

Reações de oxidação catalíticas

QFL5835-6 Catálise: uma visão integrada

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Selective oxidation remains one of the key synthetic steps for the activation of a broad range of substrates for the production of either finished products or intermediates for the preparation of pharmaceuticals, agrochemicals, as well as commodity chemicals.

alkanes
olefins
alcohols



**Epoxides, alcohols,
ketones, aldehydes,
and acids**

In contrast to **hydrogenation reactions** which are often carried catalytically with H_2 , there are relatively **few selective oxidation reactions that are catalyzed using O_2 .**

Why hydrogenation with a heterogeneous metal catalyst and H_2 is a commonplace laboratory procedure and most would not consider doing a similar oxidation process with O_2 as a standard laboratory procedure?

- H_2 has to be activated by chemisorption on a catalyst surface before it can be reacted with a substrate for hydrogenation to occur
- O_2 in its ground state is a diradical triplet species. This opens up the possibilities of competing non-catalyzed gas or liquid phase reactions in which triplet dioxygen reacts directly with the substrate without the intervention of a catalyst

- Selective oxidations using stoichiometric

oxidants: $\text{Na}_2\text{Cr}_2\text{O}_7$, KMnO_4 , MnO_2 , ...

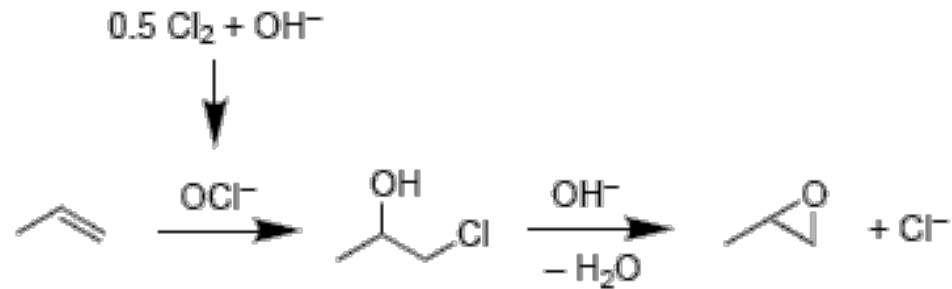
- Produce stoichiometric amounts of very toxic waste, no longer tolerable.

- Most industrial oxidation processes tend to use either chlorine or organic peroxides.

- One produces huge amounts of chloride salts and lesser, but significant, amounts of toxic chlorinated organic by-products.

- The alternative use of organic peroxides is expensive, and is also accompanied by the formation of by-products — economically disadvantageous if there is no market for them.

Epoxidation with chlorine



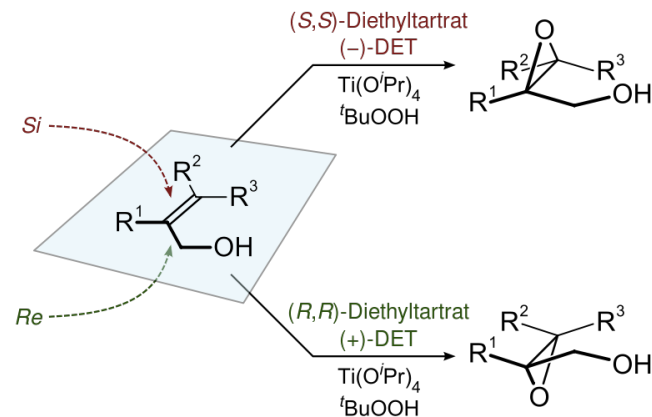
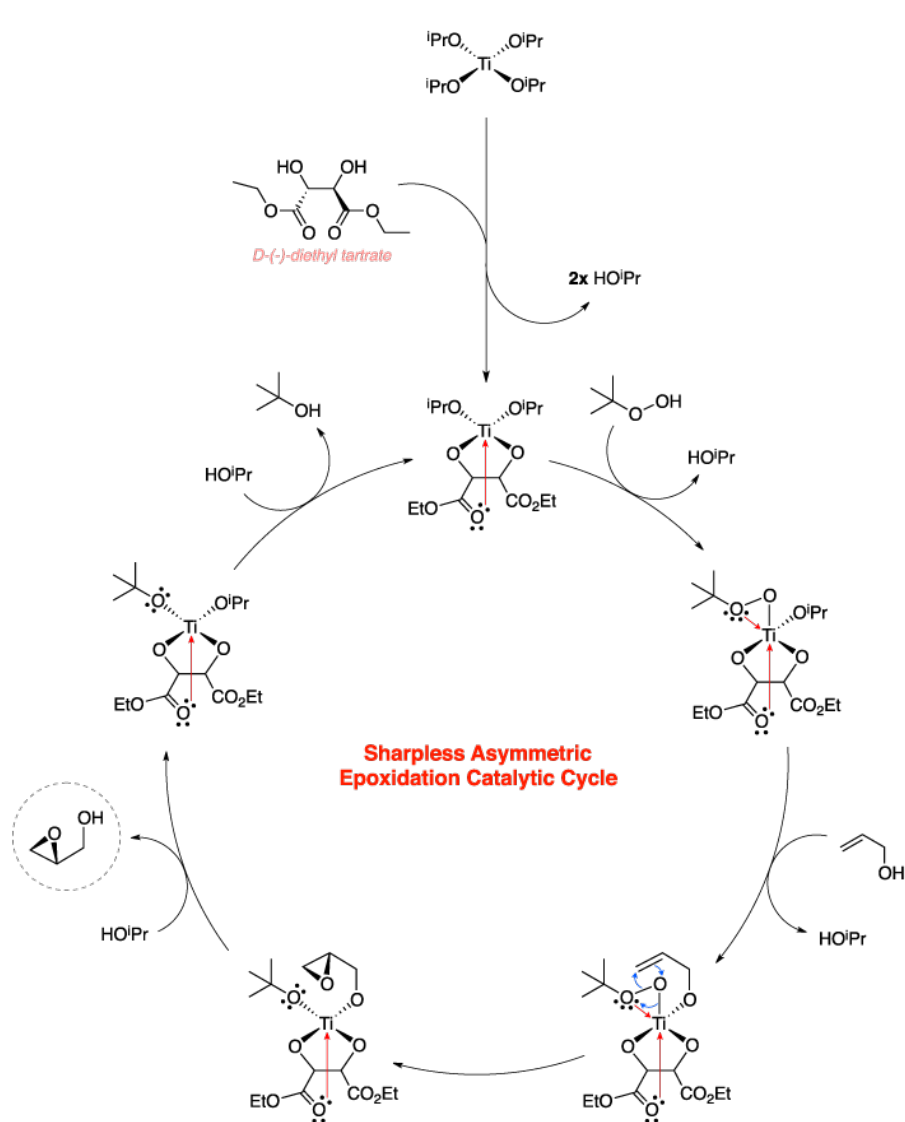
Scheme 1. Chlorohydrin process for propylene oxide.

- Chlorine
- hypochlorite
- peroxyacids

Sharpless Epoxidation

- The oxidizing agent is tert-butyl hydroperoxide

Note: The mechanism shown is using D-(-)-diethyl tartrate and is simplified for clarity. It is believed that this reaction proceeds through a dimeric titanium complex



Katsuki, T.; Sharpless, K. B. (1980). "The first practical method for asymmetric epoxidation" J. Am. Chem. Soc., 1980, 102 (18), pp 5974–5976



clean and freely
available from air

• CATALYTIC OXIDATIONS

There is a real need for new **catalytic processes** that use molecular oxygen, especially since environmental factors are of paramount importance and we need to develop atom efficient green processes.

