Petrochemistry-2014

OMICS Group Conferences
Accelerating Scientific Discovery

2nd World Congress on
Petrochemistry and Chemical Engineering

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Cyclohexane oxidation: catalytic oxidation *vs* autoxidation

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2014-10-29

Cardiff Catalysis Institute
Cardiff University

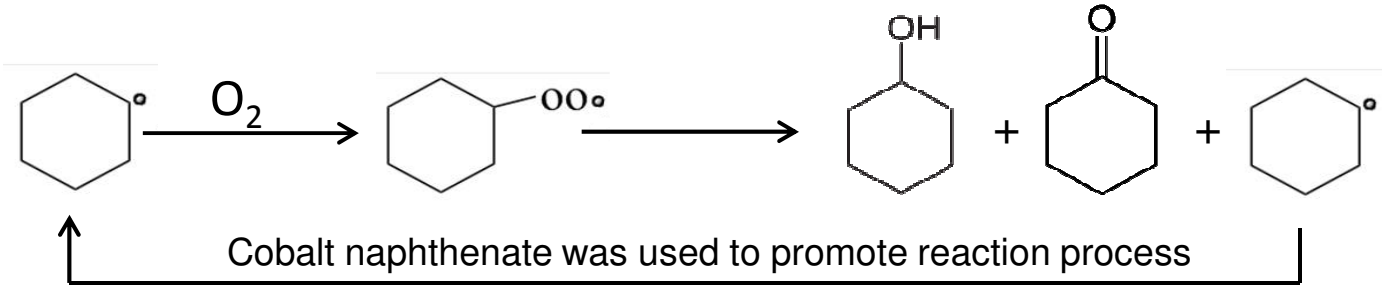
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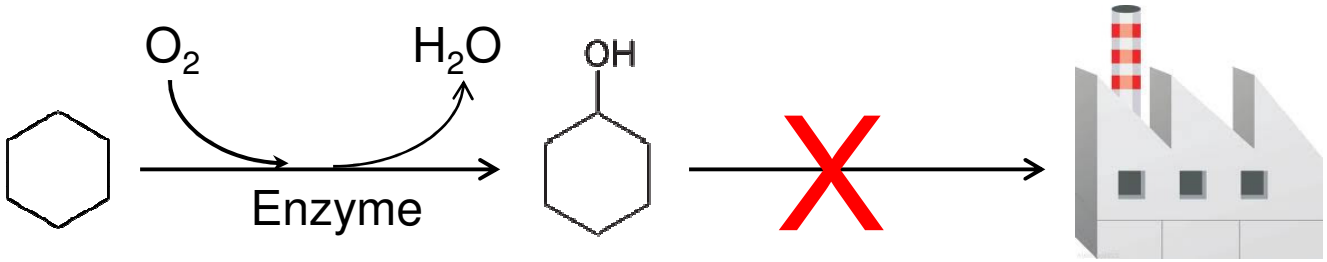
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Results and discussions:

Nano materials as catalysts for cyclohexane oxidation







Can we develop new catalysts for aerobatic oxidation of alkanes?

‘good’
‘unique’ ← Au *new* ? → ‘poorly’
‘excellent’

↓

catalytic behavior? chemical kinetics? mechanism?

