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Modification of the surface reactivity and selectivity of mixed oxides in oxidation reactions due to coadsorbate species

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Abstract

The influence of coadsorbate species on the surface properties of mixed oxides in the selective oxidation of hydrocarbons is shown to highlight the concept of the possibility to tune the reactivity and selectivity with gas phase dopants and the role of coadsorbate species in the reaction mechanism of selective oxidation. Although few literature data are available on these topics, the examples discussed illustrate that a better understanding of these phenomena is a key to the design of better catalysts and a critical factor in understanding the real nature of the surface processes during the catalytic reaction. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Several important industrial oxidation reactions are made using gas phase processes on solid catalysts based on mixed oxides and as a consequence considerable attention has also been focused on investigation of surface mechanisms responsible for the selective behavior. A classical example of very extensively investigated system from the mechanistic point of view is the selective oxidation or ammoxidation of propene on bismuth molybdate catalysts [1–4]. The reaction involves a complex multistep transformation and is basically the same irrespective of the presence or absence of ammonia, apart from the transformation of molybdenum metal-dioxo species (O=Mo=O) to metal-diimido species (NH=Mo=NH). The rate determining step is the abstraction of an α-methyl hydrogen from a lattice oxygen linked to a bismuth ion to form a π-allyl intermediate coordinated to a molybdenum ion. The metal-oxo or -imido group then attacks the allyl intermediate forming a σ-bonded oxygen- or nitrogen-allyl species which then transforms to acrolein or acrylonitrile by further abstraction of an α-hydrogen. The –OH groups formed during the abstraction of the two hydrogen atoms react then to form water which desorbs from the catalyst. At the end gaseous oxygen, adsorbed dissociatively probably at the bismuth site, reoxidizes the active sites reforming the starting bismuth–molybdenum active sites. There are several key hypotheses in this mechanism which should be pointed out because they have had a considerable influence on the subsequent studies of the surface mechanisms in selective oxidation reactions:

1. The reaction occurs at a specific single site (a bismuth–molybdenum center) which possesses all

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the functions necessary to complete the transformation from the reactant to the product. There is no movement on the surface or desorption/readsorption of the intermediate species.
2. The selective oxidation/ammoxidation occurs with a Mars-van Krevelen type mechanism, i.e. the adsorbed hydrocarbon reduces the oxide center which is later reoxidized by gaseous oxygen. There is no bulk or surface oxygen transport to reoxidize the reduced center.
3. Gaseous oxygen is rapidly dissociated and transformed to lattice oxygen having a nucleophilic character without the formation of adsorbed oxygen species with electrophilic character such as O_2^-, O^-, etc.
4. Only a single pathway of reaction exists from the reactant to the product.
5. The reaction occurs through redox reactions only at the oxide center without participation of other coadsorbate species in the reaction mechanism.

The same hypotheses have been applied in several of the proposed reaction mechanisms of selective oxidation at oxide surfaces, although clearly further studies have in part modified the above view. For example, the analysis of the behavior of multicomponent bismuth molybdate catalysts [5] has shown that bulk diffusion of oxide ions plays an important role in the enhancement of the catalytic activity and the migration of oxide ions is mainly accelerated by lattice vacancies. The surface picture suggested by these studies is that the catalytic behavior is not associated with a specific localized active site, but collaboration between different kinds of active sites proceeds quite efficiently. One site activates molecular oxygen while another site mainly consumes it for the reaction. This indication is in line with the theory of remote control proposed by Delmon and Ruiz [6,7] that oxidation and reduction occur at different, spatially separated, sites on the surface of the catalyst. It is worth noting that in these cases the attention is shifted from a localized reaction mechanism analogous to that occurring at complexes in the liquid phase to a true reaction mechanism on solid surfaces in which the collective properties of the surface are the key factor.

Nevertheless this recent evidence indicate that it is probably not correct to discuss a selective oxidation transformation in terms only of a reaction at a specific localized site. Most of the reaction mechanisms of selective oxidation are based implicit on this assumption, as shown for example in a recent review on the mechanisms of propene and propane transformation over mixed oxides [8]. Furthermore, consideration is made of the possibility that coadsorbate species (i) modify the intrinsic activity/selectivity of the surface, (ii) modify the pathways of transformation or (iii) play directly a role as co-catalysts. These coadsorbate can be both reactants or their products of transformation and gas phase additives added specifically to increase the catalytic behavior. For example, the role of water in improving the selectivity in several reactions of selective oxidation is known [9], but usually water is considered to help only the desorption of the products or to limit the adsorption of reactants due to competitive chemisorption [10]. In the presence of steam, on the contrary, the coordination characteristics of the active centers and the surface acido-base characteristics of the catalyst can also be modified. In a recent work [11] it was shown that in the case of Cu–ZrO_2 catalysts water has a much more complex effect. Water in the gas phase (i) influences the degree of hydroxylation of the surface and thus coordination environment of copper sites as well as (ii) acts as a coordination ligand. Both effects were found to determine the coordination and redox activity of copper sites with a consequent effect on the catalytic reactivity of copper sites in N_2O decomposition [11]. CO_2 [12], SO_2 [13], etc. are other gas phase additives which often lead to an improvement in the behavior in selective oxidation reactions.

Less studied is the possibility of adding various organic additives to the gas phase to improve the catalytic performances. When these additives (or their products of transformation) form adsorbed species relatively stable during the catalytic reaction, it may be expected that they can influence the surface reactivity in a number of ways: (i) changing the nature of surface metal-complexes active in the reaction, (ii) blocking some sites responsible for side reactions, (iii) enhancing or inhibiting surface transport of spillover oxygen or hydrogen species, (iv) favouring charge separation or transport in electron redox reactions and (v) playing a direct catalytic role, stabilizing by coordination some intermediates or mediating directly the oxygen or hydrogen transfer. Carbonaceous species formed on the surface of oxidation catalysts during reaction should also be included in this general concept of surface modifications by coadsorbate species. There is various evidence showing that the active sites in oxidative dehydrogenation of styrene probably be associated with the carbonaceous species on the surface of the catalyst [14,15] and similarly these species are responsible for the selective behavior of silica in the ammoximation of cyclohexane [16].