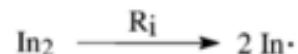
It is surprising that there have been few new approaches in the design of selective oxidation catalysts using molecular oxygen in the past forty years.¹ **The major advances in selective oxidation were marked out over 50 years ago.**

- titanium silicalite TS-1
 - epoxidation of alkenes (H_2O_2)
- iron-doped ZSM-5 zeolite
 - oxidation of benzene to phenol (N_2O)

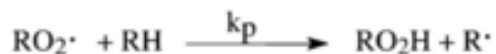
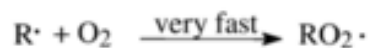
¹G. J. Hutchings, Chem. Commun., 2008, 1148–1164

•Autoxidation mechanism

Initiation:



Propagation:



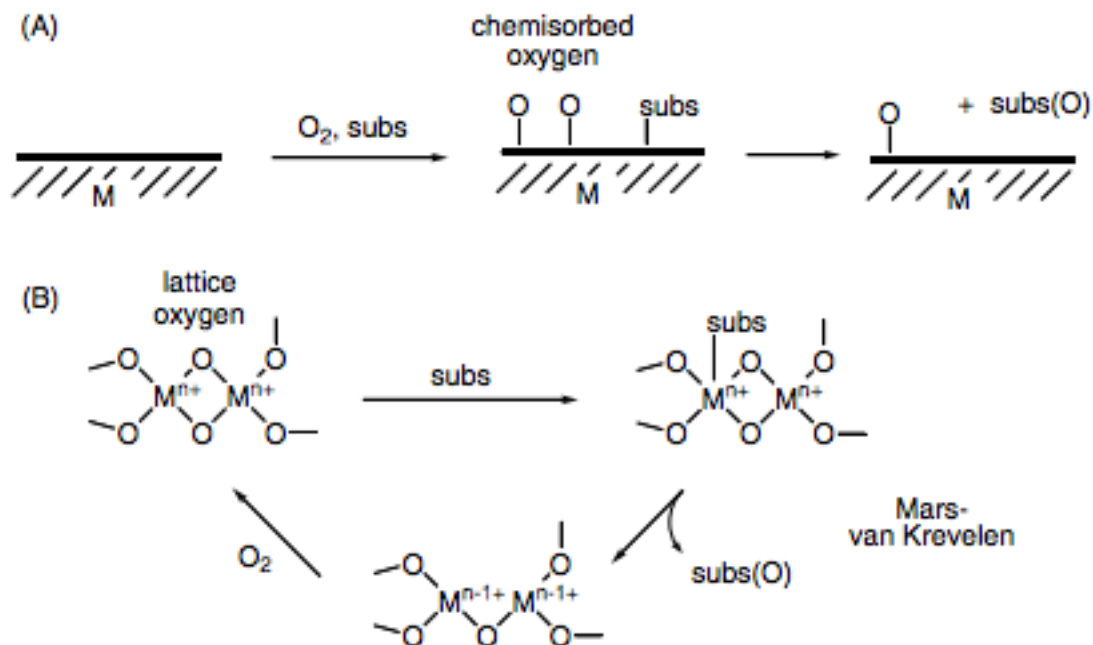
Termination:



Fig. 4.3 Mechanism of autoxidation.

Radical scavenger: butylated hydroxytoluene(BHT). BHT is an antioxidant that reacts with free radicals, delaying oxidative processes.

- Oxidation at metal or oxide surfaces



SCHEME 1.3 Oxygen activation on the surface of heterogeneous catalysts. (A) Through chemisorption; (B) by replenishing consumed lattice oxygen.

•Oxidation with redox catalysts

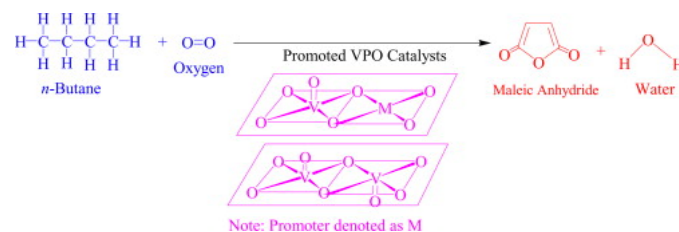
Redox catalysts: V, Mo, Fe

- Low selectivity: the oxygenated products are more reactive than the starting materials, e.g. alkanes.

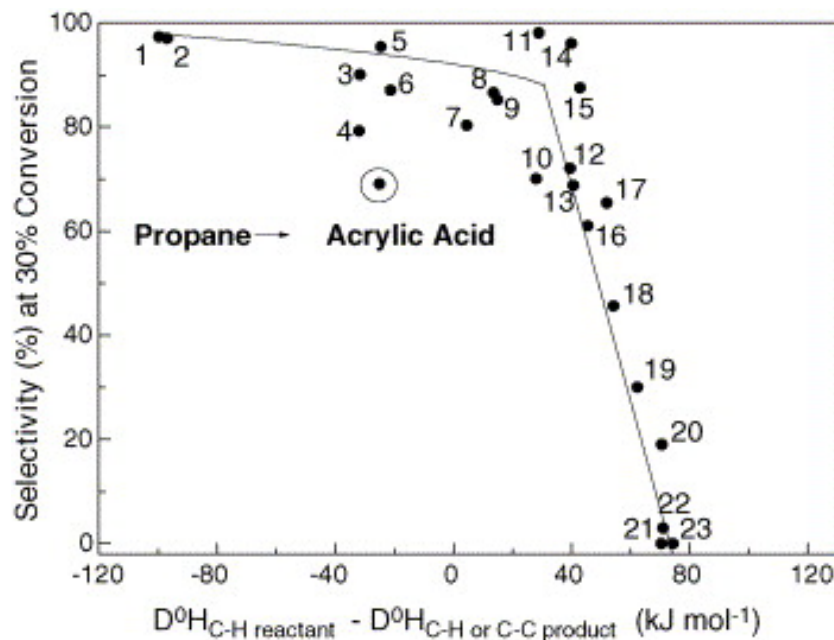
- High temperature
- Highly active catalysts

- Industrial application of catalytic oxidation of alkanes:

Oxidation of butane to maleic anhydride
($(VO)_2P_2O_7$ - VPO))



The role of reactant and product bond energies in determining limitations to selective catalytic oxidations (Applied Catalysis A: General 137 (1996) 179-191)



if this bond energy difference (weakest bond in reactant and product) is less than 30 kJ mol^{-1} very high product selectivity is possible, whereas for differences greater than 70 kJ mol^{-1} near zero selectivity is always recorded.

Fig. 1. Selectivity in product vs. $D^0H_{C-H \text{ reactant}} - D^0H_{C-H \text{ or } C-C \text{ product}}$ at 30% conversion for the indicated reactions [1]: 1, ethylbenzene to styrene; 2, 1-butene to butadiene; 3, acrolein to acrylic acid; 4, toluene to benzoic acid; 5, ethane to ethylene; 6, n-butane to maleic anhydride; 7, toluene to benzaldehyde; 8, propene to acrolein; 9, 1-butene to 2-butanone; 10, isobutane to isobutene; 11, methanol to formaldehyde; 12, methacrolein to methacrylic acid; 13, propane to propene; 14, ethanol to acetaldehyde; 15, isobutene to methacrolein; 16, n-butane to 1-butene; 17, benzene to maleic anhydride; 18, propane to acrolein; 19, methane to ethane; 20, isobutane to methacrylic acid; 21, ethane to acetaldehyde; 22, methane to formaldehyde; 23, isobutane to methacrolein.

- Oxidation by O₂ chemisorption

CO oxidation

M. Haruta¹ was the first to show that CO oxidation could be performed at ambient temperatures by using gold dispersed on oxide surfaces.

