Catalytic Wet Oxidation (CWO) in Waste Water Treatment

(Introduction of a new Technology).

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CONTEXT OF CWO IN WASTE WATER TREATMENT

Problem: Treatment of waste water streams containing toxic & non-biodegradable organics at dilute concentrations.

- Phenols → Chemical & petrochemical industries…
- Chlorophenols → pulp & paper industry (Cl bleach).

Proposed treatment method:

Heterogeneous Catalytic Wet Oxidation (CWO) conducted at low severity (T, P)

- Catalyst (solid) recoverable & reusable.
- Catalyst deactivation due to heavy polymeric deposits.
- Low selectivity towards CO_2.

GENERAL OBJECTIVES

Development of:

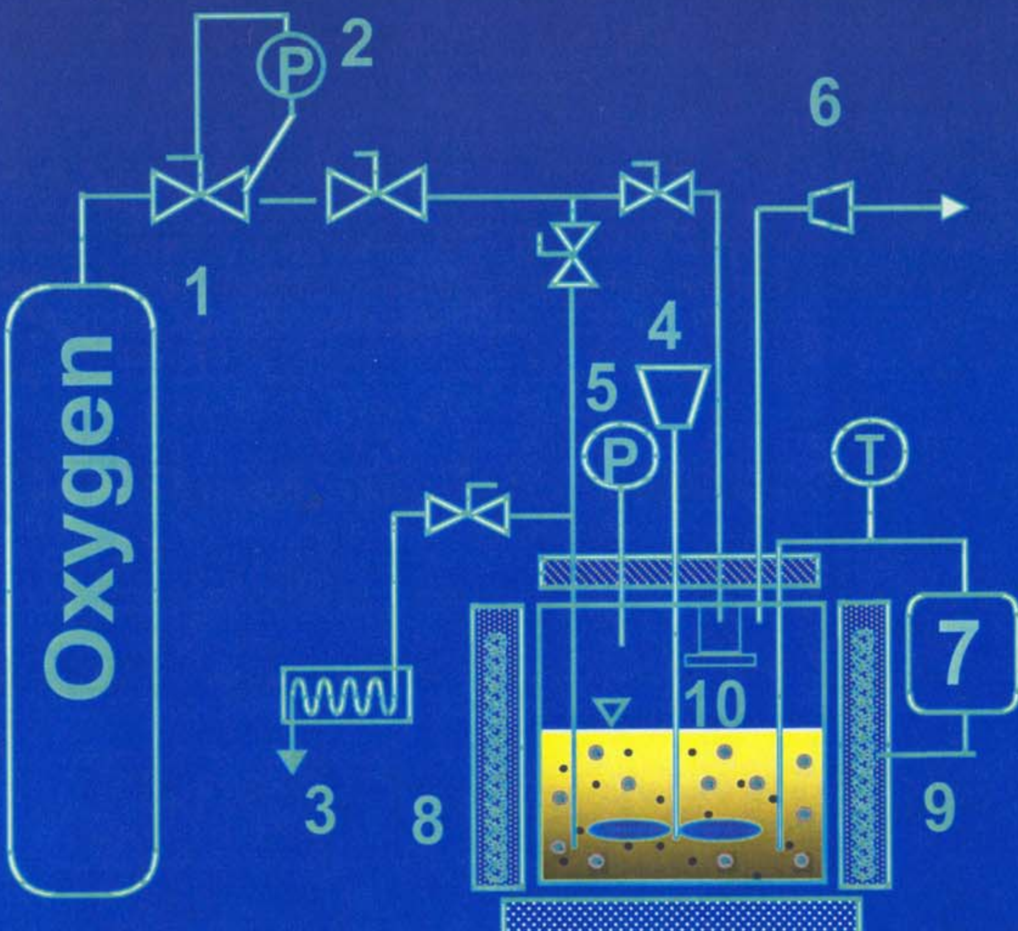
- **Selective & cokeless industrial catalysts;**
- **Trustful CWO kinetics accounting for deactivation.**
- **Economically and process wise acceptable to industries.**

SPECIFIC OBJEVTIVES

- **CWO of model phenol solution over MnO_2/CeO_2**
    - **Pollutant and TOC removal,**
    - **Catalyst characterization,**
    - **Kinetic modeling,**
    - **Fate of removed C & catalyst selectivity,**
    - **MnO_2/CeO_2 noble metal promotion.**

- **CWO of a model Chloroguaiacol solution**
    - **TOC & pollutant removal**
        - **Effect of catalysts (noble metal; oxides),**
        - **Effect of temperature,**
        - **Intermediates identification.**

EXPERIMENTAL



1- Oxygen cylinder
2- Pressure regulator
3- Liquid sampling
4- Magnet drive
5- Pressure gauge
6- Relief valve
7- Temperature controller
8- Slurry reactor
9- Heating jacket
10- Reagent injection device

Range of operating conditions:

Initial pollutant concentration	**1-10 g/L**
Catalyst loading	**1-5 g/L**
BET surface area	
Mn/Ce	107 m^2/g
Pt-Mn/Ce	102 #
Pt/Al_2O_3	190 #
Co/Bi	64 #
$CuO.ZnO/Al_2O_3$	10 #
Particle diameter	<0.147 mm
Oxygen partial pressure	0.5-1.5 MPa
Temperature	80-200 ^oC
Stirrer speed	750 rpm

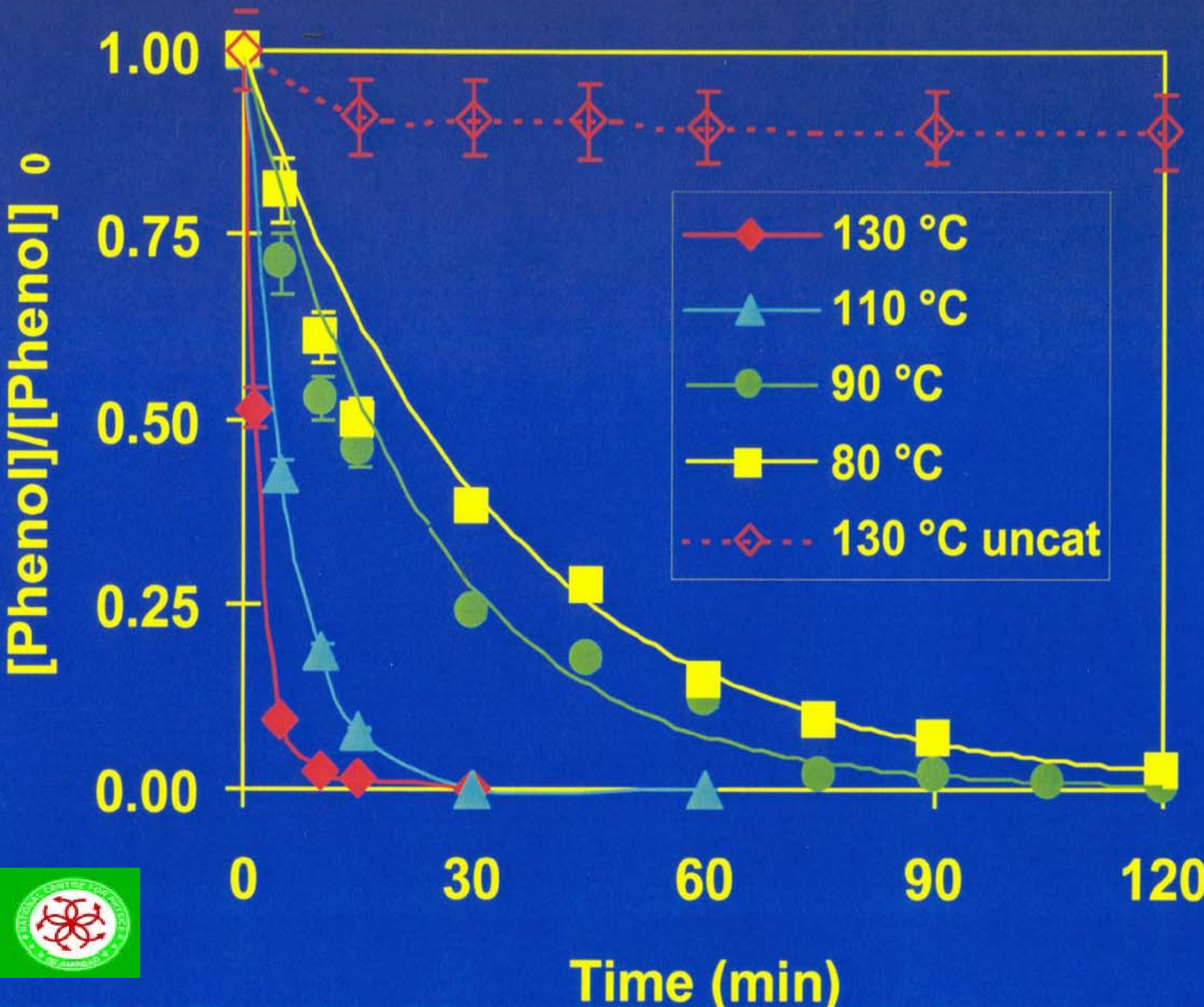
Analytical techniques:

Liquid phase: GC-MSD, HPLC, TOC.

Catalyst: BET, CHN, XPS, TPO-MS, TPR, SEM.