Since in most of the cases the possible role of coadsorbate in modifying the surface reactivity is not specifically considered, clear evidence on this subject is not available in the literature. Nevertheless we will discuss here some indirect evidence to highlight the importance of correct consideration of the role of coadsorbate on the surface reactivity for tuning of the surface properties, design of new surface reactions and better understanding of the catalytic chemistry at solid surfaces.

2. Direct role of coadsorbate in the mechanism of selective oxidation

The direct role of carbonaceous species on the mechanism of oxidative dehydrogenation of ethylbenzene or alkanes and in some cases also of selective oxidation is well documented [14–18], although the nature of the surface sites on the carbonaceous material responsible for this behavior is not very clear. Instead, evidence has not been reported about a possible role of not-condensed species, although in several cases the bond between organic species and the surface sites is so strong that a significant amount of these species is present on the surface during the catalytic reaction. However, the complexity of the investigation necessary to evidence a possible cocatalytic role of coadsorbate species, excluding at the same time other effects clearly present such as competition for chemisorption, etc., usually prevents obtaining clear information on direct participation of coadsorbate in the reaction mechanism.

Therefore, we will discuss here indirect evidence based on the analogy with the reaction mechanisms in homogeneous liquid phase oxidation which can serve as a guideline to approach the investigation on this subject. In fact, it has been clearly demonstrated that the activity of homogeneous catalysts depends considerably on the nature of the ligands not only due to a modification of the electronic properties of the metal center of the complex, but also because the ligand ‘assists’ the catalytic transformation forming specific bonds with the substrate/intermediate [19]. Furthermore, there are several examples in which an organic molecule ‘mediates’ the selective oxidation. A recent interesting example [20] shows that in the Pd(II)-catalyzed alkene acetoxylation or Wacker type oxidation, the reoxidation of reduced palladium can be made efficiently by a molybdovanadophosphate (PVMoO)/hydroquinone/O_2 system. The primary agent for Pd^0 oxidation is a quinone (for example, benzoquinone) which forms from the corresponding hydroquinone by reaction with the MoVP which is then reoxidized by gaseous oxygen. The hydroquinone–quinone transformation thus mediates the direct oxidation of Pd^0 by PVMoO which is not a fast reaction.

Solid supported or unsupported Pd^{2+}-phosphomolybdovanado heteropoly acids are also active in the gas phase at low temperature (about 100°C) Wacker-type oxidation [21,22], in particular for the 1-butene to 2-butanone oxidation. The reaction is selective, although the catalytic activity progressively declines due to both the progressive reduction of the heteropolyacid and the accumulation of organic species on the catalyst surface. Periodic reoxidation at high temperature with oxygen is thus necessary. It is interesting to note that the rate of formation of the product initially increases (Fig. 1) in contrast with the expected progressive deactivation due to the effects described above. The initial increase in the formation of 2-butanone may derive simply from the fact that the overall apparent rate of reaction is controlled by the rate of desorption of the product and thus an initial accumulation on the surface is necessary before its presence in the gas phase becomes evident, although the initial increase in productivity is too marked to be justified by a desorption-controlled mechanism only. It is not unlikely that the initial induction time is due at least in part to the formation of organic species which mediate the reoxidation of reduced palladium similarly to what occurs in the liquid phase. Infrared data indicate the effective presence of large amounts of organic species on the surface of the catalyst during catalytic reaction [21], but do not allow clarification of a possible role of these species in the reaction mechanism due to the presence of several different species. It

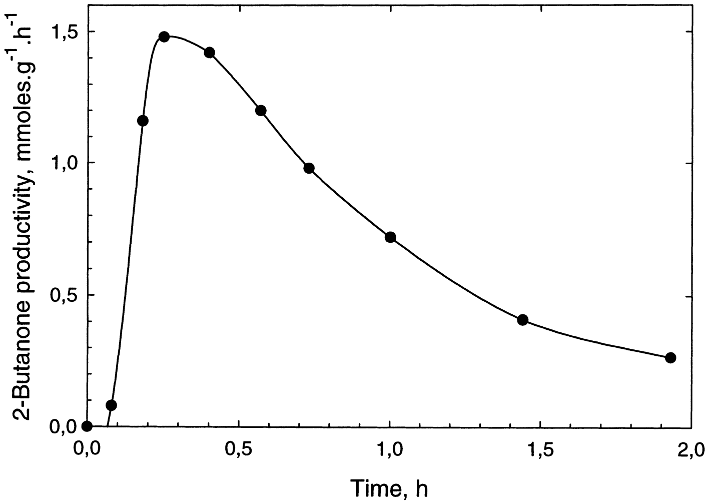

Fig. 1. Productivity to 2-butanone from 1-butane over Pd^{2+}-$H_3PV_2Mo_{10}O_{40}$ as a function of time on stream. Reaction temperature 80°C; feed: 0.5% 1-butene, 20% O_2, 10% H_2O in helium.

will be interesting, therefore, to demonstrate whether or not the homogeneous mechanism is present also in the heterogeneous system, for example analyzing the effect on the reaction rate of adding small amounts of benzoquinone. Nevertheless this example show that the role of organic species as cocatalysts in selective reactions at solid surfaces cannot be ruled out and should be considered in discussing the catalytic data.