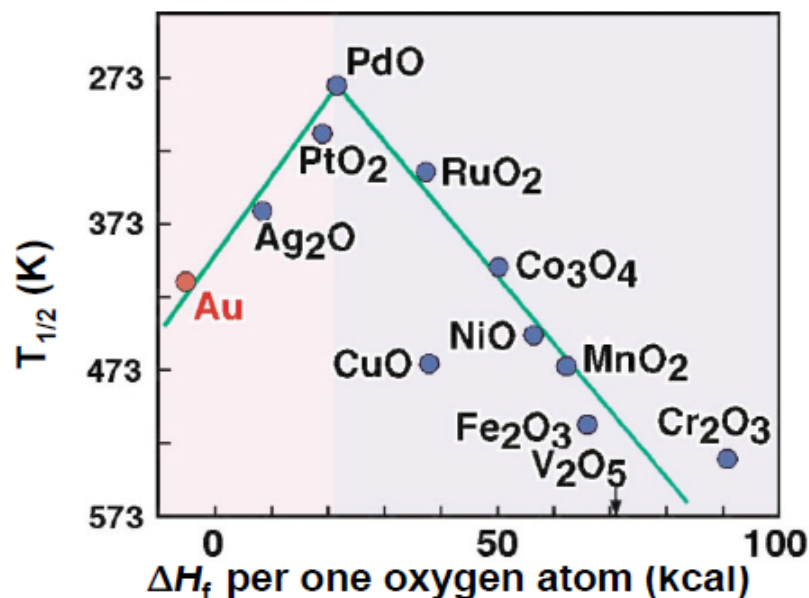
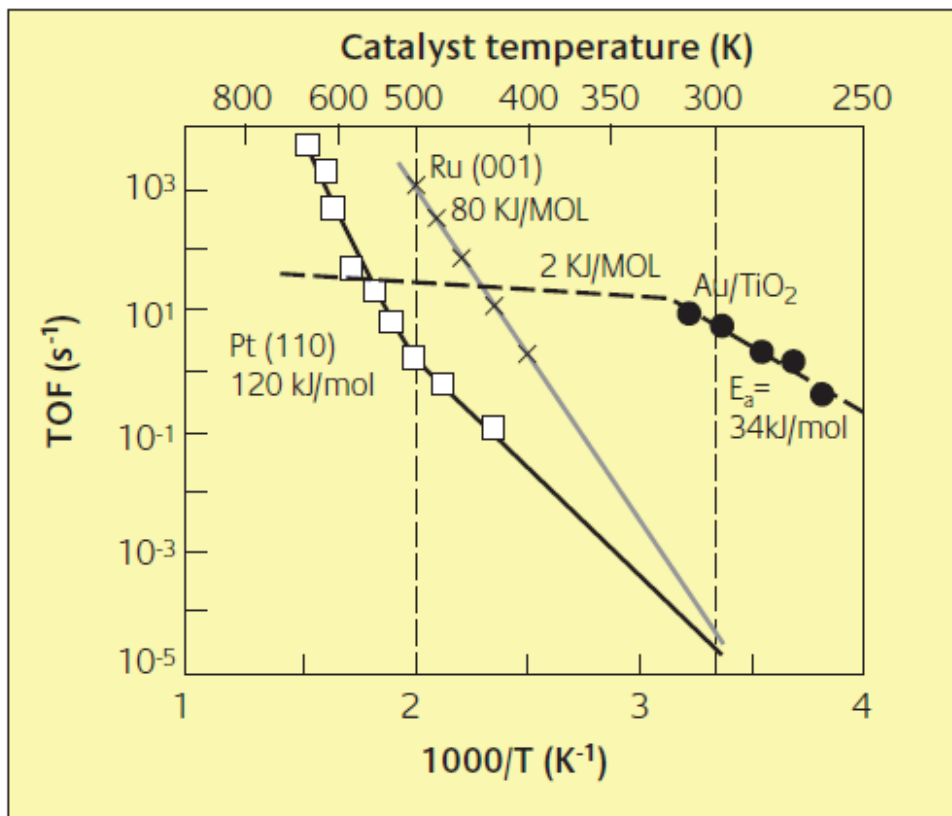


Fig. 1. Catalytic activity of metal oxides for H₂ oxidation as a function of their heat of formation per one oxygen atom. $T_{1/2}$ is the temperature for 50% conversion of H₂ obtained by a fixed bed flow reactor in a stream of 1 vol.% H₂ in air under a space velocity of $2 \times 10^4 \text{ h}^{-1}/\text{ml} \cdot \text{g-cat}$.

The active gold catalysts were composed of Au nanoparticles homogeneously dispersed on metal oxide supports such as Fe₂O₃, Co₃O₄, and NiO

¹Haruta, M.; Kobayashi, T.; Sano, H.; Yamada, N. Chem Lett 1987, 405.

CO oxidation



CO oxidation

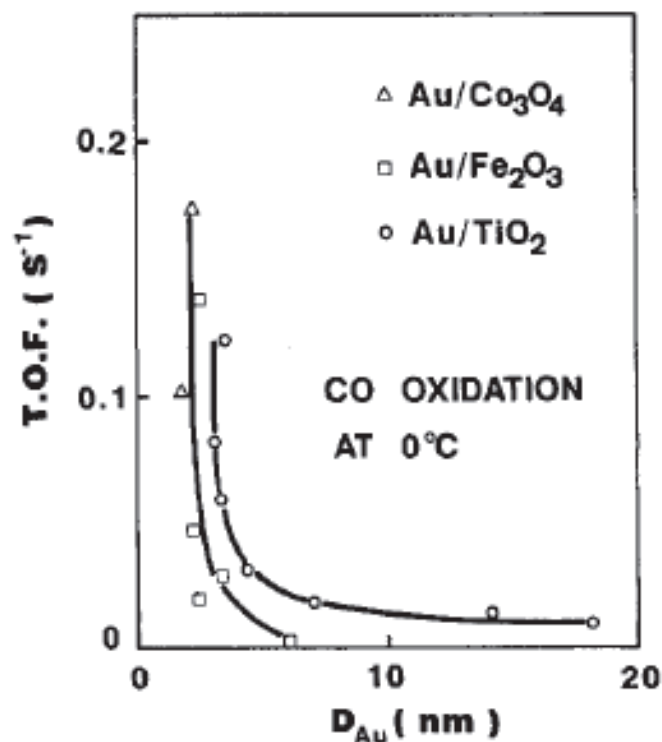
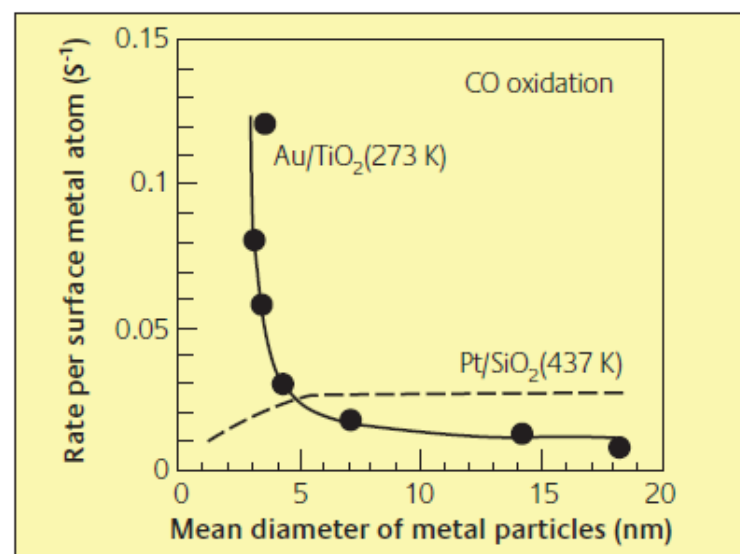


Fig. 4. Turnover frequencies based on surface exposed gold atoms as a function of the mean particle diameters of gold in CO oxidation at 0°C . Δ , $\text{Au}/\text{Co}_3\text{O}_4$; \square , $\text{Au}/\alpha\text{-Fe}_2\text{O}_3$; \circ , Au/TiO_2 .

Comparison with platinum:



CO oxidation

CO oxidation is an essential goal for fuel cell technology where residual traces of CO have to be removed from the H_2 that is used as the fuel source. However, this requires preferential oxidation of CO in the presence of CO_2 , H_2O and a massive excess of H_2 .

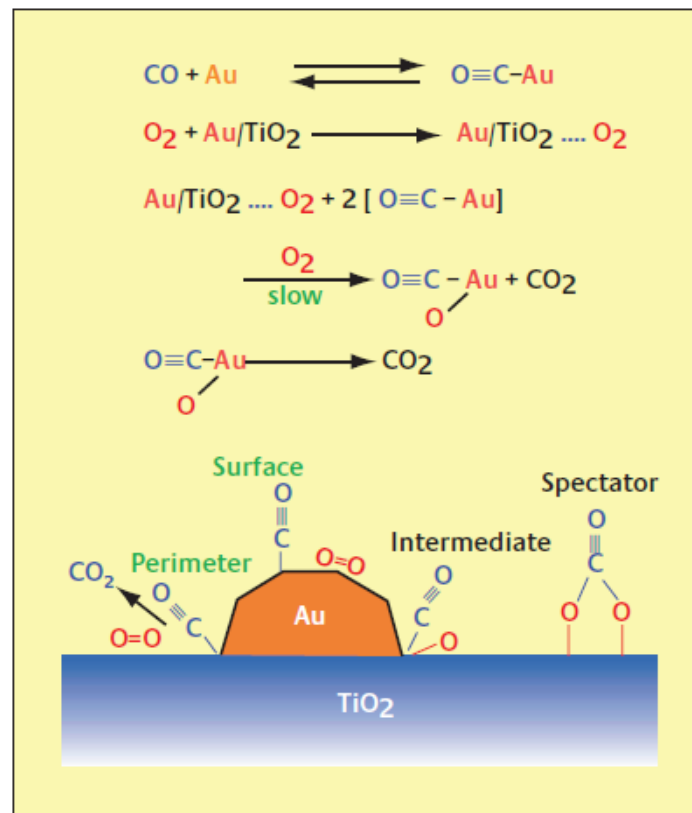
- Why gold is such an effective catalyst for the oxidation of CO?
- What is the mechanism by which supported gold nanocrystals oxidize CO?
- What is the nature of the active site and is it the same for all supported gold catalysts?

