

Chemical basis of metal catalyst promotion

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Chemical basis of metal catalyst promotion

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A survey is presented of the different modes of action of metal catalyst promoters. Broadly two main categories can be distinguished: structural and bifunctional promoters. In structural promotion the promoting atoms do not participate themselves in the elementary steps of a catalytic reaction. Bifunctional promoters participate themselves chemically in the catalytic reaction. Five different kinds of structural promotion can be recognized: *ensemble-size regulating; valence-state promotion; polarizing-structural promotion; surface-phase and cluster complex promotion; particle size stabilizing*. Each subcategory is discussed shortly and when relevant illustrated with a practical example. Three different kinds of bifunctional promoters can be distinguished: *Polarizing-bifunctional promotion; direct-bifunctional promotion; chemical-bifunctional promotion*. Whereas conceptually different, subcategories are not always easily experimentally distinguishable. Of most of the different kinds of promotion theoretical treatments exist. Quantum-chemical studies are referred to in the text.

1. Introduction

In catalysis one is mainly interested in dissociation reactions of adsorbed molecules or recombination reactions of molecules or adsorbed molecule fragments. For a chemisorbed molecule to dissociate a surface atom ensemble is required consisting of a minimum number of surface atoms [1]. It may be converted by an insertion type of reaction to a larger molecule. Such a reaction requires a small ensemble and may even occur on a single surface atom [2]. Many other reactions are conceivable that have different ensemble-size requirements. Under catalytic conditions often different modes of reaction compete. Even a single crystal surface, with crystallographically equivalent atoms, provides many different reaction paths for chemisorbed molecule fragments to react.

In a practical catalyst usually several different surface planes are exposed to particles of different particle size. This even increases the number of possible reaction paths. Therefore metal catalysts can be considered intrinsically non-selective. This is the basis of the selectivity problem of heterogeneous catalysis [3].

The role of promoters or modifiers is to enhance selectivity by changing the active catalyst surface such that the number of reaction paths offered to adsorbed molecules decreases and a selected reaction path dominates. A promoter is an additive added to the catalyst when the catalyst is prepared, a modifier alters selectivity and activity by introduction of the coadsorbent during reaction from the gas or liquid phase. For convenience in the following we will denote both as promoters.

The most general way to distinguish those additives is to describe them as structural [4] or bifunctional promoters [5]. Structural promoters act primarily because they affect the solid state chemistry of the catalytically active metal surface. They do not participate in the catalytic event themselves. This is different for the bifunctional promoters. Then adsorption complexes between adsorbate molecule fragments and promoter atoms play an essential role. Of course this schematization is ideal and in reality the structural and bifunctional role may occur together. If one wishes to develop a quantum-chemical theory of metal promotion [6], it is essential to be aware of the very different chemical phenomena that are con-

tained within the concept of metal catalyst promotion.

2. Structural promotion

Structural promotion may occur in several different ways. We will analyse in this section the several different structural promotion effects. The ensemble effect [1a] is one of the classical examples. The ensemble effect reduces non-selective reactions involving dissociation of adsorbed molecules by coadsorption of catalytically non-reactive elements. We will mention two examples.

By the use of transition metals alkanes can be converted to aromatics. Reaction conditions have to be chosen such that this reaction is thermodynamically feasible. The catalytically active catalyst component chosen is usually Pt. Non-selective reactions change the number of carbon atoms in the product molecules, producing light gas and coke on the catalyst that poisons catalyst activity. Since the non-selective dissociative reaction paths require large ensembles of surface atoms, they can be suppressed by coadsorption of S during the reaction (modifier) or alloying with inert metal atoms, e.g. Sn. The action of S can be enhanced by coalloying with an element that strongly adsorbs S, so that at the high reaction temperature requirement S is maintained with a high surface concentration. The beneficial effect of alloying with Re is thought to be due to this mechanism [7]. In the absence of S, alloying with Re enhances non-selective reactions. It then acts as a negative bifunctional promoter (see next section).

Another example of an ensemble effect is provided for by the role of alkali or alkali earth hydroxide addition to a Rh catalyst used to produce methanol [8a] from the reaction of CO and H₂ or to produce aldehydes by reaction of ethylene with CO [8b]. The reaction to be suppressed is the dissociation of CO.

As has been demonstrated theoretically [1b] as well as experimentally [9] dissociation of CO requires large surface ensembles. The presence of alkali and alkali earth salts on the metal surface suppresses the surface ensemble size of the catalytically active center and hence CO dissociation.

As a result methanol production as well CO insertion into an alkene is enhanced. Both reactions only require small surface ensembles. According to the ensemble effect the selectivity change is the result of the suppression of non-selective reaction paths by site blocking.

Many cases are now known where promoters affect the solid state chemistry of the catalytically active surface phase. Catalytically active phases can be stabilizing containing surface atoms in a particular valence state. Such structural promoters may be called valence state promoters. A prototype for this kind of promotion is the action of Cl in the silver catalyst used for the epoxidation of ethylene [10]. Selective epoxidation [10b, 10c] occurs by a silver-oxygen surface molecule complex that is charge deficient. At the oxy-chloride surface formed by coadsorption of Cl. The selective epoxidation reaction between electrophilic oxygen and the electron-rich bond of ethylene is optimized. Elsewhere a quantum-chemical study of this effect has been published [11].

