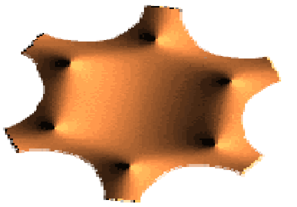


External noise-induced phenomena in nonlinear surface reactions

Miguel Pineda and Raúl Toral

IFISC (CSIC-UIB) Palma de Mallorca – Spain.

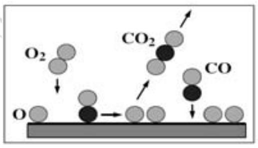
mpineda@ifisc.uib-csic.es; raul@ifisc.uib-csic.es

Introduction

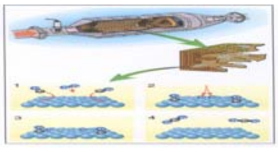
The influence of external noise on minimalistic models for the catalytic CO oxidation on Ir(111) and Pt(111) is studied by means of the adiabatic elimination technique. Two models, which reproduce the bistable behaviour usually observed in CO oxidation on noble metals, are analyzed. The noise is superposed on the fraction of CO in the constant gas flow directed at the surface and the resulting stochastic systems are reduced after the adiabatic elimination of oxygen coverage. This reduction allows us to analyze theoretically the interplay between external noise and the kinetic bistability of CO oxidation. We report the phenomena of noise-induced shifts of steady states and noise-induced jumps between stable steady states. We also present evidence for noise-induced transitions from mono- to bistability. The theoretical results are compared with simulations of the original two-variable stochastic reaction systems.

Catalytic CO oxidation

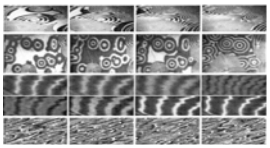
Mechanism



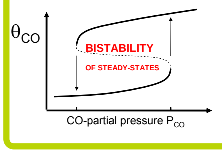
Applications (car converters)

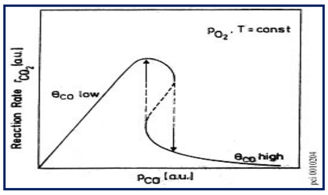


Dissipative structures (patterns)



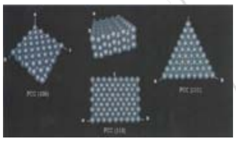
Kinetic Bistability





Deterministic approach

Single crystal approach



CO oxidation on Ir(111)

$$\frac{d\theta_{CO}}{dt}=\overbrace{Y_{CO}k_1\left(1-\frac{\theta_{CO}}{\theta^s_{CO}}-\frac{\theta_O}{\theta^s_O}\right)}^{adsorption}-\overbrace{k_2\theta_{CO}}^{desorption}-\overbrace{k_3\theta_O\theta_{CO}}^{reaction}$$

$$\frac{d\theta_O}{dt}=\overbrace{(1-Y_{CO})k_4\left(1-\frac{\theta_{CO}}{\theta^s_{CO}}-\frac{\theta_O}{\theta^s_O}\right)^3}^{adsorption}-\overbrace{k_3\theta_O\theta_{CO}}^{reaction}$$

$$0<\theta_{CO}<\theta^s_{CO}=1,\ 0<\theta_O<\theta^s_O=1$$

CO oxidation on Pt(111)

$$\frac{d\theta_{CO}}{dt}=\overbrace{Y_{CO}k_1\left(1-\frac{\theta_{CO}}{\theta^s_{CO}}-\frac{\theta_O}{\theta^s_O}\right)}^{adsorption}-\overbrace{k_2\theta_{CO}}^{desorption}-\overbrace{k_3\theta_O\theta_{CO}}^{reaction}$$

$$\frac{d\theta_O}{dt}=\overbrace{(1-Y_{CO})k_4\left(1-\frac{\theta_{CO}}{\theta^s_{CO}}-\frac{\theta_O}{\theta^s_O}\right)^2}^{adsorption}-\overbrace{k_3\theta_O\theta_{CO}}^{reaction}$$

$$0<\theta_{CO}<\theta^s_{CO}=0.5,\quad 0<\theta_O<\theta^s_O=0.25$$

$$\boxed{\begin{aligned}&\phi_{CO}+\phi_O=\phi_T\,(cm^{-2}s^{-1})\\&\frac{\phi_{CO}+\phi_O}{\phi_T}=1\\&Y_{CO}+Y_{O_2}=1\end{aligned}}$$