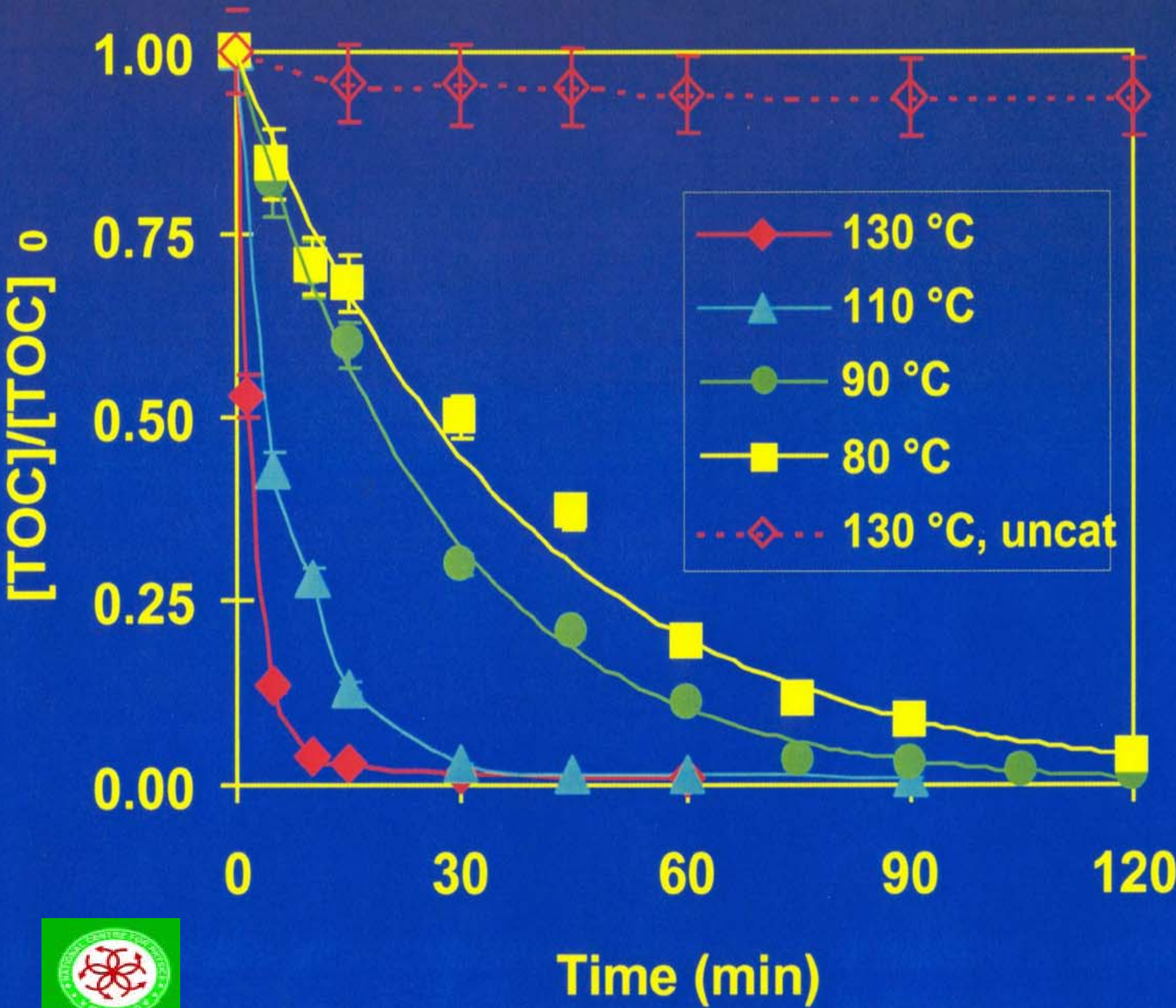
RESULTS

Effect of temperature on phenol CWO over MnO_2/CeO_2



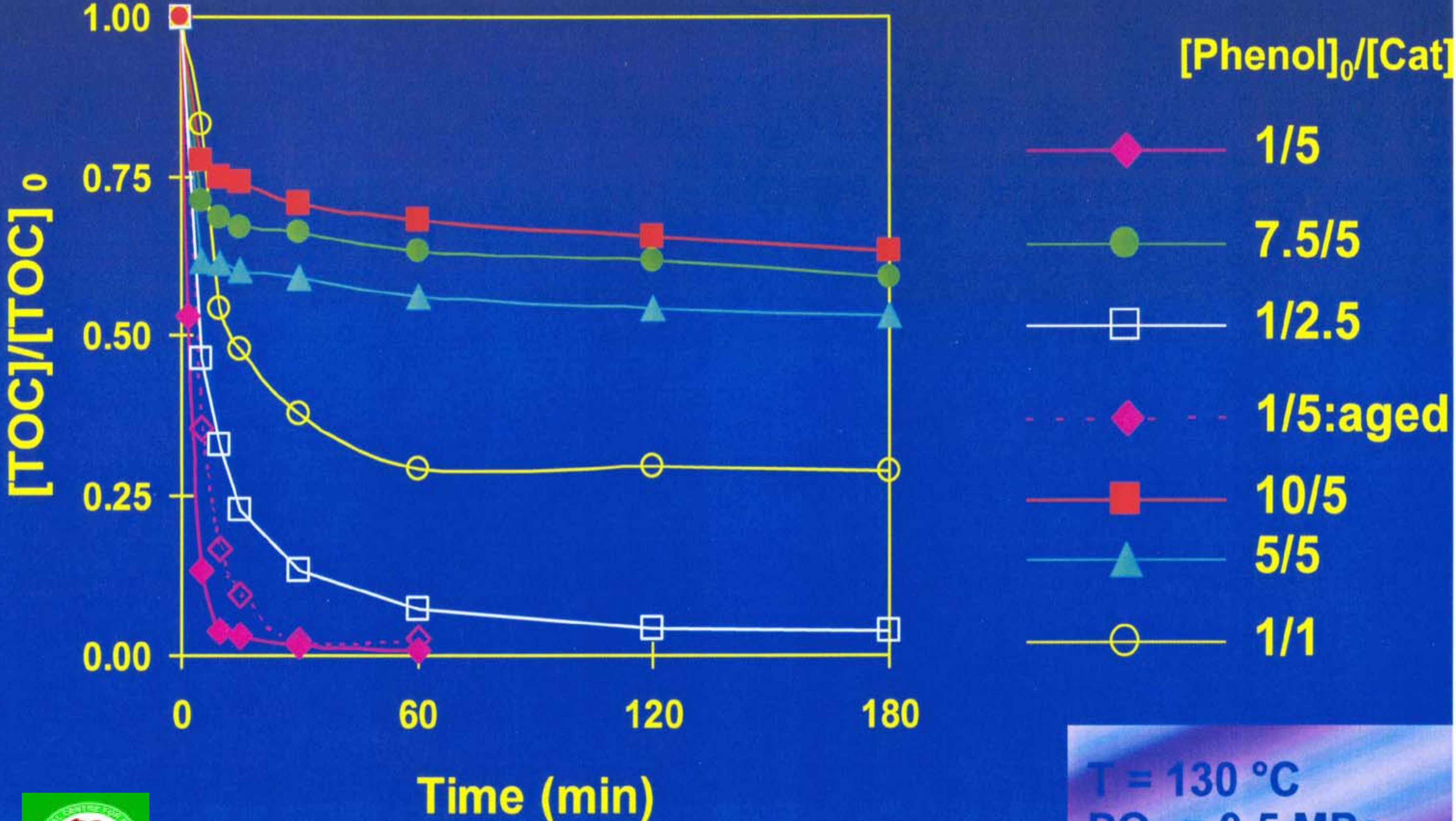
$[Phenol]_0 = 1 g/L$
$(TOC)_0 = 766$ ppm
$PO_2 = 0.5$ MPa
[Cat] = 5 g/L

Effect of temperature on TOC reduction during CWO of phenol over MnO_2/CeO_2



$[Phenol]_0$ = 1g/L
$(TOC)_0$ = 766 ppm
PO_2 = 0.5 MPa
[Cat] = 5 g/L

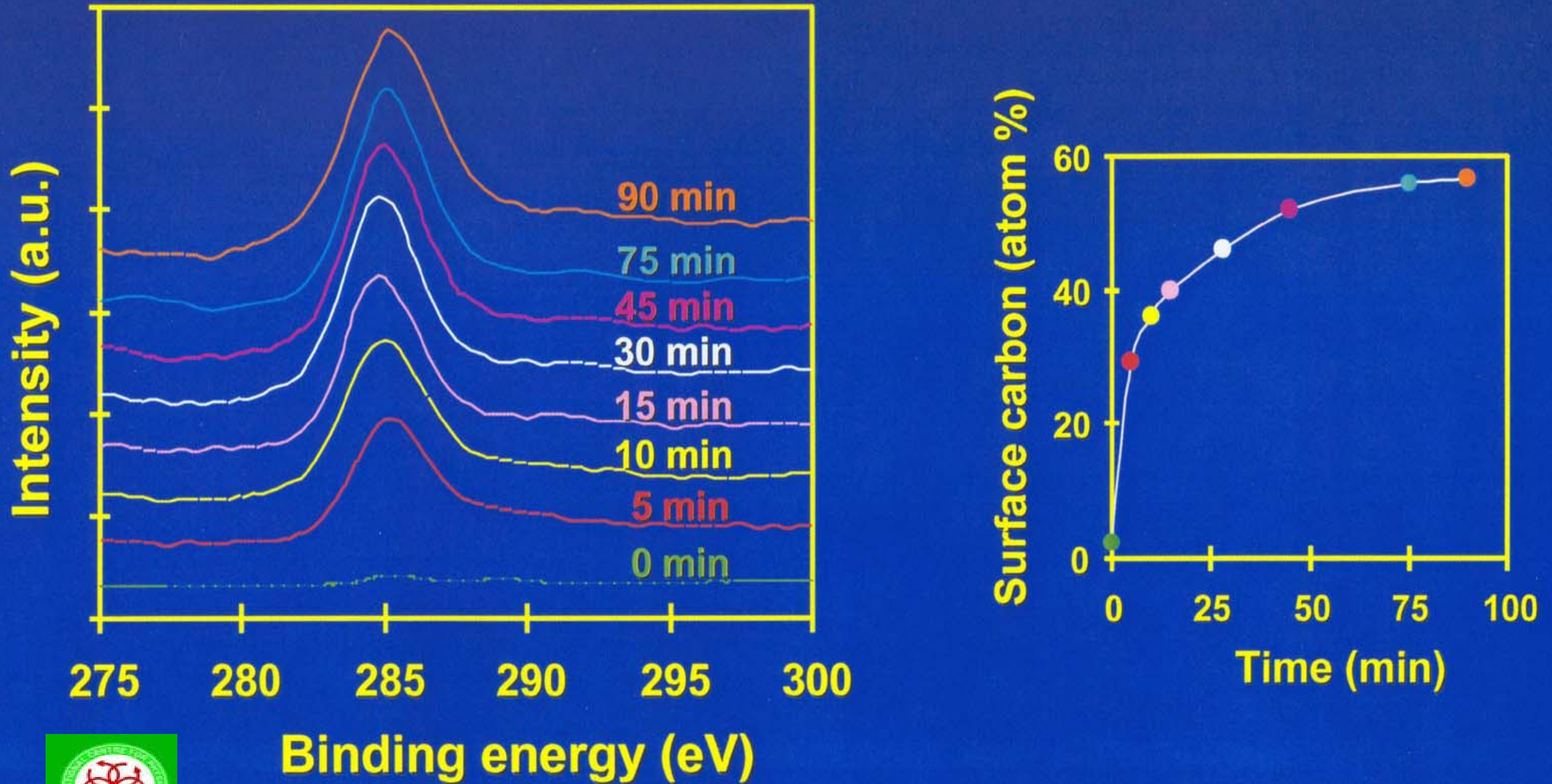
Effect of phenol initial concentration and catalyst loading on TOC removal in the presence of MnO_2/CeO_2



