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Review

Environmental catalysis

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Abstract

This review article was constructed around the first Algerian–French congress aimed on emerging materials which was held at Tamanrasset by the end of February 2003. The aim of this review is to point out that a lot of work has been done in heterogeneous catalysis to better understand the active sites responsible for the catalytic reactivity. Most of these researches were performed under reducible atmosphere, on metallic catalysts, to improve our knowledge about hydrocarbon reforming catalysts. Starting from this base which was recalled through various classes of important studies such as: (i) the dilution of the active sites, (ii) the use of bimetallics, (iii) the use of well-crystallised surfaces and (iv) the influence of the metal–support interactions; a development and an opening is made on the three-way catalysis and the DeNO$_x$ reactions. The objectives being to point out the very important influence of the experimental conditions and of the gas phase compositions which may induce very strong surface modifications of the initial metallic aggregates. Moreover, it will depend on the reactions, i.e. isomerisation, oxidation, reduction where the active site may also be composed of, in addition to the metallic crystallites, the participation of the oxygen of the support.

A tentative for a general interpretation of the observed results is given by the use of the variations of the local density of states and of the "d" band centre energy.

Keywords: Hydrocarbon reforming reactions; Skeletal rearrangement of alkanes; Particle size effects; Alloys and bimetallic effects; Support influence; Well-defined surfaces; Three-way catalysis; NO$_x$ reduction; DeNO$_x$ process

1. Introduction

Sometimes a title is so used, so omnipresent, that its meaning is very small; but its basic sense is so important that we must not pass it under silence and say nothing. To this "Environmental Catalysis" is linked the notion of sustainable development. From the book edited by Janssen and van Santen [1] there is a good definition of sustainable development "which is a process of change in which the exploitation of resources, the direction of investments, the orientation of technological development and institutional change are all in harmony and enhance both current and future potential to meet human needs and aspirations". In this definition we find words as future, employment and technical development. With respect to this last issue catalysis plays an innovative role in the development of new technologies to prevent and reduce all types of emissions.

Another aspect in the past few years is the huge increase in the interest in nanotechnology, a term that was virtually unheard of a decade ago. In fact, the length scale of importance in heterogeneous catalysis has been known by researchers to be nanometer or smaller for many years [2]. Catalysts represent the oldest commercial application of nanotechnology.

Finally in the development of catalyst-based technologies the catalysts were mostly optimised for activity all through the 20th century. Catalysis research in the 21st century should focus on achieving 100% selectivity for the desired product in all catalyst-based processes [3,4]. This way can achieve clean manufacturing without by-products. This eliminates the need for waste disposal, and provide environmental sound green catalysts-based chemical processes [4].

Moreover, we know how important is pollution linked to transportation, hence, from all the points raised above it seems necessary to make a review about what was done concerning catalysis and automotive pollution control and to point out the influence of the active sites which have nanometric scales.

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I shall not develop this manuscript around new materials but only about those already used for years with a new look on the results. The intention being to develop new ideas from former results.

This review article will be divided into three parts devoted, respectively, to hydrocarbon reforming reactions, three-way catalysis and $DeNO_x$ catalysis. These three topics were developed during the first Franco-Algerian meeting devoted to emerging materials which was held at Tamanrasset from 23 to 25 February 2003.

The quality of diesel or gasoline is the first step to take into account when you are concerned by automotive pollution control. Too often there is not a global approach between the quality of the mixture of petrol and the efficiency of the catalysts used for automotive gas emissions. This situation can be understood from an economical point of view as two different huge industries are concerned and their interests are opposed; but from a scientific point of view we have to fill this gap and to erect a bridge between these two industries.

2. Hydrocarbon reforming reactions

2.1. Introduction

Due to the gasoline engine process, to get the best yield, the chemical nature of the gasoline should have a low content of double bonds, either aromatics or olefins; be almost free of heteroatoms except for oxygen and have a narrow boiling point distribution. It has a low-volatility and a high octane number. Therefore highly branched paraffins with 8–10 carbon atoms would best fulfil all the requirements. Isooctane, which has an octane number equal to 100 by definition, is the reference structure and it can be assumed as a model; other molecules should come as close as possible [5]. In other words it means that we have to find catalysts able to give branched hydrocarbons. At the opposite, in the Section 4, devoted to $DeNO_x$ reactions, we shall discuss about the quality of the Diesel fuel and the meaning of the cetane number, where linear hydrocarbons are favoured.

It is not the purpose of this article to review all the mechanisms of reactions undergone by the carbon skeletons of aliphatic and alicyclic hydrocarbons in the presence of metallic catalysts but we want to stress the influence of the dispersion of metal particles in skeletal isomerisation reactions as well as cyclisation, ring opening and hydrogenolysis reactions.

From the pioneer works of the group of Gault and coworkers [6,7], it has been clearly pointed out that catalysis by oxide-supported metals may take place on the metal surfaces alone, and more open surface sites with lower packing density as stepped platinum surfaces have a greater reactivity in H–H, C–H and C–C bond breaking than low index crystal surfaces [8,9]. In parallel to these studies the influence of the particle size was pointed out since 1969. Boudart [10] defined two types of reactions: “structure-insensitive” or facile reactions and “structure-sensitive” or demanding reactions. A facile reaction may be defined as one for which the specific activity of the catalysts is practically independent of its preparation mode [11]. From these observations extensive studies on the influence of particle size in reactivity of alkanes have been undertaken for about half a century. Such an investigation is directly correlated to the concept of active centres which can be already found in Taylor’s 1925 paper in which he wrote: “there will be all extremes between the case in which all the atoms in the surface are active and that in which relatively few are so active” and “... the amount of surface which is catalytically active is determined by the reaction catalysed” [12].

All the experiments devoted to hydrocarbon reforming reactions are usually performed under reductive atmospheres where a mix of hydrogen and hydrocarbon passes through the catalyst bed. In general these experiments take place under stationary conditions in reactant compositions, temperature and gas flow velocity. The temperature range to perform such reactions is between 150 °C and up to 550 °C. Most of the studies which we are going to give the results of were made on metal-supported catalysts in which the metal (Pt, Pd or Ir) was deposited on a catalytically more or less inert carrier. Besides these model “industrial” catalysts, single crystals and stepped surfaces were also used to characterise the active sites.

2.2. Results and discussion about skeletal rearrangement of alkanes

Several questions at that stage have to be asked:

(a) Where does the catalytic reaction occur?
(b) What are the parameters which govern the catalytic reaction; are they electronic and/or geometric effects?
(c) Are catalytic properties governed by individual atoms or by ensemble atoms?
(d) Do catalytic reactions, in the adsorption step, follow a dissociative or an associative process?

We are going to answer these questions one after the other on the base of an ensemble of convergent experiments, as it is shown in Fig. 1. These experiments were conducted since 1965 up to 1980 to better understand the catalytic active sites.

