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Study of surface reaction mechanisms by $^{16}O/^{18}O$ and H/D isotopic exchange

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Abstract

Surface diffusion of active species is a general phenomenon in catalysis: rates of migration often being much higher than turnover frequencies of reaction, surface species can migrate and visit a great number of active sites in between two successive catalytic cycles. $^{16}O/^{18}O$ and H/D isotopic exchange is a very useful technique to elucidate reaction mechanisms involving mobility steps of O- and H-containing reactive species. The method is based on the measurement of the rates of exchange between gaseous $^{18}O_2$ (or D_2) and ^{16}O species (or OH) species of the support via metal particles, small metallic clusters acting as porthole of O or H on the support. Simple kinetic models allow to calculate surface and bulk diffusivities on the oxide used as support. As a rule, a significant O mobility can only be observed above 200 °C for most oxides. Furthermore, very great differences of diffusivity (five orders of magnitude) are recorded between silica (on which OH groups are virtually immobile) and oxides like ceria exhibiting a very high oxygen mobility. Differences of diffusivity (two orders of magnitude) are much less for hydrogen than for oxygen. This method can give useful information about reactions catalyzed by metal/oxide systems in which surface diffusion can play a decisive role in the mechanism: steam reforming, water gas shift, hydrocarbon oxidation, aromatic hydrogenation, methanol synthesis, coke formation). For oxides such as $Ce_xZr_{1-x}O_2$ mixed oxides, O mobility is so high that surface and bulk mobility can no longer be distinguished. More complex kinetic models requiring computer simulation of *all the steps* of adsorption, desorption, diffusion and exchange simultaneously have been developed.

Keywords: Surface diffusion; $^{18}O/^{16}O$ and H/D isotopic exchange; Rh catalysts; Rh/CeO_2 catalysts; Water gas shift; Steam reforming; Catalytic hydrocarbon oxidations

1. Introduction

Let us consider a heterogeneous catalytic reaction A + B in gas or liquid phase. In what follows, pore diffusion is a sufficiently fast process to have no impact on the apparent rate of reaction. One of the most popular approach for describing the catalytic reaction is the Langmuir–Hinshelwood mechanism controlled by the surface reaction between A_{ads} and B_{ads}. The two molecules can react if and only if they are adsorbed on adjacent sites (Fig. 1a). The rate is given by Eq. (1):

$$r = k\bar{C}_A \times p_B \tag{1}$$

where $\bar{C}_A$ is the surface concentration of molecule A and p_B is the probability to find a molecule B in a position adjacent to A_{ads}. Let θ_A and θ_B be the surface coverages of A_{ads} and B_{ads} and N_S, the number of surface sites, then we have: $\bar{C}_A = N_S\theta_A$ and $p_B = \theta_B$ provided that A_{ads} and B_{ads} are statistically distributed at the surface. Eq. (1) becomes:

$$r = kN_S\theta_A\theta_B \tag{2}$$

This is the classical expression of the rate derived from a LH mechanism with surface reaction as rds. In Fig. 1a, A_{ads} and B_{ads} are supposed to be immobile on the surface: they can react or they desorb.

2. The concept of surface diffusion in heterogeneous catalysis

If the rate of surface diffusion is sufficient, B may adsorb and react on molecules A in non-adjacent positions. By analogy

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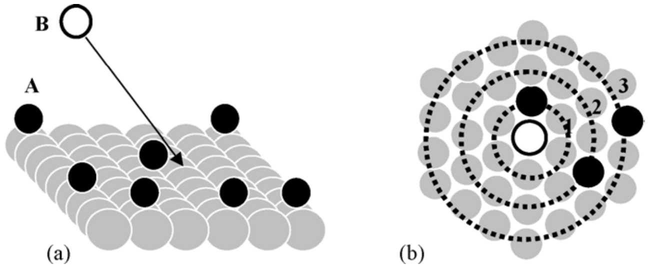

Fig. 1. Catalytic reaction A + B on a metallic surface: (a) classical Langmuir–Hinshelwood model without surface diffusion: A does react with B only if B adsorbs on adjacent positions; (b) model with surface diffusion: B can react with molecules A located in the first sphere of reaction or, after diffusion, with molecules A located in the second, third, ... spheres.

with coordination chemistry, we can define one or several spheres of reaction (Fig. 1b).