T = 130 °C
PO_2 = 0.5 MPa

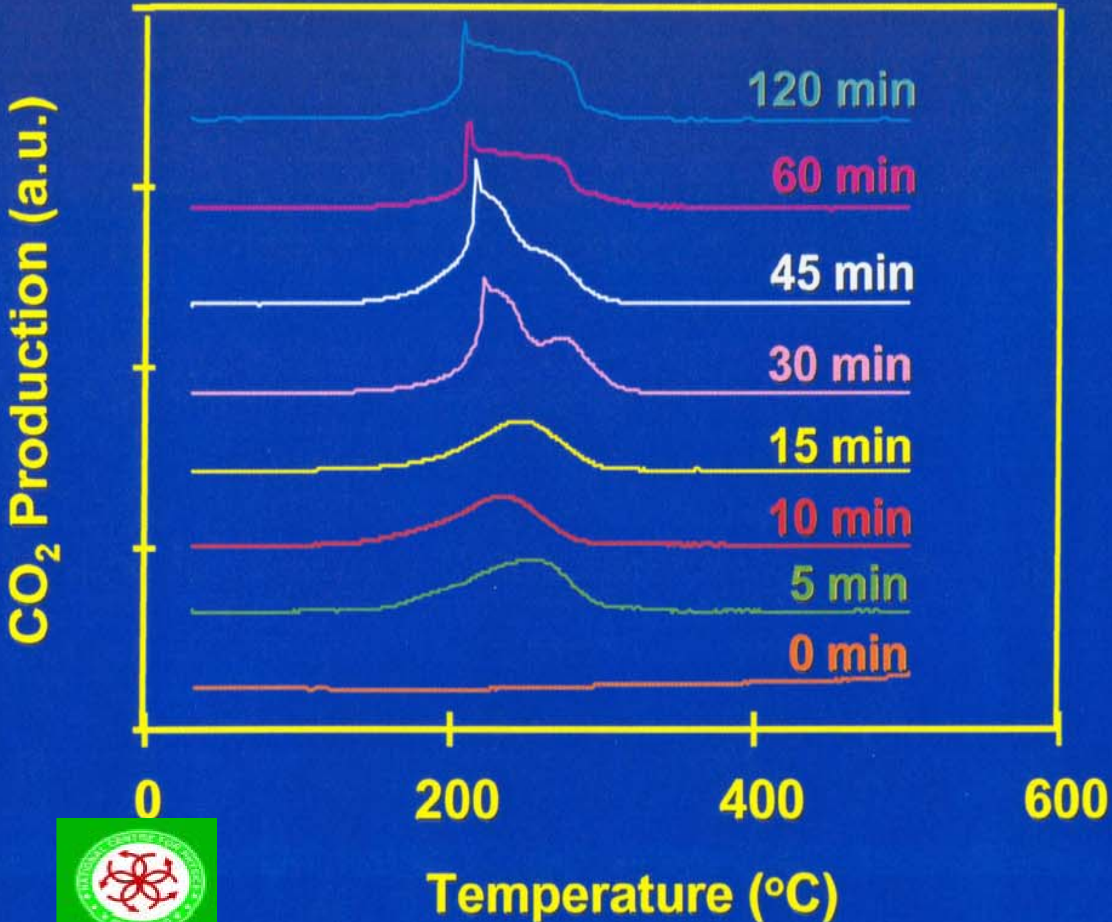
XP C1s peak spectra of catalyst samples withdrawn @ # CWO reaction times

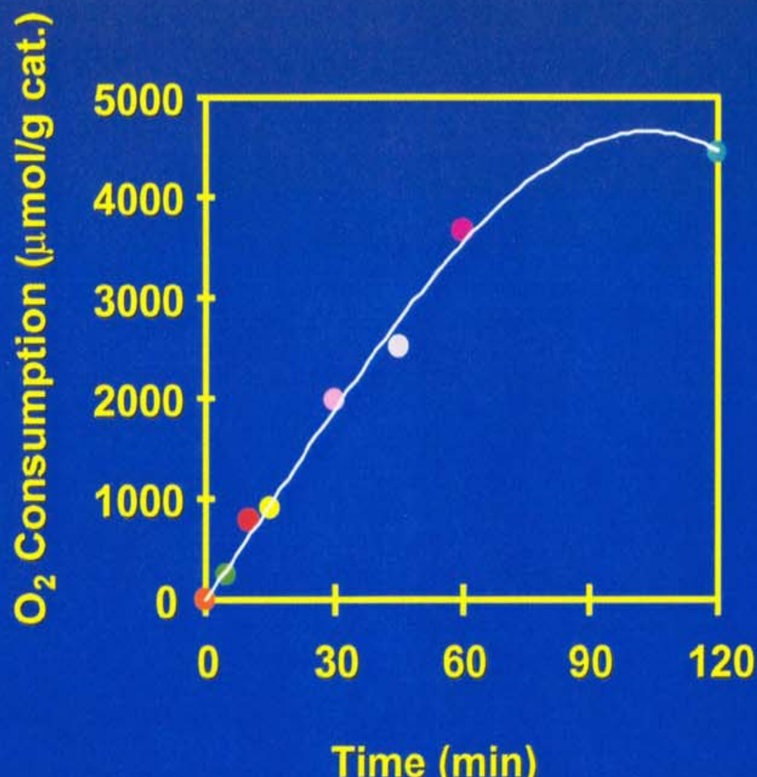
[Phenol]$_0$ = 1g/L; (TOC)$_0$ = 766 ppm; PO_2 = 0.5 MPa;T = 80 °C; Mn/Ce



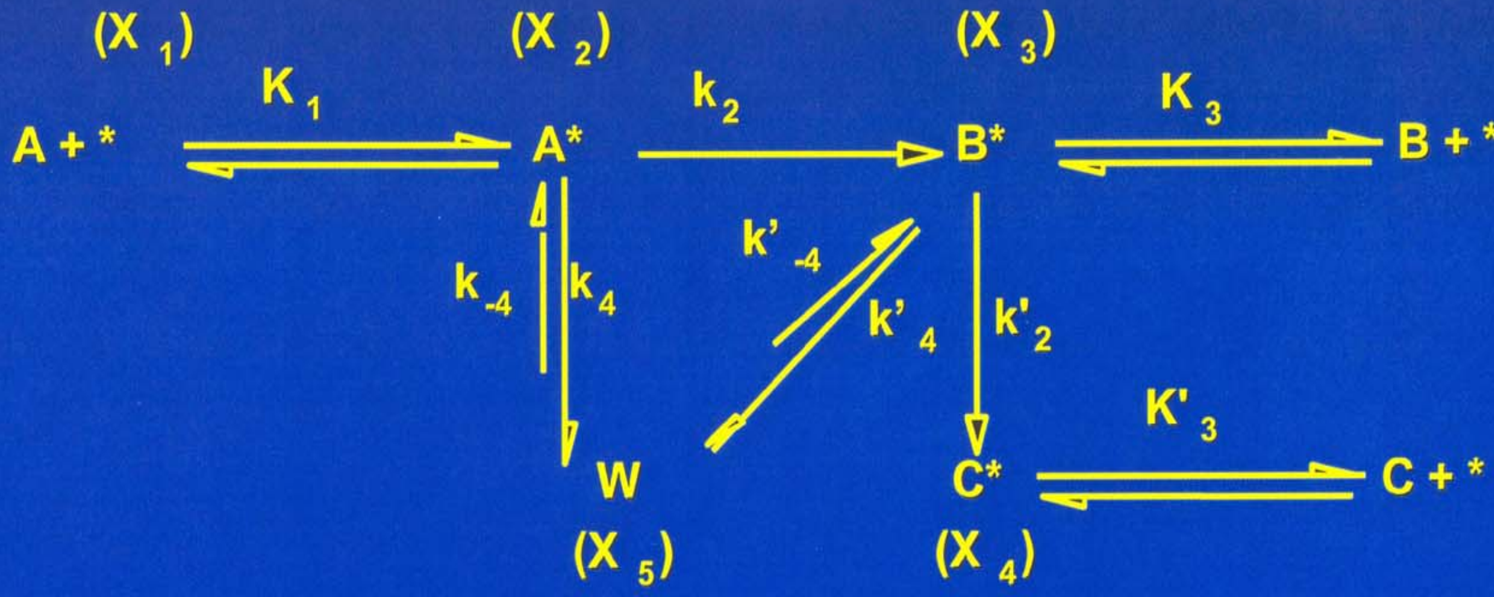
CO_2 production during TPO of catalyst samples withdrawn @ # CWO reaction times