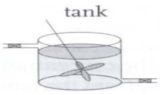
Ir(111)	Pt(111)
$\phi=0.878MLs^{-1}$	$\phi=0.878MLs^{-1}$
$S_{CO}=1$	$S_{CO}=0.84$
$S_O=0.11$	$S_O=0.06$
$\nu_d=1\times10^{13}s^{-1}$	$\nu_d=1.24\times10^{15}s^{-1}$
$E_d=33.4\,kcal/mol$	$E_d=34.9\,kcal/mol$
$\nu_r=10^5ML^{-1}s^{-1}$	$\nu_r=1.645\times10^{14}ML^{-1}s^{-1}$
$E_r=9.55\,kcal/mol$	$E_r=24.1\,kcal/mol$

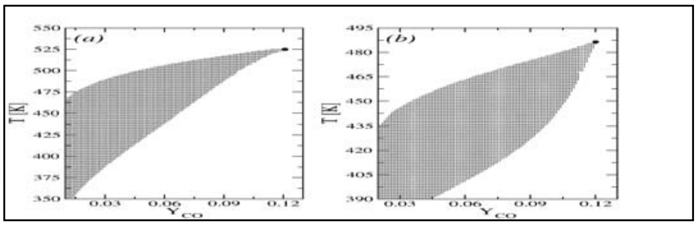
$S_{CO,O}=Sticking$ coefficient of CO or O

$$k_1=S_{CO}\phi_T,\quad k_4=2S_O\phi_T,\quad k_2=\nu_d e^{-E_d/RT},\quad k_3=\nu_r e^{-E_r/RT}$$

Mean-field-type analysis

$$\boxed{\begin{aligned}&1)\ CO(gas)+*\xrightarrow{k_1}CO(ads)\\&2)\ CO(ads)\xrightarrow{k_2}CO(gas)\\&3)\ CO(ads)+O(ads)\xrightarrow{k_3}CO_2(gas)\\&4)\ O_2(gas)\xrightarrow{k_4}2O(ads)\end{aligned}}$$





External noise in CO oxidation

Stochastic approach

$$\boxed{Y_{CO}\to Y_{CO}+r\eta(x,t)}$$

$$\langle\eta(t)\rangle=0$$

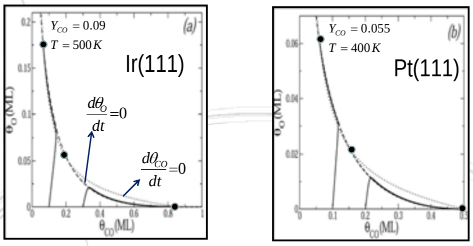
$$\langle\eta(t)\eta(t')\rangle=\delta(t-t')$$

$$\frac{d\theta_O}{dt}=f^O(\theta_{CO},\theta_O)+g^O(\theta_{CO},\theta_O,r)\eta(t)$$

$$\frac{d\theta_{CO}}{dt}=f^{CO}(\theta_{CO},\theta_O)+g^{CO}(\theta_{CO},\theta_O,r)\eta(t)$$

Two algebraic equations from the stochastic approach

Time scale separation (r=0)



