallites can grow according to quite complex laws, depending on the atmosphere surrounding the catalyst (23).
 - c) The catalyst itself, when in an unsupported form, such as for oxides. Some associations, in mixed oxides, considerably increase the resistance to aging (24).
- 3) Aging by chemical and structural modifications. Some well known examples are the deactivation of supported cobalt or copper oxides by their reactions with alumina carriers, to give inactive spinels (25).
 - 4) Aging by volatilization. A well known example concerns the elimination of Ru in oxidative media, by the volatilization of some Ru oxides. Numerous ways of stabilization have been tried without clear success, i.e. alloying with other metals, or incorporation into peculiar structures such as perovskites (26) (27). Another example concerns the formation of volatile halides or oxyhalides of catalytic metal, with halogens coming from the gasoline.
 - 5) Aging, finally, due to poisoning by various elements contained in the fuel, which can be essentially lead, phosphorus, halogens, sulfur, etc. ... Lead is added gasoline as T.E.L. ou T.M.L., to improve octane number. Halogens are added to eliminate lead oxides as volatile lead halides. Phosphorus compounds give detergent properties to the fuel. Sulfur compounds come from insufficient desulfuration of gasoline. I shall describe only, and even briefly, this type of aging, which is quite complex itself due to the numerous parameters of action. Indeed, the poisons are various and can act differently, according to the catalyst nature, the atmosphere surrounding the catalyst, the temperature, the converter type, and so on.
This description will be made solely for oxidation catalysts, for which a more complete investigation has been made. Then, the overall evolution of performances, during aging, in the case of a three way catalyst, will be presented.

6.1. AGING FOR OXIDATION CONVERTERS

It can be useful to disentangle the specific effects of each poison, before seeing the influence of their association which, of course does not necessarily proceeds according additive laws. In each case one would have to determine the nature of initial poison compounds, which governs their possibility of diffusion towards the external catalyst surface, then into the catalyst pores. Considering lead compounds, for example, they are initially in the form of quite small solid particles of lead oxide which can be deposited on the periphery of the catalyst. But they can be quickly transformed into volatile lead halides, and so became, able to penetrate into the catalyst pores. Then, the nature of poisoning has to be examined, i.e.: simple geometric contamination, or chemical poisoning which can be irreversible (therefore cumulative) or reversible (therefore depending on partial pressure of poison compounds). Such properties depend on the geometric position, on the nature, and the stability of poison

compounds fixed on the catalyst surface. Considering phosphorous or sulfur compounds, for example, they act differently, if they are in the form of volatile oxides or in the form of much more stable (and so more harmful) compounds, such as phosphates, sulfates, oxyhalides, etc., formed by eventual combination with the carrier, the metal, the lead, etc. ... Moreover, aging can be quite different for the oxidation of CO or of each hydrocarbon. Generally, but not always, we can consider that hydrocarbon oxidation is more reduced than CO. For all these reasons, it appears impossible, today, to present a synthetic review of aging, even limited to oxidation catalysts. But it seems possible to illustrate, by some examples, some typical aspects of this aging.

It has to be noticed that the works of different authors make extensive use of the simulation concept, and this in two directions. One direction concerns the aging phenomenon itself, by use of synthetic mixtures (or gasoline) containing the studied poisons, and by performing aging in laboratory tests or in burners as well as in engines. The second direction concerns the measurement of catalytic performances, before and after aging, as already presented.

— For aging with lead compounds alone, researchers have shown, for example, the great difference in sensitivity that can exist between elements such as Pt or Pd, as illustrated by figure 21

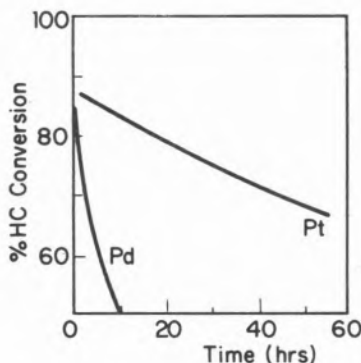


Fig. 21

Resistance of platinum and palladium to poisoning by 0.4 g Pb/gal fuel.