$[Phenol]_0$ = 1g/L; $(TOC)_0$ = 766 ppm; PO_2 = 0.5 MPa;T = 80 °C; Mn/Ce

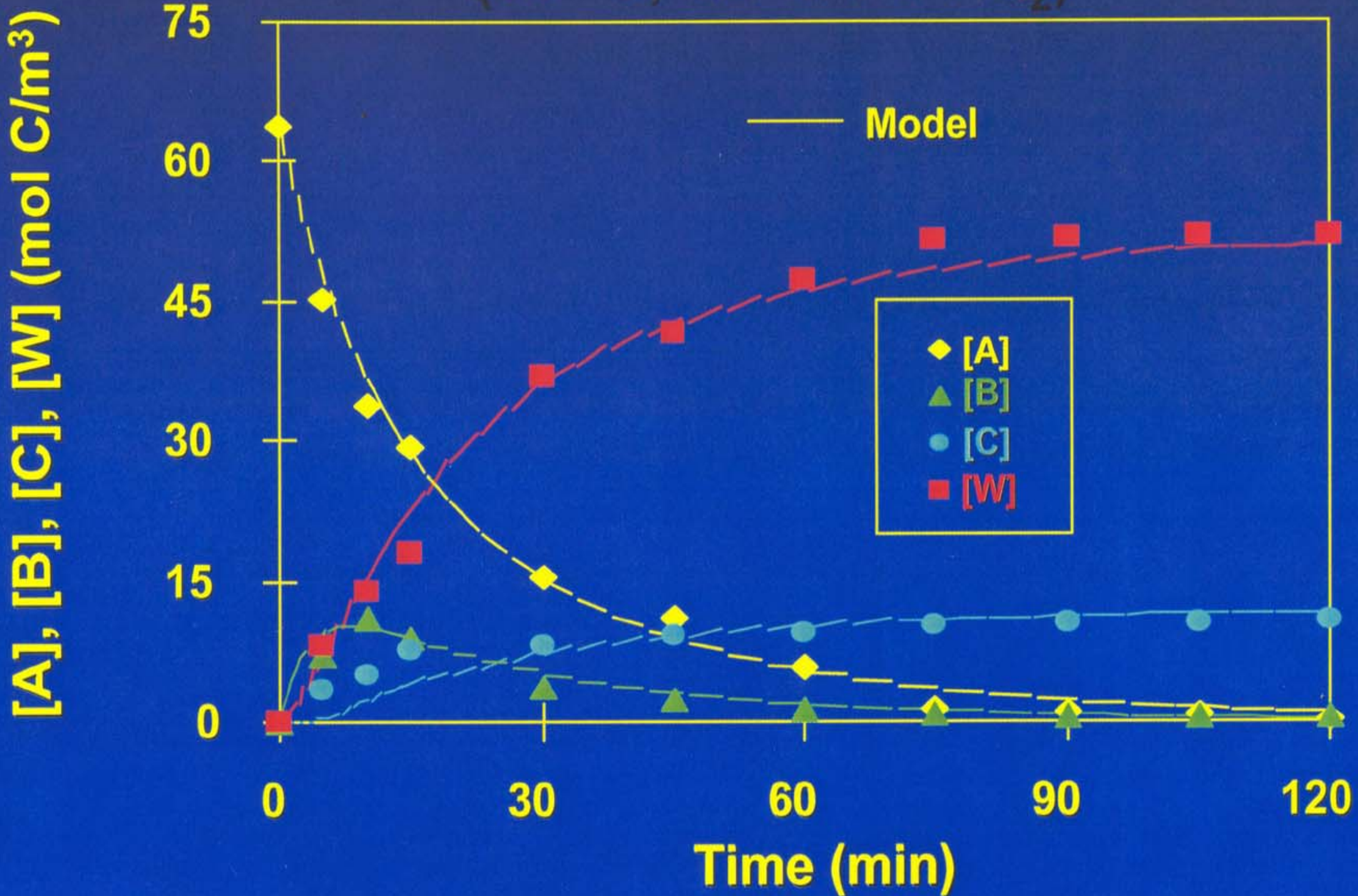




Proposed reaction scheme for phenol CWO with formation of carbonaceous deposits



Measured and predicted time profiles for phenol CWO (90 °C, 0.5 M Pa PO_2)



