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From the Molecular Level to Chemical Engineering Models in Heterogeneous Catalysis. New Discoveries and Their Impact

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Overview

Important phenomena in catalysis are attributed to surface mobility, changes of surface structure and spillover processes. On the other hand, modifying (so-called 'doping') substances and often several phases are included in the majority of the most active catalysts. We examine here the role of mobility phenomena in modifying many aspects of the dynamics of catalytic reactions: activity, selectivity, bistability and ageing. The role of surface mobility is emphasized, especially in the cooperation between different phases or surface domains of different composition.

Oxidation of CO on a Cu-Modified Pt(111) Phase

In certain ranges of experimental conditions, the oxidation of CO on Pt(111) exhibits bistability. For example, when the CO pressure (p_{CO}) is raised from a low value, the reaction rate increases and then drops abruptly at p_{COmax} . When diminishing p_{CO} from high values, the high rates are recovered only at a pressure (p_{COmin}) well below p_{COmax} . The reason is that a compact adsorbed CO layer can form at high p_{CO} , preventing the dissociative adsorption of molecular oxygen.

Dissociatively adsorbed oxygen on Cu(111) islands epitaxially deposited on Pt(111) can trigger the oxidation of CO adsorbed on Pt(111), in conditions where pure Pt(111) is poorly active. In experiments with decreasing p_{CO} , the high rate regime is attained for values higher than

p_{COmin} . A reaction front expands from Cu to the whole Pt surface [1]. The reason is that small amounts of adsorbed O-atoms on Cu(111) cross the Cu/Pt border, react with the CO-saturated Pt(111) surface and thus create vacancies in the close-packed CO adlayer. Pairs of vacancies permit the dissociative adsorption of O_2 . A diffusion-reaction front progresses across the

whole Pt(111) surface, restoring the high rate. Other experiments show that very low Cu coverages on Pt(111) increase the rate of front propagation. This demonstrates that doping with Cu has two different effects: *i*) triggering the reaction and *ii*) accelerating it when the system is in the low activity bistability branch.

Cooperation between Phases in Selective Oxidation (Remote Control)

Spillover (S.O.) is defined as a phenomenon in which a mobile surface species formed on one phase migrates and jumps onto (spills over on) a different surface. S.O. species bring about special effects in catalysis [2][3], particularly the creation of catalytic sites [3]. The most conspicuous result is a very strong synergy between two or several distinct phases such as the one observed between $\alpha\text{-Sb}_2\text{O}_4$ (emitter of $\text{O}_{\text{S.O.}}$) and SnO_2 in the selective oxidation of isobutene to methacrolein (Fig. 1). The pure compounds give only CO_2 and H_2O , but a substantial yield in