J. Catal. 2010, 270, 16; PCCP 2012,14, 16279

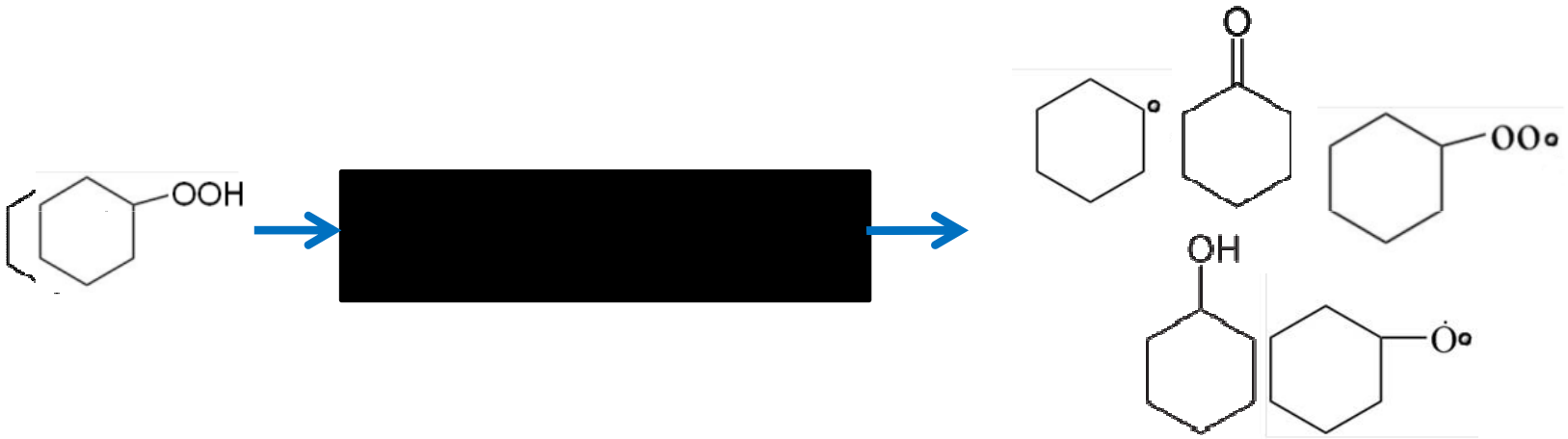
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What can we do?

Can we catch **intermediates**?

Can we identify interaction between reactants and catalysts?

Can we identify evolution of products?



‘hot’ and ‘mess’ conditions

many side reactions

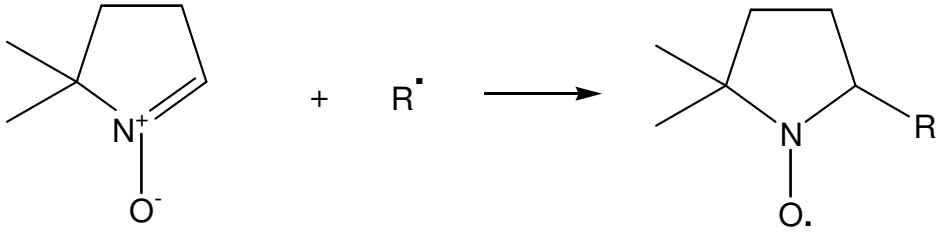
‘cold’ and ‘clean’conditions

only one reaction

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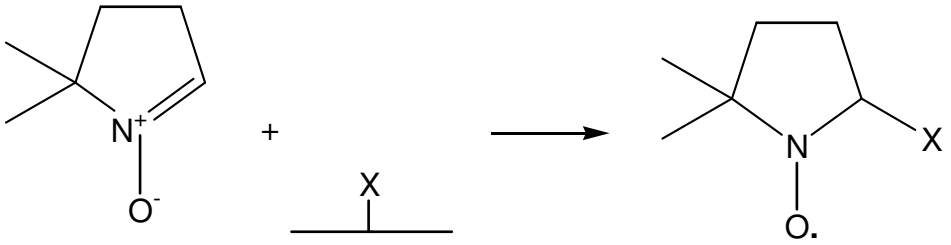
EPR spin trapping methodology



Trapping of a free radical

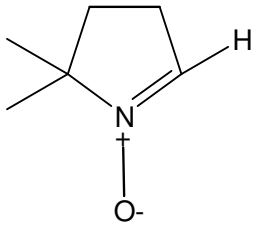
Spin trapping Molecule (diamagnetic)

Spin adduct (paramagnetic)

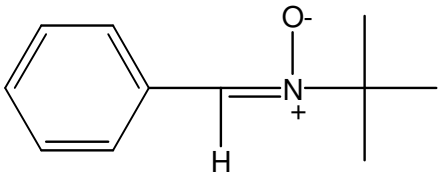


Trapping of species adsorbed over surfaces

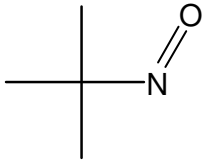
Spin traps used in this study:



5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO)