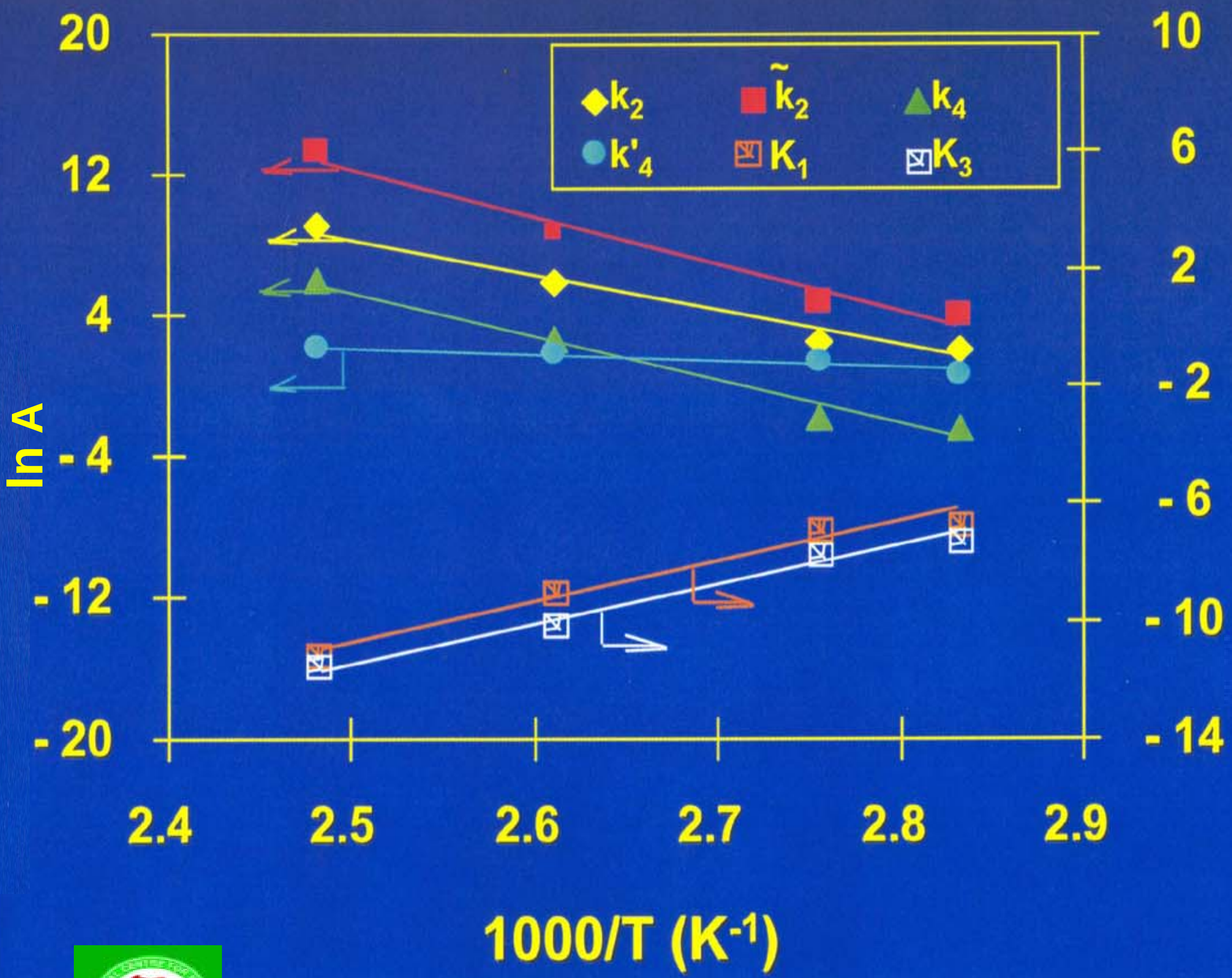
A: Phenolic Carbon

B: Dissolved intermediates carbon

C: Total Inorganic Carbon

W: Solid carbon

Arrhenius and Van't Hoff plots for rate & equilibrium constants



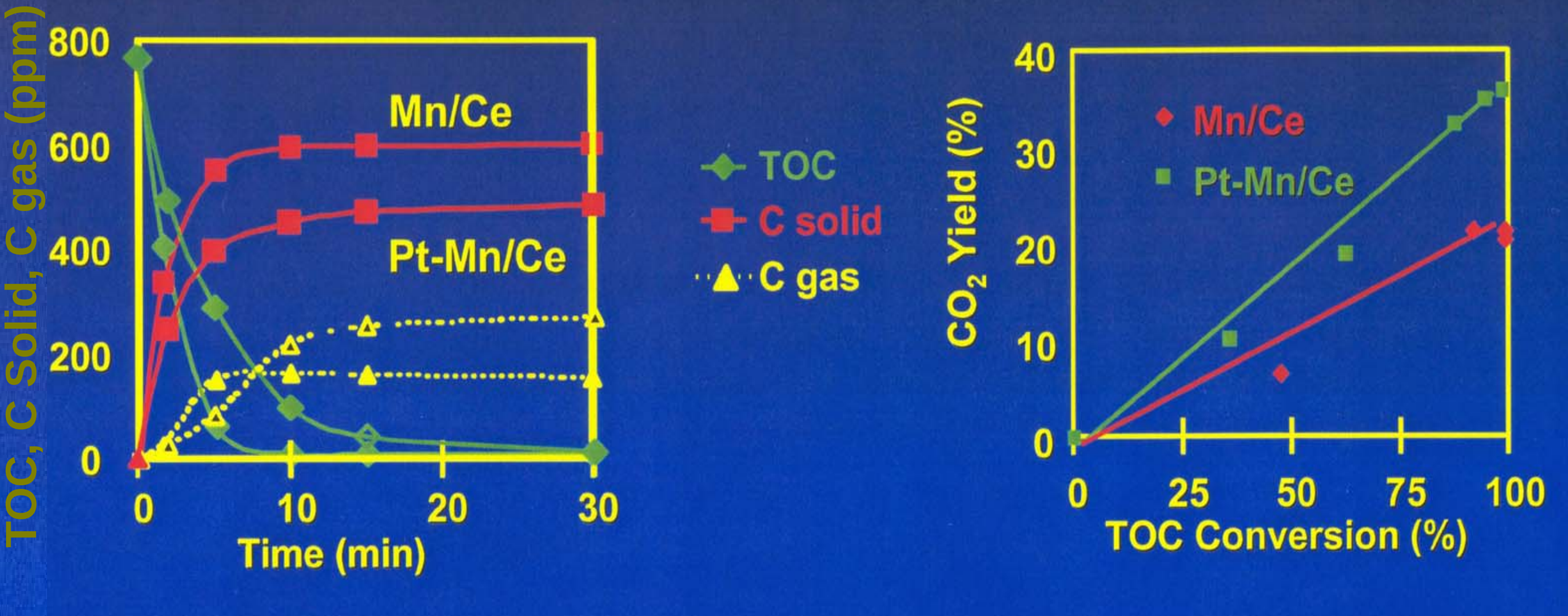
Activation energies

k	E (kJ/mol)
k_2	174
k_2'	227
k_4	212
k_4'	34

Adsorption enthalpies

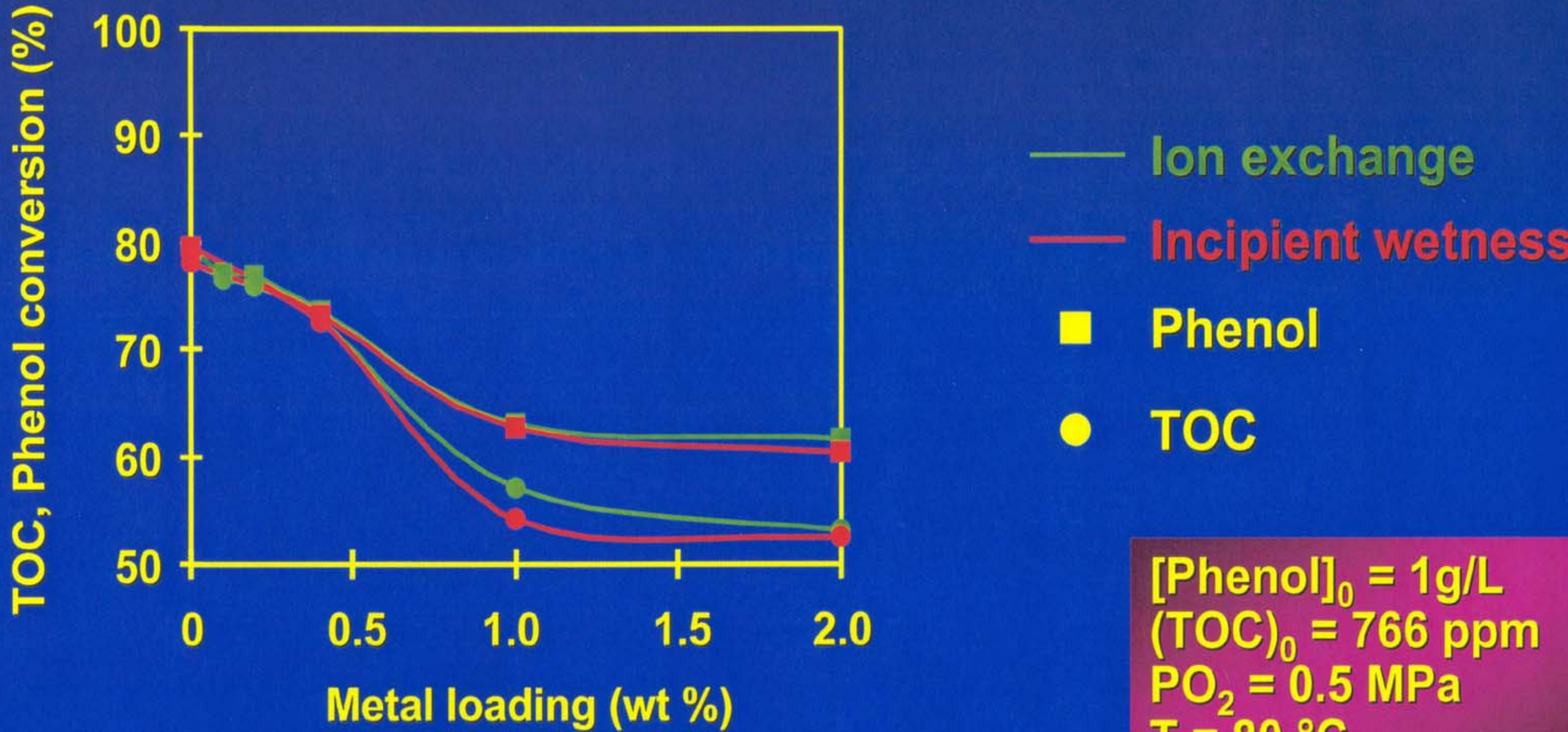
k	E (kJ/mol)
k_2	174
k_2'	227

TOC, solid carbon, gaseous carbon (CO_2) time profiles, and CO_2 yield versus TOC conversion



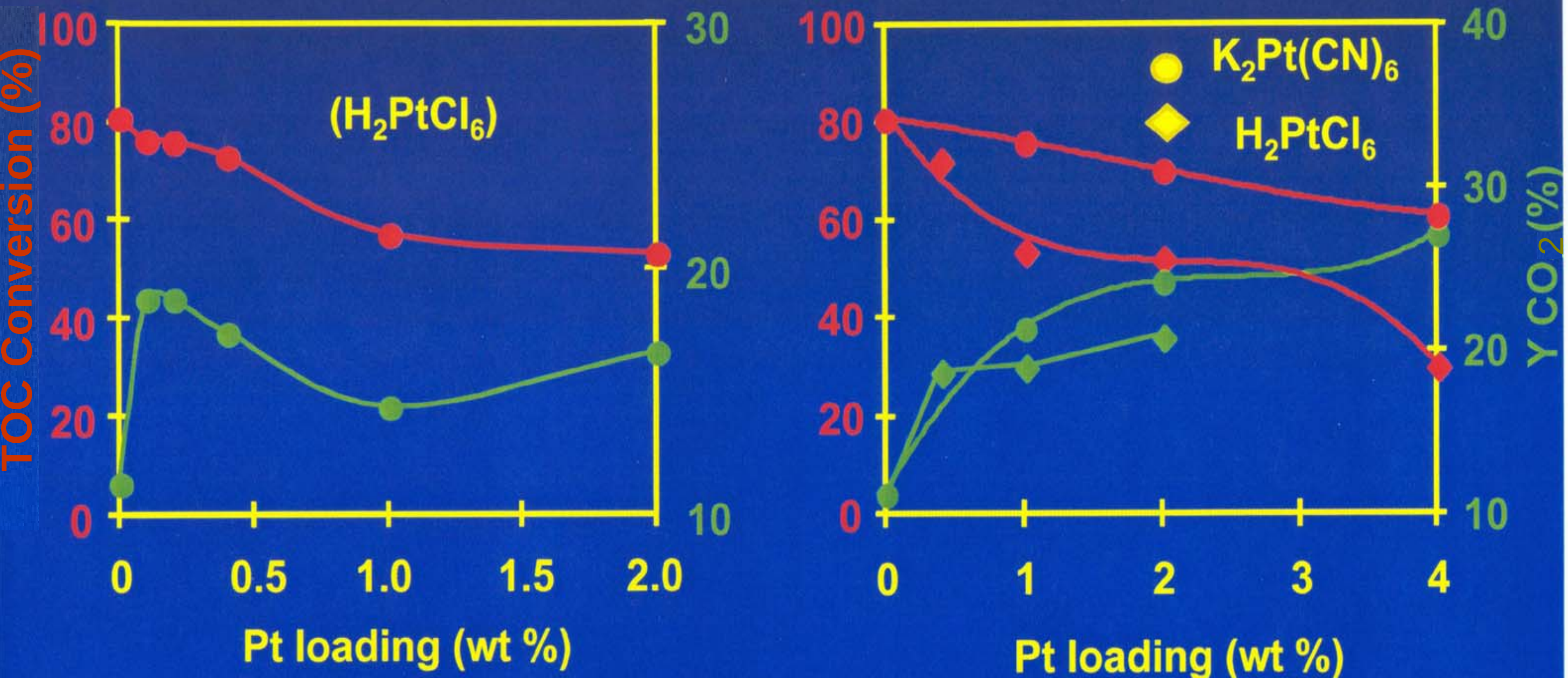
$[Phenol]_0 = 1 g/L$
$(TOC)_0 = 766$ ppm
$PO_2 = 0.5$ MPa
T = 130 °C