2.2.1. Particle size effects [6,7]

Two basic mechanisms were proposed for the skeletal isomerisation of hydrocarbons on metals. The bond shift mechanism (Fig. 2a) explains the isomerisation of short molecules. When the carbon chain is long enough, another mechanism takes place, which involves dehydrocyclisation to an adsorbed cyclopentane intermediate followed by ring cleavage and desorption of the products (Fig. 2b). On most platinum catalysts, either films or supported platinum with moderate degree of dispersion, both

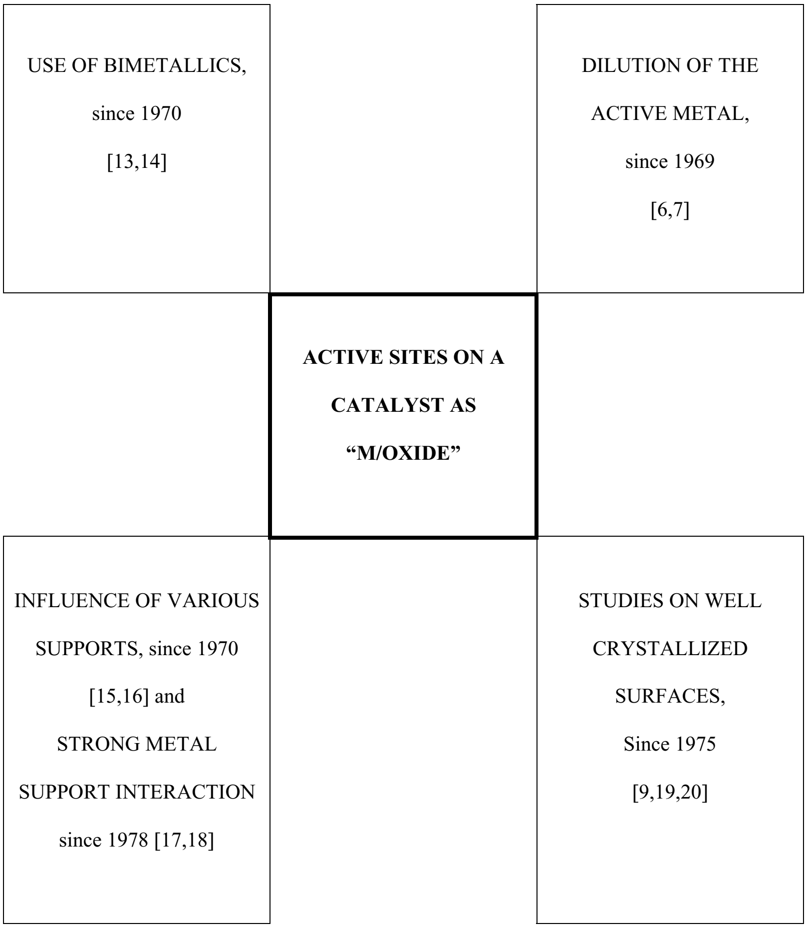


Fig. 1. Convergent studies to approach a better understanding of the active sites.

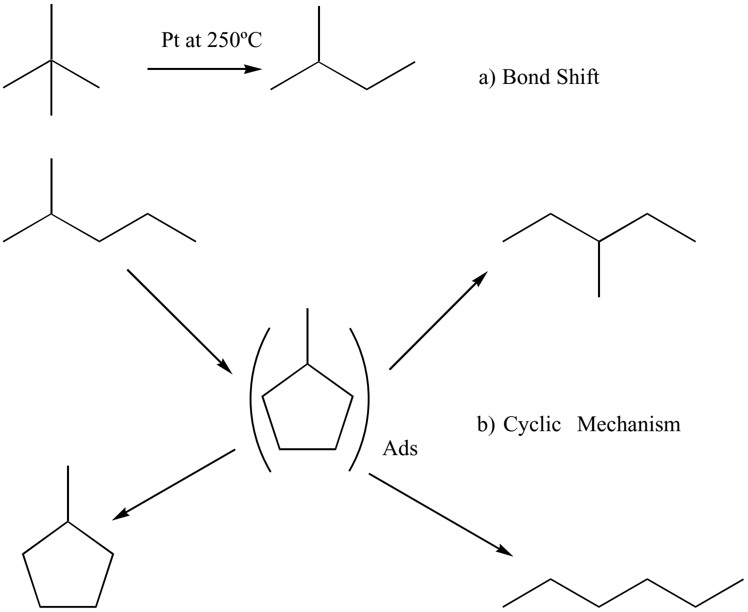


Fig. 2. (a) Bond shift (BS) and (b) cyclic mechanism (CM) for skeletal isomerisation of alkanes.

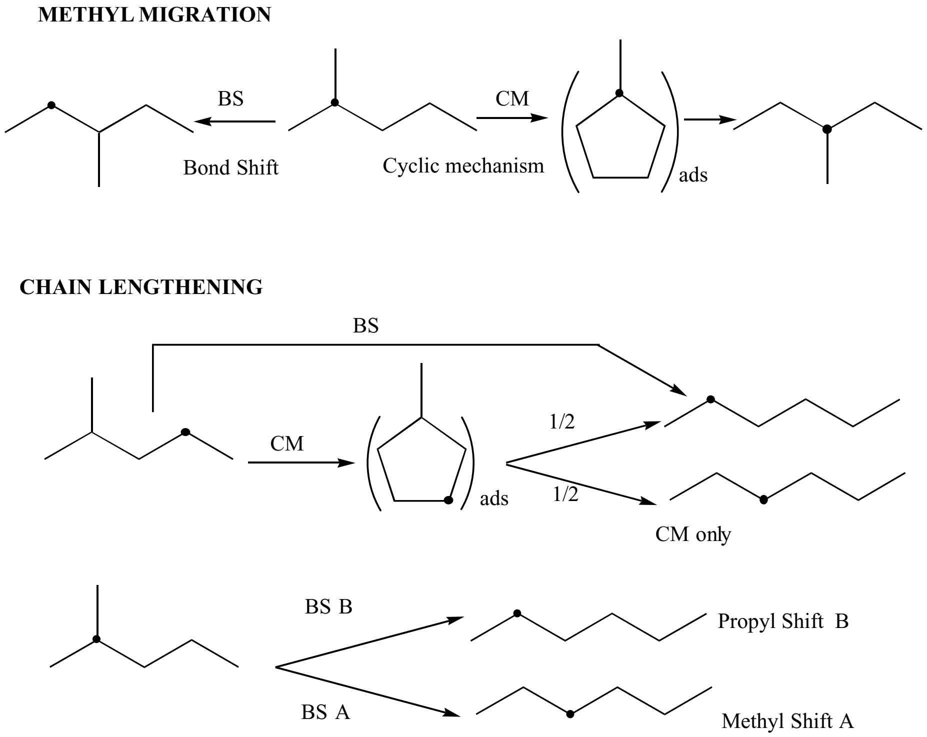


Fig. 3. Bond shift and cyclic mechanism for the isomerisation of 2-methylpentane to 3-methylpentane and *n*-hexane. Use of ^{13}C labelled hydrocarbons.

the cyclic and the bond shift mechanisms take place. The first problem which arises, then, is that of determining, in each case, the contribution of each mechanism. This problem may easily be solved by using tracer techniques [7]. Fig. 3 shows how the use of 2-^{13}C-2-methylpentane allows a distinction to be made between the cyclic and the bond shift mechanism in the case of the isomerisation of 2-methylpentane to 3-methylpentane. Similarly, 2-^{13}C and 4-^{13}C-2-methylpentanes yield *n*-hexanes labelled on different positions according to whether the chain lengthening occurs by cyclic or bond shift mechanism.

