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 $P_{CO_{\text{max}}}$ When diminishing $P_{CO}$ from high values, the high rates are recovered only at a pressure ($P_{CO_{\text{min}}}$) well below $P_{CO_{\text{max}}}$. 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 $P_{CO_{\text{min}}}$. 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 Cu-Sb$_2$O$_4$ (emitter of O$_{\text{so}}$) and SnO$_2$ in the selective oxidation of isobutene to methacrolein (Fig. 1). The pure compounds give only CO$_2$ and H$_2$O, but a substantial yield in

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{methylacrolein.png}
\caption{Methylacrolein yield in the oxidation of isobutene, as a function of catalyst composition. Same conditions and overall weight of Sb$_2$O$_4$ + SnO$_2$ in all experiments [4].}
\end{figure}

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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 $\alpha$-Sb$_2$O$_4$. Such a special phase produces spillover oxygen Os.o. The role of Os.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$_3$ 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 Os.o. This was proven directly [6][7]: MoO$_3$ crystallites get faceted in the presence of Os.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, $R_{\text{in}}$ (weight ratio of the potentially active phase in the mixture):

$$\text{rate} = F_{\text{rc}}(R_{\text{in}}, P_{O_2}, P_{\text{HC}}, T) \cdot \frac{k_{\text{red}} P_{\text{HC}} \cdot k_{\text{ox}} P_{O_2}}{k_{\text{red}} P_{\text{HC}} + k_{\text{ox}} P_{O_2}}$$

where $k_{\text{red}}$ and $k_{\text{ox}}$ are the rate of reduction and reoxidation of the catalyst surface, and $P_{O_2}$, $P_{\text{HC}}$ the partial pressures of oxygen and hydrocarbon reactant, respectively [8]. A comprehensive dynamic model permits the calculation of function $F_{\text{rc}}$ [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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