Effect of Pt-loading & loading method on TOC and phenol conversions



$[Phenol]_0$ = 1g/L
$(TOC)_0$ = 766 ppm
PO_2 = 0.5 MPa
T = 80 °C
t = 60 min

TOC conversion and CO_2 yield versus Pt-loading on Mn/Ce

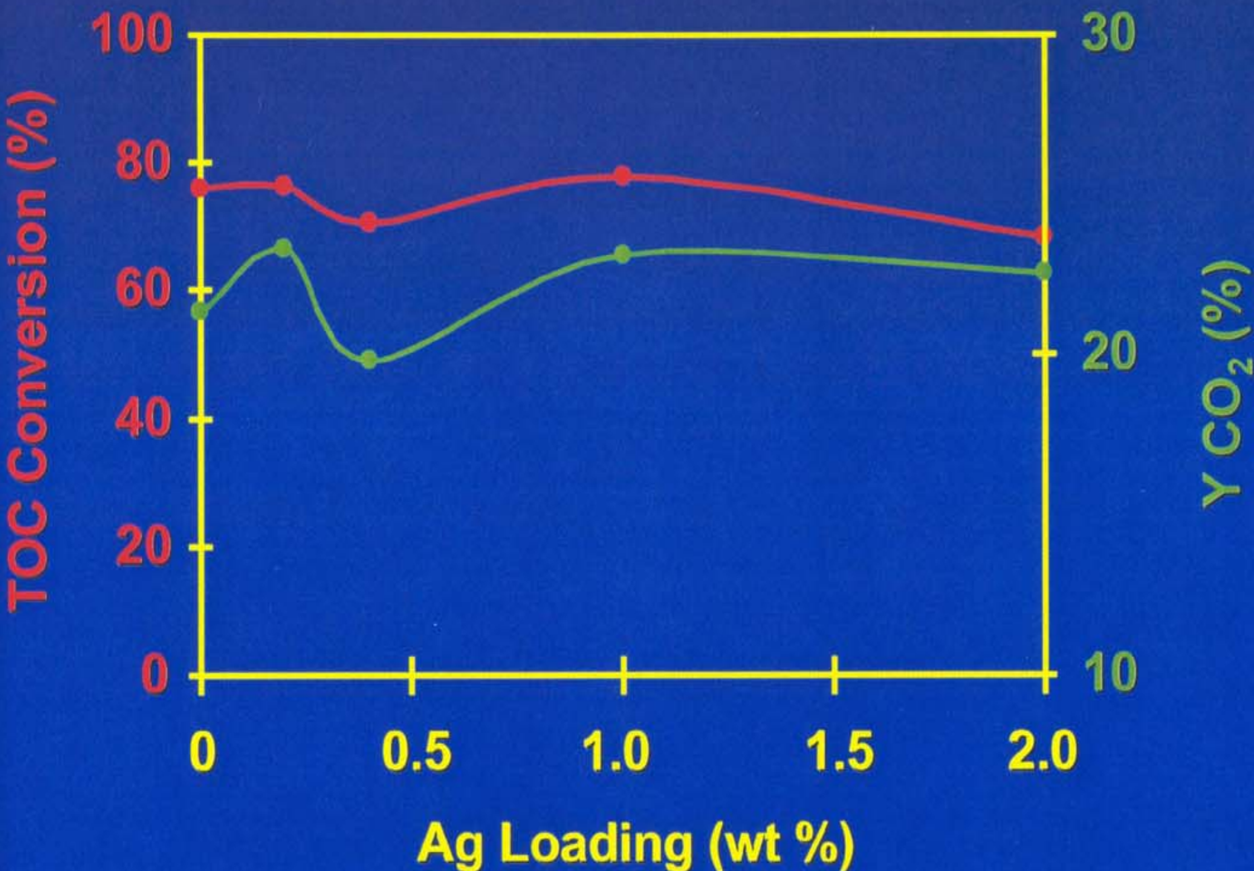


Ion exchange

$[Phenol]_0$ = 1g/L
$(TOC)_0$ = 766 ppm
PO_2 = 0.5 MPa
T = 80 °C
t = 60 min

Incipient wetness

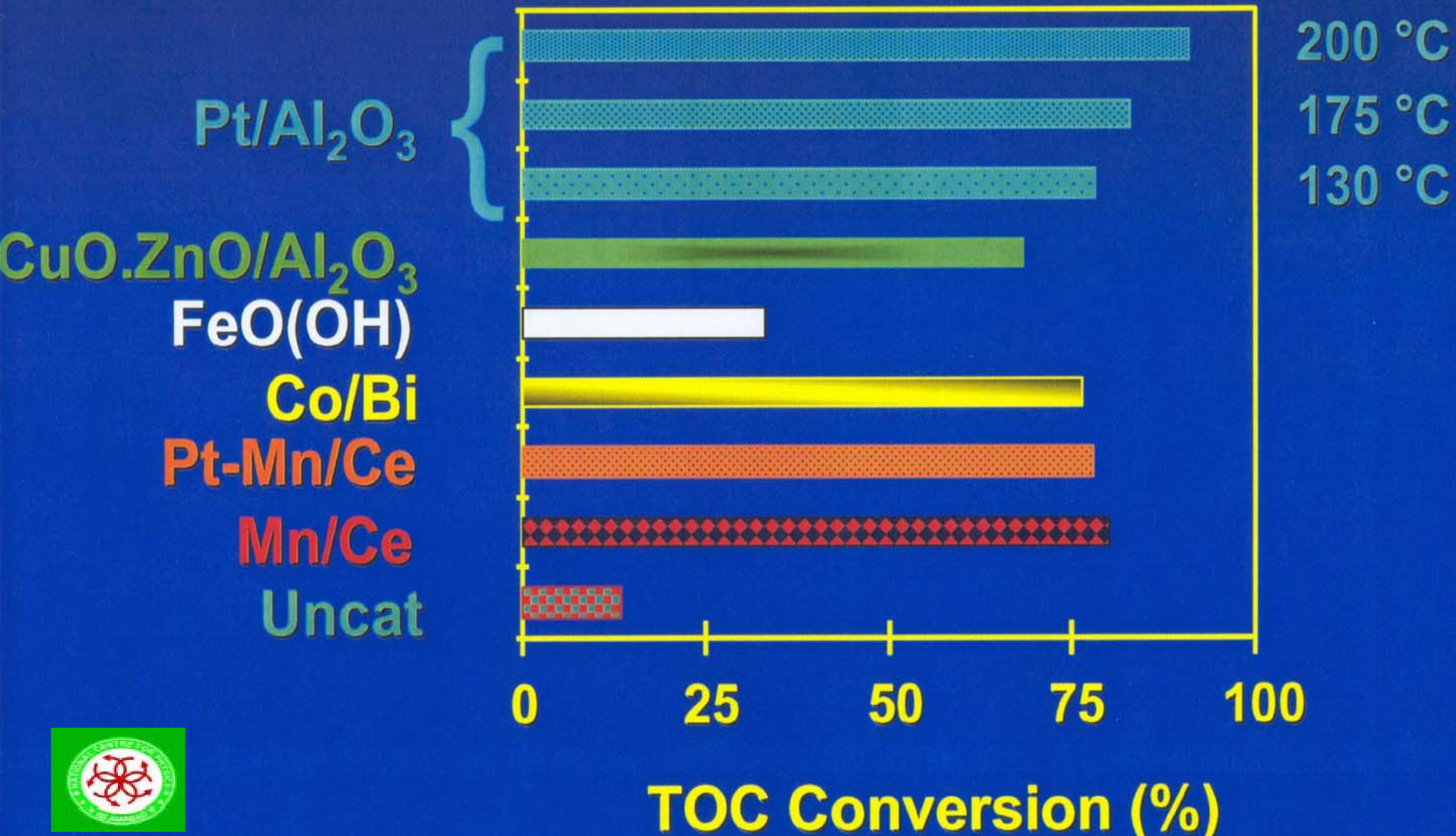
TOC conversion and CO_2 yield versus Ag-loading on Pt (1 wt %)-Mn/Ce



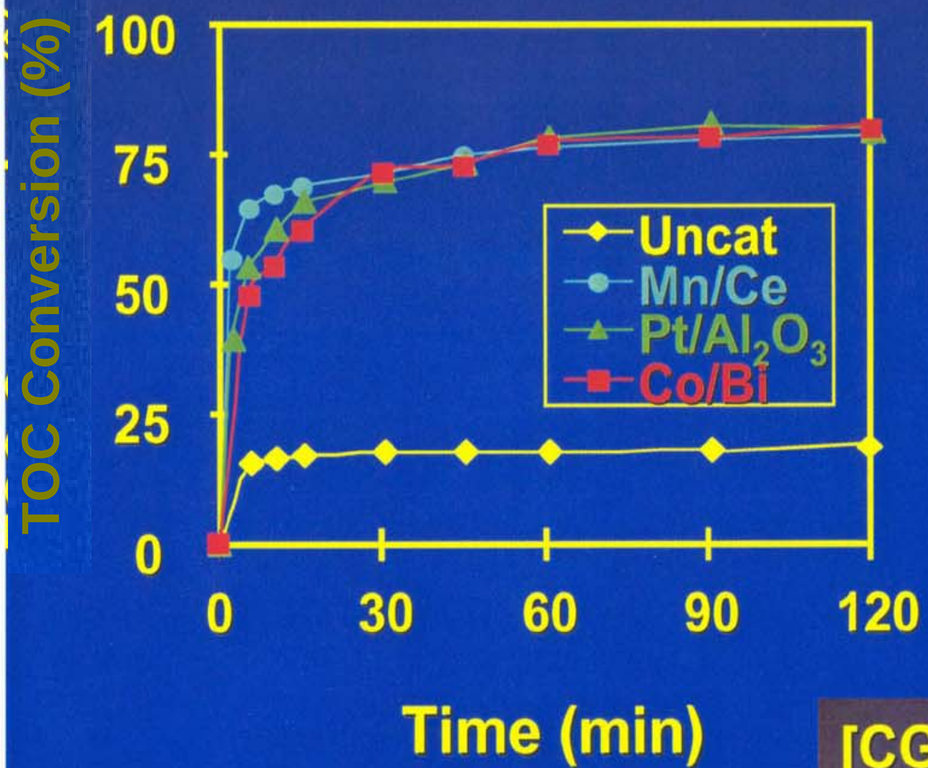
$[Phenol]_0$ = 1g/L
$(TOC)_0$ = 766 ppm
PO_2 = 0.5 MPa
T = 80 °C
t = 60 min

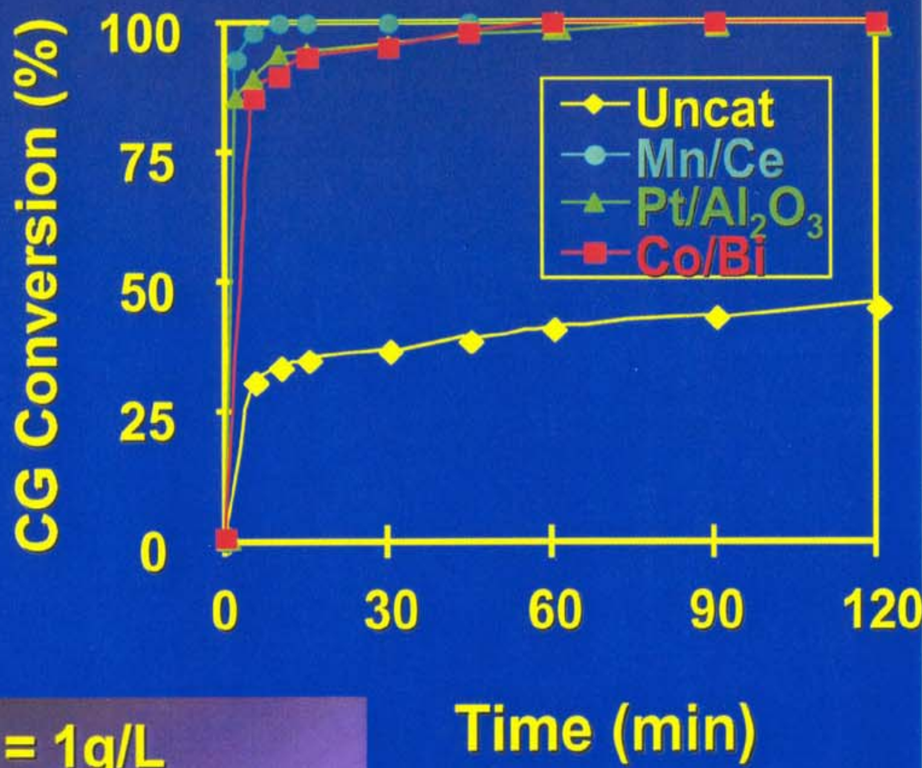
Screening tests: TOC removal vs. # solid catalysts (CWO of chloroguaiacol)