A different example of selective oxidation mediated by surface anchored species was given recently by Tsubokawa et al. [23]. Alcohols and diols are not readily oxidized by Cu^{2+} salts, but in the presence of nitroxyl radicals immobilized on silica and ferrite react quickly to give the corresponding aldehydes, ketones and lactones. The alcohols are oxidized with oxoaminium moieties (N=O) on the silica and ferrite surface, which were formed by the reaction of the nitroxyl radical (N–O$^{\bullet}$) moieties with Cu^{2+}. The oxoaminium moieties are reduced to the corresponding hydroxylamine moieties (N–OH) reoxidized by the Cu^{2+} salt. The surface nitroxyl radical thus mediates the selective oxidation of the alcohol with strong analogies with that observed in homogeneous catalysis for the oxygen transfer reactions from coordinated ligands containing groups such as the nitro group [24]. For example, a cobalt–nitrosyl (Co–NO) complex reacts with O_2 to form a nitro complex (Co–NO_2) able to transfer oxygen to various organic species (propene is oxidized to acetone) reforming the starting cobalt–nitrosyl complex. The nitrosyl complex thus mediate the oxygen transfer from gaseous oxygen to the organic molecule.

On heterogeneous catalysts similar observations have been made in terms only of rate of hydrocarbon activation. For example, methane reacts very slowly with oxygen over H-zeolites even at very high temperatures (up to 600°C), but in the presence of NO also the reaction quickly proceeds at 300°C [25]. Other coadsorbate species, such as sulphate, have also been shown to play an active role in facilitating the dissociative adsorption of saturated hydrocarbons on solid catalysts [26]. Evidence for the applicability of these concepts of oxidation mediated by coadsorbed species to synthesize organic products on solid surfaces instead is not available, although the method can be particularly useful in developing oxidation systems active at low temperature and thus applicable for the synthesis of fine chemicals.

2.1. *Role of coadsorbate in enhancing the rate of hydrocarbon activation*

Although examples are limited, there is some interesting evidence showing the possible role of coadsorbate in enhancing the rate of hydrocarbon activation in oxidation reactions.

A first example is given by the study of the ammoxidation of propane to acrylonitrile over Ga–Sb-oxide based catalysts [27,28]. Over these catalysts, the rate of propane selective oxidation increases with introduction of ammonia to the reaction mixture and similarly the rate of acrylonitrile formation also increases. For example, the rate of propane conversion at 550°C passes from about 3×10^{11} to 5.5×10^{11} molecules. $C_3H_8\,cm^{-2}\,s^{-1}$ as the concentration of ammonia in the feed increases from 0% to about 0.5% [28]. Worth noting in this case and differently from other catalysts for propane ammoxidation [29], is that the increase in the product formation rate is not a result of a decline in formation of carbon oxides. Therefore, ammonia modifies the surface characteristics enhancing the rate of alkane activation. Infrared spectroscopic data on the ammonia interaction with the Ga–Sb-oxide catalyst [30] indicate that both ammonia adsorption and catalyst treatment with a reaction mixture produce the NH_2^- amide groups which can serve as base sites to catalyze the propane activation via a carbanion intermediate further transformed to propene. Adsorbed ammonia species then react with the propene intermediate to form acrylonitrile. Ammonia has thus in this case a double role: it is the reactant necessary to (i) form the product and (ii) generate surface adsorbed species which play a cocatalytic role in the mechanism of alkane activation (Fig. 2).

A different example is given in the gas phase oxidation with oxygen of alkylaromatics over Fe–Mo/borosilicate [31]. The addition of carbon dioxide to the feed significantly promotes hydrogen abstraction and thus the rate of alkylaromatic conversion, although it adversely affects oxidation of the resulting alkenyl group to oxygenates. Although the mechanism of this effect was not investigated, it is reasonable to suppose that the CO_2/acid carbonate cycle is that responsible for the increased rate of alkylaromatic hydrogen abstraction. Also in this case a coadsorbate species participates in the reaction mechanism significantly changing the surface reactivity.

Less clear is the effect of carbon dioxide in inhibiting the further selective oxidation of the aromatic alkenyl intermediate. Following the above hypothesis, the adsorbed CO_2 abstracts the hydrogen atoms from the alkylaromatic and reacts with oxygen to form the acid carbonate species which then dissociates to CO_2 and H_2O. The oxygen necessary to oxidize the aromatic alkenyl intermediate is thus intercepted from the CO_2 to form the acid carbonate, leading on the one hand to an enhancement in the rate of alkylaromatic activation, but on the other hand to inhibition of further oxidation of the intermediate of oxidative dehydrogenation. This example illustrates how it is possible in some cases to significantly alter the surface behavior, not only in terms of reactivity, but also of selectivity and nature of the products formed.

This example also indicates that a coadsorbate species may act as a trap or sink of the surface mobile oxygen species involved in the mechanism of selective oxidation. The potentiality of exploitation of this concept in controlling the surface reactivity via oxygens traps or sink adspecies should be further demonstrated, and can be a very fruitful direction of research.

2.2. *The role of coadsorbate in relation to the gas to solid interaction*

The effect of gas-phase dopants cannot be rationalized correctly, if the nature of the reactant-solid surface interaction is also not taken into account. An example of this effect is given by the study of the effect of SO_2 in *o*-xylene on V-TiO_2 [32] and *n*-butane oxidation on $(VO)_2P_2O_7$ [13]. In both cases an anhydride forms on V-based catalysts, but the chemisorption properties of the two hydrocarbons are very different.