CO oxidation

Proposals have included the **size** and **morphology** of the gold particle and its **interface with the support**, the **metal oxidation state**, and **support effects**.

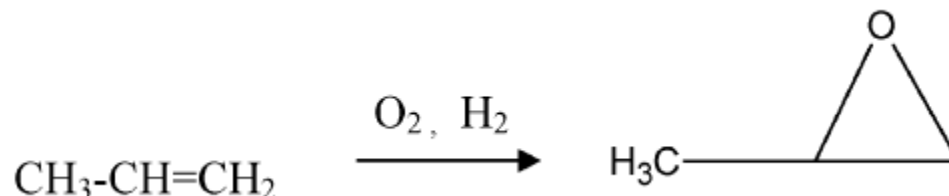
EXAFS, XPS, Mössbauer, IR of CO adsorbed, O₂ adsorption and the reaction of O₂ with CO, ¹⁸O₂ isotope experiments, etc. -

Metallic Au surfaces are necessary for CO adsorption and that the peripheries act as reaction zones with O₂



M. Haruta / Catalysis Today 36 (1997) 153–166

Propene epoxidation



All attempts to produce PO commercially by direct oxidation of propene, in a similar way to the silver promoted synthesis of ethylene oxide, have till now been unsuccessful and the majority of PO is still manufactured by the chlorohydrin process and the indirect hydroperoxide processes.

Table 1 Reaction of propene with hydrogen and oxygen over Au-, Pd-, Pt-TiO₂ catalysts

Catalyst	Reaction temperature/°C	C ₃ H ₆ Conv. (%)	Selectivity (%)			
			PO	C ₃ H ₈	CO ₂	Acetone
1%Au-TiO ₂	50	1.1	> 99	—	—	—
1%Au-TiO ₂	80	0.8	—	< 10	> 70	—
1%Pd-TiO ₂	25	57.1	—	98	1	0.4
1%Pt-TiO ₂	25	12.1	—	92	6	2

Propene epoxidation

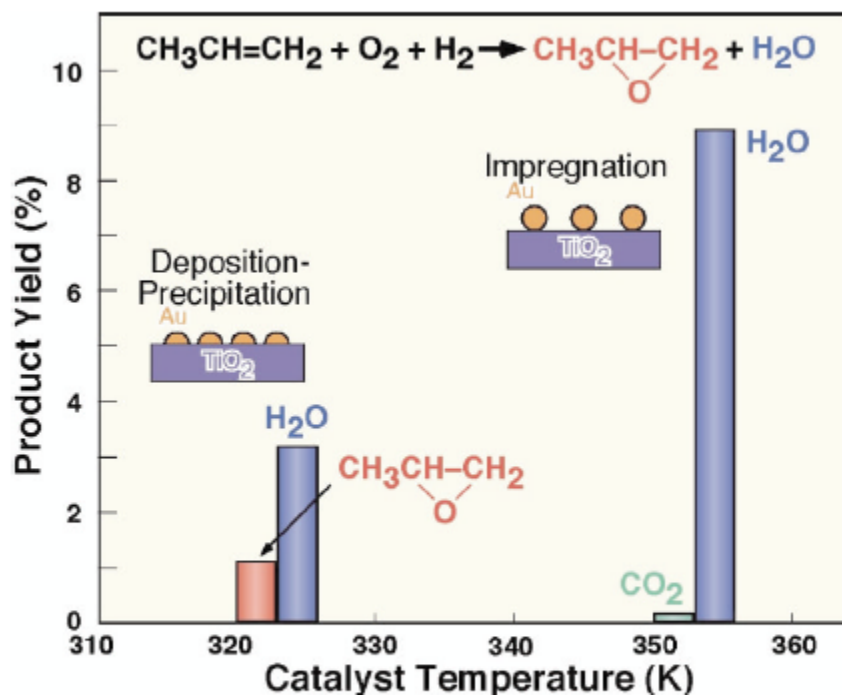
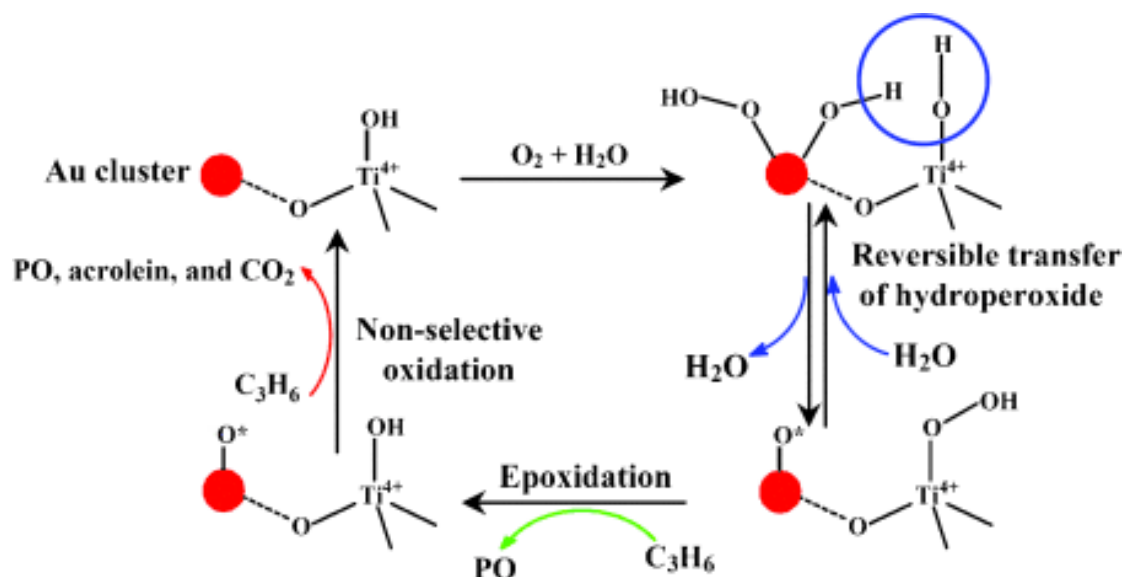


Fig. 3. Product yields of the reaction among C₃H₆, O₂, and H₂ over Au/TiO₂ catalysts prepared by the deposition-precipitation and impregnation methods. Reactant gas, C₃H₆:O₂:H₂:Ar = 1:1:1:7, Space velocity; 4000 h⁻¹.ml/g-cat.

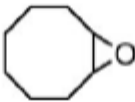
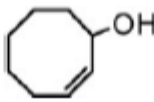
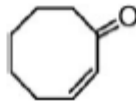
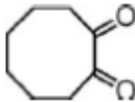
Propene epoxidation

“The resulting titanium hydroperoxide species (Ti–OOH) are the actual reaction partners for the propylene, which is converted to propylene oxide.”



