Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

1. CO reverse-spillover effect on CO oxidation

The reverse-spillover of CO has an important effect in CO oxidation on supported clusters. It corresponds to the capture by the metal clusters of CO molecules physisorbed on the support. The reverse spillover phenomenon is illustrated on figure SI-1.

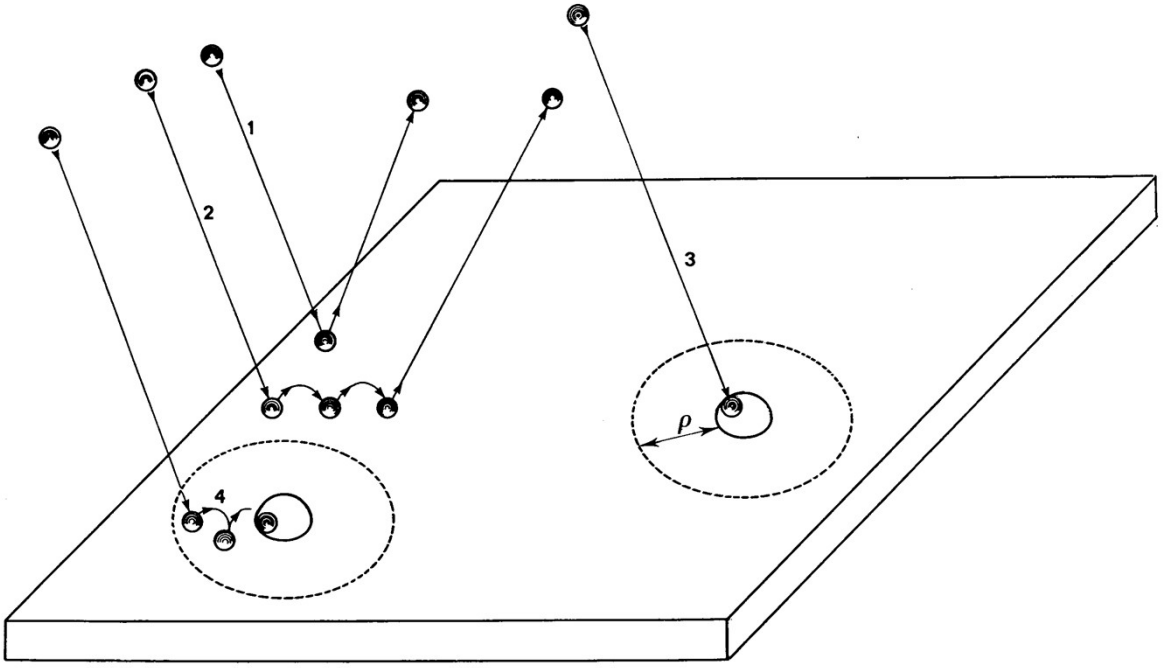

Figure SI1-1: Illustration of the reverse spillover phenomenon. CO molecules impinging on the sample surface can be either reflected (1), physisorbed on the substrate where they diffuse before desorbing (2) or they directly chemisorb on a metal cluster (3). There is a second channel for CO molecule to chemisorb on metal cluster: during its diffusion travel on the substrate, a physisorbed CO molecule can be captured by a metal cluster (4). One can define around each cluster a capture zone, of width ρ, where all physisorbed CO molecule will become chemisorbed on the metal cluster.

Qualitatively, it increases the flux of CO molecules arriving on the clusters. This extra CO flux increases when the size of the clusters decreases or when the substrate temperature drops and it decreases when the distance between the clusters becomes equal or smaller than the mean diffusion length (Xs) of CO molecules on the substrate. An analytical solution of this problem, taking into account the competition between clusters for the capture of CO molecules diffusing across the support surface,

has been given for the first time by C.R. Henry [1]. The ratio of the TOF for supported clusters (TOF_{clus}) and the TOF without the effect of the reverse spillover of CO (TOF_{cor}) is given by the following relation:

$TOF_{clus}/TOF_{cor} = 1+\alpha Xs\ P(x,y)\ /R$

With $P(x,y) = [\ I_1(y)K_1(x)- K_1(y)I_1(x)] / [I_0(x)K_1(y) + I_1(y)K_0(x)]$

I_i and K_i are the modified Bessel function of *i*-th order and x= R/Xs, y = L/Xs;

R is the cluster radius, L is the half-distance between neighboring clusters and α is the adsorption probability of CO on the clean support,

$Xs = a_0 \exp(E_a-E_d)/2kT$.

E_a and E_d are the adsorption and the diffusion energies of a CO molecule on the support surface, k the Boltzman constant, T the substrate temperature and a_0 the distance between to neighboring adsorption sites on the support.

This model has been already applied for Pd clusters on alumina ultrathin films on Ni_3Al (111) [2]. For this system, we have derived the value of the following parameters:

E_a-E_d = 0.15 eV, α = 0.4.

At 533 K, Xs is equal to 2.04 nm. The width of the capture zone, ρ , is close to Xs. The density of clusters (n_s= $6.5x10^{12}$ cm^{-2}) is given by the lattice parameter of the dot structure of alumina ultrathin film (4.1 nm). For clusters containing 180 atoms the radius is 1.08 nm, the distance between two neighboring clusters being 4.1 nm one immediately see that the collection zones overlap (1.08+2.04 > 4.1/2) even for 19 atoms clusters for which the radius is 0.6 nm there is a strong overlap of the capture zones. In these conditions, for each cluster sizes, the spillover effect reaches a maximum value [2]. However when cluster size decreases the reverse-spillover effect becomes more important.