SO_2 is a gas phase component often cofed in small amounts (a few ppm) together with hydrocarbons and

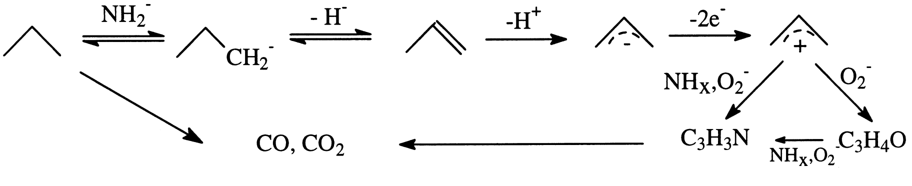

Fig. 2. Reaction mechanism proposed for propane ammoxidation over Ga–Sb-oxide based catalysts [27].

air in industrial practice especially in the past. Although very few fundamental studies have been made to understand in detail the mechanism of action of SO_2 in promoting selectivity, there are two reasonable interpretations of the effect of SO_2: (i) it forms vanadyl-sulphate thus blocking redox reactivity of some surface V^{5+}-sites and (ii) it forms locally low Tamman temperature (LTT) species analogous to those observed for V_2O_5 catalysts for SO_2 oxidation [33], thus promoting amorphization and spreading of supported vanadium-oxide and oxygen mobility with a consequent beneficial role in the rate of oxidation of the hydrocarbon. In both cases, the effect of SO_2 can be interpreted in terms of strong coadsorbate action, because both species formed in the presence of SO_2 slowly decompose stopping the feed of SO_2.

These two interpretations of the effect of SO_2 are in apparent contradiction: in the first case the lattice oxygen donor ability (LODA) should decrease, whereas in the second case an increase in LODA would be expected. Both effects probably are present simultaneously with the dominant effect depending on the nature of the catalyst, and its beneficial or negative effect on the selectivity depending on the nature of chemisorption of the hydrocarbon on the solid surface.

The formation of LTT vanadium-oxide species requires the presence of a V_2O_5-like phase such as on the supported vanadium-oxide selective for *o*-xylene oxidation [34]. Due to the aromatic ring, the adsorption of the alkylaromatic on the catalyst surface is much stronger than the adsorption of an alkane such as *n*-butane, as clearly shown from IR and chemisorption studies [34,35], even taking into account the differences in catalyst characteristics in the two examples discussed. Furthermore, the rate of benzylic hydrogen abstraction (rate determining step in *o*-xylene oxidation [34]) is much higher than that of paraffinic H abstraction from *n*-butane (rate determining step in this second case [35]). It is thus possible to schematically indicate that the number of active oxygens near an adsorption site for the activated hydrocarbon (briefly NOH) should be significantly lower in the case of *o*-xylene oxidation than for *n*-butane oxidation. There are various concurrent reasons on which this statement is based: (i) a high surface coverage by the hydrocarbon should limit oxygen chemisorption and catalyst reoxidation, (ii) a high ratio between the rate of lattice oxygen consumption by reaction with hydrocarbon and lattice oxygen replenishment via gaseous O_2 decreases the number of active oxygens available for insertion into hydrocarbon molecule, and (iii) a high number of chemisorption sites per unit surface area geometrically decreases the oxygen sites near adsorption sites.

Reported in Fig. 3(a) is a schematic representation showing this concept of different surface situation in the two cases of *o*-xylene and *n*-butane oxidation. Although the above considerations clearly indicate that the selective oxidation of an hydrocarbon is a dynamic process of transformation, the model is simplified in the representation (Fig. 3) in terms of surface distribution of active lattice oxygens (–O) and adsorbed hydrocarbons plus a simplified reaction network of transformation which summarizes the kinetics of transformation. We may also assume that the rate of hydrocarbon or products transformation depends on the number of active oxygens (NOH) [36]. Clearly, this simplified model will not give mechanistic insights on the reaction mechanism, but only illustrates the concept of a link between kinetics of transformation and surface modifications by adspecies, as regards both reactants and gas phase dopant (SO_2) adsorption.

Let us now analyze the case of *o*-xylene oxidation (Fig. 3(a)). If the adsorbed hydrocarbon is not rapidly oxidized to the final product (phthalic anhydride), the surface concentration and residence time of the intermediate species (assumed as *o*-methyl benzoic acid) becomes higher and thus decarboxylation and further oxidation to carbon oxides is possible. If a rapid formation of the anhydride instead occurs, a more stable product forms which can then desorb. The oxidation of the anhydride requires first hydrolysis to the diacid and then decarboxylation, but the Brϕnsted acid sites which catalyze the hydrolysis are blocked by the chemisorption of the hydrocarbon and thus the consecutive oxidation of the anhydride is a slower process. The role of Brϕnsted acid sites in catalyzing side reactions will also be discussed in the following section. The action of SO_2, which promotes the local formation of LTT vanadium oxide species showing enhanced oxygen mobility (Fig. 3(a)), is thus to increase the rate of oxidation up to final anhydride, avoiding side reactions on the intermediate species. This does not considerably affect the rate of consecutive oxidation of the anhydride and thus the