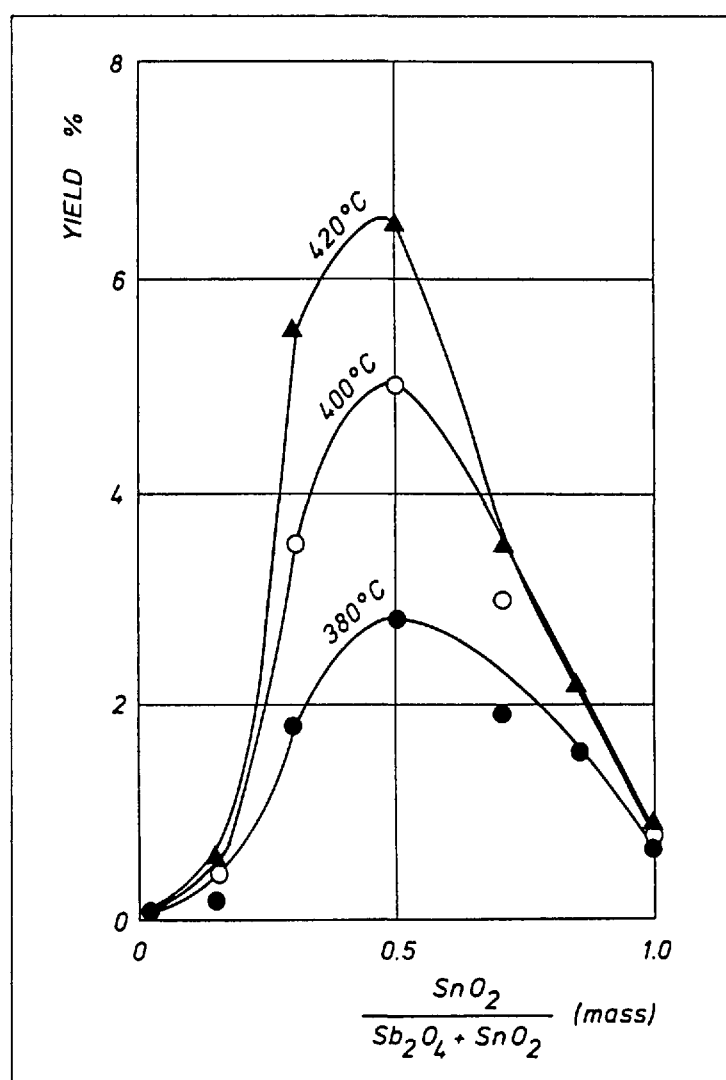


Fig. 1. Methacrolein yield in the oxidation of isobutene, as a function of catalyst composition. Same conditions and overall weight of $\text{Sb}_2\text{O}_4 + \text{SnO}_2$ in all experiments [4].

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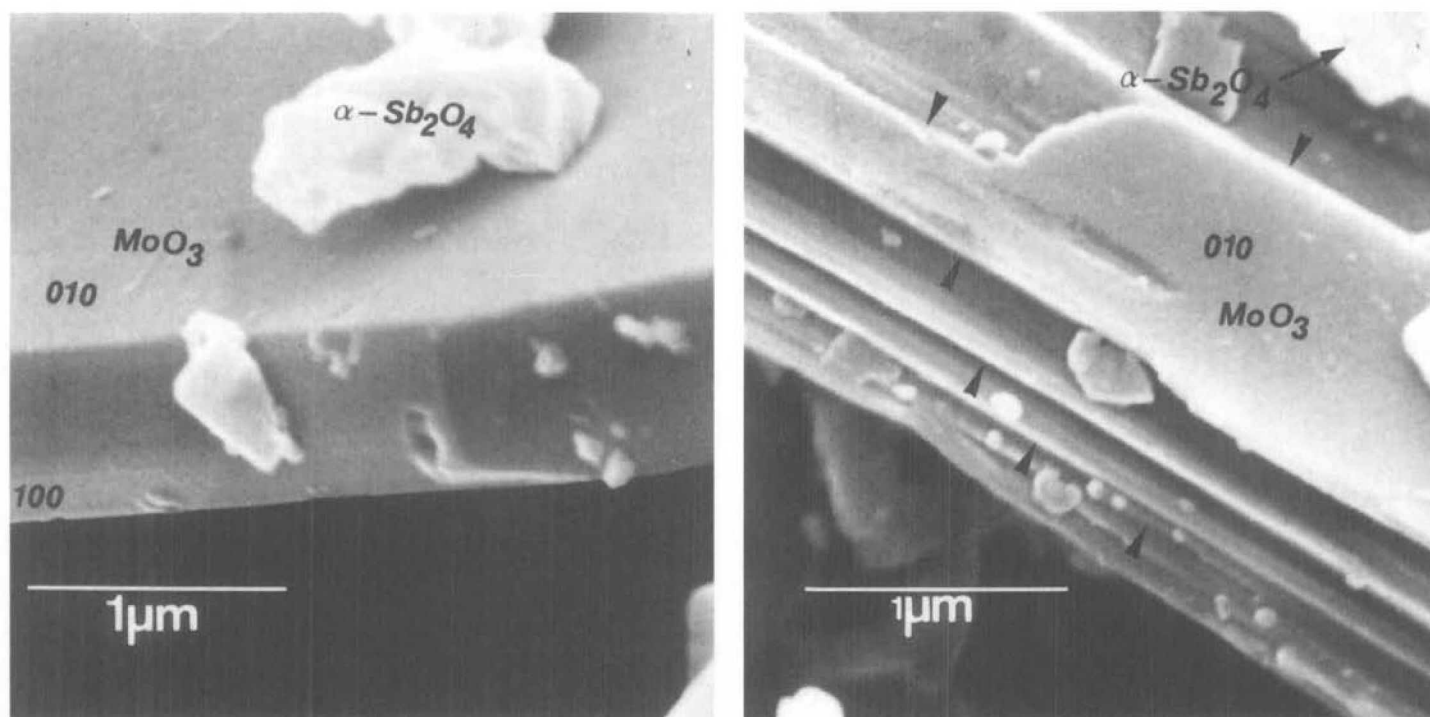