$[CG]_0$ = 1g/L; $(TOC)_0$ = 529 ppm; PO_2 = 0.5 MPa; T = 130 °C; t =1hr



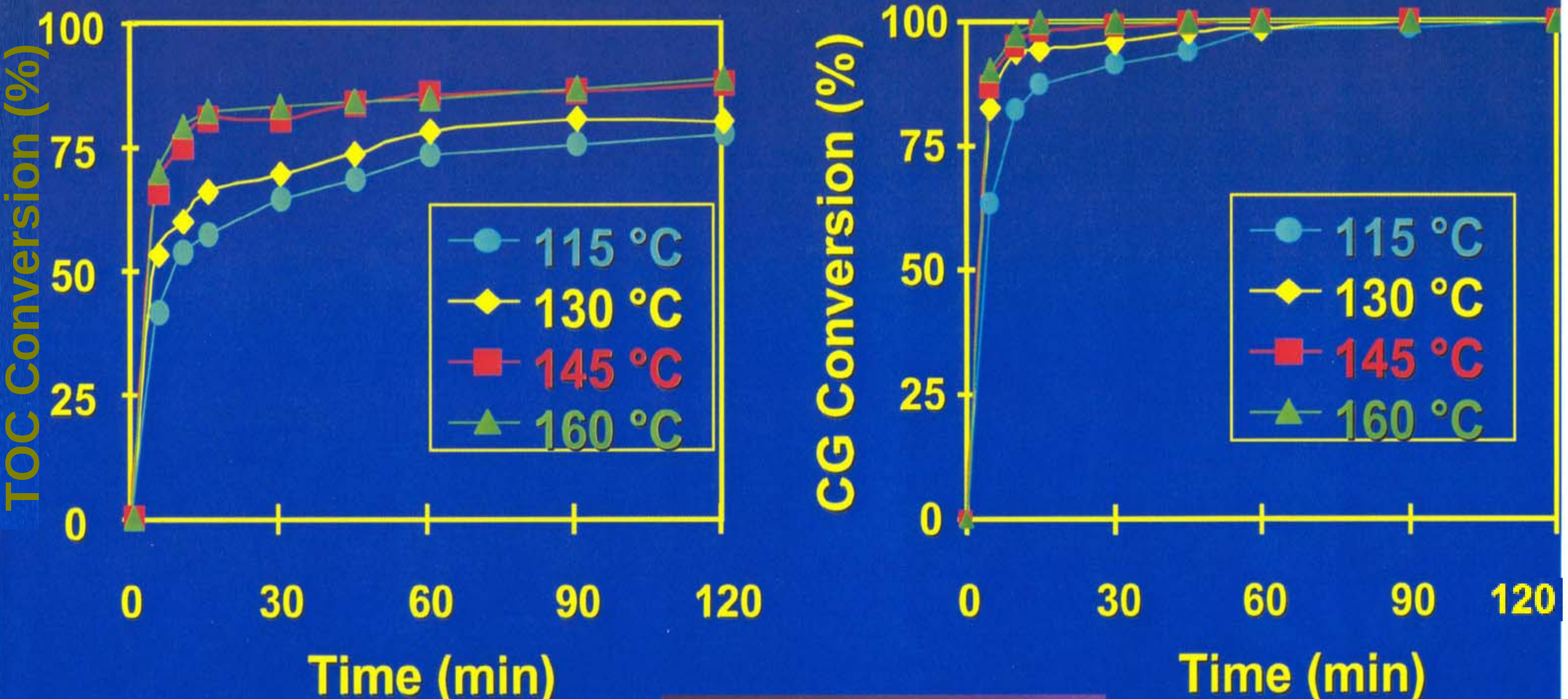
Effect of catalyst on TOC & chlorogaïacol degradation rate





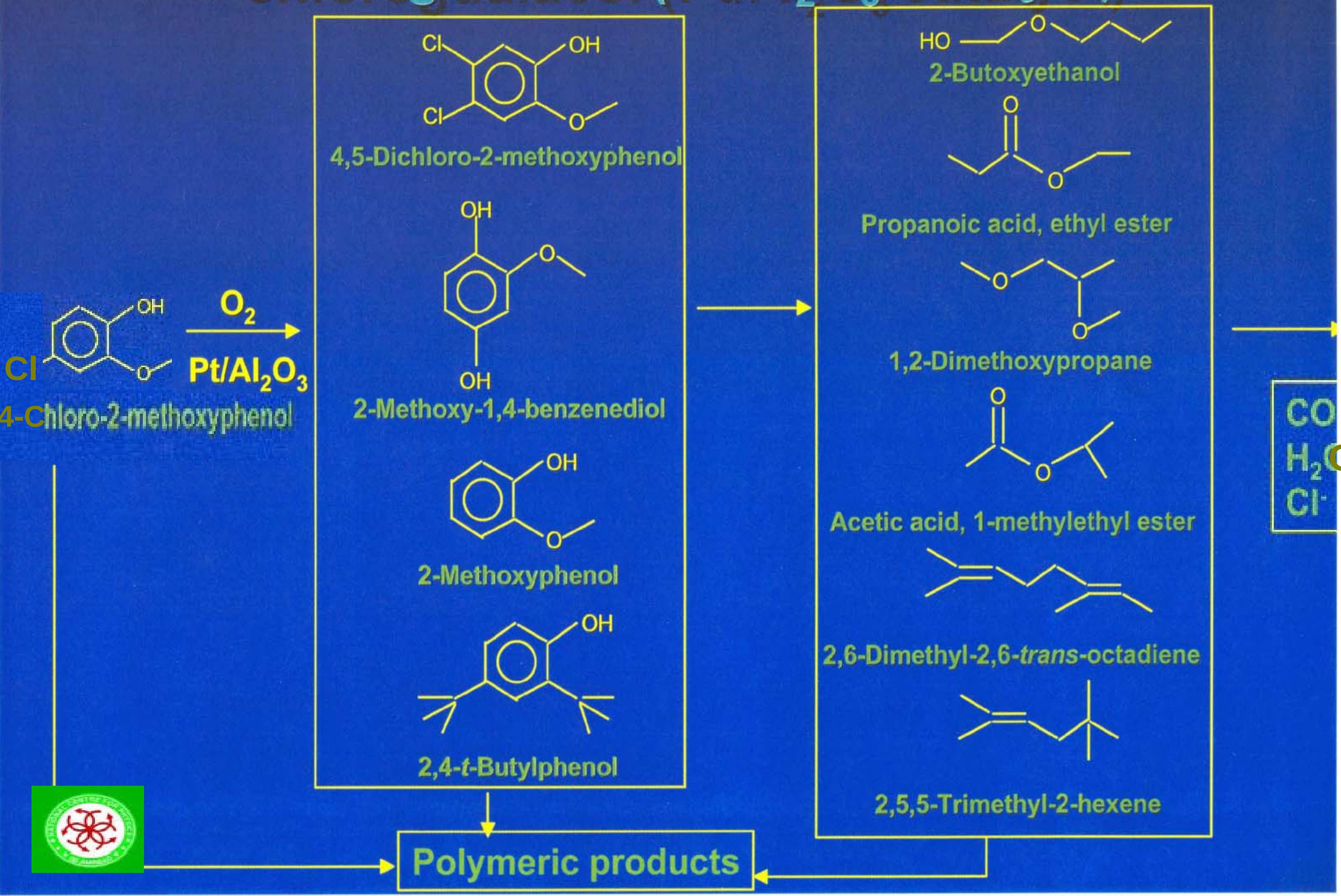
$[CG]_0$ = 1g/L
$(TOC)_0$ = 529 ppm
PO_2 = 0.5 MPa
T = 130 °C

Effect of CWO temperature on TOC & chlorogaïacol degradation rate over Pt/Al_2O_3