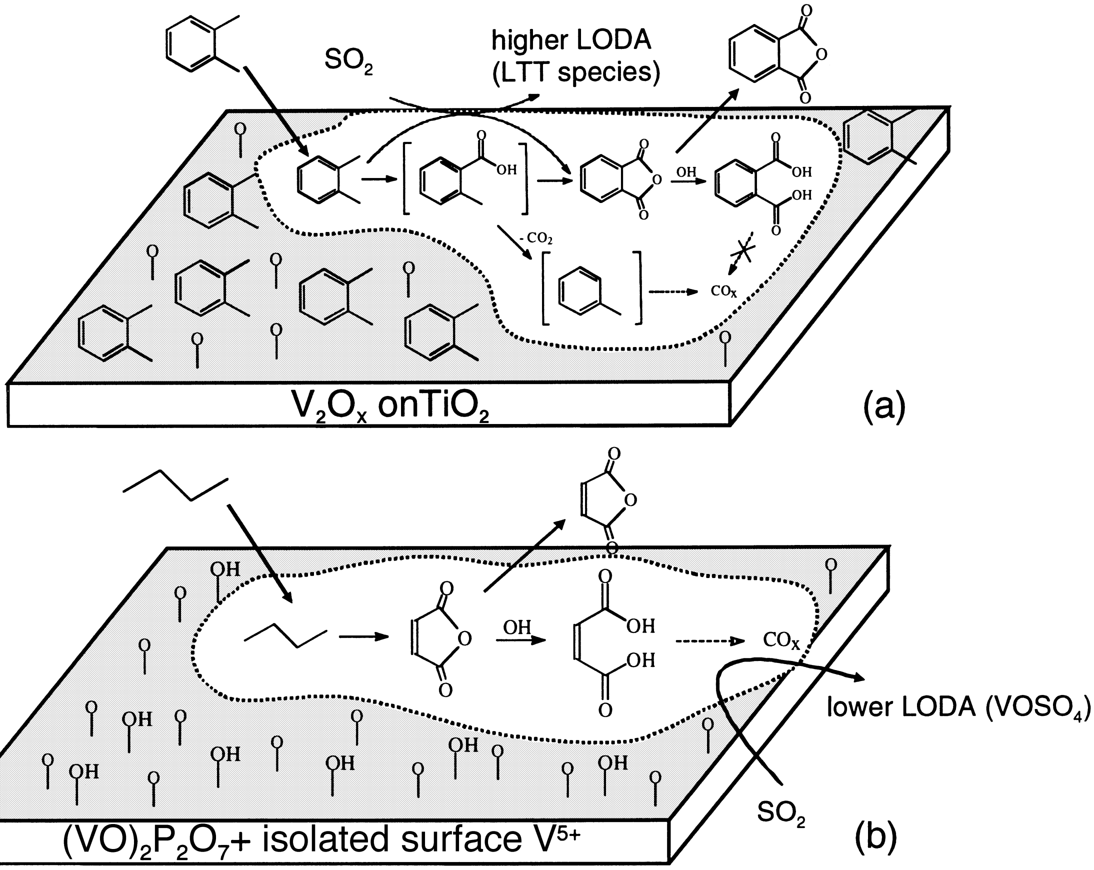

Fig. 3. Schematic representation of the different effect of SO_2 in relation to the kinetics of oxidation and chemisorption properties of *o*-xylene on V_2O_x on TiO_2 and *n*-butane on vanadyl pyrophosphate catalyst. Note: lattice oxygen donor ability (LODA), low Tamman temperature V-oxide species (LTT).

overall effect is an increase in the selectivity to anhydride.

A different case occurs for alkane selective oxidation over vanadium–phosphorus oxides. As schematically drawn in Fig. 3(b), due to the negligible chemisorption of *n*-butane as such, the low surface concentration of products of *n*-butane transformation (this aspect is further discussed in the next sections) and the low rate of *n*-butane conversion, a higher number of active oxygens per adsorption site as well as the presence of a larger number of free Brønsted acid sites during the catalytic reaction are expected in this case. Therefore, the transformation to the anhydride is fast, but the hydrolysis of the anhydride to the acid is also fast. The loss of selectivity thus derives principally from the consecutive oxidation of the maleic acid which is catalyzed by the presence of surface V^{5+} sites. This agrees with the much more enhanced loss of selectivity with increasing hydrocarbon conversion in *n*-butane oxidation than in *o*-xylene oxidation [9]. The reaction of SO_2 with these isolated surface V^{5+} sites to form species ($VOSO_4$) with a reduced redox activity thus allows in this case an increase in the overall selectivity, because the rate of the consecutive oxidation of the adsorbed anhydride decreases. In agreement, the promotion effect of SO_2 in *n*-butane oxidation is especially to increase the selectivity at high conversion [13]. The mechanism of promotion of SO_2 in this case is thus the opposite of that discussed for *o*-xylene where the intrinsic selectivity in the direct formation of the anhydride is promoted rather than a reduction in the rate of its consecutive conversion. The reason is the different nature of the active surface during catalytic reaction and the different nature of adspecies.

This example of the different action of SO_2 in *o*-xylene and alkane oxidation thus illustrates that the role of coadsorbate in modifying the surface selectivity can be different, not only as a function of the nature of the catalyst, but also as a function of the nature of the surface modifications due to adspecies.

2.3. *Role of coadsorbate in changing the surface pathways of reaction*

Coadsorbate species may have not only a direct role in the mechanism of synthesis of the key product, but also have an important effect on the selective synthesis of the product, because their presence blocks side reactions. An interesting case is when the modifier of the intrinsic surface reactivity of the oxide is one of the reactants. An example of this case is given by the role of ammonia in the synthesis of acrylonitrile from propane on V–Sb-oxide catalysts [29,37]. When ammonia is added in small amounts to the propane+O_2 feed the propane conversion decreases considerably and the selectivity increases, not however, to the product of N-insertion (acrylonitrile) as expected, but rather to the intermediate propene [38]. Only after a further increase in the NH_3 concentration in the feed, does acrylonitrile formation start to increase. The role of ammonia is thus not only that of a reactant. Indeed, ammonia has a more complex behavior as evidenced by infrared (IR) studies on the surface reactivity and properties of V–Sb-oxides in relation to the mechanism of propane (amm)oxidation [37].