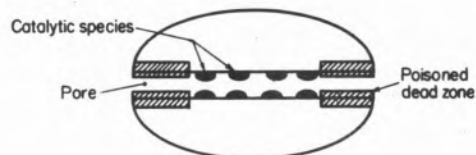
Catalyst: 1000 cm² 0.1% Pt or 0.1% Pd on Al₂O₃ at 550°C

(28). Higher poisoning of Pd has been interpreted as the harmfulness of mutual solubility of Pd and Pb oxides (29).

Moreover, the quite harmful effect of preferential deposition of lead at the periphery of the catalyst has been observed and interpreted as illustrated by figure 22. The inactivity of pore mouths leads to the complete limitation of the overall rate of oxidation, by diffusion through the «dead zone». The fundamental consequence of this, is a very low apparent activation energy in the high temperature range (figure 23). The practical consequence is the impossibility of reaching total conversion, even by using quite high temperatures, as shown by figure 24 (27).

— For aging with phosphorous compounds alone, many researchers have found a higher poisoning effect than with lead compounds

PELLETS (high limitation)



WASH-COAT OF MONOLITHS (lower limitation)

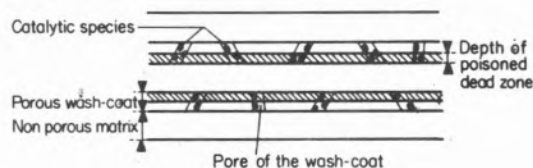


Fig. 22

Pore mouth poisoning inducing diffusional limitation

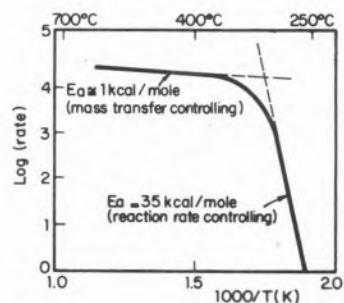


Fig. 23

Arrhenius plot for a lead-poisoned catalyst after 250-hr accumulation using fuel with 0.1 g Pb/gal

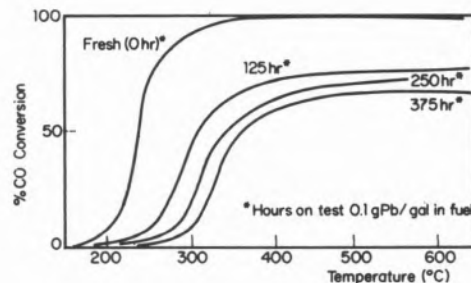


Fig. 24

Laboratory evaluation of a lead-poisoned Pt-Al₂O₃ catalyst GHSV: 90,000/hr⁻¹; lead accumulation: 0.1 g Pb/gal; converter: 2300 cm² radial flow at 590°C

alone, as shown by figure 25 (30). Moreover, it appears in these works that phosphate compounds, formed by combination with the carrier, are accumulated more clearly than for lead compounds, at the periphery, hence the greater reduction in activity.

— With both lead and phosphorus, some researchers have found a

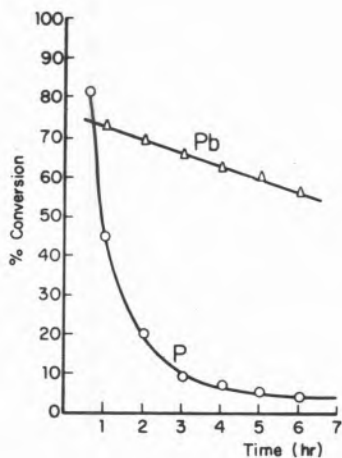


Fig. 25

Typical poisoning deactivation curves simulated experiments; O, phosphorus and Δ , lead

weaker poisoning effect than with each one separately (30). This can be due to the formation of less harmful lead phosphate. But it seems that some controversy then exists about the experimental facts themselves.