The following table gives the values TOF_{clus}/TOF_{cor} as a function the mean radius of the clusters.

N	19-34	35	50	80	180
R (nm)	0.60	0.63	0.71	0.83	1.08
TOF_{clu}/TOF_{cor}	2.51	2.39	2.13	1.86	1.51

From the table we see effectively that the effect of the reverse spillover decreases when the cluster size increases, then the reverse spillover cannot be at the origin of the increase of the TOF observed in the experiments.

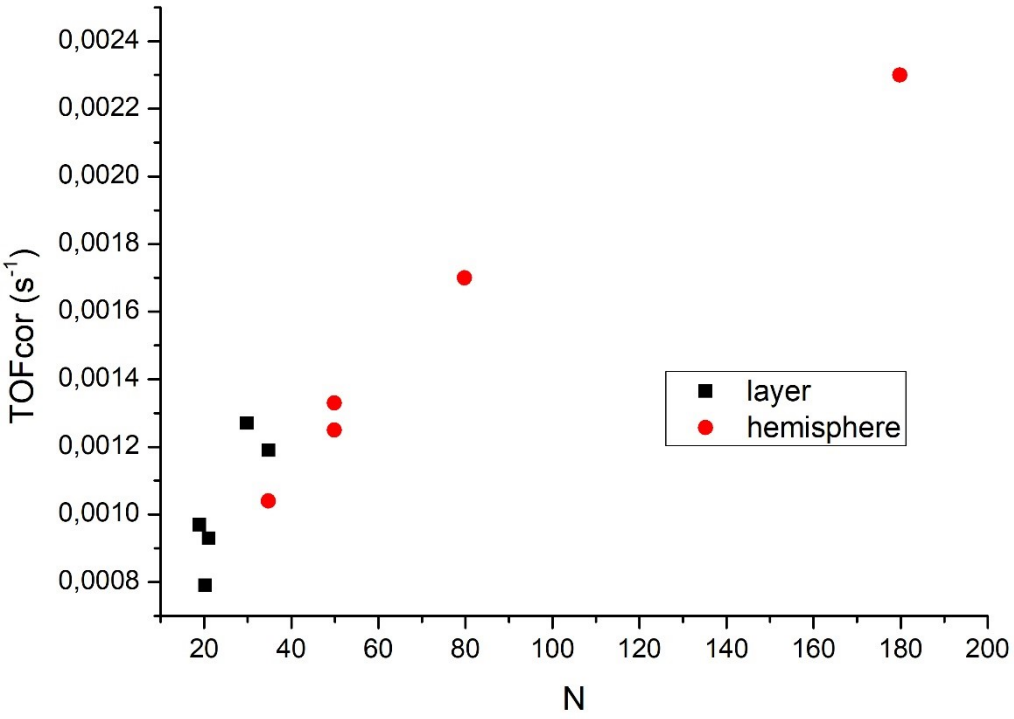

Figure SI1-2: Plot of TOF_{cor} as a function of N for the layer model (black squares) and the hemisphere model (red points).

On figure SI1-2 we see that after removing of the reverse-spillover effect the TOF is not a constant as it would be if there was no size effect but, on the contrary, it increases with N and the increase is even larger than for the TOF vs N curve (see figure 7). This curve shows that there is clearly an intrinsic size effect for clusters containing less than 180atoms.

From the value of Xs we see that Xs/L is very close to one, that means that the capture zone around the clusters overlap. In case of strong overlap TOF_{clus}/TOF_{cor} has a simplified expression :

$TOF_{clus}/TOF_{cor} = 1 + \alpha(1-A_c)/2A_c$, where $A_c = 2\pi Rn_s$ is the percentage of the substrate covered by the clusters.

[1] C.R. Henry, On the effect of the diffusion of carbon monoxide on the substrate during CO oxidation on supported palladium clusters. Surf. Sci.(1989)519-526

[2] G. Sitja, C.R. Henry; Molecular beam study of the oxidation of carbon monoxide on a regular array of Palladium clusters on alumina. J. Phys. Chem. C 121(2017)10706

2. Layer model for 19, 31 and 37 atoms having one layer, two and three layers, respectively.

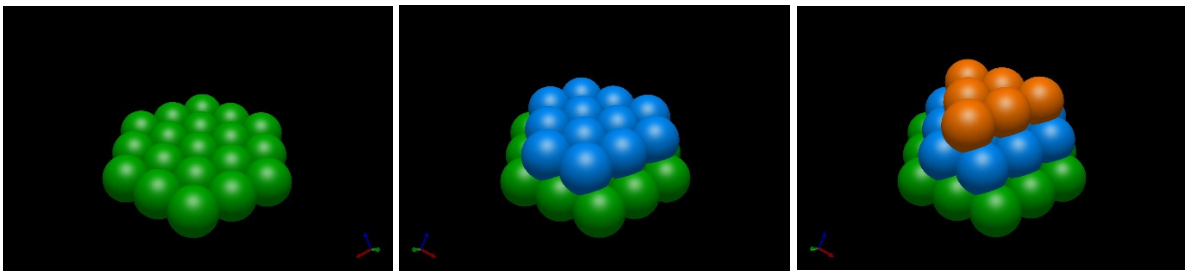

Figure SI2-1: Ball models of clusters containing 19, 31 and 37 atoms (from left to right).