Of particular interest is the comparison of the different results obtained after adsorption on the catalyst of some of the precursors of the intermediates in propane oxidation on V–Sb-oxide and their change as the catalyst temperature increases, when ammonia is only present coadsorbed on the catalyst or when it is also present in the gas phase [37]. Ammonia is chemisorbed on V–Sb-oxide both as ammonium ion by reacting with Brϕnsted acid sites or as coordinated ammonia on Lewis acid sites [38], but with increasing catalyst temperature ammonia adspecies can also be oxidized to N_2+H_2O from catalyst lattice oxygen. Although the coordinated ammonia adspecies is probably the precursor species for the oxidation of ammonia via heterolytic splitting [38], the higher stability of the latter species as well as the reaction of the formed water with Lewis acid sites to generate Brϕnsted acid sites [9] determines a net formation of Brϕnsted acid sites as a consequence of the partial oxidation of ammonia, although in the controlled conditions of IR experiments [37] the amount of residual ammonia adspecies is still enough to allow the theoretical synthesis of acrylonitrile from adsorbed organic species. When only ammonia adspecies are present together with organic adspecies during the IR high temperature experiments there is thus the formation of free Brϕnsted acid sites which, on the contrary, further react with gas phase ammonia to form ammonium ions in the second type of coadsorption studies. The presence of free Brϕnsted acid sites the reactivity of which is not blocked by reaction with ammonia determines a significant change in the surface reactivity and pathways of transformation. The overall reaction network in propane ammoxidation on V–Sb-oxides [37] is reported in Fig. 4(a). Various reaction pathways of transformation are present, with some of them also leading to the same final product (acrylonitrile), although characterized by different selectivities due to the different possibilities of side reactions which, in turn, are influenced differently by the presence of free Brϕnsted acid sites whose reactivity is not blocked by reaction with ammonia.

An instructive specific example is the case of the competitive pathways from intermediate acrolein. This adspecies can be converted either directly to acrylonitrile probably via imine species or via a further oxidation step to form an acrylate species. The latter species quickly reacts with adsorbed ammonia to form an amide species which at high temperature further converts to acrylonitrile. However, in the presence of free Brϕnsted acid sites the amide can be hydrolyzed to form free, weakly coordinated, acrylic acid which is the precursor to the formation of carbon oxides (Fig. 4(b)). The acrylonitrile itself can also be hydrolized to the amide and then to the acid in the presence of free Brϕnsted acid sites and further to carbon oxides.

There are other points in the surface reaction network where free Brϕnsted acid sites catalyze side

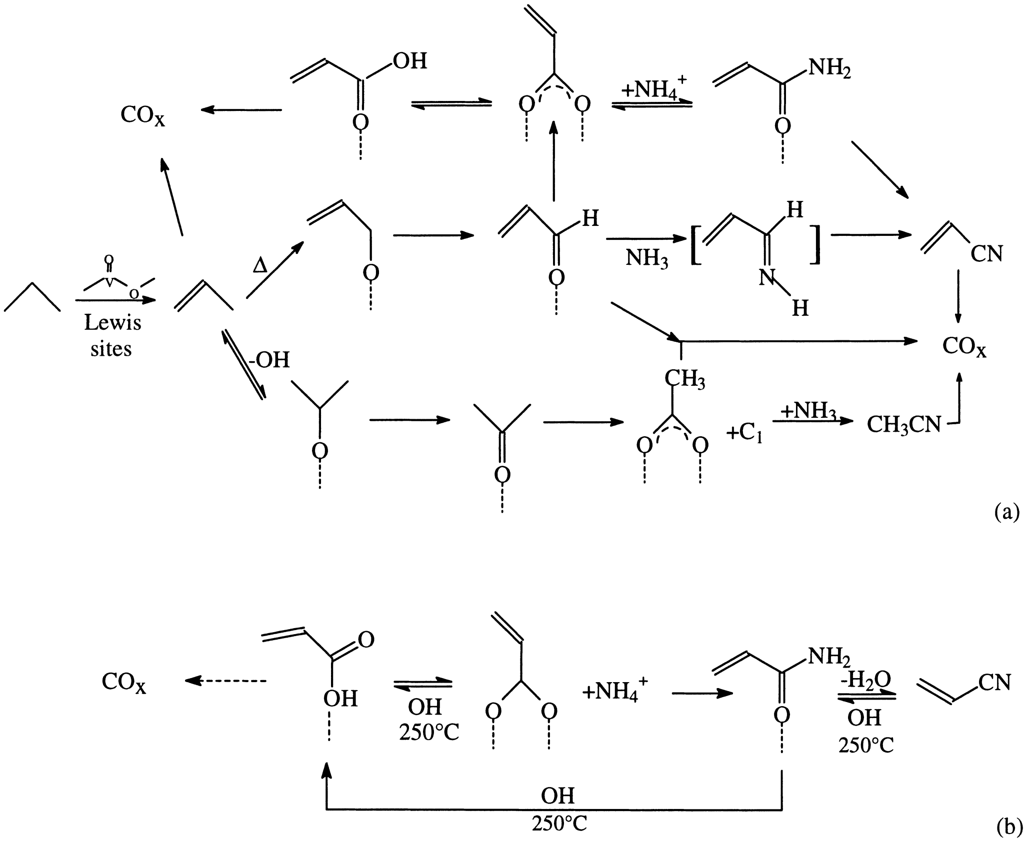

Fig. 4. Surface reaction network in propane ammoxidation on V–Sb-oxides (a) and detail of the effect of Brϕnsted acid sites on the reaction pathways from acrylic acid to acrylonitrile (b) [37].

unselective reactions. As indicated in Fig. 4(a), there are two possible routes of transformation of intermediate propene, one by reaction with free Brϕnsted acid sites to form an isopropylate intermediate then further rapid transformation to acetone, precursor for carbon chain degradation, and a second selective pathway by allylic lattice oxygen addition to form an alcoholate species precursor of acrolein formation. Also in this case the inhibition of free Brϕnsted acid site reactivity by reaction with ammonia favours the selective route and thus overall selectivity. This explains why there is on the same catalyst a very drastic increase in selectivity to partial oxidation products (from nearly zero to over 80%) in going from oxidation to ammoxidation conditions. In olefin (propene) oxidation the increase is much less enhanced [9], because the interaction of the olefinic double bond with the Brϕnsted acid sites already inhibits their activity.