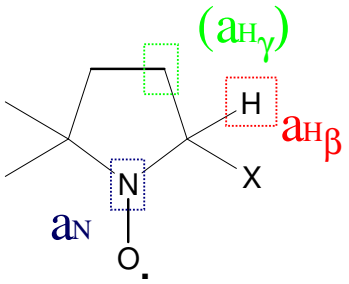


N-*tert*-Butyl-α-phenylnitrone (PBN)

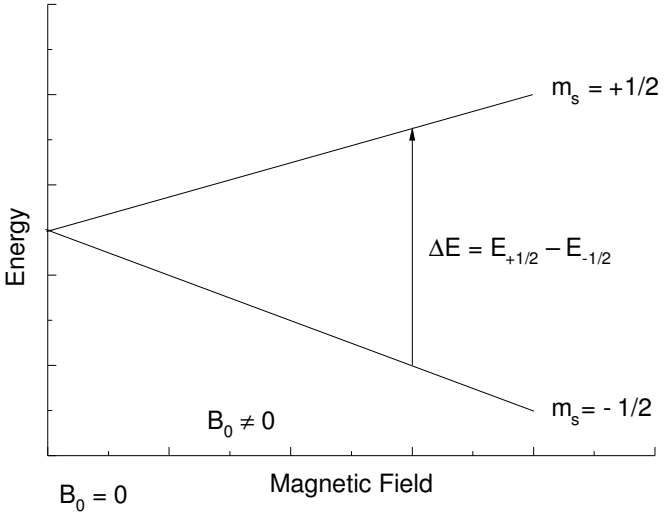


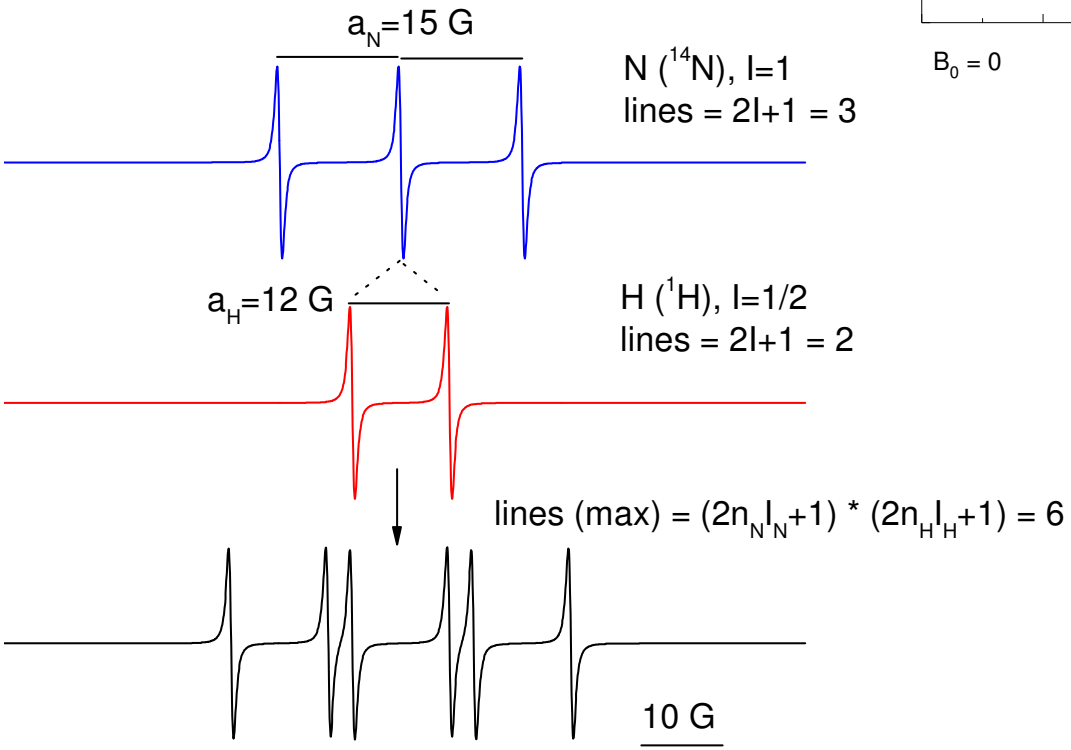
2-methyl-2-nitrosopropane (MNP)

EPR spin trapping methodology



$$\Delta E = g_e \mu_B B_0$$





What is real role of Au?