The description of the isomerisation mechanisms as being of bond shift or cyclic mechanism is very rough; structural effects, especially those resulting from substitution of hydrogen atoms in the reacting molecules, have also been considered. Such effects are very pronounced in the case of methylcyclopentane hydrogenolysis, one of the steps involved in the cyclic mechanism. Such a reaction takes place according to two different mechanisms, one selective and the other non-selective. For the former reaction only di-secondary $-CH_2-CH_2-$ bonds are broken on catalyst of low dispersion (10% Pt/alumina); at the opposite, for the latter reaction, an almost equal chance of rupturing any $-CHR-CHR'-$ bond of the ring takes place on highly dispersed catalysts such as 0.2 wt.% Pt/alumina; but breaking of cyclic C–C bonds containing a quaternary carbon atom never occurs [21].

Now we are going to correlate these reaction mechanisms with the size of the metal particles and more generally with the structure of the metal surface. One could expect that selective hydrogenolysis, favoured on large metal particles, requires a larger number of metal atoms than non-selective hydrogenolysis, which takes place on extremely dispersed catalysts. Similarly, isomerisation of 2-methylpentane to 3-methylpentane takes place predominantly according to a bond shift mechanism on catalysts of low dispersion and according to a cyclic mechanism on catalysts with very small metal particles; this again could imply a larger number of metal sites for the former than for the latter reaction [21–24]. It was shown [25] that the percentage of cyclic mechanism in the isomerisation of 2-methylpentane to 3-methylpentane as a function of metal dispersion remains roughly constant (ca. 20%) over a large dispersion range (0–50%) and increases above 50% dispersion. Careful determination by electron spectroscopy and SAXS of metal particle size distributions shows that there are no crystallites smaller than 1 nm in the catalysts of low dispersion while they are present in increasing amounts with increasing dispersion in those catalysts for which an enhancement of the cyclic mechanism is observed. From these results, it was suggested that both types of isomerisation sites include edge atoms; and an upper limit of metal particle size around 2.5 nm was defined below which selective hydrogenolysis is no longer possible.

These experiments were able to show the particle size effects in isomerisation and hydrogenolysis reactions. Other approaches were also undertaken to better understand the “nature” of the active sites.

2.2.2. Alloys and bimetallics influence [13,14]

By the use of alloys the debate about the electronic and geometric effects was at its maximum and very good articles written by Ponec [14,26] clarified this point. Alloying of metals may result in important changes in their activity and selectivity in catalytic reactions. These changes are experimentally well established but theoretically still difficult to understand as a lot of parameters have to be taken into account; among them, there are surface segregation and the thermodynamic of its formation.

When a metal which is active in a certain reaction is alloyed with an inactive one, two effects can be conceived [27]:

(a) *A "geometric" or "ensemble size" effect*. By alloying, the number of contiguous identical atoms is clearly decreased. Catalytic reactions which require large ensembles of active atoms will then obviously be suppressed more strongly than reactions which require only small ensembles.
(b) *An "electronic" or ligand effect*. The electronic structure of the metals may be changed by alloying. If so, then the bond strength of the adsorbed species and thereby their reactivity may change as well.

In spite of the difficulties to understand the "real" behaviour of such systems, these studies always bring a huge amount of results which improve the knowledge of the global catalytic reactions. In fact, a large amount of alloys or bimetallics was studied since the first one prepared by Kluksdahl; it was a Pt–Re catalyst [28].

2.2.3. Support influence [17,18]

The other approach to the understanding of active sites concerned the influence of the support on the intrinsic properties of the supported metals. The phenomenon of "strong metal–support interaction" (SMSI) has attracted interest and has principally been interpreted since 1984 on the basis of decoration of the metal surface, partially or largely, by the support [18]. When a SMSI effect takes place it was originally reported that the hydrogen uptake on platinum could be restored after oxidation at 673 K [17]. Subsequent studies have found that the adsorptive properties of the metal could be partially restored even by oxygen exposure at room temperature [29] or by exposure to steam at 525 K [30]. Since the activity in hydrogenolysis reactions is affected strongly by the onset of SMSI, reactivity is a better probe than chemisorption for monitoring the reversal of SMSI.

After, around 1990, this simple view has been questioned and the role of electron transfer between support and metal, originally proposed by Schwab and Pietsch [31] and Solymosi [32] has been revived.

Studies of Clarke et al. [33] have shown that high temperature reduced (HTR) Pt/TiO_2 catalysts exhibit SMSI as inferred from negligible hydrogen chemisorption take-up and moderate activity for skeletal reactions of alkanes. The interest in titania supports is heightened by their unique ability to enhance the reactivity of metal in hydrogenation of CO [34] or molecules that have CO functional groups [35], while suppressing hydrogenolysis of hydrocarbons such as ethane [36] or *n*-butane [37]. The SMSI effect appears to be prevalent on both small and large metal particles.

At that point we may underline that such SMSI may take place in automotive exhaust catalysts as they are forced to high temperatures and changes in gas compositions from reductive to oxidant as we shall see in the next section.

There is only one step jumping and to enter in the area of active supports as solid acid supports and substitutes of platinoids and their (induced) influence on the supported metals. On one hand, bifunctional catalysis operates either following the "classical" mechanism proposed by Mills et al. [38] which comprises dehydrogenation of alkanes on the metal surfaces, isomerisation of the protonated alkenes on the acid sites, and hydrogenation of the isomerised alkenes on the metal surfaces, or the presence of a metal–proton adduct $[H\text{–}(M_m)(H^+)_x]^{x+}$ site which combines metallic and acid sites and consequently the migration step occurring in the former mechanism between the two sites, metallic and acid, is suppressed [39,40]. And, with the solid acid support participation, it is generally agreed that acid-catalysed hydrocarbon conversion reactions proceed by way of highly reactive, positively charged intermediates, that are referred to carbocations.

On the other hand, the generation of new acid sites on mixed oxides was first proposed by Thomas [41], further developed by Tanabe and Takeshita [42] and by Connel and Dumesic [43]. The latter have studied the generation of new acid sites on a silica surface by addition of several kinds of dopant cations. There seems to be a common idea in these works that the generation of new acids sites is ascribed to the charge imbalance at locally formed M(1)–O–M(2) bondings, where M(1) is the host metal ions and M(2) the doped and/or mixed metal ions. The charge imbalance might be expected even on single-component metal oxides consisting of small particles, since the electronic properties of small-sized metal or oxide particles are widely accepted to be somewhat different from those of the bulk materials [44]. These differences are attributed to the surface imperfections, which can be metal or oxygen vacancies, causing the local charge imbalance. From the work done by Nishiwaki et al. [45] on TiO_2 catalysts with various particle sizes from around 5 to 25 nm; they noticed that the highest acid strength increases with a decrease in the particle size, indicating the generation of new and strong acid sites on small-sized TiO_2 particles. This is likely to be due in this case to the presence of many oxygen vacancies existing on the surface of small-sized TiO_2 particles. The oxygen vacancies generate considerable numbers of dangling bonds, whose energy levels are located in the band gap region between the valence and the conduction bands. Electrons trapped in these levels may cause the local charge imbalances and hence the generation of new and strong acid sites over the surface of finely divided TiO_2 particles.