Oxidation of higher alkenes

Table 6 *cis*-Cyclooctene oxidation with molecular oxygen in the absence of a solvent^{a,132}

Catalyst	TBHP/g	Conv. (%)	Selectivity (%)				$\sum_{\text{sel}} C_8$
							
1% Au/graphite	0.12	7.9	81.2	9.3	4.1	0.5	95.1
1% Au/graphite	0.02	7.1	79.2	6.8	3.0	0.5	89.5
1% Au/graphite	0.002	1.3	82.6	7.4	2.1	0.6	92.7
No catalyst	0.008	2.0	Trace	0.0	0.0	0.0	—
Graphite	0.008	2.3	Trace	0.0	0.0	0.0	—

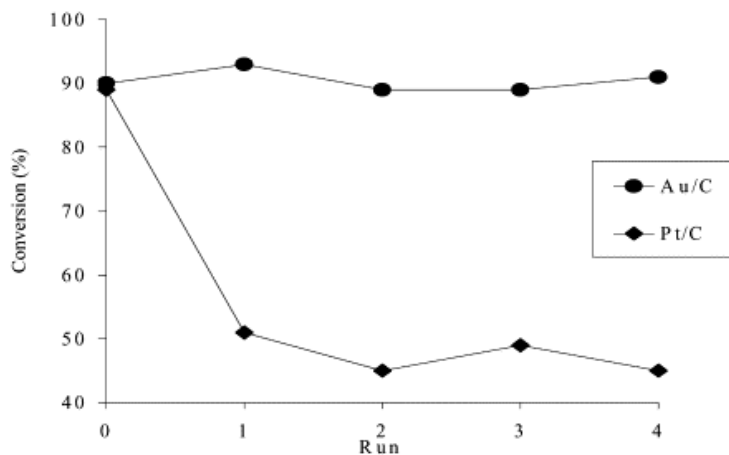
^a Reaction conditions: 0.12 g catalyst, *cis*-cyclooctene (10 ml, 0.066 mol), 80 °C, 24 h, in a stirred autoclave with O₂ 3 bar. TBHP = *tert*-butylhydroperoxide.

Oxidation of alcohols

•Michele Rossi et al.

Comparing the catalytic activity of Au and Pt nanoparticles

•Oxidation of *n*-propanal

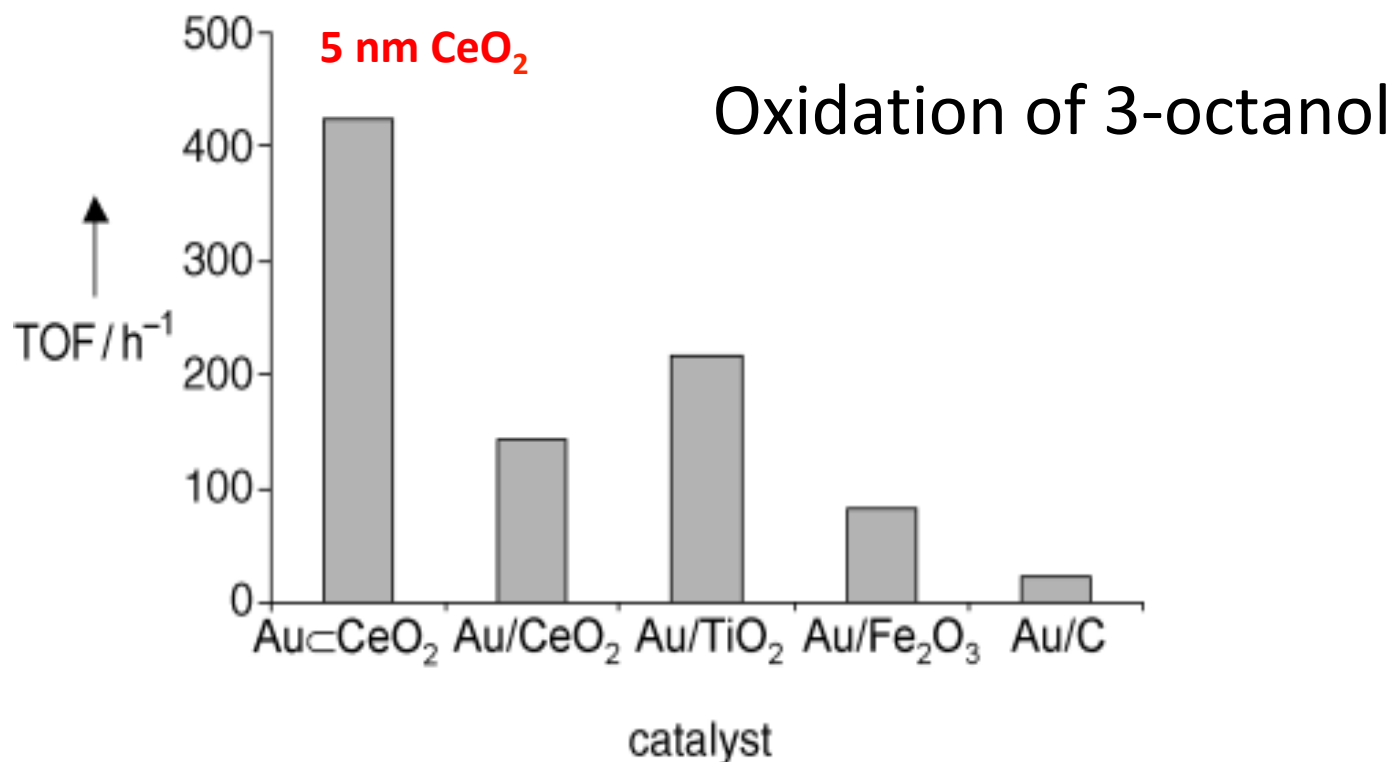


•Oxidation of aldehydes

Reagent	Conversion (%) ^a			
	Water		Water/acetonitrile (9/1 (v/v))	
	1% Au/C	5% Pt/C	1% Au/C	5% Pt/C
<i>p</i> -Me-PhCHO	8	6	3	2
PhCHO	24	20	5	5
<i>p</i> -F-PhCHO	24	21	4	5
<i>n</i> -C ₆ H ₁₃ CHO	9	9	4	3
<i>n</i> -C ₂ H ₅ CHO	90	81	25	41

•Avelino Corma et al.

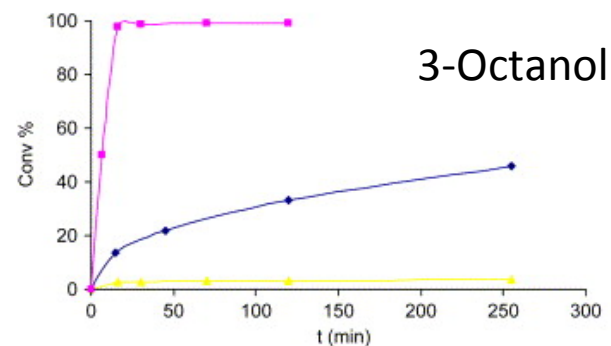
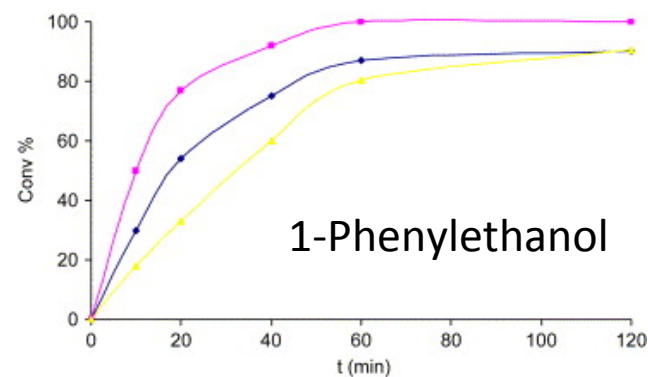
Effect of support on gold catalysis



•Avelino Corma et al.

