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PROMOTION AND SUPPORT EFFECTS IN SYNGAS REACTIONS

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A short review is presented on the problems of selectivity in the syngas reaction. Attention is mainly given to the role of promoters in these reactions. Several mechanisms of promotion are critically reviewed and analyzed.

1. Introduction

Synthesis gas reactions on metals offer to a scientist, who is interested in fundamental problems of selectivity in catalysis, an interesting field to explore. Synthesis gas reactions lead to a great variety of products, therefore the selectivity problems are very important here. The product pattern can be influenced substantially by the choice of the metal, alloying (bimetallics formation) and the use of promoters. There are many open problems in all these directions.

Synthesis gas reactions can be directed into the three principal directions: (i) synthesis of hydrocarbons (ii) synthesis of methanol and (iii) synthesis of higher oxygen containing molecules (oxygenates). There are already some simple rules available concerning the manipulation of the selectivity.

a) The main mechanism of converting CO into CH_x units, can be characterized as a "dissociation(CO)-hydrogenation(C + H)" reaction, in contrast to the "hydrogenation-dissociation" reaction [1]. The CH_x units recombine by a step by step polymerization (this leads to the Flory-Schultz-Anderson distribution of products) into hydrocarbons. Pure, unpromoted and unsupported metals are sufficiently active and selective, but promoters are used to improve the performance of the practical catalysts [2]. The optimum catalysts are the metals which dissociate CO at the temperature of reaction or at a still lower one (Fe) [13]. Promoters are thus useful but not essential here.

b) There is no unambiguous evidence that an unsupported, unpromoted and chemically pure metal can catalyse the CH_3OH synthesis. There are some claims

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in this directions but it can be suspected that actually an unintentional promotion took place then. For example, by minute contaminants in the commercial supports when supported metals are used, or by oxides originated from the crystal holders (often oxidized Ta) when single crystals are tested etc. (see another paper by the authors in this issue). On the other hand, it has been established with Pd, Pt and Rh that the presence of unreduced M^{n+} centres, stabilized by the promoter (notice, that support can appear on the metal and play a role of a promoter [4]), is beneficial for the CH_3OH synthesis [5].

c) Pure metals don't produce any C2 + alcohols at all. They show in some cases (Rh) only a very low activity in aldehyde formation [6]. Higher alcohols are only produced, when the metal catalyst is promoted by a metal oxide, whereby "selfpromotion", such as by FeO_x on Fe etc. can also likely occur [6,7].

2. Phenomenology of promotion

There seems to be sufficient and convincing evidence available that various oxides promote dissociation of CO [8]. Of course, there is always [9] an optimum concentration of the promoter on the metal surface, probably corresponding with the maximum perimeter of promoter patches on the metal. Any further increasing of this concentration makes the blocking effect of the promoter (itself a compound not active in syngas reactions) to prevail. It is easy, to accept that the rate is simultaneously proportional to the perimeter length L and the fraction of the surface not covered $(1-\theta_p)$ by the promoter. The latter fraction supplies H_{ads}, CO_{ads}, and stored the intermediates:

$$\text{rate} = \text{const.}\ L(\theta_p)\cdot(1-\theta_p)\cdot f(p_{H_2}, p_{CO}).$$

The function $\theta_p(1-\theta_p)$ has a maximum at $\theta_p = 0.5.$ and $L(\theta_p)$ is a function with a maximum, too. As already mentioned above, the presence of promoters is indispensable when CH_3OH or higher alcohols have to be produced. With regards to the C_{2+} oxygenates, it is already clear that promoting oxides promote hydrogenation of aldehydes or ketons [10]. Another, but still open question is whether the CO-insertion step is promoted too.