Finally, a way to understand the active sites is to find compounds able to mimic them. Platinum-like behaviour of tungsten carbide was first pointed out by Muller and Gault [15] and Levy and Boudart [16]. For example, a study of the reaction of 1,1,3-trimethylpentane, in the presence of metal films (Fe, Co, Ni, W, Rh, Pt and Pd) showed that only platinum rearranged the reactant to appreciable amounts of xylene [15]. However, on tungsten, after an induction period, gem-dimethylcyclopentane, benzene, toluene and xylenes were formed. If originally, on "fresh" tungsten and tungsten carbides, with hydrocarbons, a very fast extensive hydrogenolysis to methane mostly occurs [46,47], on such compounds, in the presence of oxygen, this extensive hydrogenolysis is inhibited in favour of skeletal rearrangement reactions which seem to take place following a bifunctional mechanism. It was suggested that the presence of carbon in tungsten carbides modifies the electronic surface properties of tungsten in such a way that they resemble those of platinum. X-ray photo-electron spectra of tungsten, tungsten carbide (WC) and platinum, presented by Colton et al. [48] confirmed this idea.

2.2.4. *Use of well-defined surfaces [9,19,20]*

The fourth approach to study active sites is to investigate the atomic scale of hydrocarbon catalysis over single crystal surfaces. Prior to that, traditional approaches focus on reaction kinetics of practical catalysts consisting of very small, between 1 and 10 nm, metal crystallites dispersed on various supports. But little is known about the working structure and the chemical state of the active catalyst surface. Important break through has been done by the groups of Berkeley [49,50], Strasbourg [9,51] and Berlin [52]. The decisive role of surface irregularities (steps and kinks) in breaking strong C–O, N–O, C–H, C–C and other bonds was elucidated in these works on stepped surfaces.

In the case of the isomerisation of 2-methylpentane to 3-methylpentane and *n*-hexane, we noticed [9] a complete change in reaction mechanisms from "normal" crystallites, larger than 2 nm, to extremely small metal particles; and this result was confirmed by experiments performed on single crystals exposing various stepped surfaces as the $[6(1\,1\,1) \times (1\,0\,0)]$ and the $[5(1\,0\,0) \times (1\,1\,1)]$ according to Somorjai and coworkers nomenclature [50]. These surfaces, especially that with (1 1 1) terraces and (1 0 0) steps, simulate extremely well supported Pt/Al_2O_3 catalysts of low dispersion.

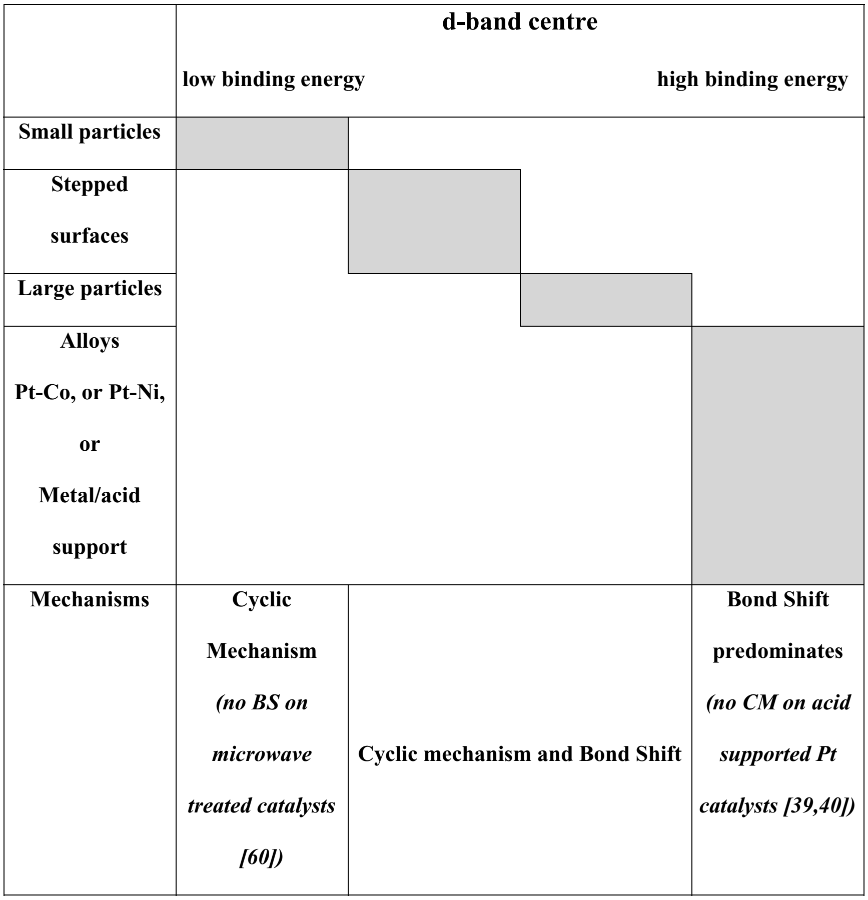


Fig. 4. Correlation made between the d-band centre variation and the alkane isomerisation reactions. NB: no bond shift reaction was observed on microwave treated catalysts [60].

Furthermore, work with stepped platinum surfaces has clearly shown that a stepped surface with either (1 1 1) or (1 0 0) terraces has an enhanced activity for both bond shift and cyclic mechanism compared with a planar (1 1 1) surface. Moreover, it was shown by LEED [53] that hydrogen induces step coalescence and terrace broadening on a stepped surface of platinum $[m(1\,1\,1) \times (1\,0\,0)]$ in the temperature range 470–770 K and the final orientation was, for $m = 6$, the structure $[11(1\,1\,1) \times (3\,1\,1)]$. Thus, under reaction conditions, the nature of the initial crystallographic orientation may have changed, and according to van Hardeveld and Hartog such (3 1 1) orientation corresponds to the B5 sites [54]. Such a site can be associated to the bond shift mechanism.

If we have to make an intermediate conclusion we should raise the relation which exists between the electronic structure of the platinum (metallic) aggregates and their selectivity. In fact, when a reactant is adsorbed on surface atoms there is an electron donation from the reactant to the surface atoms and a back donation from the surface atoms to the reactant [55,56]. At this level of discussion we can sum up our observations as: (i) noticeable isomerisation requires a high density of low-coordination sites, (ii) the cyclic mechanism percentage (CM) increases at the expense of the bond shift mechanism when the surface atom coordination decreases, so that CM becomes dominant only on highly dispersed Pt particles, which cannot be mimicked by stepped surfaces. Now, that the importance of low-coordination sites has been stressed, we can discuss this point in terms of the local electronic changes which take place correlatively at these sites. It has long been known that the valence band width increases with roughly the square root of the coordination number [57] so that the local density of states distribution should be reduced for the sites responsible for the cyclic mechanism. Moreover, for more than half filled d-band metals such as Pt, the d-band centre moves up to lower binding energies as the coordination decreases [58].