Comparing the catalytic activity of Au and Pd nanoparticles

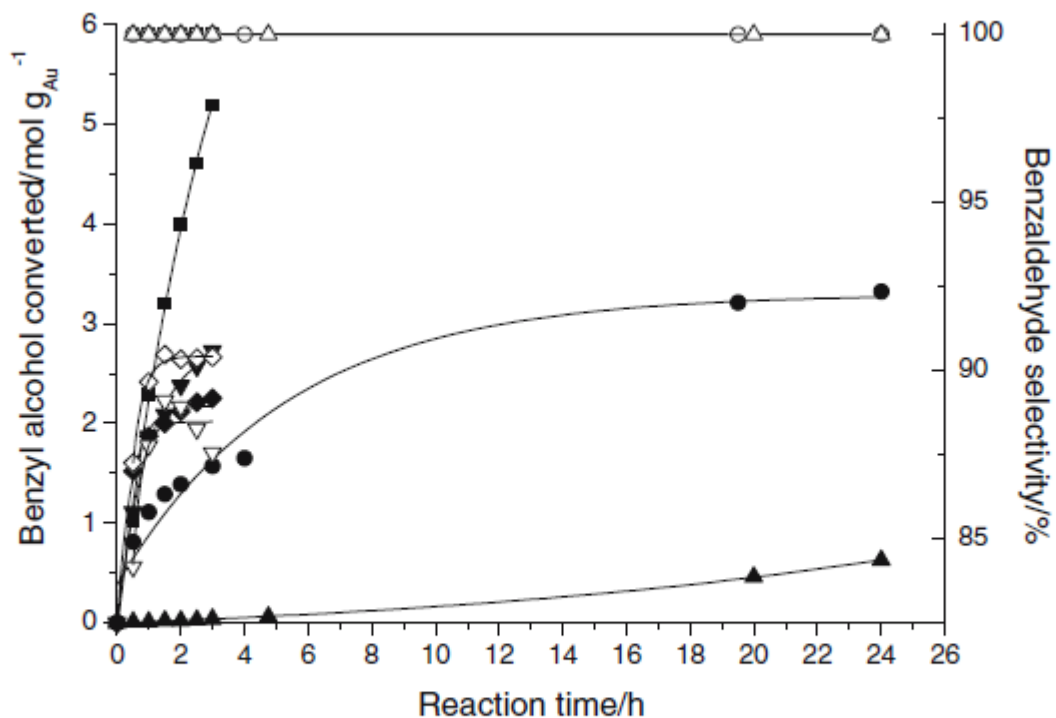
Substrate	T (°C)	Catalyst	Ketone yield (%)	TOF (h ⁻¹)
1-Phenylethanol	160	Au/CeO ₂	33	12,480
		Pd/CeO ₂	>95	32,558
	120	Au/CeO ₂	>95	1511
		Pd/CeO ₂	91	645
3-Octanol	120	Au/CeO ₂	>95	2337
		Pd/CeO ₂	3	63



Pd/CeO₂ ▲, Au/CeO₂ ■ e Pd/apatite ◆

•G. H. Hutchings, *et al.*

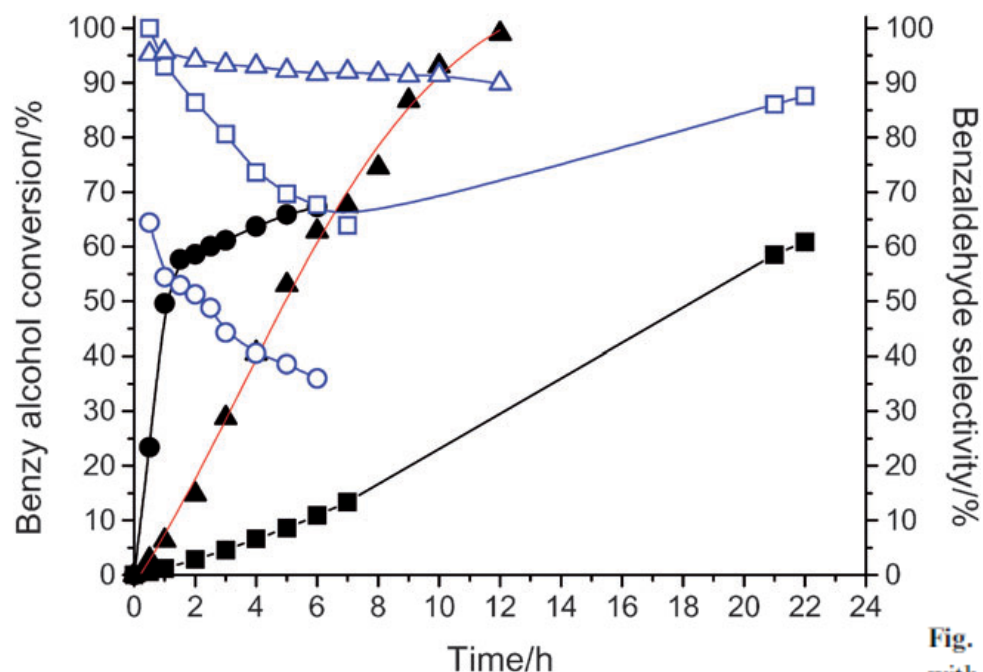
Oxidation of benzyl alcohol – effect of support



Oxidation of benzyl alcohol in the absence of solvents using gold catalysts as a function of reaction time; conversion – solid symbols, selectivity – open symbols; (■) Au/SiO₂; (●) Au/CeO₂; (▲) Au/TiO₂; (▼) Au/Fe₂O₃; (◆) Au/C.

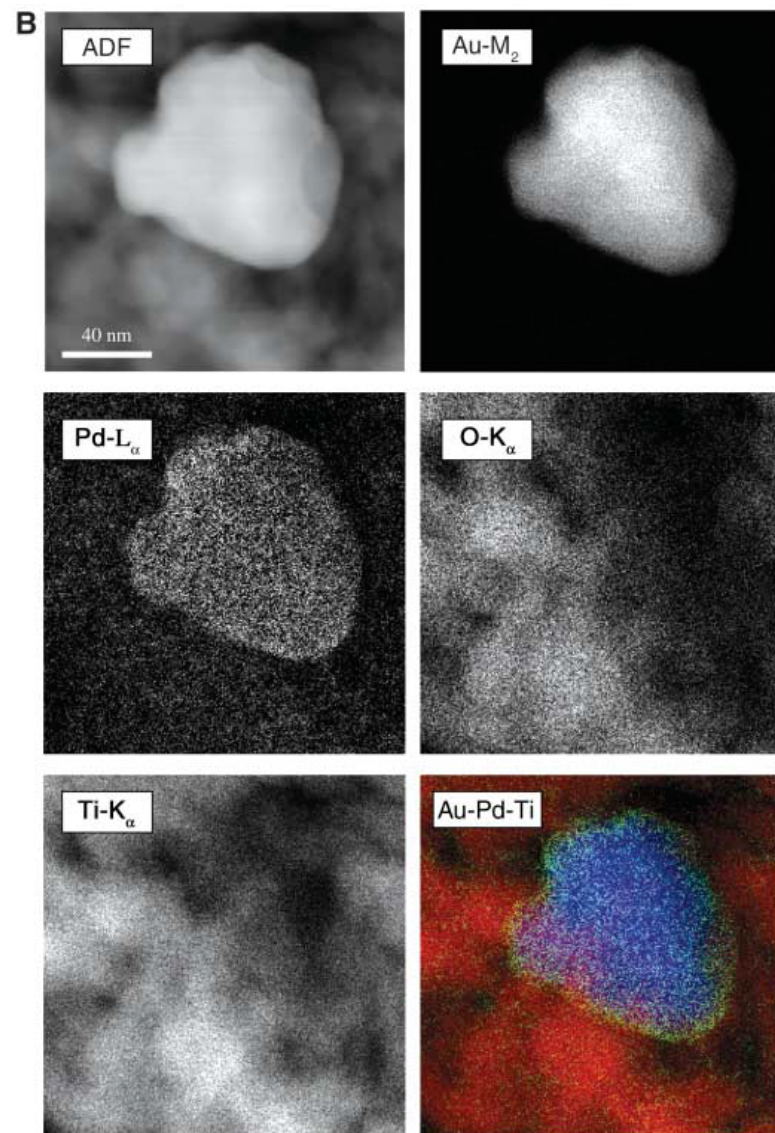
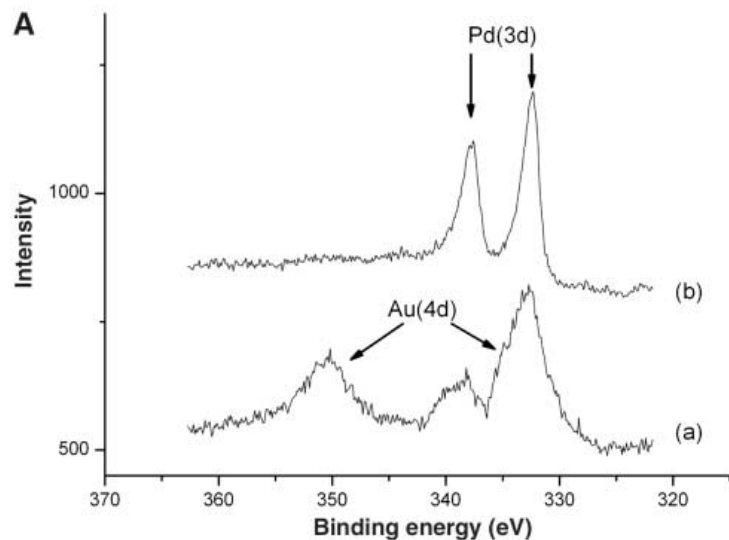
•G. H. Hutchings, *et al.*