The role of Cs is to stabilize this silver-oxychloride phase under reaction conditions. The molecular complex is sketched in fig. 1. The action of Cs is related to that of Re in the forming catalyst. The latter stabilizes the sulfide phase under the particular reaction conditions applied. Oxygen and chloride are valence state promoting. Re and Cs are examples of surface phase stabilizing promoters. They form a third category of structural promoters.

Ponec et al. [12] have demonstrated experimentally as well as theoretically [13] that methanol selective catalysts based on Pd have to contain ions. These ideas are consistent with quantum-chemical studies on organo metallic complexes of Pd [2a, 2b, 13]. The activation energy barrier for

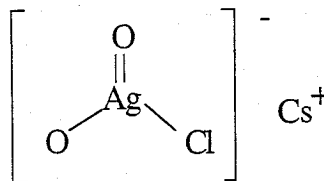


Fig. 1. The silver-oxychloride surface complex for selective ethylene epoxidation (schemata): valence state promotion combined with surface phase structural promotion.

CO insertion into the metal–hydrogen bond is lowered if the transition state complex leading to formyl formation can donate electrons into empty transition metal d-orbitals of suitable symmetry. Pd atoms contain ten d-valence electrons. Ions have empty d-holes available. Because Rh already contains one electron less than Pd, the need to form an ion is less. Clearly additives that promote the presence of surface ions can be considered valence state promoting. Again chlorine can act as such, but also alkali cations, as has been especially demonstrated for the case of the Cu catalyst [14].

Whereas methanol formation on Pd occurs by way of the formyl intermediate, on Cu methanol formation occurs by way of the formate. Shustorovich [15] has very elegantly demonstrated that on Cu the formyl reaction path becomes inhibited and formate formation becomes favoured by reaction of CO with a surface hydroxide. The presence of Cu^+ ions will not lower the activation barrier for formyl formation because the d-valence electron band remains completely occupied. However the presence of Cu^+ may favour the surface complex CuOH , which has a low activation-energy to formate formation with CO. Cations that stabilize Cu^+ ions can be considered valence state promoting. Another example of valence state promotion is the $\text{Ce}_{2+x}/\text{Ru}$ complex formed upon reduction of Ce in CeRu alloys [16]. Walker et al. [16] interpreted XANES data of $\text{CeH}_{2+x}/\text{Ru}$ particles such that electrons are transferred from CeH_{2+x} to Ru, altering the catalytic properties of small Ru particles such that nitrogen dissociation is enhanced.

Related to valence state promotion is the polarizing action of cations with a high charge adsorbed or sited next to small metal particles. Such as polarizing promotion is sketched in fig. 2a. Small particles embedded in a zeolite, located next to a highly charged cation, become polarized such that charge depletion occurs on those atoms most remote from that cation. For a complete quantum-chemical analysis we refer to ref. [17]. Metal atom charge depletion enhances the frequency of adsorbed CO [17a]. It also causes the interaction energy with adsorbing closed-shell molecules as H_2 or methane to increase [17b]. Metal cluster polarization is responsible for the

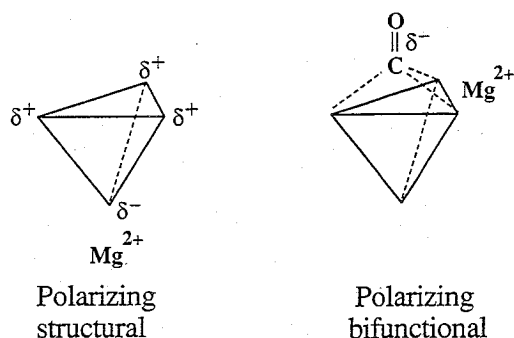


Fig. 2. Polarizing promotion (schematic). (a) Polarizing structural promotion. (b) Polarizing bifunctional promotion.

enhanced metal activities observed for zeolites containing small metal particles next to highly charged cations. It has been called the Schwab effect of the second kind [18].

Finally in zeolites stabilization of specific metal cluster complexes may occur. Such complex promotion has been demonstrated by Bartomeuf et al. [19a]. They demonstrated the stabilization of Cini's negatively charge Pt–carbonyl clusters in Na^+ zeolite. Sheu et al. [20] have reported stabilization of analogous complexes in zeolites and their destruction by the presence of protons in the zeolite.

In summary four types of structural promotion have been discussed:

- ensemble-size regulating,
- valence-state promotion,
- polarizing-structural promotion,
- surface-phase and cluster-complex promotion.

Classical structural promoters that act as stabilizers to prevent particle size sintering or to enhance particle size dispersion have to be added. They have been discussed extensively elsewhere [4].

3. Bifunctional promotion

Whereas in the previous section additives were discussed that were supposed to have no chemical activity of their own or did not directly interact with adsorbates here these additional effects are considered.