Ammonia is thus not only a reactant for the synthesis of acrylonitrile from C_3 hydrocarbons, but also plays a main role as a self modifier of the surface reactivity. The effect is especially remarkable in alkane oxidation, because the lower interaction of the hydrocarbon with surface sites (Brϕnsted acid sites, in particular) prevents the inhibition of the reactivity in catalyzing side reactions of these surface sites by interaction with the hydrocarbon itself. In order to increase the selectivity in alkane oxidation it is thus necessary to operate with a high hydrocarbon concentration, because the higher amount of olefins formed also causes a self modification of the surface reactivity. This concept will be further demonstrated in the following section.

2.4. Role of the surface concentration of coadsorbate on the surface behavior

The strong chemisorption of one of the reactants can inhibit the chemisorption of the others and thus it is expected that the surface reactivity may depend on the amount of these strongly chemisorbed adspecies. An example of this situation is given by a study of the dependence of the surface reactivity of vanadyl pyrophosphate in propane ammoxidation on the amount of chemisorbed ammonia [39,40]. The experiments to analyze this question were made in the following way. First ammonia was chemisorbed at about 400°C up to complete saturation of the sorption capacity and then gas phase or weakly coordinated species were removed with a flow of pure He. After this preadsorption, a flow of propane (about 7%) in helium with or without oxygen (about 8%) was fed to the catalyst while monitoring the change in the distribution of products with time on stream. By estimating the amount of ammonia which thermally desorbed in separate experiments and that consumed by nitrogen balance, it was possible to derive the change in the surface reactivity as a function of the residual amount of ammonia adspecies [39]. In the absence of oxygen in the feed the catalyst was not very active, giving only propene as the main product. In the presence of oxygen in the feed, instead, an interesting behavior was observed which is summarized in Fig. 5 where the yields of products and propane conversion are reported as functions of the residual fractional amount of ammonia adspecies, i.e. the residual adsorbed moles of ammonia with respect to the saturation coverage at the same reaction temperature. When ammonia coverage is nearly complete, the catalyst is less active, but highly selective, i.e. very low amounts of carbon oxides form. After removing part of the ammonia adspecies, the catalyst reactivity increases (propane conversion increases) after an initial decrease, possibly due to an effect of ammonia similar to that discussed in Section 2.2 for Ga–Sb-oxide based catalysts. It is also interesting to note that decreasing the surface coverage of ammonia adspecies increases the formation of acrylonitrile, the only product of nitrogen insertion and the formation of which was thus expected to be maximum for full ammonia surface coverage. The reason for this is probably that chemisorbed ammonia inhibits chemisorption of oxygen at surface Lewis acid sites and thus avoids oxidation of the intermediate propene, a necessary step to acrylonitrile [40]. Differently from the V–Sb-oxides discussed in the previous section, lattice

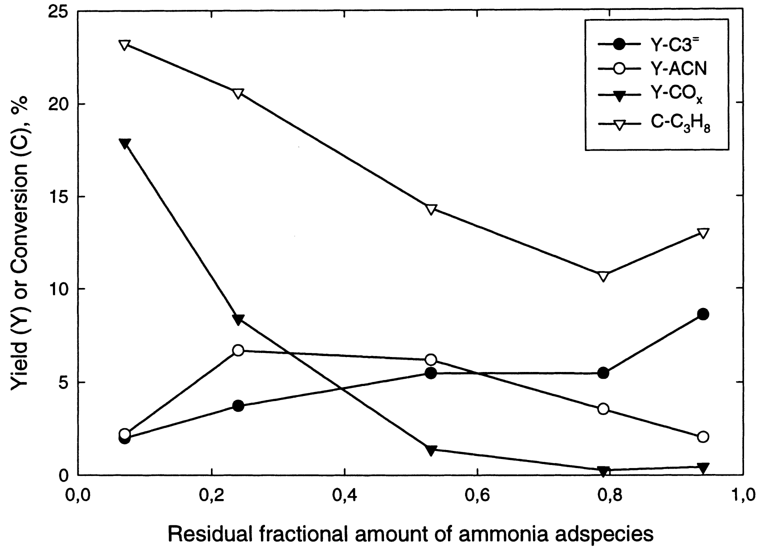

Fig. 5. Yield of propene ($C_3^=$ =), acrylonitrile (ACN) and carbon oxides (CO_x) at 406°C as a function of the residual fractional amount of ammonia adspecies (with respect to saturation coverage at the same temperature) during transient catalytic experiments feeding about 7% propane and 8% O_2 on vanadyl pyrophosphate with ammonia preadsorbed at 400°C [39].

oxygen of vanadyl pyrophosphate is much less prone towards oxidation of the adsorbed hydrocarbon. On vanadyl pyrophosphate, therefore, the selective synthesis of acrylonitrile from propane requires an optimum concentration of ammonia and oxygen adspecies which, however, can be obtained only in transient conditions. In fact, the behavior in stationary conditions is close to that observed for full ammonia coverage [39]. The further depletion of ammonia adspecies (Fig. 5) leads to a decrease in acrylonitrile formation and a considerable increase in formation of carbon oxides, in agreement with the previous discussion on the role of ammonia adspecies in the modification of the surface selectivity.

This example shows that the concentration of adspecies, in relation with possible competitive adsorption phenomena or inhibition of reactivity of surface sites, is another important parameter determining both the rate of hydrocarbon conversion and the selectivity to its products of transformation. This example also shows that operations in unsteady-state conditions may allow in some cases significant improvements in selectivity, because it is possible to achieve better control and optimization of the concentration of coadsorbed species.