Entry	Catalyst	Au loading (wt %)	Initiator	Conversion (%)	Selectivity (%)					K/A ratio
					K	A	CHHP	AA	Total	
1	Au/MgO - Imp	1	-	1.93	30	51	7	0	88	0.58
2	Au/MgO - Imp	0.1	-	1.75	35	44	15	0	94	0.8
3	Au/MgO - Imp	0.01	-	1.35	28	36	27	0	91	0.78
4	autoxidation	-	-	1.10	19	22	57	0	98	0.86
5	Au/MgO - Imp	1	AIBN	4.50	34	51	6	0	91	0.67
6	autoxidation	-	AIBN	6.75	32	57	2	0	91	0.56
7	Au/MgO - Imp	1	TBHP	5.01	29	50	0	19	98	0.58
8	autoxidation	-	TBHP	6.61	33	52	0	15	100	0.63

Slightly higher than blank

Mass production of peroxide ⟶ *What's role of Au?*

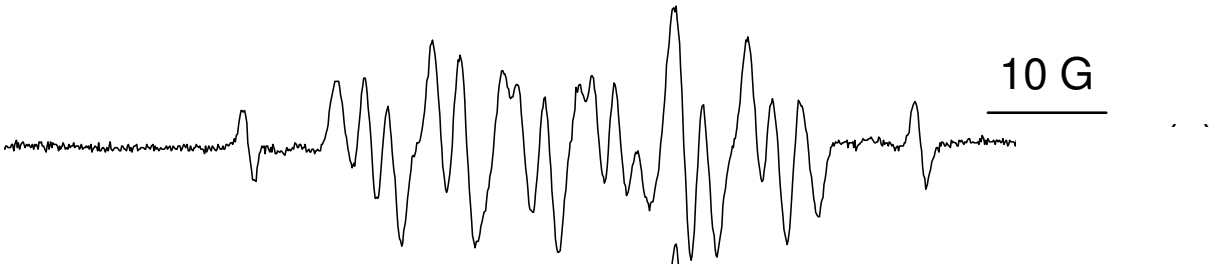
Higher A/K ratio

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C_6H_{11}-OOH → C_6H_{11} -OO• + $C_6H_{11}O$•

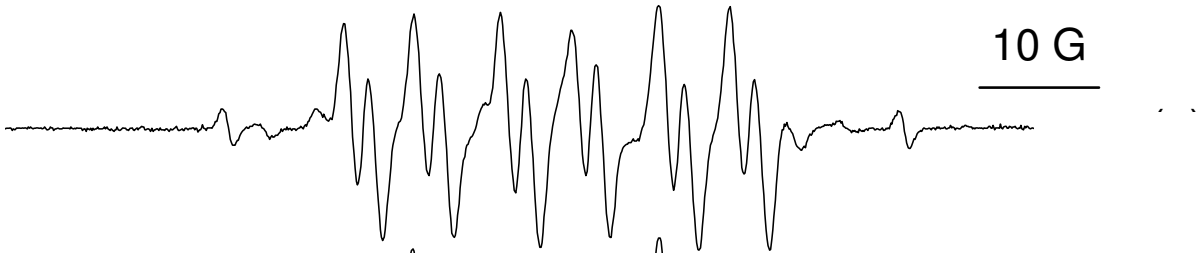
Autoxidation



Spin adducts	Relative amount (%)		
	DMPO-O-C_6H_{11}	DMPO-OO-C_6H_{11}	DMPO-C_6H_{11}
Autoxidation	50	44	-