The presence of promoters is certainly indispensable also in the synthesis of methanol. A discussion is still going on concerning the questions of what the promoters really do and what the active centres are. In particular, the discussion is vivid with regard to the commercial Cu catalysts. In the view of almost all commercial producers of CH_3OH synthesis catalysts, the promoters just stabilize proper dispersion and proper shape of the Cu^0 metal particles, see e.g. [11]. Some authors ascribe a more active role to the promoter (e.g. ZnO), such as generating hydrogen atoms or bearing active intermediates [12]. The French authors [13] favour the idea of a bifunctional catalysis: a metal (Pt, Pd) generates H_{ads} which, after a spill-over migration, reacts with CO on the support, whereby not all oxides are equally suitable to mediate the spill over migration. In principle, in Cu/ZnO systems a similar mechanism could be working.

3. Mechanisms of promotion

Some specific (and unique for the given case) mechanisms of promotion have been already mentioned above. However, there are also some more *general* suggestions in the literature on the mechanism of promotion, which need to be considered. Let us turn now our attention to them.

3.1. A THROUGH-THE METAL INTERACTION

In this line of thinking, several effects [a)–c)] are most frequently assumed to exist.

a) The promoting species changes the population of certain specific valence band orbitals (e.g. d-orbitals) of the metal particles and influences by that the adsorption (e.g. the binding by backdonation) and reactivity of CO or other intermediates.

b) The promoter causes a very limited shift of electrons to or out of the metal particles, whereby the additional (+) or (−) charge is "smeared out" over the particle, causing changes in its adsorption or catalytic properties.

c) The electrostatic potential created by the promoted species changes the properties of the particle, by an influence "through the metal". However, neither of these ideas are physically correct, as we shall see immediately.

Ad a) One can make approximate but sufficiently accurate calculations, (following the textbooks on solid state physics [14]), estimating how many electrons can be transferred between a metal and a semiconductor (support, or promoter). It is at maximum 1–3 electrons per 100 metal atoms on the interface. A cubic metal particle with 5 atoms at the edge can thus take or loose abt. 1 electron. This is to be compared with 1250 valence electrons totally involved with a metal like Pt.

Ad b) The additional charge stays localized near to the promoting species. This is nicely seen when inspecting the figures in papers by Norskov et al. [15]. These authors analyzed the case of e.g. Na atoms on a metal. In the real case of promotion by compounds, such as Na_2O, Na_2CO_3 or NaOH on the metal, the transfer of electrons into the metals (mostly assumed) is impossible from Na^+ and it is certainly limited also from "O" of the Na–O–species. The situation with an Na atom on a jellium metal is schematically shown in fig. 1.

Ad c) Several calculations show that the penetration of the electrostatic potential into the metal is minimal. It is spacially very much localized [16] due to the screening by the metal electrons. This, together with the argument concerning

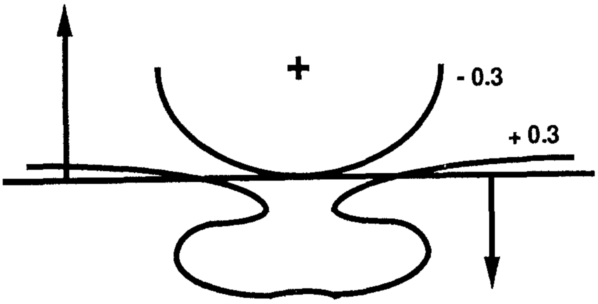

Fig. 1. Contour values for +0.3 V and −0.3 V of the electrostatic potential round an Na atom placed in (+) above a "jellium" metal. Potential is induced by electron transfer from Na into the metal. The arrow directed inside the metal represents 0.15 nm (to be compared with lattice plane distances in metals); the arrow directed out of the metal is on a distance of 0.35 nm from a centre of Na atom and by its length (0.25 nm) it indicates where the perpendicularly standing CO would (approximately) reach.

b) indicates that any transferred charge is unlikely to be uniformly "smeared out" over the whole particle.