To surface scientists autonomous promotor reactivity is well-known from the work of Lackey et

al. [21] and Ponec [22]. If alkali metal adsorbed to a transition metal surface is present at high surface concentration two-dimensional alkali metal cluster formation may occur. In the case of K upon contact with CO this may result in the formation of $K(CO)_x$ compounds, well-known in inorganic chemistry. Upon heating carbonate, the oxide and carbon may be formed [23]. This is an example where the coadsorbate potassium metal goes through an intermediate phase $K(CO)_x$, before it will arrive in the state stable under catalytic conditions (K_2CO_3 , K_2O). In this state it may act as a structural promotor or bifunctional promotor.

Extensively studied is coadsorption of a small quantity of alkali metal [22,24]. When present at low surface coverage alkali atoms interact strongly with the transition metal surface and a surface and a surface dipole develops. The alkali metal atoms become slightly positively charged. This charge is locally screened by polarization of the transition metal atoms in contact with the alkali layer. The local electrostatic field generated by the chemisorbed potassium surface dipole layer influences molecules adsorbed to transition metal atoms close to the cation. This favours such that electron backdonation between metal surface and adsorbate [22,25]. A force between adsorbate and alkali atom may result such that adsorbed molecules bend towards the alkali ion [22,26].

The direct electrostatic interaction between cation and adsorbate we will call polarizing bifunctional promotion. For a cluster in a zeolite it has been sketched in fig. 2b. Comparison with fig. 2a illustrates the difference with polarizing structural promotion.

CO adsorbed to dissolved transition metal complexes has been found to become activated by the direct interaction with cations [27]. Guided by the observation of low CO infrared adsorption frequencies Sachtler et al. [8b] have proposed direct bifunctional promotion (see fig. 3) to be responsible for the activating effects of reducible acidic

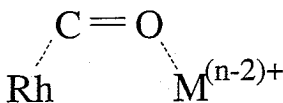


Fig. 3. Direct bifunctional promotion (schematic).

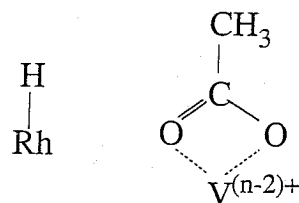


Fig. 4. Chemical bifunctional promotion (schematic).

oxides as V_2O_5 , TiO_2 , Nb_2O_5 , Mn_2O_3 on synthesis gas conversion. It is now well established that coadsorption of these oxides to a transition metal surface lowers the activation energy [28] for CO dissociation.

Currently it is not known whether direct bifunctional promotion, resulting in a valency change of the promoting cation when CO dissociates (the dissociated oxygen atom changes to promoting cation), or polarizing bifunctional promotion, causing enhanced CO bond weakening in the transition state is responsible. In the latter case no valency change of promoting cations occurs. Isotope labelling studies [28c] have shown that the increase in ethanol production from CO and H_2 by coadsorption of reducible acidic oxides on Rh is not due to a change of the rate of CO insertion into precursor species $M-CH_x$, but due to the increased steady state concentration of $M-CH_x$ species. This surface concentration is enhanced by the increased rate of CO dissociation. The rate of hydrogenation of aldehyde precursors is also significantly enhanced [28c], similar as the increase in hydrogenation activity of aldehyde to alcohol by the same promotors [29]. Consistent with the idea of a direct bifunctional interaction, the aldehyde carbonyl group may directly interact to exposed M^{n+} ions. They can be considered to act as a Lewis acid. The enhanced aldehyde residence time then results in an increased hydrogenation rate. Alternatively aldehyde may form a metal acetate intermediate with the promoting oxide, which subsequently is hydrogenated to the alcohol by hydrogen activated on Rh. The latter kind of bifunctional promotion is a chemical bifunctional promotion (see fig. 4). Acetate formation has been reported to occur under these conditions [8b, 30]. As a third possibility polarizing bifunctional activation, due to the dipole field of promoting

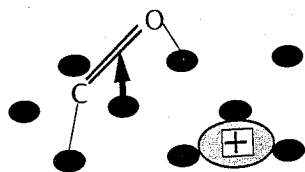


Fig. 5. Polarizing bifunctional promotion of a CO molecule dissociating on a surface (schematic). The arrow indicates increased electron backdonation.

cations may occur giving rise to an enhanced aldehyde residence time. This is sketched in fig. 5.

The promoting effect of alkali cations on the rate of methanol formation catalyzed by Cu, may also be due to chemical bifunctional promotion. NaOH and KOH are able to form mono-alkali formate upon reaction with CO at relatively mild conditions. Hydrogen dissociated by Cu may produce methanol by hydrogenation of the mono-alkali formate.

In summary three kinds of bifunctional promotion can be defined:

- polarizing-bifunctional promotion,
- direct-bifunctional promotion,
- chemical-bifunctional promotion.

Experimentally under catalytic conditions these conceptually different bifunctional promotion types are often difficult to discriminate. Firm experimental as well as theoretical evidence for polarizing bifunctional promotion under surface science conditions [22,31] exists.

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