- Sulfur is undesirable because it leads to the formation of stable sulfates with base metals constituting the catalyst or with lead from the gasoline (figure 26) (31).

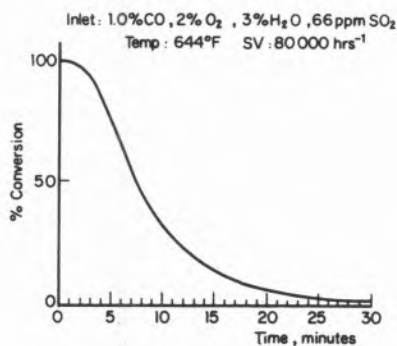


Fig. 26

Decrease in the oxidation of CO upon addition of 66 ppm of SO_2 to the inlet stream as a function of time

We must recall that in spite of thermodynamic limitations, the use of excess oxygen can lead to SO_2 oxidation into SO_3 .

- Concerning halogens, the phenomena seem complex. According certain authors (3) (32), halogens alone, would lead solely to a reversible poisoning effect; in other words to kinetic inhibition, which would disappear by the elimination of these poisons in the feed. According to others, they also lead to metal elimination as volatile oxyhalides or carbonylhalides. Some comparison can be made with the influence of halogen compounds on the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst used in catalytic reforming, on which halogens can lead both to the elimination of Pt and to its redispersion, depending on the experimental conditions. We recall that, by combination

with lead, halogens make it possible for volatile lead halides to penetrate into the pores. This gives an altogether much more uniform distribution of lead on the catalyst surface, and an increase in the total fixed lead. The final result is, however, weaker aging than with pore mouth contamination. This can be understood on the basis of the greater harmfulness of the rate limitation by diffusion through dead pore mouths.

- The influence of temperature on poisoning is complex, although some interpretations can be proposed. Some researchers have shown that aging decreases when temperature poisoning increases, as illustrated by figure 27 (33). Some others have found an

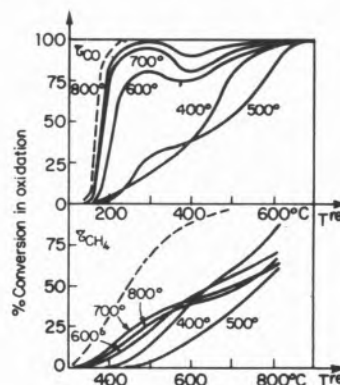


Fig. 27

Catalyst with 0.08% Pd on alumina carrier. Activity after aging during 30 h in a burner at different temperatures (0.25 g/l Pb; 1 Cl - 0.5 Br). Laboratory activity test for $\text{VVH} = 30,000 \text{ h}^{-1}$

- - - activity for the fresh catalyst
- activity after aging

enhancement of aging when temperature increases (30). These results can be reconciled by considering the range of stability of poison compounds. As long as the temperature is lower than the limit at which the instability of poison compounds appears, aging increases with temperature, by some kinetic effect. When we reach the range of thermal instability of poison compounds, aging can decrease with temperature. Such an explanation concerns rather the irreversible poisoning. For reversible poisoning, the decrease with temperature can be due to the decrease in the adsorption coefficient of the poison with temperature. Anyway, such a beneficial effect of high temperature is in line with the often claimed possibility of restoring some activity to a partially spent catalyst by forcing it to work, temporarily, at quite a high temperature (28). Of course thermal sintering can intervene at the same time, and this may be an irreversible aging factor when temperature increases.

- Interesting comparisons between sensitivity to sulfur and lead poisoning, of noble metal and base metal oxide have also been made by several researchers (3). It appears that noble metals are weakly sensitive to sulfur (for thermodynamic and maybe kinetic reasons), but that their low percentage, leads them to be sensitive to lead poisoning. On the contrary, base metal oxides are highly sensitive to sulfur (by stable sulfate formation), but their high percentage makes them weakly sensitive to lead poisoning.