There is, of course, *some* through-a-metal interaction possible between the co-adsorbed molecules. A similar interaction can be expected to occur also between the promoters and the molecules under the promoters' influence. Several authors have shown [17] that this is theoretically possible. However, one has to look on the *size* of these interactions [18]. Analysis of the relevant data shows that the through-the-metal interaction is in its strength comparable with the strength of the Van der Waals forces, or in any case, it is on the nearest neighbour place only a few percent of the chemisorption bond strengths of the influenced species. The same conclusion holds for the potential effects of the small changes of the density of states at the Fermi energy of the metal [19]. Calculations in [17] and [19] cover the same and thus the estimate in [18] universally holds.

3.2. A "THROUGH THE VACUUM INTERACTION"

There is two possibilities of promoting effects based on a sound physical bases: (i) an electrostatic field influence on the adsorbed species, and (ii) a localized chemical interaction between the promoter and the adsorbed species. Up to now, there is no direct evidence specifically confirming the role of these two mechanisms in the synthesis gas reactions, but both mechanisms are in general terms well proven. It is known that the electrostatic field influences slightly the population of the antibonding orbitals on adsorbate molecules, wherever these orbitals are present and are suitable for being populated by "backdonation" [20]. Furthermore, the dipole in the absorbed molecule can be strongly influenced [21]. Both of these effects can influence the reactivity of the adsorbed species.

Localized chemical interactions have been seen on promoted single crystal of Cu [22] and in the alkyl-shift (CO insertion) reaction (in metal carbonyls) upon promotion by Lewis acids [23]. The cation-Lewis acid influences CO on its "O"-end. It is only a speculation, but the authors of this paper think that the two last mentioned interactions play amongst others an eminent role in the formation of C_{2+} oxygenates. Interactions of this type can be involved in CO dissociation, CO insertion and hydrogenation of the –CH=O bond.

3.3. CREATION OF NEW SITES

Let us start with a list of some relevant facts.

(i) Addition to the metal of an oxide which is known to promote the CH_3OH synthesis, leads to a slower reduction and survival under mild conditions of metal ions. This is known for Pd [24,25], Rh [4,25] and Cu [26,27].

(ii) It is known that the positive charge on a metal stabilizes the potential intermediates of the synthesis. On the Pd^+ ion it stabilizes the formyls [28] and on the Cu^+ ion, it could be the molecularly adsorbed CO [29] what is stabilized.

(iii) For Pd, a good correlation exists between the activity in the methanol synthesis and the concentration of the Pd^{n+}-ions (most likely, Pd^+). As far as Cu is concerned, the authors [11] say that the activity is proportional in the Cu^0 metal surface. However, in their experiments a constant fraction of the Cu surfaces, after reaction with a given constant constant of CO_2 was always covered by Cu^{n+} species. So, a similar correlation, like for Pd, that is with Cu ionic content, might hold here too. It has been shown that for CO_2 free mixtures, the activity of Cu/ZnO was proportional to Cu^+ concentration in ZnO [12a] and in mixtures containing CO_2, the activity might be proportional to *all* Cu^+ centres, including those formed in the presence of CO_2 and those present before the reaction.

It is then, of course, very temptating to relate the facts under (i) to (iii) and to conclude that the role of the promoter is to create and preserve reaction centres (M^{n+}) which bear the essential intermediates. In this picture the role of any M^0 in the system would mainly be to supply atomic hydrogen. Also some oxides (Cr_2O_3, ZnO) can contribute to the activation of molecular hydrogen.

4. Concluding remarks

An attempt has been made above to cathegorise and to critically analyse some data and ideas concerning promotion in syngas reactions. It is also important to realize that probably in many papers in literature, one worked with un-intentionally promoted catalysts. This is certainly true for the Rh [16] and the Cu catalysts (see another paper by the authors in this issue). Since during the preparation of the catalysts, many support materials get dissolved, and after the reduction oxidic species from the support appear on the metal [4], the often observed support-effects can actually be unrecognized effects of promotion.

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