Comparing the catalytic activity of Au, Pd and AuPd nanoparticles



TiO₂-supported Au-Pd alloy nanocrystals give significantly enhanced activity for alcohol oxidation using a green chemistry approach with O₂ under mild solvent-free conditions

Fig. 15 Benzyl alcohol conversion and selectivity in benzaldehyde with the reaction time at 373 K, 0.1 MPa O₂ pressure: (■) Au/TiO₂, (●) Pd/TiO₂, (▲) Au-Pd/TiO₂; solid symbols – conversion, open symbols – selectivity (benzyl alcohol (40 ml), catalyst (200 mg), 100 °C, 0.2 MPa O₂).¹³¹



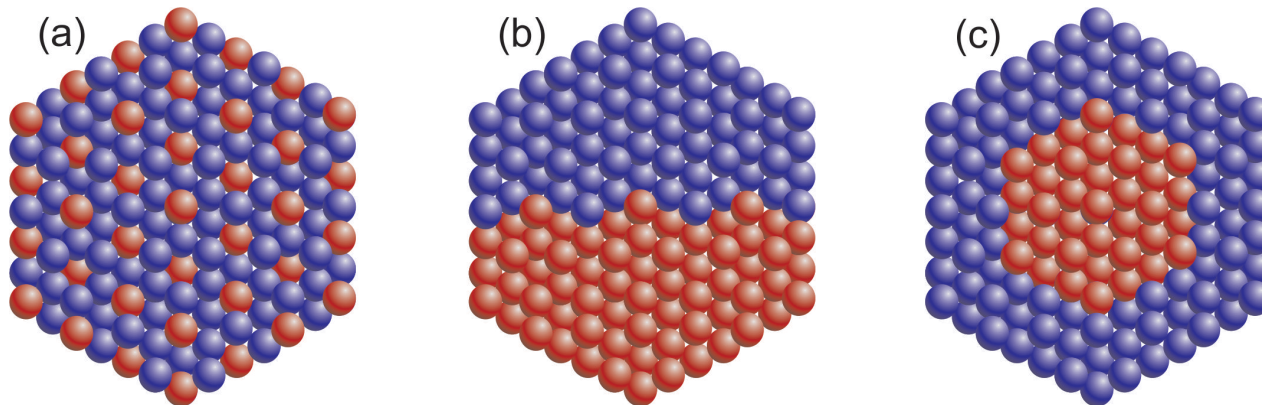
(A) Au(4d) and Pd(3d) spectra for a 2.5 weight % Au–2.5 weight % Pd/TiO₂ catalyst after different heat treatments: (a) uncalcined or (b) calcined at 673 K in air. (B) Montage showing the ADF-STEM image of a bimetallic particle and the corresponding MSA-processed STEM-XEDS maps of the Au-M₂, Pd-La, O-K_α, and Ti-K_α signals. Also shown is a reconstructed MSA-filtered Au-Pd-Ti composition map (Ti, red; Au, blue; and Pd, green).

Table 2. Comparison of the catalytic activity for alcohol oxidation to the corresponding aldehyde. Catalyst is 2.5% Au–2.5% Pd/TiO₂ unless noted otherwise; substrates oxidized without solvent unless specified; catalyst mass varied to give the metal concentrations indicated; and TOF was measured after first 0.5 hour of reaction. *T*, temperature.

Entry	Alcohol	Reaction conditions		[Metal] (10 ^{–5} mol/liter)		TOF (/hour)
		<i>T</i> (K)	<i>P</i> (10 ⁵ Pa)	Au	Pd	
1	Benzyl alcohol	373	2	63.5	118	607
2	Benzyl alcohol*	373	2	63.5	0	213
3	Benzyl alcohol†	373	2	0	118	2,200
4	Benzyl alcohol	373	1	2.1	3.9	6,190
5	Benzyl alcohol	373	2	2.1	3.9	6,440
6	Benzyl alcohol	373	5	2.1	3.9	6,190
7	Benzyl alcohol	373	10	2.1	3.9	5,950
8	Benzyl alcohol	383	1	2.1	3.9	14,270
9	Benzyl alcohol	393	1	2.1	3.9	26,400
10	Benzyl alcohol	433	1	2.1	3.9	86,500
11	1-Phenylethanol	433	1	1.8	3.2	269,000
12	3-Phenyl-1-propanol	433	1	2.1	3.9	2,356
13	Vanillyl alcohol‡	363	1	21.6	40.6	10
14	Cinnamyl alcohol§	363	1	21.6	40.6	97
15	Octan-1-ol	433	1	2.5	4.7	2,000
16	Octan-2-ol	433	1	2.5	4.7	0
17	Octan-2-ol/octan-1-ol	433	1	2.1	3.9	0
18	Octan-3-ol	433	1	2.1	3.9	10,630
19	1-Octen-3-ol	433	1	2.1	3.9	12,600
20	Crotyl alcohol	433	5	2.1	3.9	12,600
21	Butan-1-ol	433	5	2.1	3.9	5,930
22	1,2-Butanediol	433	1	2.1	3.9	1,520
23	1,4-Butanediol	433	1	2.1	3.9	104,200
24	Benzyl alcohol	433	1	2.1	3.9	12,500
25	Benzyl alcohol¶	433	1	2.1	0	12,400
26	Benzyl alcohol#	433	1	0	3.9	24,800
27	Benzyl alcohol**	433	1	2.4	4.5	36,500
28	Benzyl alcohol††	433	1	0	3.6	37,600
29	1-Phenylethanol††	433	1	0	3.1	11,600

*2.5% Au/TiO₂. †2.5% Pd/TiO₂. ‡0.2 mol/liter in toluene as solvent. §0.2 mol/liter in water as solvent. ||2.5% Au–2.5% Pd/HAP prepared by impregnation of HAP with H₂AuCl₄·3H₂O and PdCl₂. ¶2.5% Au/HAP prepared by impregnation of HAP with H₂AuCl₄·3H₂O. #2.5% Pd/HAP prepared by impregnation of HAP with PdCl₂. **2.5% Au–2.5% Pd/TiO₂ prepared with the method of Kaneda (6) using TiO₂ as support. ††0.2% Pd/HAP prepared using the method of Kaneda (6) using HAP as support.

Bimetallic nanomaterials for the design of advanced catalysts

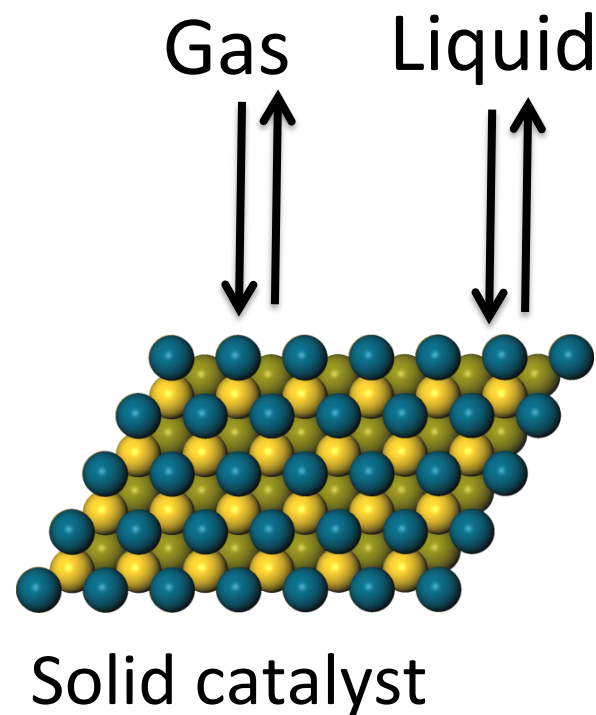


(a) alloy, (b) cluster-on-cluster, (c) core-shell

- High atomic structural complexity:
 - Distribution of metal domains?
 - Composition (bulk and surface)?
- Composition homogeneity among particles
- Atomic rearrangement and restructuring under heating/working conditions