In conclusion, all research done on poisoning, and, more generally, aging now casts some light on the comprehension of these problems and provides some means of action to reduce deactivation.

In this way we can see that industrial oxidation catalysts, having excellent activity and stability qualities, have been manufactured. They are used in the U.S.A. and Japan to help out in respecting the standards that now exist in these two countries, concerning maximum CO and hydrocarbon emission rates.

6.2. AGING FOR THREE-WAY CATALYSTS CONVERTERS

Only two types of information will be presented. One is taken from a publication accurately describing rigorous experiments with three-way catalysts (21). Two others come from a patent or technical paper (34) (35).

In the first one, I have chosen an example, for a given three-way catalyst, of how aging evolves in reduction and oxidation, as a function of the redox potential, which is a parameter that is quite similar to the A/F ratio. The performances are presented for three states of operating, i.e. for a fresh catalyst; after simulated driving for 40,000 km with lead-free isooctane; and after simulated driving for 40,000 km with isooctane containing 7.93 g/m³ Pb, 0.56 g/m³ P, and 0.02 wt % S. Figure 28 shows that aging in the absence of lead induces a narrowing of the window from 0,3 A/F unit to 0.1 A/F unit, while with lead it is impossible to obtain conversions higher than 70 %, for both types of reaction. These results show how difficult it can be to maintain performances within the specifications that governments want to have obeyed.

However, several affirmations appear here and there, by which authors affirm that they have overcome the problem of aging. In a patent by Du Pont (34), a catalyst with a perovskite structure, A B O₃, such as for example (S_r L_a) (Co Ru)₂ O₃, with 1-20 % of the B sites occupied by Ru or Pt, is claimed to have excellent performances for reduction and oxidation. Moreover these performances are apparently maintained during a run of 1000 hr with a lead containing gasoline. Another item from the Los Angeles Times (35) tells us that a three-way catalytic converter on a Volvo car has

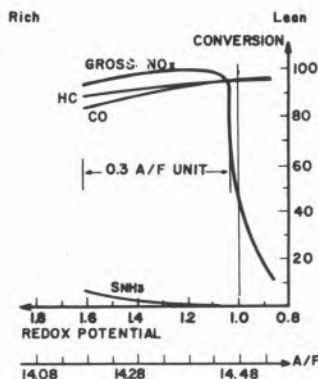


Fig. 28. A

3-way catalyst ; 550 °C ; 60.000 h⁻¹ . Effect of A/F on conversion. Fresh catalyst.

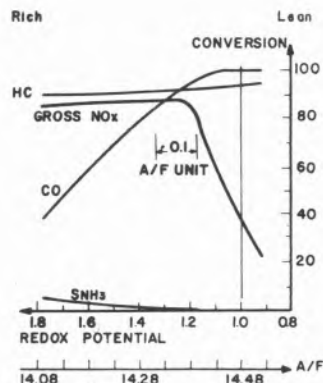


Fig. 28. B

3-way catalyst ; 550 °C ; 60.000 h⁻¹ . Effect of A/F on conversion. Aged catalyst (lead-free iso-octane, 40 000 km)

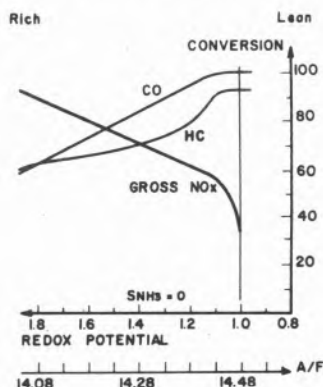


Fig. 28. C

3-way catalyst ; 550 °C ; 60.000 h⁻¹ . Effect of A/F on conversion. Aged catalyst (iso-octane with 7.93 g/m³ Pb, 0.56 g/m³ P, 0.02 wt % S)

performed over a 50,000 mile span at pollution levels lower than required by federal regulations. This catalyst is reputedly made of Pt and Rh to achieve both oxidation and reduction. But it seems that a key question was whether this three-way converter could be adapted to cars with the carburetors found in most American models.