Small metallic or oxide clusters used in heterogeneous catalysis are typically of 1–10 nm in size. In most cases, turnover frequencies (TOF) are comprised between 0.1 and a few $(\text{second})^{-1}$, which means that the duration τ of one catalytic cycle is comprised between 0.1 and 10 s. Under these conditions, diffusion rates are often higher or much higher than the reaction rates themselves. To demonstrate this, let us compare the mean size of the spheres of reaction (equal to the particle size at the most) and the distance l covered by the diffusing species during one catalytic cycle. Many reactions on metals involve atomic species of hydrogen or oxygen with coefficient of surface diffusion D_s in the order of $10^{-8}\ \text{m}^2\ \text{s}^{-1}$ for hydrogen and of $10^{-10}\ \text{m}^2\ \text{s}^{-1}$ for oxygen [1]. Distances l covered by diffusing species during a time t are given by Eq. (3):

$$l = \sqrt{D_s t} \qquad (3)$$

which shows that H and O atoms may migrate over distances around 10^{-4} and 10^{-5} m for 1 s, i.e. over distances much greater than the particle sizes currently encountered in catalysis. Actually, the rates of diffusion are extremely high on metals, each hydrogen or oxygen atom being able to ‘‘visit’’ all the surface sites of every particles in a time much smaller than the reaction time (duration of a catalytic cycle).

3. Some examples of reactions involving surface diffusion steps

3.1. Water gas shift and steam reforming

Water gas shift (WGS, Eq. (4)) and steam reforming (SR, Eq. (5)) may obey mechanisms involving surface diffusion as rate determining steps over certain supported metal catalysts:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (4)$$

$$C_nH_m + 2nH_2O \rightarrow nCO_2 + \left(2n + \frac{m}{2}\right)H_2 \qquad (5)$$

Two kinds of mechanisms are generally admitted for the WGS reaction: (i) dissociative mechanisms (either via H_2O or CO dissociation) and (ii) associative mechanisms. In this latter type of mechanism, CO would be adsorbed on the metal while H_2O would be activated on the support on which reactive OH species are formed. Formate species [2–4] (or in some instance, special carbonate species [5,6]) are then produced by *association* of CO_{ads} and OH_{ads}. In the final step, the formates decompose into CO_2 and H_2. Depending on the sites (metal or support) where the formate species are formed and decomposed, the mechanism may involve OH, CO or formate surface diffusion between metal and support sites (or vice versa).

Copper appears to be the most active metal in this reaction, which justifies its use in industrial processes ($Cu/ZnO/Al_2O_3$ catalysts [7–9]). This is a reaction sensitive to the nature of the support: Pt and Rh catalysts are much more active when they are supported on alumina than on silica or carbon [2]. A similar support-sensitivity was reported by Barbier and Duprez [10] and Panagiotopoulou and Kondarides [11,12] who showed that the activity of Pt catalysts was in the order: $Pt/CeO_2 \gg Pt/Al_2O_3 \gg Pt/SiO_2$. In every case, differences of one or two orders of magnitude in activity were observed between the different supports. The mechanism proposed by Grenoble et al. (Fig. 2) is based on the observation that formates or formic acid decompose mainly into $CO + H_2O$ on metals or on basic sites while they decompose into $CO_2 + H_2$ on acid sites. Owing to selectivity of transformation, formates species appear as likely intermediates in the WGS reaction.

Steam reforming over Rh catalysts obeys a mechanism largely depending on OH group mobility on the support. Table 1 summarizes the results obtained by Duprez et al. [13–15] and by Grenoble [16] in aromatic steam dealkylation.

The reaction is not very sensitive to the nature of metal: there is less than one order of magnitude between the activity of the most active metal (Rh) and that of the less active metal (Ir). Contrasting with this catalyst behavior, the reaction is strongly sensitive to the nature of support, specially with Rh: there are at least three orders of magnitude differences between Rh/Cr_2O_3 and unsupported rhodium. Excepted in this later case, all the supported Rh catalysts had similar dispersions, which confirm that support effects are not due to particle size effects. The mechanism proposed for this reaction is a *bifunctional* mechanism involving active sites of metal (M) for hydrocarbon activation and active sites of support (S) for water activation. The support must be considered here as an active phase of the catalysts. It should be hydrophilic and should possess very mobile OH groups. The final step is a reaction between HC fragments and OH’s on the metal [13,16].