A change in the electronic structure of the platinum surface through oxidation provides the best explanation for the oxygen effects observed. It is likely that pre-oxidation renders the platinum surface, especially kink sites, electron deficient and more like iridium or osmium [49]. Moreover, metallic oxides are frequently employed as promoters in the preparation of practical catalysts, as we shall see in the next sections, and changes in the metal work function is often observed for these supported metals. For example potassium is electron donor and will promote Fischer–Tropsch catalysts and can enhance the aromatisation activity of *n*-hexane but the condition is that the additive free catalysts is monofunctional [59].

Coming back to our objective, to get high octane or cetane numbers, the unique parameter, in fine (in heterogeneous catalysis), is the local electronic structure of the surface sites accessible to the molecule during the reaction. And in Fig. 4 are summarised the various points discussed above.

With all these several points in mind we can now tackle the other two aspects concerning the “three-way catalysts” and the “DeNO$_x$” catalysts.

3. Three-way catalysis

3.1. Introduction

Why do we need catalysts in automotive emission control?

In addition to the primary products carbon dioxide and water, combustion of fossil fuels such as gas, oil or coal with the air produces pollutants such as carbon monoxide (CO), hydrocarbons (HC), nitrous oxides (NO$_x$), sulphur dioxide (SO$_2$) and, in diesel engines, fine particles of solid material (diesel soot) which contaminate the atmosphere if they are not eliminated.

The automobile is not the only machine which uses the combustion process to obtain energy. It is also used in many industrial branches. The consumption of gasoline and diesel fuel has remained roughly the same since 1960 amounting to approximately 25% of the worldwide crude oil consumption. It is therefore no wonder that scientists and engineers started considering how to limit the emission of pollutants from motor vehicles over 20 years ago. The first legal regulations were passed in the seventies in the USA and Japan; then other industrialised countries followed. When considering in 1997 the 500 million motor vehicles around the world, and the fact that the worldwide consumption of crude oil has nearly tripled since 1960, it is of vital importance to reduce the emissions from automobile engines [61].

Here start the difficulties. The catalysts used for such reactions: oxidation of CO and of HC and reduction of NO$_x$ (three reactions to perform; hence they are named as “three-way catalysts”) will never operate under steady state conditions. Catalyst temperature will increase rapidly after engine starting, and the exhaust flow rate and composition will fluctuate rapidly under all modes of operation. Numerous studies have shown that the performance of catalysts under dynamic conditions differs greatly from their performance under steady state conditions. Thus it is mandatory to evaluate and compare the performance of three-way catalysts on the basis of tests that involve dynamic conditions [62].

The variation in engine exhaust emissions is shown in Fig. 5 where pollutant concentration is plotted against equivalence ratio (λ); this being the ratio between the air:fuel at a particular point and at stoichiometry [63].

The actual air to fuel ratio (A/F) at stoichiometry is dependent on fuel composition but is generally considered to be around 14.6, where the value of $\lambda = 1$. If the engine is tuned rich of stoichiometry, hydrocarbon and carbon monoxide emissions are high, nitrogen oxide emissions are low and the oxygen content of the exhaust is minimal. As the engine tune is moved towards stoichiometry, hydrocarbon and car-

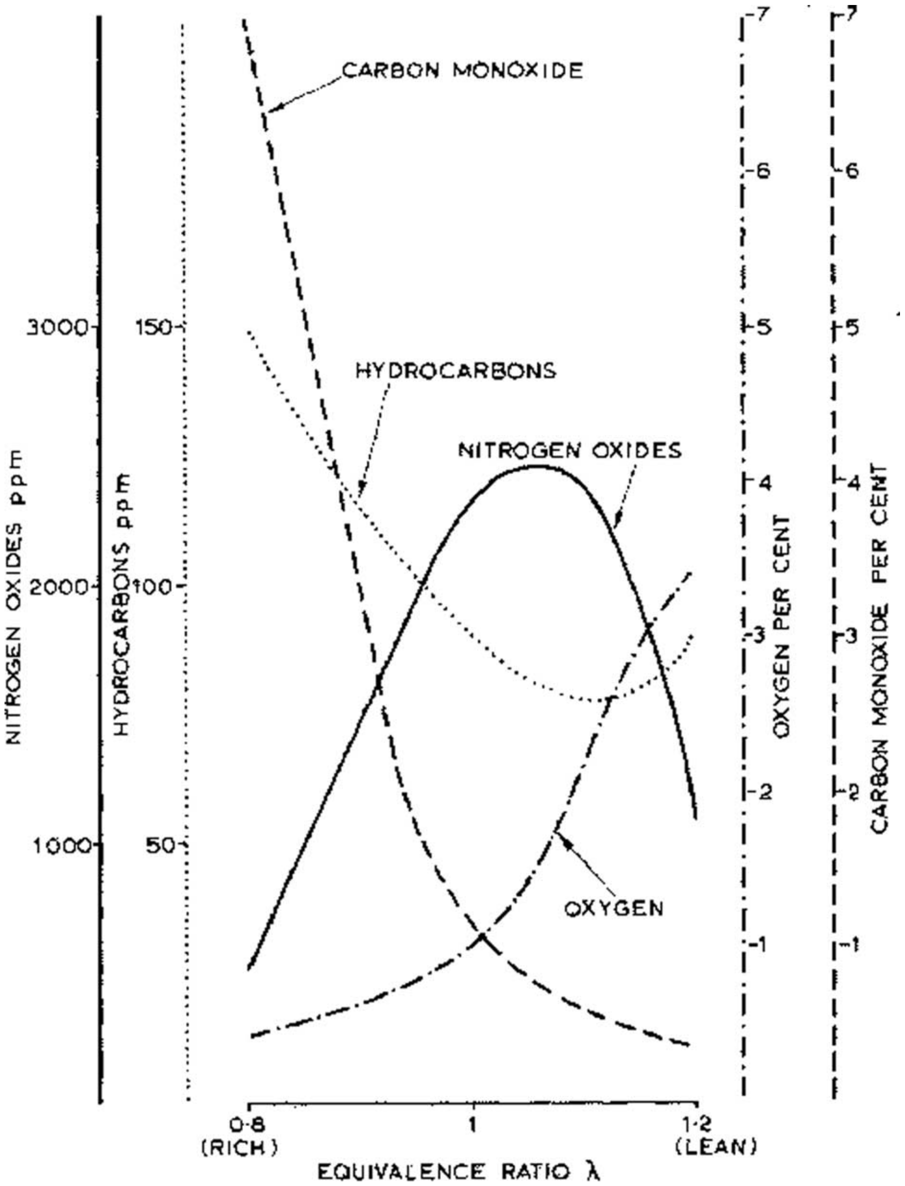


Fig. 5. Exhaust emissions vary according to engine tune, that is air to fuel ratio (A/F) or equivalence ratio (λ). If the engine is tuned rich of stoichiometry ($\lambda < 1$), hydrocarbon and carbon monoxide emissions are high and nitrogen oxide emissions are low. As the tune is moved towards stoichiometry, hydrocarbon and carbon monoxide emissions fall but nitrogen oxide emissions rise to a maximum just lean of stoichiometry [63].

bon monoxide emissions fall but nitrogen oxide emissions rise to a maximum just lean of stoichiometry.