Adiabatic reduction

1) Fast variable

$$\frac{d\theta_O}{dt}=f^O(\theta_O|\theta_{CO})+g^O(\theta_O|\theta_{CO},r)\eta(t)$$

$$\bar\theta_O=\langle\theta_O\rangle\longrightarrow$$ *Gaussian approximation*

Novikov`s theorem

$$\left\langle g^O(\theta_O)\eta(t)\right\rangle=\frac{g^O(\theta_O)}{2}\frac{\partial g^O(\theta_O)}{\partial\theta_O}$$

$$\boxed{\frac{d\bar\theta_O}{dt}=f^O(\bar\theta_O,\theta_{CO})+\frac{g^{CO}(\bar\theta_O,\theta_{CO})}{2}\frac{\partial g^{CO}(\bar\theta_O,\theta_{CO})}{\partial\bar\theta_O}=0}\quad\text{(a)}$$

2) Slow variable

$$\frac{d\theta_{CO}}{dt}=f^{CO}[\theta_{CO},\bar\theta_O(\theta_{CO})]+g^{CO}[\theta_{CO},\bar\theta_O(\theta_{CO},r),r]\eta(t)$$

$$\boxed{F=f^{CO}(\theta_{CO},\bar\theta_O)-\frac{g^{CO}(\theta_{CO},\bar\theta_O,r)}{2}\frac{\partial g^{CO}(\theta_{CO},\bar\theta_O,r)}{\partial\theta_{CO}}=0}\quad\text{(b)}$$

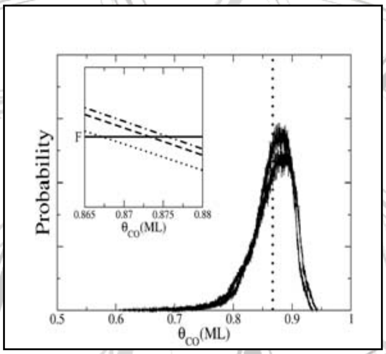
External noise-induced phenomena

Noise-induced shift of steady states

$r=0.0$
$r=0.08$
$r=0.095$

CO oxidation on Ir(111)

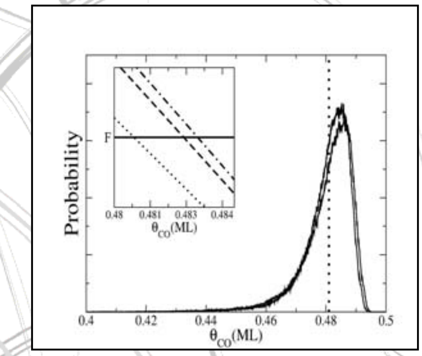
$T=500K\quad Y_{CO}=0.1$



$r=0.0$
$r=0.1$
$r=0.115$

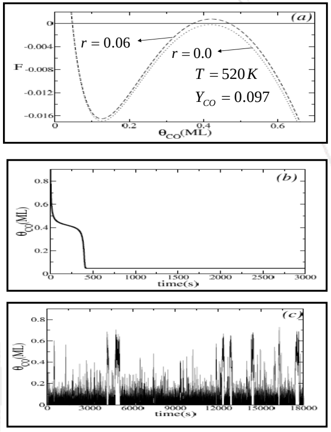
CO oxidation on Pt(111)

$T=470K\quad Y_{CO}=0.12$

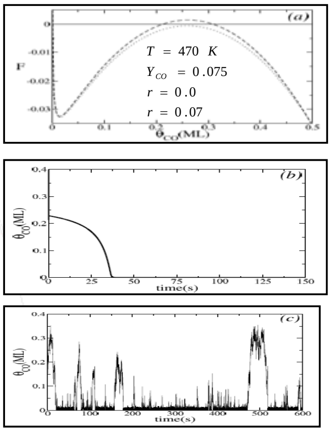


Noise-induced transitions from mono- to bistability

CO oxidation on Ir(111)



CO oxidation on Pt(111)



Summary and conclusions

- Deterministic and stochastic models for the catalytic CO oxidation on Ir(111) and Pt(111) were analyzed. It was shown that these models reproduce bistability. The phenomena of noise-induced shifts of steady states and noise-induced transitions from mono- to bistability have been also theoretically and numerically reported [J. Chem Phys. **130**, 124704 (2009)].