The kinetic derivation of this mechanism including a limiting step of OH transfer from the support to the metal led to the following expression of the TOF on Rh catalysts [13]:

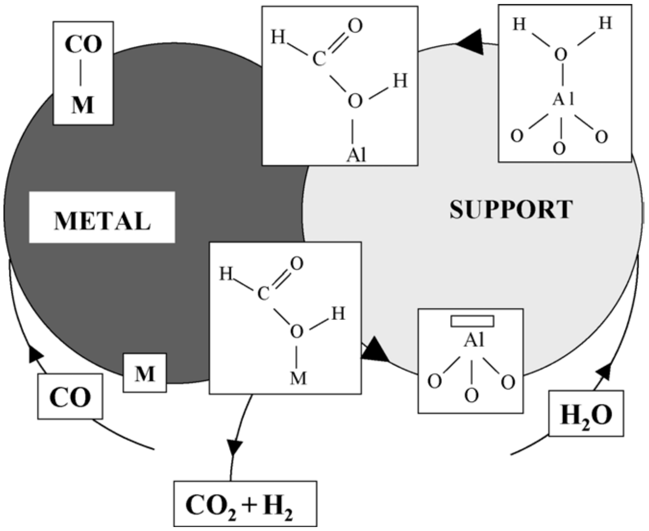

Fig. 2. Associative mechanism of WGS with formate intermediates. CO is adsorbed on the metal. Formates species are produced by insertion of CO in OH groups of the support. They are decompose into $CO_2 + H_2$ on the metal (after Ref. [2]).

$$\mathrm{TOF} = \frac{r}{M_0} = K(S_0^2 I_0)^{1-n} P_\mathrm{T}^n P_\mathrm{W}^{m(1-n)} \tag{6}$$

where P_T and P_W are the partial pressures in toluene and water; r the reaction rate (mol h^{-1} g^{-1}); M_0 the metal site density; S_0 the support site density and I_0 is the perimeter of the metal particles (per gram of catalyst). The specific perimeter is given by:

$$I_0 = \beta x_\mathrm{m} D^2 \tag{7}$$

where β is a parameter depending on the particle shape, x_m the metal loading and D its accessibility (%). On Rh catalysts, the kinetic order with respect to toluene n is close to zero [13,16] while that with respect to water is close to 0.5. Turn over frequencies should then be proportional to I_0. This was verified on some series of Rh catalysts of different loading and dispersion [13,17]. Eq. (6) was also proved to represent satisfactorily the rates of n-heptane steam reforming reported by Kikuchi et al. [18].

Table 1
Activity of metals and support effect in toluene steam dealkylation

Metal/Al_2O_3	Relative TOF	Rh/support	Relative TOF
Rh	100	Cr_2O_3	300
Pd	28	Al_2O_3	100
Pt	18	TiO_2	20
Ni	17	SiO_2	10
Co	15	C	1
Ru	14	Rh black	0.1
Ir	13		

Reaction conditions: 440 °C, 1 atm, H_2O/toluene molar ratio = 7 (from Ref. [15]).

3.2. Mild oxidation reactions

Mild oxidation reactions are also good examples of reactions that may imply mobility of reactive oxygen species. The classical Mars–Van Krevelen mechanism is per se a mechanism involving O migration. Hydrocarbons are accommodated on oxometallic sites (C sites) by hydrogen abstraction. Adsorbed HC (often allylic species) are then selectively oxidized by oxo species from the solid, which gives rise to oxygenated products (aldehydes, ketones, acids, . . .) and anionic vacancies. In the final step, the anionic vacancies are filled in by O^{2-} coming from accommodation sites of gaseous dioxygen (O sites). As C sites and O sites are not (forcedly) in adjacent positions, an oxygen flux should occur through the catalyst or at its surface to allow O sites to feed C sites with reactive oxygen species. An example is given in Fig. 3 for the mild oxidation of propene into acroleine over bismuth molybdate catalysts [19].