Of course, as far as lead contamination is concerned, another way to reduce aging consists in reducing the lead percentage in gasoline. The problem of a balance between the two solutions is both quite simple and quite complex. It is quite simple in its principle, for we just have to calculate, or estimate, the right economic balance between the cost attributed to aging problems in the presence of lead, and the cost for obtaining high-quality lead-free gasoline. To solve this problem of optimization, we must of course take into account the known fact that the «first» percentages of lead addition (leading thus to slight aging) lead to a greater improvement in antiknock properties, than the ultimate percentages. In a symmetrical way, the «first» improvement, by increasing the proportion of light isoparaffins and of aromatics, in a lead-free gasoline, is less costly than the ultimate one. On the other hand the real problem is quite complex for the following reasons :

- It is difficult to estimate the exact resistance to aging in the presence of lead for each catalyst.
- The production of high antiknock gasoline, in the absence of lead, would lead to a small revolution in the refinery scheme. Moreover, such gasoline could cause health problems due to the high percentage of aromatics.
- All this helps to feed the understandable opposition of the lead industry to lead elimination.

In conclusion, the complex, but not unsolvable, problem of the catalytic control of automobile emissions is governed by the balance between several variable factors. Of course the optimization criterion is the economics of the whole system. At the same time, the price of health must be taken into consideration, but this would make up the subject for another talk. At any rate, through the Minotaur's labyrinth of catalytic emission-control, Catalytic Engineering appears as Ariadne's thread which acts as the guide to attaining the most effective route. At the same time, it is nice to see that this extremely applied type of research makes extensive use of all fundamental knowledge acquired in the field of catalysis.

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DISCUSSION

R. DARRAS : It seems to me that the originality and difficulty of cleaning automotive exhaust gases by catalysis is that the catalyst must be efficient and resistant in a large range of temperatures, corresponding to the various working conditions of the motor. Could you indicate some ways of ideas to choose or to find a catalyst filling this unusual condition ?

R. MONTARNAL : The problem of good performances at low temperatures, concerns mainly the oxidation activity, which is specifically needed early in a driving cycle beginning by a cold start, because the reducing atmosphere caused by functioning of the choke, creates large amounts of CO and HC initially. It can be solved by using precious metals, which generally are quite active at low temperature. For an simple oxidation converter, or for a three-way catalyst converter, Pt and Pd can be used, as being highly active species. For a dual converter, the reducing converter is used as oxidation reactor during cold starting. It seems however better to use Rh or Ir in this reactor instead of Pt or Pd, to be able to promote the selective reduction of NO into N₂, during reductive utilisation. But then, during oxidative period, the activity with Rh or Ir is lower than it would be with Pt or Pd.

The problem of high temperatures concerns specifically the resistance to aging and more peculiarly to sintering. For deposited

catalysts, it needs to dispose of thermally resistant carriers. Such carriers exist to day for temperatures as high as 1000°C (alumina carriers for example). Moreover, one must avoid sintering of the deposited species, or avoid their elimination as volatile compounds. The optimal catalytic formulas can then be more difficult to define due to the complex influence of the reactional atmosphere (oxygen, halogens, sulfides or sulfur oxides ...).

D. TRIMM : Can you precise the best means to realize the NO reduction in presence of a great excess of oxygen ?

R. MONTARNAL : In the case of spark ignition engines, excess of oxygen in the exhaust gas can be avoided by operation in the air/fuel region rich of stoichiometry. The adverse effect of short time incursion in the region lean of stoichiometry can be compensated by the use of catalysts containing an «oxygen-storage» component.

For lean-burn gasoline engines or for Diesel engines both giving great excess of oxygen in the exhaust gases, NO reduction rate becomes very low due to the elimination of reducing reactants (H₂, CO, hydrocarbons) by reaction with oxygen.

NO decomposition to nitrogen and oxygen proceeds likewise at a rate several order of magnitude to low to be of practical interest.