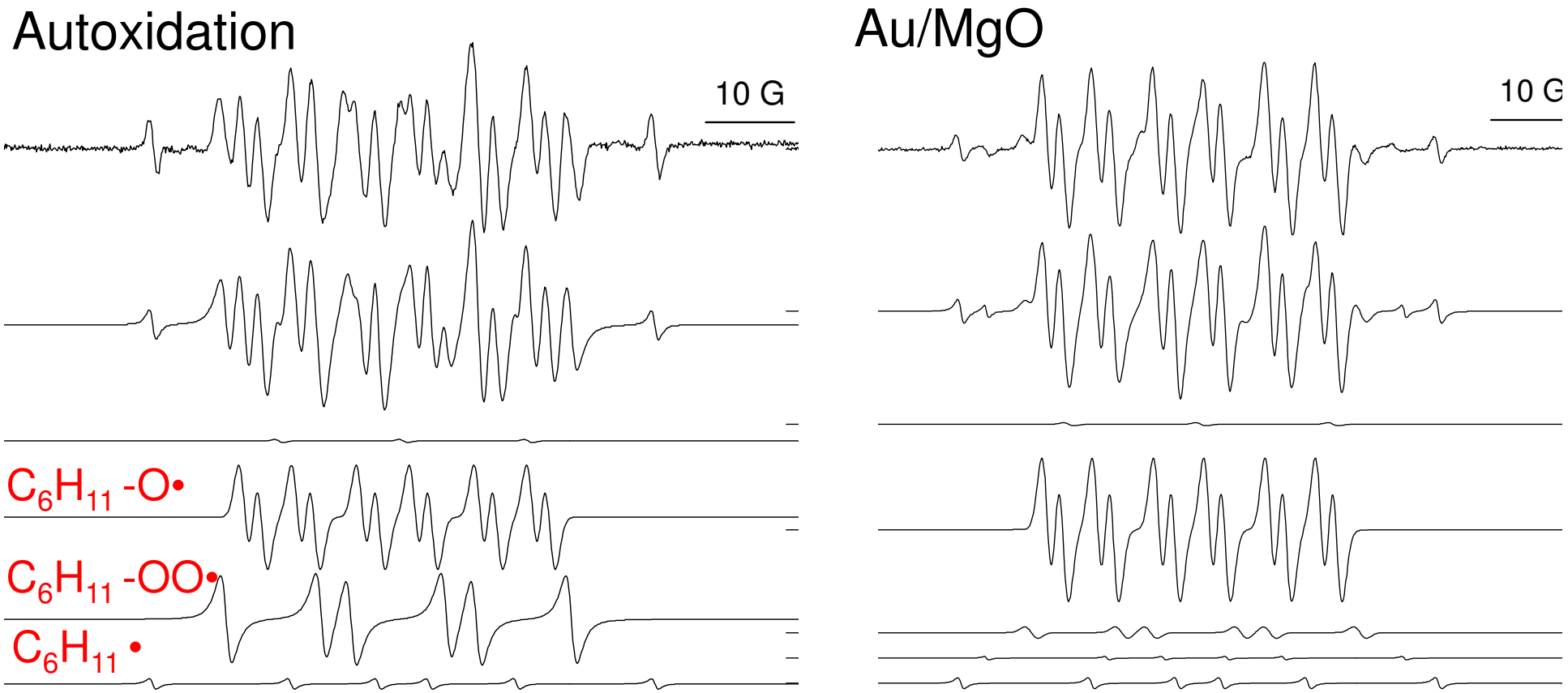
C_6H_{11}-OOH → C_6H_{11} -OO• + C_6H_{11}O•

Au/MgO



Spin adducts	Relative amount (%)		
	DMPO-O-C_6H_{11}	DMPO-OO-C_6H_{11}	DMPO-C_6H_{11}
Au/MgO	81	8	4

C_6H_{11}-OOH → C_6H_{11}-OO• + C_6H_{11}O•



Spin adducts	Relative amount (%)		
	DMPO-O-C_6H_{11}	DMPO-OO-C_6H_{11}	DMPO-C_6H_{11}
Autoxidation	50	44	-
Au/MgO	81	8	4

Catalyst or initiator?

Both: it can act as catalyst for intermediate decomposition to promote autoxidation

Why gold is unique but bad?

diffusion control: autoxidation is very fast!

activity

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Conclusion:

Noise raises from side-reactions, surface changing under chemical environments, complicated composition of catalysts:

High-vaccum surface characterization (clear but weak)

molecular probes instead of real reactants/active sites

In-situ characterization (strong but noisy)

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