The catalytic cycle is shown here with propene and oxygen activation steps on adjacent Bi–O–Mo entities. It is known however that the sites where dioxygen is adsorbed are not identical with the sites where lattice oxygen are consumed: the role of oxygen lattice diffusion [20], the specificity of basal faces of MoO_3 in orientating the reaction [21–23] and the cooperation between phases (MoO_3 with antimony oxides, iron molybdates or iron-cobalt molybdates with bismuth molybdates) [24–26] are proofs of the multi-site Mars and Van Krevelen mechanism. In many mild oxidation reactions, a good balance between acid–base and redox properties is required for a good activity and selectivity of the catalysts, which underlines the complexity of the solids used in these reactions [27].

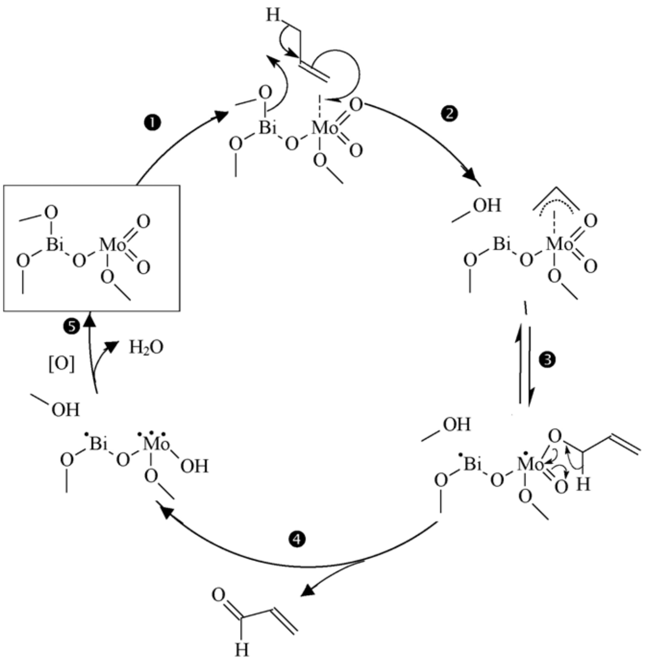

Fig. 3. Mechanism of oxidation of propene into acroleine over bismuth molybdate catalysts. After adsorption (step 1) and H abstraction (step 2), the allylic species is oxidized into acroleine (step 3) which is desorbed (step 4). Step 5 corresponds to O activation of the catalyst by refilling of the anionic vacancies.

3.3. Total oxidation in automotive converters or in combustion

Transient oxidation reactions in automotive converters are known to take advantage of the ability of certain components of the catalysts to store oxygen (when it is abundant in gas phase) and to release it (when the O_2 concentration decreases in gas phase). This property of three-way catalysts, named oxygen storage capacity (OSC) involves fast oxygen transfer between metal particles and oxide phases (typically CeO_2-based components) storing oxygen [28]. Ceria is now replaced by $Ce_xZr_{1-x}O_2$ mixed oxides with much higher thermal resistance and OSC properties [29,30]. Fig. 4 compares the OSC properties of CeO_2 and $Ce_{0.68}Zr_{0.32}O_2$ oxide. It was shown that the excellent storage capacity of $Ce_xZr_{1-x}O_2$ oxides was linked to the bulk oxygen mobility much higher in mixed oxides than in ceria.

3.4. Reactions and processes involving H mobility

Hydrogenation of aromatic hydrocarbons over metal catalysts is generally considered as structure insensitive, turnover frequencies on a given metal being virtually independent from the particle size. However, many studies have shown that the reaction might be sensitive to the nature of support: for instance, Rh/Al_2O_3 is almost four times more active than Rh/SiO_2 in benzene hydrogenation [31]. Similar trends were observed by Vannice and Vasiur Rahaman in the hydrogenation of benzene, toluene and xylene over Pd [32] and Pt catalysts [33]. To explain these results, Vannice et al. proposed that aromatic hydrocarbons could be adsorbed on support acid sites in the vicinity of metal particles and then react with spilled-over hydrogen. Experiments carried out over mechanical mixture of Pt/Al_2O_3 and alumina led to a similar conclusions [34]. This concept resembles the concept of spheres of reaction depicted in Fig. 1 with an extension of the metal site area to a contiguous domain of the support around each metal particles.