A different case of effect of the surface concentration of adspecies in the modification of the intrinsic surface selectivity is given by the analysis of the effect of propane concentration in the feed on the selectivity of vanadyl pyrophosphate. In this case, different from the previous examples discussed, the modification in the surface reactivity is induced by the products of reaction.

On the same catalyst active and selective in *n*-butane oxidation to maleic anhydride (selectivities up to about 80%) and in the same reaction conditions propane is instead nearly completely oxidized to carbon oxides (selectivity to partial oxidation products lower than about 5%) [41,42]. One explanation of this observation is the different stability of the products of partial oxidation obtained in the two cases [43], although their chemical characteristics do not fully justify the remarkable difference in selectivity. However, it is possible to observe that the analysis of the residual adsorbed species after catalytic reaction in the case of *n*-butane oxidation indicates the presence of significant amounts of strongly adsorbed species [44] (between the detected products of thermal desorption maleic and phthalic anhydride, crotonaldehyde, etc.) absent in the case of propane oxidation. This suggests

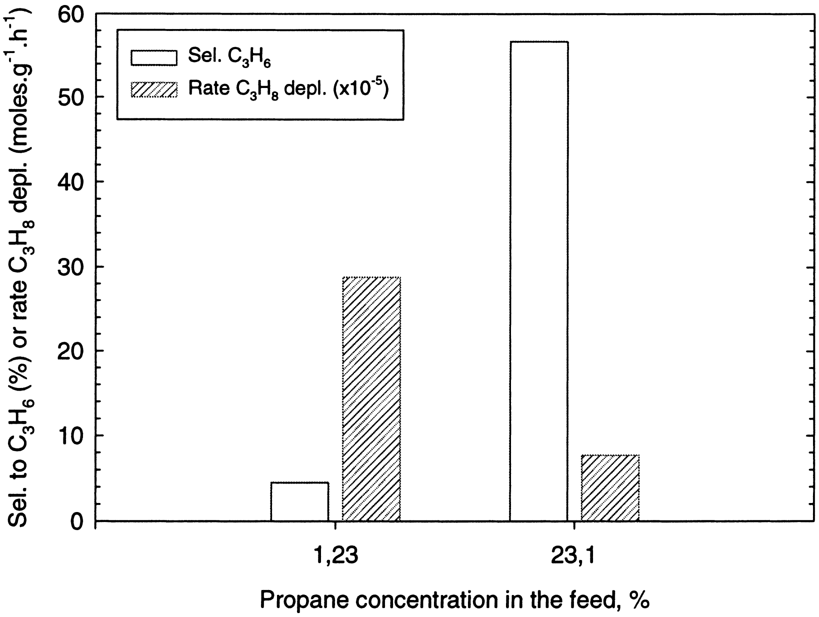

Fig. 6. Selectivities to propene from propane and rate of propane depletion at 322°C in propane oxidation on $(VO)_2P_2O_7$ using a feed mixture containing in both cases 10.2% O_2, but 1.2% or 23.1% of propane [42].

that the modification of the surface reactivity by these strongly chemisorbed adspecies, present in *n*-butane but not in propane oxidation, is co-responsible for the change in the surface selectivity of vanadyl pyrophosphate in C_3–C_4 alkane oxidation together with the difference in the rate of consecutive oxidation of the products of reaction.

Based on the previous discussion, it is thus expected that by increasing the propane concentration it is possible to compensate for the lower interaction with surface sites of the products of propane oxidation with respect to those in *n*-butane oxidation by increasing their amount. The data reported in Fig. 6 show that effectively by increasing the propane concentration in the feed from about 1% to 25% at a fixed oxygen concentration it is possible to increase the selectivity to partial oxidation products considerably from nearly zero to about 60% [42]. The drastic increase in the selectivity shown in Fig. 6 is due reasonably to the combined effect of control of NOH sites (as shown by the decrease in the rate of propane depletion in Fig. 6) and modification of the surface properties by chemisorption of the products (propene) formed. This example further illustrates the importance of a correct understanding of phenomena due to coadsorbate species to control and tune the reactivity and selectivity properties of oxide surfaces in selective oxidation reactions.

3. Conclusions

The examples discussed show that various possible effects are to be expected on the surface reactivity and selectivity in the presence of coadsorbate species together with the reactant or intermediates: (i) modification of the coordination and electronic properties of a surface metal ion and (ii) direct participation of the adsorbed species in the reaction mechanism, assisting the metal ions in the catalytic transformation (for example, helping to hold the intermediate coordinate to the site in a specific mode) or directly mediating oxygen, hydrogen or electron transfer to or from the reactant/intermediate. There are, however, further possible functions of the coadsorbate species in modifying the surface properties: (i) change in the surface acido-base properties which can catalyze side reactions, (ii) blockage of chemisorption sites to control, for example, the amount of surface oxygen species, and (iii) inhibition of the diffusion of surface species into the reacting molecule. Coadsorbate species, i.e. all strongly held adspecies on the surface which are not reaction intermediates, may be either the reactants themselves and the products of their transformation or gas phase dopants. In several cases it was observed that the intrinsic surface properties of oxides are significantly altered by the presence of these coadsorbed species and that the catalytic behavior (for example, in comparing alkane and alkene oxidation, the behavior of different alkanes, the effect of hydrocarbon conversion on the selectivity, etc.) cannot be rationalized without taking into account these effects.

A correct understanding of the modification of the surface reactivity and selectivity of mixed oxides in oxidation reactions due to coadsorbate species is thus a necessary approach for a better knowledge of catalytic surface phenomena, and for the tuning and design of new catalysts.

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