3.2. Results and discussion

The objective of these catalysts is to remove simultaneously hydrocarbons, carbon monoxide and nitrogen oxides. The noble metal most closely associated with the catalytic reduction of NO_x in exhaust is rhodium on which NO is dissociatively adsorbed [64]. Rhodium has high activity for selectively reducing NO_x to nitrogen with low ammonia formation. And it makes a significant contribution to CO oxidation [65]. While platinum and palladium also catalyse simultaneously CO and hydrocarbon oxidation; CO is associatively adsorbed on Pt and Pd as noticed by Broden et al. [64].

In addition to the noble metals, autocatalysts contain several base metal additives which contribute significantly to catalyst performance and durability. Ceria has been shown to have multiple functions [66]: one is its ability to store oxygen, presumably by oxidation of ceria, derived from NO_x decomposition during fuel lean air/fuel ratios (net oxidising) excursions and thereby enhance NO_x conversion to N_2. Stored oxygen is then available for reaction with CO and hydrocarbons during subsequent fuel-rich air/fuel ratio excursions. Ceria has been shown to enhance the decomposition of NO by extending the time before the noble metal catalyst is deactivated by the accumulation of surface oxygen derived from NO decomposition [67]. That is, Rh/CeO_2 is deactivated more slowly than Rh/Al_2O_3 during NO decomposition, probably due to oxygen spillover from the noble metal to the reduced ceria.

Ceria favourably alters the reaction kinetics of CO oxidation and NO_x reduction over ceria containing rhodium catalyst [67]. Ceria addition to an alumina-supported rhodium catalyst was shown to enhance NO reduction activity at low temperature by decreasing the apparent activation energy for the reaction of CO with NO and by shifting to positive-order the dependence of the rate on NO partial pressure [68]. Enhancement of catalyst performance at low temperature is needed in order to decrease the emissions immediately following start-up of the vehicle. Moreover, in absence of water, an increase in ceria loading has no effect upon CO conversion, but when water is present a dramatic effect is observed, with increasing ceria loading causing an increase in conversion. This leads to the conclusion that ceria is promoting the water-gas shift reaction [66]: $CO + H_2O \rightarrow CO_2 + H_2$.

A comparative study by Oh et al. [69] of the kinetics of the NO–CO reaction over single-crystal Rh(1 1 1) and Rh(1 0 0) and alumina-supported rhodium catalysts revealed different kinetic behaviours. The Rh single crystals exhibited lower apparent activation energies and higher specific rates than those over the supported Rh/Al_2O_3 catalyst.

In addition to the special "touch" to prepare these catalysts the following transient chemical processes can affect the dynamic behaviour of these catalysts [70]:

1. Changes in the activity of a catalyst: (i) through changes in poisoning and (ii) through changes in oxidation states of the active metals.
2. Changes in the accumulation of reactive species on a catalyst which can affect dynamic behaviour: (i) through reaction of accumulated species and (ii) through inhibition of catalytic reactions by reactive species adsorbed on the active metals. At that point the memory effects induced by transient processes will concern CO disproportionation, oxygen storage and water-gas shift reaction.

All these reactions are controlled by the presence of the active sites which are composed of a mix between the metal and the oxides and the relative rates to pass from the reduced to the oxidised state and vice versa. Moreover, if a bimetallic Pt–Rh is formed, a rhodium surface enrichment occurs. The role of platinum is also important because of its contribution to the redox process. The reduced platinum assists probably the activation of oxygen upon rhodium during the lean transition and then provides active sites available for the CO adsorption during the rich transition [71,72].

In situ study of three-way catalysts using the X-ray absorption spectroscopy (XAS) technique was undertaken in which the ejected photo-electron acts as a probe of the surrounding environment in a manner similar to electron scattering. Since the absorption edges of the different elements are well separated in energy, which is the case for the Pt L_{III} edge, 11 564 eV, and the Rh K edge, 23 220 eV, the technique is element specific and able to examine the surroundings of Rh or Pt in the presence of the support [73,74]. With these $Pt–Rh/CeO_2/Al_2O_3$ catalysts an important alloyed phase is observed between Pt and Rh when these catalysts are aged, next to monometallic Pt and Rh, which are also present but in lower contribution. It means that the activity of these systems is mainly due to the alloyed phase. Furthermore, the mean sizes of the particles are around 3 nm from EXAFS experiments and 8 nm from TEM measurements. This discrepancy shows that EXAFS is specific of the elements but not of the present phases and TEM gives the particle size distributions; both techniques give an idea about the real situation.

Referring to the work of van Zon et al. [75] about the estimation of the metallic particle sizes obtained by EXAFS it was observed that for two catalysts 1% Rh/Al_2O_3 and 1% $Rh/CeO_2/Al_2O_3$, the mean metallic particle sizes were around 1 and 0.6 nm, respectively, showing the dispersion effect of ceria as expected and described in the literature [76].

To study such complicated systems we need in situ EXAFS experiments which can be used to characterise: (i) the change of the cerium oxidation state during fast redox processes for wash coated ceria plus alumina associated with platinum and rhodium catalysts. XANES spectra on the Ce L_{III} edge can record, in a fast acquisition mode, the kinetics of the reduction and oxidation processes on the time scale of a few seconds [77], (ii) the change of the rhodium surrounding environment during and after excursions in rich or lean atmospheres, and (iii) the three-way catalysts under oscillating gas mixtures by following both the catalytic activity and the changes of the EXAFS data.

The three-way catalysts effectively reduce nitrogen oxides and simultaneously oxidise carbon monoxide and hydrocarbons for stoichiometric emissions. However, the relatively better fuel economy of lean burn gasoline engines and diesel engines call for methods to reduce NO_x in lean exhausts. This point will be discussed now.

4. NO_x reduction: $DeNO_x$ processes

4.1. Introduction

All the situations above were related to gasoline fuel characterised by a high octane number which is correlated to the relative importance of branched hydrocarbons. Now we are going to examine the emission from: (i) the same fuel as used previously, but working under lean conditions and (ii) the diesel fuel defined versus the cetane number which is related to the relative amount of linear hydrocarbons.

We are now faced to eliminate four pollutants: CO, HC, NO_x and particulates. We shall mainly focus here on the NO_x reduction to nitrogen molecule.

NO is the simplest thermally stable odd-electron molecule known and is the major component of NO_x in the exhaust gases [78], and it is well known that NO is thermodynamically unstable relative to N_2 and O_2 at temperatures below 1200 K, and its catalytic decomposition is the simplest and most desirable method for its removal [79]. To date, however, no suitable catalyst with sustainable high activity has been found. This is due to the fact that oxygen contained in the feed or produced in the decomposition of NO, competes with NO for adsorption sites. As a result, high reaction temperature and/or gaseous reductant is required to remove surface oxygen and regenerate catalytic activity. Several solutions to this problem have been suggested, but currently two major approaches have reached the production stage. One is the selective catalytic reduction, where ammonia or hydrocarbons are added to the exhaust to selectively reduce NO_x. Another approach is the NO_x storage concept, which was introduced by Toyota [80]. The principal idea here is to add a NO_x storage component, usually an alkali earth oxide, to the catalyst in order to store NO_x under lean conditions [80–83]. To regenerate the catalyst and reduce the stored NO_x, the engine is tuned to stoichiometric or rich conditions for short periods. We are confronted with two situations either the catalysts used will stay under oxidative atmosphere or the gas composition above it will oscillate, for a short period of time, about 1 s, under reductive atmosphere.