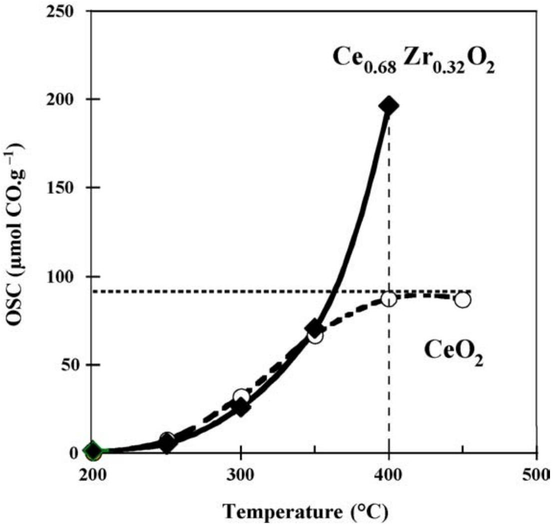

Fig. 4. Oxygen storage capacity of ceria and cerium-zirconium oxide. OSC is limited to one monolayer over ceria while almost all the bulk of $Ce_{0.68}Zr_{0.32}O_2$ can be involved in the oxygen storage process.

The role of H spillover in methanol synthesis was investigated by isotopic exchange methods by Jung and Bell [35]. Adsorbed water inhibits H_2 dissociation on ZrO_2 but not on Cu. The authors concluded that water facilitates the transport of H(D) atoms formed on the surface of Cu across the surface of ZrO_2 as a consequence of hydrogen bonding between adsorbed H_2O and HO–Zr groups. H(D) transport from Cu to zirconia plays a decisive role in formate species formation on zirconia, which is a key-step in the final step of methanol formation.

Coking of supported metal catalysts by cyclopentane is another example of the specific role of H spillover in catalysis. Cyclopentane (CPA) dehydrogenates over Pt/Al_2O_3 into cyclopentene (CPE) and cyclopentadiene (CPD), which polymerizes into coke molecules on acid sites of the support [36,37]. If the unique role of Pt were to dehydrogenate cyclopentane, the same amount of coke would be produced by reaction of alumina with an equilibrated mixture CPA/CPE/CPD. This is not the case: much more coke is formed by reaction of cyclopentane with Pt/Al_2O_3 than by reaction of a mixture CPA + CPE + CPD on bare alumina. There is another effect of Pt on coke formation, which was ascribed to coke consolidation by deep dehydrogenation of the CH_x polymeric species. This dehydrogenation step is largely favored by H back-spillover from the CH_x/Al_2O_3 species to Pt particles. In the absence of Pt, H back-spillover could not occur and hydrogen atoms remains confined on the support, which leads to a severe inhibition of coke formation.

4. Measurement of O and H mobility by isotopic exchange

To validate the possible role of O or H mobility in catalytic processes, it is necessary to have a confident measurement of surface and bulk coefficient of diffusion. The principle of the measurement is based on the exchange between gaseous $^{18}O_2$ and ^{16}O species of the support via the metal particles [38,39]. Gaseous oxygen molecules should be in equilibrium with adsorbed oxygen species on the metal. These species diffuse on to the support through the metal/support interface.

MS analyses of oxygen isotopomers allow to determine the fraction α_g of ^{18}O atoms in gas phase and to calculate the number Ne of exchanged atoms as a function of time t. The evolution of Ne with $\sqrt{t}$ (Eq. (8)) leads to the coefficient of surface diffusion D_s provided that two conditions are fulfilled: (i) adsorption/desorption of O_2 on metal particles should be very fast; (ii) direct exchange of O_2 with the support should not occur at a significant rate at T(K).

$$\mathrm{Ne} = \frac{2}{\sqrt{\pi}} C_{\mathrm{m}}^{18} I_0 \sqrt{D_s t} \tag{8}$$

I_0 is the length of the metal/support interface, i.e. the total perimeter of the metal particles per m^2 of catalyst, and C_{m}^{18} is the surface concentration (at m^{-2}) of ^{18}O atoms on the metal.