Fig. 2. Scanning electron microscopy pictures of $\text{MoO}_3 + \alpha\text{-Sb}_2\text{O}_4$ mixture: a) before test, b) after reaction, in the oxidation of isobutene to methacrolein. The crystallite of pure MoO_3 after test remains identical to that of micrograph (a) [6].

acrolein is observed when particles of the separately prepared oxides are gently mixed together [4]. Such effects are observed for 30 couples of mechanically mixed oxides active in almost all sorts of selective oxidations [4][5].

In many practical catalysts, one phase has little or no activity of its own. A typical example of such a phase is $\alpha\text{-Sb}_2\text{O}_4$. Such a special phase produces spillover oxygen $\text{O}_{\text{S.O.}}$. The role of $\text{O}_{\text{S.O.}}$ is to keep the surface of the catalytically active phase (e.g. SnO_2 and, still more typically, MoO_3) in a high oxidation state. This, in turn, stabilizes the adequate coordination of the active atom (e.g. in corner-linked MoO_6 octahedra) [3][4]. The concept led, among others, to the prediction that the surface of MoO_3 crystallites should reconstruct differently during a catalytic reaction, according to the presence or not of spillover oxygen $\text{O}_{\text{S.O.}}$. This was proven directly [6][7]: MoO_3 crystallites get faceted in the presence of $\text{O}_{\text{S.O.}}$ (Fig. 2) and AFM (= Atomic Force Microscopy) shows special structural features which probably maximize the exposition of surfaces with the structure of the (100) face, known to be selective in allylic oxidation.

A mathematical model based on the classical Mars-van Krevelen mechanism, but taking into account diffusion of S.O. species and the remote control process, gives the reaction rate per unit weight of catalyst of varying composition, R_m (weight ratio of the potentially active phase in the mixture):

$$\text{rate} = F_{\text{rc}}(R_m, p_{\text{O}_2}, p_{\text{HC}}, T) \cdot \frac{k_{\text{red}} p_{\text{HC}} \cdot k_{\text{OX}} p_{\text{O}_2}^{0.5}}{k_{\text{red}} p_{\text{HC}} + k_{\text{OX}} p_{\text{O}_2}^{0.5}}$$

where k_{red} and k_{OX} are the rate of reduction and reoxidation of the catalyst surface, and p_{O_2} , p_{HC} the partial pressures of oxygen and hydrocarbon reactant, respectively [8]. A comprehensive dynamic model permits the calculation of function F_{rc} [9]. The above equation is the first published in scientific literature representing in a comprehensive, nonempirical way the influence of gas composition, temperature and catalyst composition.

Hydrotreating Reactions

A similar remote control plays an extremely important role in the various reactions involved in the hydrotreating of petroleum-derived products. A global vision of the state of the working catalyst at the atomic level can also be developed. The model has been extremely fruitful for discovering new catalyst formulations, new architecture of catalyst pellets, new kinetic models. This leads to new chemical engineering concepts [10][11].

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