We shall only analyse the case where the catalysts are always under lean conditions and where the selective catalytic reduction (SCR) is performed with alkanes and/or alkenes (HC-SCR). The standard gas composition is about: $O_2 \sim 4–5\%$, NO ∼ 700 ppm (0.07%) and HC ∼ 1000 ppm (0.1%), the complement is helium up to atmospheric pressure.

In order to study the NO_x reduction mechanisms with hydrocarbons, labelled compounds were also used as: ^{15}NO and $^{18}O_2$.

4.2. Results and discussion

First of all an in situ EXAFS study has been done on a pre-reduced and pre-oxidised 1% Pt/γ-Al_2O_3 catalysts in order to determine the effect of NO (in that case around 1% of NO in nitrogen) versus temperature at atmospheric pressure on the platinum particles. Changes were observed in the crystallite morphologies from 200 °C, due to sintering processes on the pre-reduced catalyst [84]. On the pre-oxidised one the phenomenon was much less pronounced. Even if particle coarsening is expected when alumina-supported platinum catalyst is submitted to an oxidative atmosphere, like oxygen, it appears that the phenomenon is more pronounced under NO. Indeed, Lööf et al. [85] have observed a similar effect on the same kind of catalysts. Moreover, it was noticed that the rate of sintering is dramatically enhanced under NO, compared to oxygen [86]. The sintering could occur through the formation of platinum–NO complexes, enriched with oxygen or not.

As we always have to keep in mind the effect of oxidation–reduction cycling or only oxidation on the particle size distributions these results are important. The growth of crystallites is caused by migration of individual atoms or molecules on a substrate; this is called Ostwald ripening [87,88]. As oxides have a lower melting point and a lower sublimation energy than metals, therefore these compounds are more likely to sinter via the mechanism of atom migration than the metals. Oxidising atmosphere is more conducive to sintering than inert or reducing atmosphere [88]. In any case the key point is the ability for each metal to retain the high activity thanks to the presence of low-coordination sites.

Furthermore, when performing experiments, with labelled compounds $^{18}O_2$ and ^{15}NO with propene as reductant, in the temperature range 150–250 °C we noticed, from Arrhenius plots determined from initial rates, the presence of two temperature domains 150–200 and 200–250 °C [89,90]. At low temperature range, propene and ^{15}NO disappearance reactions have the same apparent activation energy value while at high temperature range, propane and $^{18}O_2$ consumption reactions have similar activation energy value. Such a behaviour is in accordance with the fact that, at low temperature, the sticking coefficient of NO (σ_{NO}) is higher than the oxygen one (σ_{O_2}) [91,92], and when the temperature increases, σ_{NO} decreases and σ_{O_2} increases which leads, in fine, to a complete oxidation of the propane with $^{18}O_2$. Moreover, it was noticed that initially an exchange reaction took place in the adsorbed phase between $^{15}N^{16}O$ and $^{18}O_2$ giving $^{15}N^{18}O$. This result points out that an intermediate species such as $[^{15}N^{16}O^{18}O]$ does participate to the reaction [89,90].

From these results two different mechanisms were suggested for the reduction of NO by propene on alumina-supported 0.2 wt.% Pt.

(a) At low temperature we suggest the following steps:
  - The olefin, electron donor, is adsorbed on the terrace atoms acting as electron acceptor.
  - NO is adsorbed on the edge, corner or kink atoms, and accept electrons from them by back donation.
  - NO acts as a nucleophilic reactant which attacks the olefin, electrophilic centre.
  - A nitroso compound is formed which is tautomerised into an oxime; then dimerisation of the oxime occurs and oxidative degradation gives nitrogen molecules.

(b) At high temperature, the first step is a partial oxidation of the olefin to a ketone adsorbed as NO, on terrace atoms acting as electron withdrawing ensemble. An enolic form takes place which attacks NO, electrophilic reactant in that case. After the reaction pathway is the same as above: a nitroso compound is formed which is tautomerised into an oxime; then dimerisation of the oxime occurs and oxidative degradation gives nitrogen molecules (Fig. 6).