Heterogeneous catalysis = surface catalysis¹

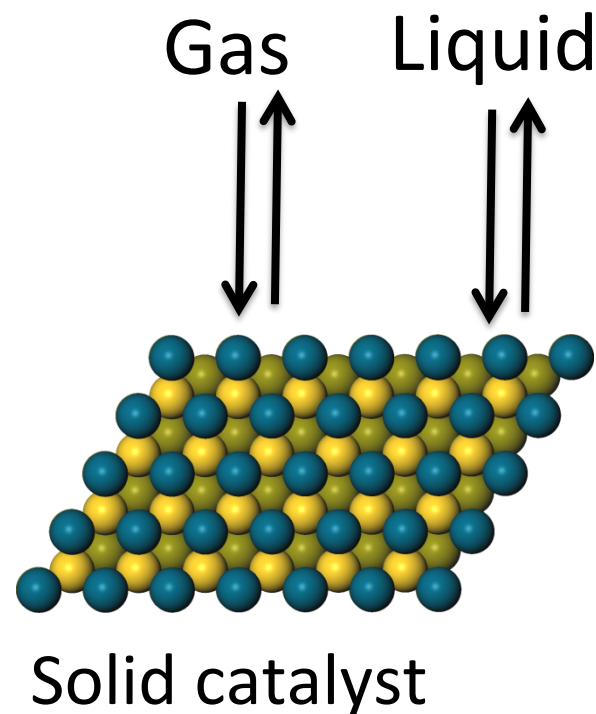
- 1) Adsorption
- 2) Reaction
- 3) Desorption



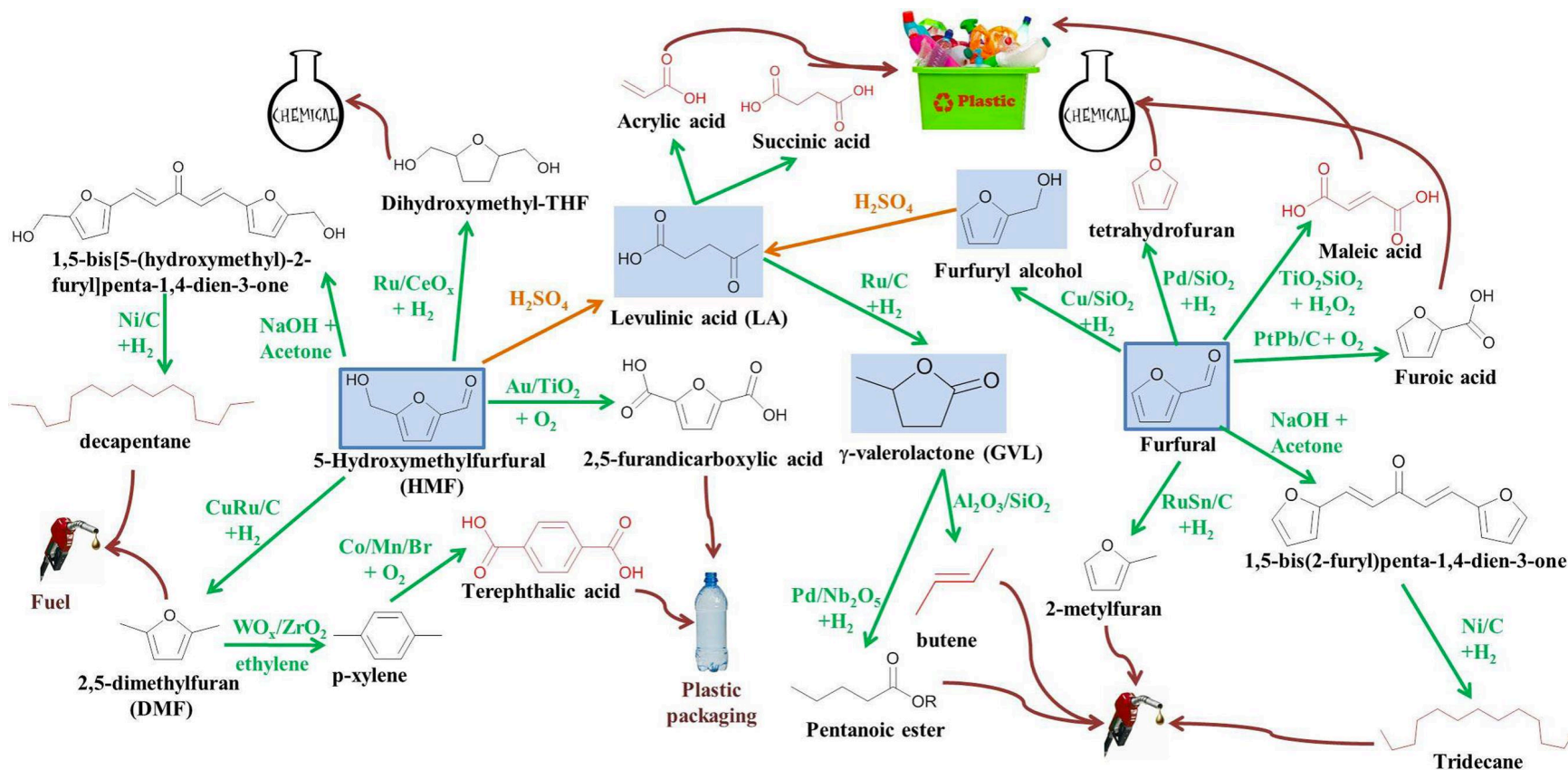
Heterogeneous catalysis = surface catalysis¹

Extremely sensitive to
surface and subsurface
composition?

How to control (and
know) the surface
composition of bimetallic
catalysts?

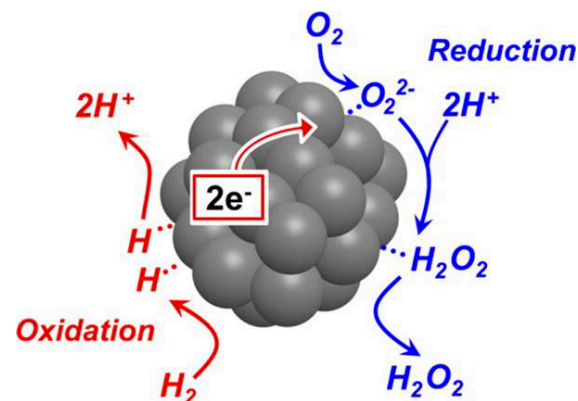
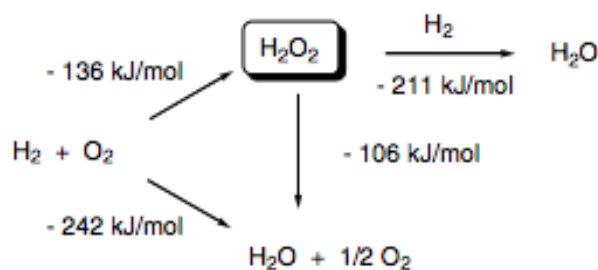
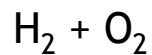
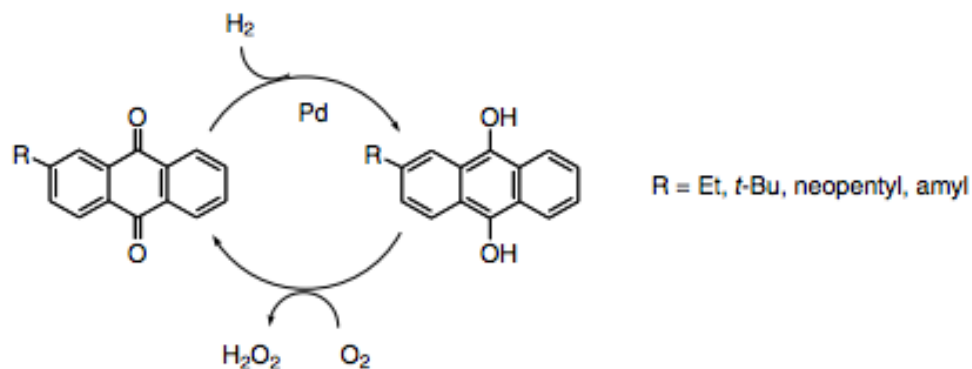


Biorefinery platform molecules



Direct synthesis of H₂O₂

Anthraquinone process



J. Am. Chem. Soc., 2016, 138 (2), pp 574–586