Eq. (8) is the integral form of the Fick's law for a surface diffusion around metal particles assimilated to circular sources. If the metal dispersion and loading are $D\%$ and $x_m\%$, respectively, the specific perimeter of the particles is given by Eq. (7). For cubic or hemispherical particles and for most metals, $10^5 < \beta < 10^6\ \mathrm{m\ g^{-1}}$ [38], which gives values of I_0 in the range of 10^7 to $10^9\ \mathrm{m\ g^{-1}}$ for conventional metal catalysts (≈0.5% metal; 50% dispersion). This extraordinary high length can explain the impact of surface mobility in bifunctional catalysts with sites A on the metal and sites B on the support or at the metal/support interface, e.g.: Pt/CeO_2 [40] and Pd/CeO_2 [41] in dynamic oxygen storage, Au/ZrO_2 in CO oxidation [42], Rh–Cu/$ZrCeO_x$ in TWC reactions [43], Pt/$ZrCeO_x$ in CH_4 partial oxidation [44].

At higher temperatures, surface diffusion is very fast and bulk diffusion (coefficient D_b) can be observed. The whole surface (metal + oxide) being in equilibrium with the gas phase, the following equation can apply for calculating D_b:

$$-\mathrm{Ln}\,\frac{\alpha_g}{\alpha^*} = \frac{2}{\sqrt{\pi}}\,\frac{\rho A}{N_g}\,\sqrt{D_b t} \qquad (9)$$

α^* is the value of α_g at the beginning of bulk exchange (after full exchange of the surface), ρ the atomic density of the solid, A the BET area of sample and N_g is the number of O atoms in gas phase.

The results obtained on a series of Rh/oxide catalysts are represented on Fig. 5. Very great differences can be observed: O mobility is very fast on ceria while, at the opposite, silanol groups are virtually immobile. These results explain why silica is a very poor support for reactions involving OH mobility (SR, WGS, certain oxidation reactions) while ceria is an excellent support for these reactions.

As a rule H diffusion is observed at much lower temperatures than O diffusion (20–100 °C) [45] as confirmed by quantum chemistry computation [46].

The simple models leading to Eqs. (8) and (9) are valid for oxides not exchanging oxygen at a very fast rate. In the case of oxides with very high O mobility, such as $Ce_xZr_{1-x}O_2$ oxides, oxygen exchange is so fast that surface and bulk diffusion cannot be discriminated. Fick's law has to be integrated simultaneously at the surface and in the bulk. A more complex kinetic model has been developed to calculate D_s and D_b for these oxides [47,48].

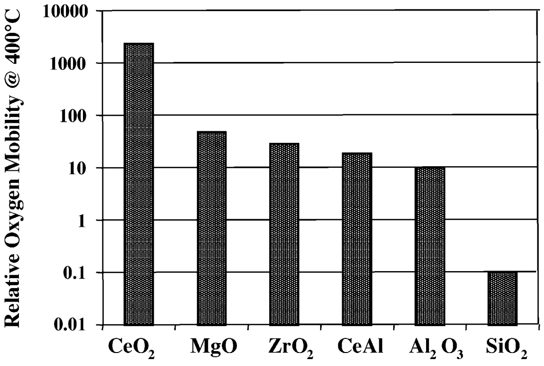

Fig. 5. Relative oxygen mobility at 400 °C on different oxides (base 10 for alumina, $D_s = 2 \times 10^{-18}\ \mathrm{m^2\ s^{-1}}$). CeAl is a 10% CeO_2/Al_2O_3 oxide. The coefficients of surface diffusion were measured with Rh as O porthole on the oxides.

5. Conclusions

Many reactions obey mechanisms involving surface diffusion of intermediates or reactive species. Therefore, additional terms representing surface diffusion steps should be added to the classical ''Langmuir–Hinshelwood'' mechanisms. Isotopic exchange is a powerful technique for the measurement of coefficients of surface and bulk diffusion in oxides. This technique can give useful information on the diffusing species (specially superoxides and peroxides). However, other techniques (FTIR, Raman, RPE, RMN) should be coupled to isotopic exchange to fully identify these species.

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