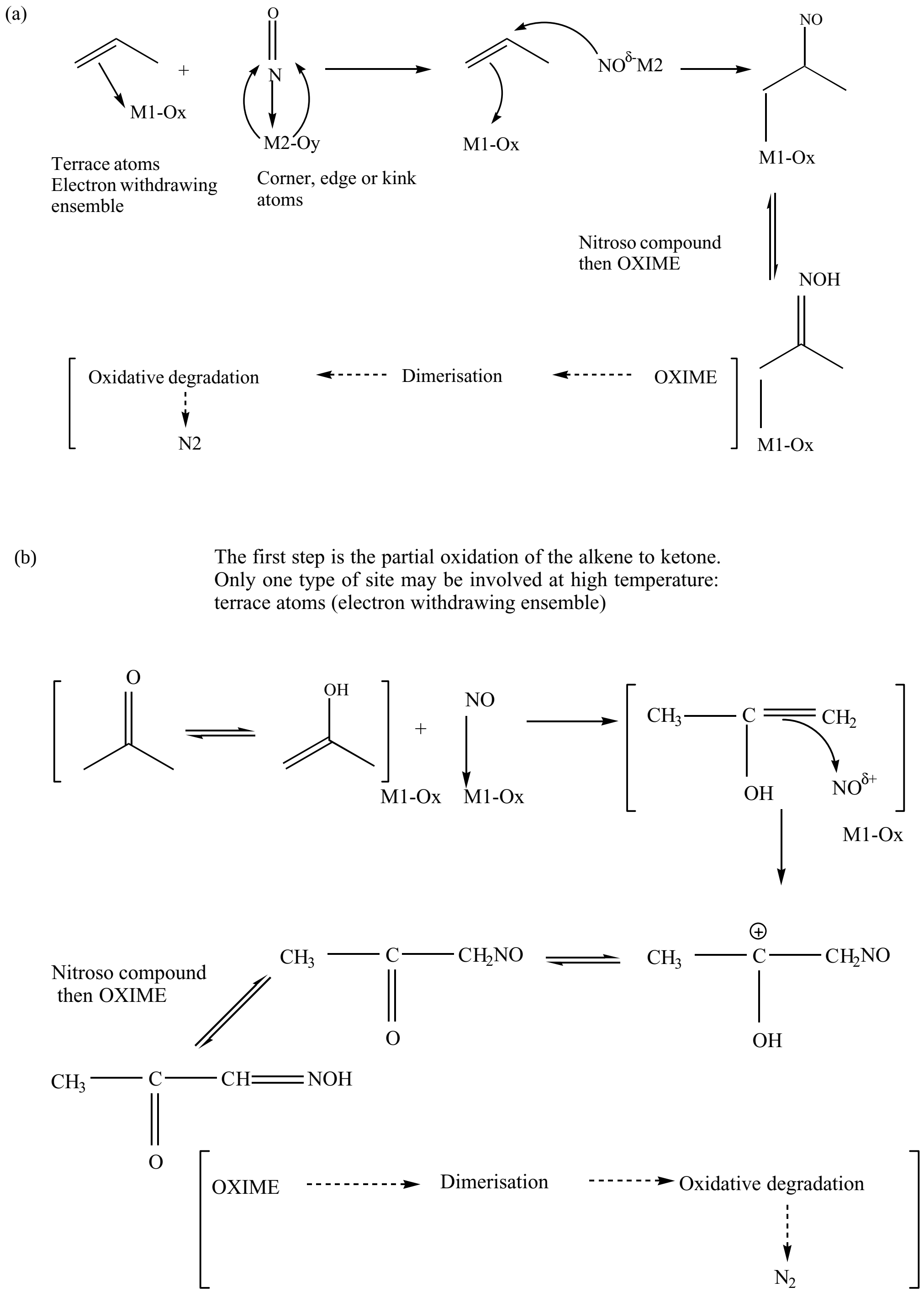
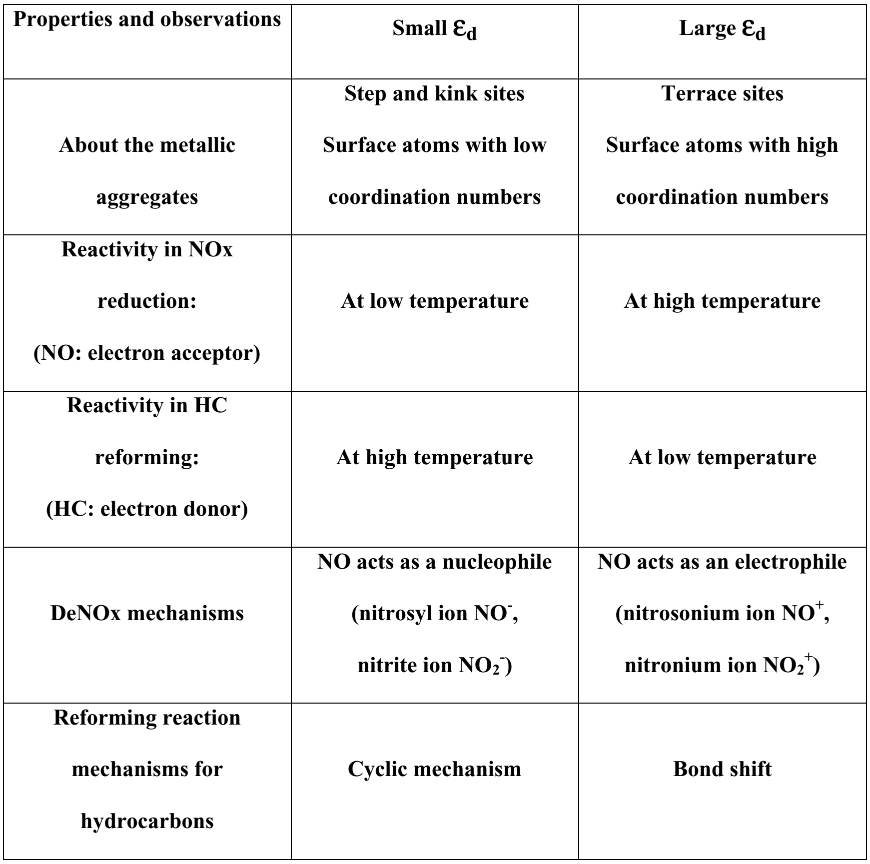


Fig. 6. Proposed mechanisms for NO reduction by propane at (a) low and (b) high temperatures.

In these reaction sequences it has been pointed out the strong influence of the sites of adsorption: terrace, edge, corner or kink atoms in the pathway to follow. We may think that these active sites consist of special arrangements of step and terrace atoms that are aligned correctly to produce high reactivity and selectivity [93].

To conclude this part we know that the effects of the nature of the reducing agent and promoters on the reactions are important and can be summarised as follows:

- At comparable HC chain length, saturated HC are much less effective compared to unsaturated ones. It can be explained by the fact that it is easier to oxidise NO to NO_2 than to break a C–H bond from the alkane species.
- The use of carbonyl or nitro-compounds [94] as well as alcohols [95] results in high activity at low temperature. The more the reactants are adsorbed, the higher the nitrogen production is. To interpret these results, strong adsorption phenomena have to be invoked.



Properties and observations	**Small ε_d**	**Large ε_d**
About the metallic aggregates	**Step and kink sites** **Surface atoms with low coordination numbers**	**Terrace sites** **Surface atoms with high coordination numbers**
Reactivity in NOx reduction: (NO: electron acceptor)	**At low temperature**	**At high temperature**
Reactivity in HC reforming: (HC: electron donor)	**At high temperature**	**At low temperature**
DeNOx mechanisms	**NO acts as a nucleophile (nitrosyl ion NO^-, nitrite ion NO_2^-)**	**NO acts as an electrophile (nitrosonium ion NO^+, nitronium ion NO_2^+)**
Reforming reaction mechanisms for hydrocarbons	**Cyclic mechanism**	**Bond shift**

Fig. 7. Relations between reforming reactions of hydrocarbons performed under reductive atmosphere and $DeNO_x$ reactions occurring under oxidative atmosphere; variation of ε_d.

- The use of promoters does not give clear answers about the beneficial effect or not on the selectivity in N_2/N_2O ratio [95] even the reactivity is changed. It shows that a comprehensive knowledge of the exhaust lean technology is still missing.

5. General conclusion

Automotive three-way catalysts have represented over the last 25 years one of the most successful stories in the development of catalysts. But we still have a lot to do before understanding these reactions.

In 1991, from a great variety of experimental evidence regarding the relationship between catalytic activity, strong adsorption strength and surface roughness, Somorjai summarised these points in what he called: “the three puzzles of surface science” [96–98].

(a) Strong sites for chemisorption are at the same time sites of high catalytic activity. In particular, the rougher the surface, the higher is its catalytic activity.
(b) Bond breaking takes place in a narrow temperature range characteristic of the adsorbate–adsorbent system.
(c) This range shifts to lower temperatures in the presence of stronger adsorptive sites, or rougher surfaces.

To explain these points the role of the metal surface reconstruction induced by dissociative chemisorption has to be taken into account. Moreover, we have to learn more about the modification of the work function of a solid when a reactant is adsorbed on its surface. For instance, hydrocarbons act as electron donors, at the opposite oxygen and NO act as electron acceptor. Hence a decrease or an increase of the work function should be observed respectively.

Such results lead to the consideration of the variations of the d-band centre: ε_d [58]. We underlined that, for low binding energy (low negative values of ε_d), on one hand, the cyclic mechanism was predominant, on the other hand, the $DeNO_x$ reaction occurs at low temperatures, on low-coordinated atoms, NO acting as a nucleophile. For high binding energy, bond shift mechanism predominates, and the $DeNO_x$ reactions take place at high temperatures, NO acts as an electrophile, Fig. 7.

Concomitantly to these researches in exhaust catalysts, new formulations are studied to get higher selectivities in reforming reactions either for branched or linear hydrocarbons.

These reflections will be sterile if these ideas were not discussed in a larger community than chemists only. It was the case at the *colloquium on emerging materials* which was opened to a larger community included physicists and chemists. At the interface of these disciplines we may find out the various pathways involved in *environmental catalysis* and answer about “the three puzzles of surface science”.

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