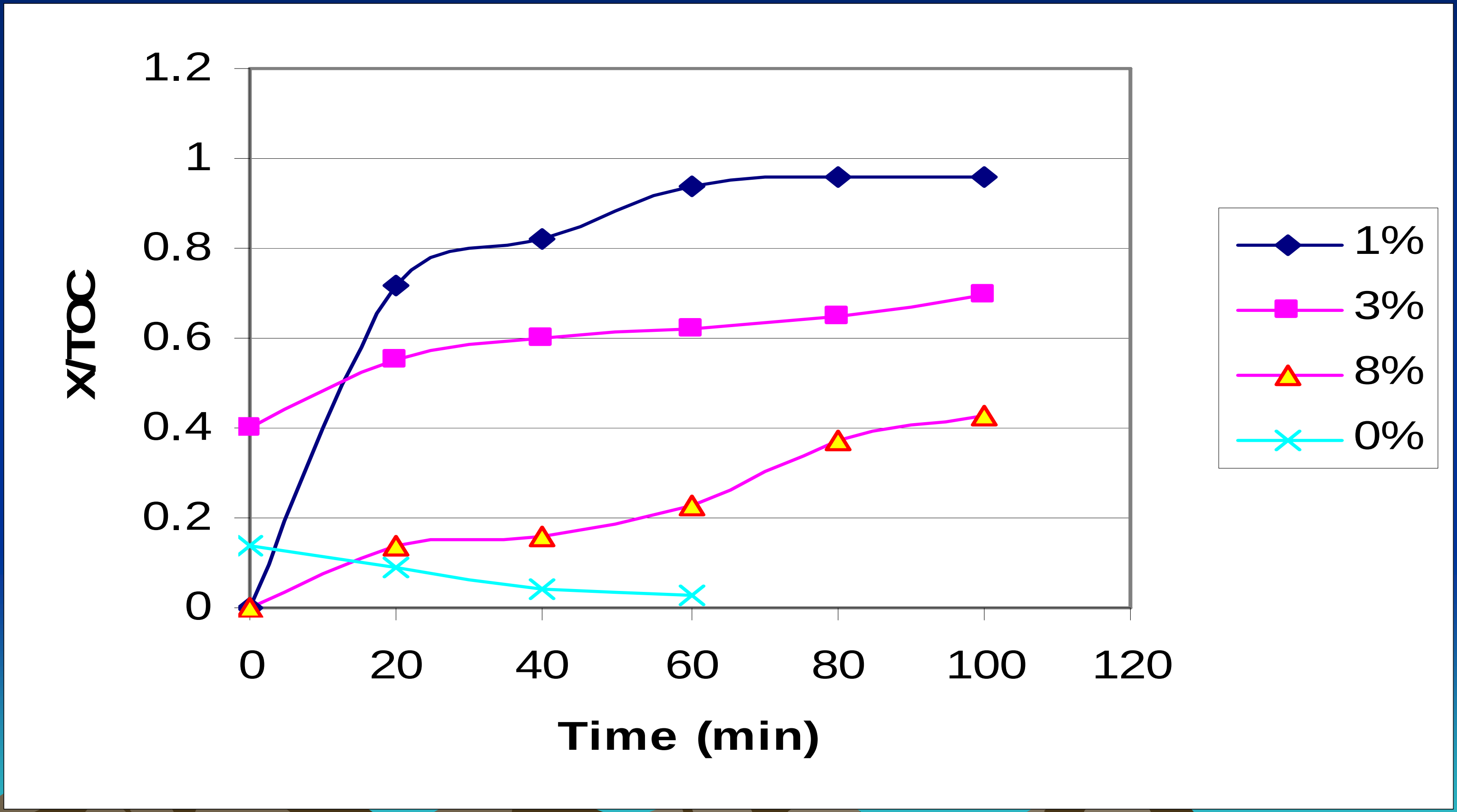


$[CG]_0$ = 1g/L
$(TOC)_0$ = 529 ppm
PO_2 = 0.5 MPa

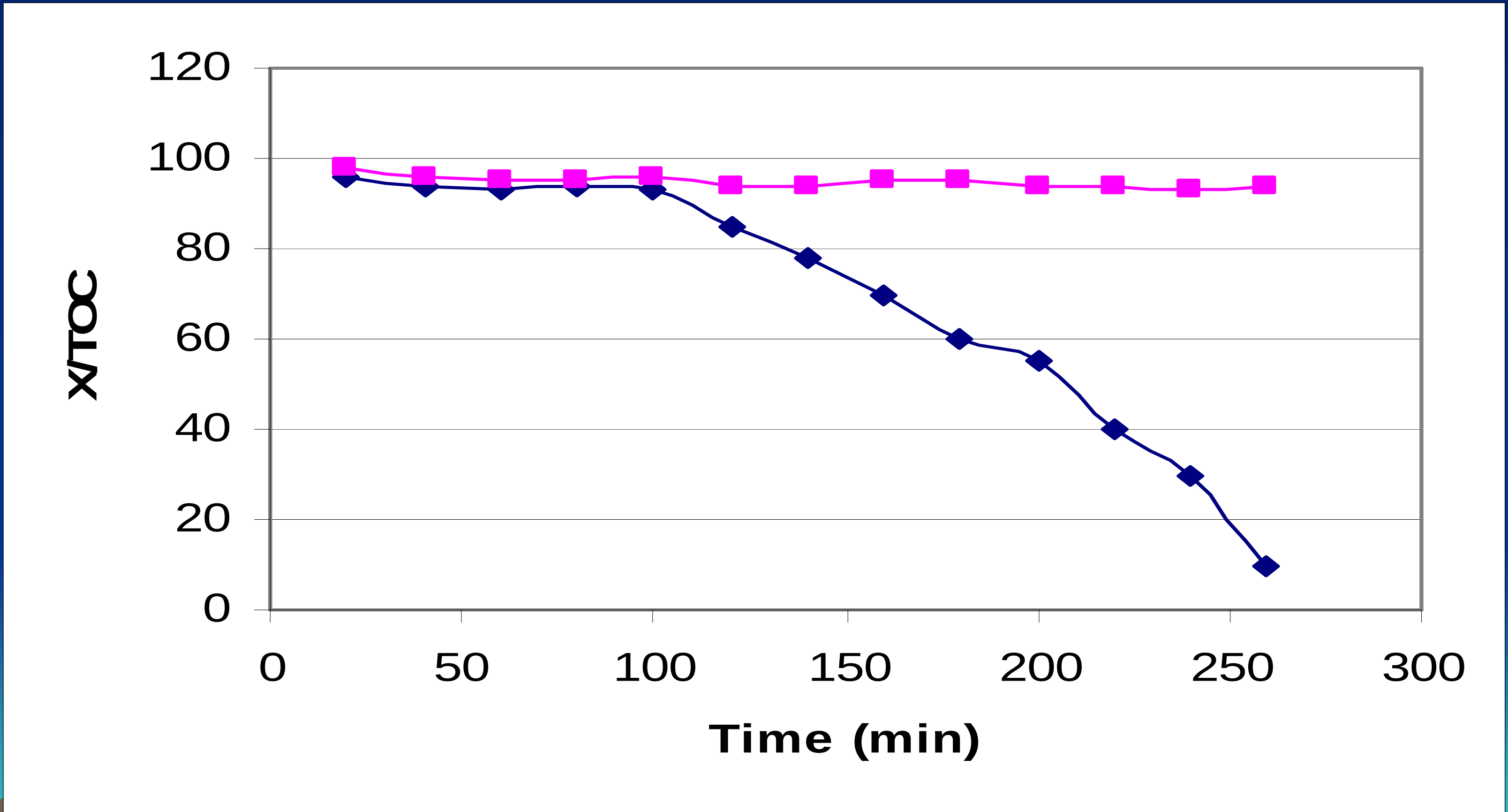
Major CWO ring & break-down intermediates of chloroguaiacol (Pt/Al_2O_3 catalyst)



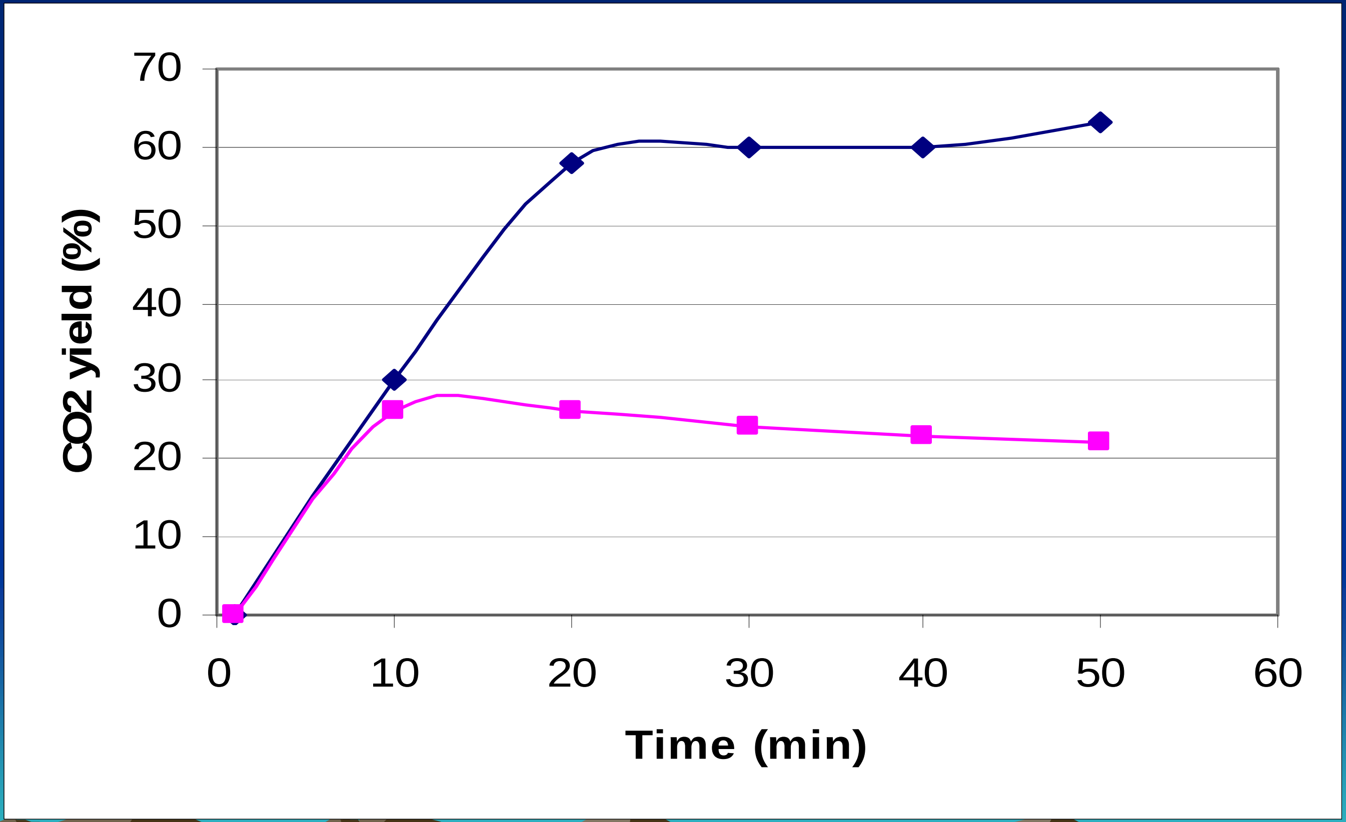
Catalyst Stability Increase. K doping and Zeolite support



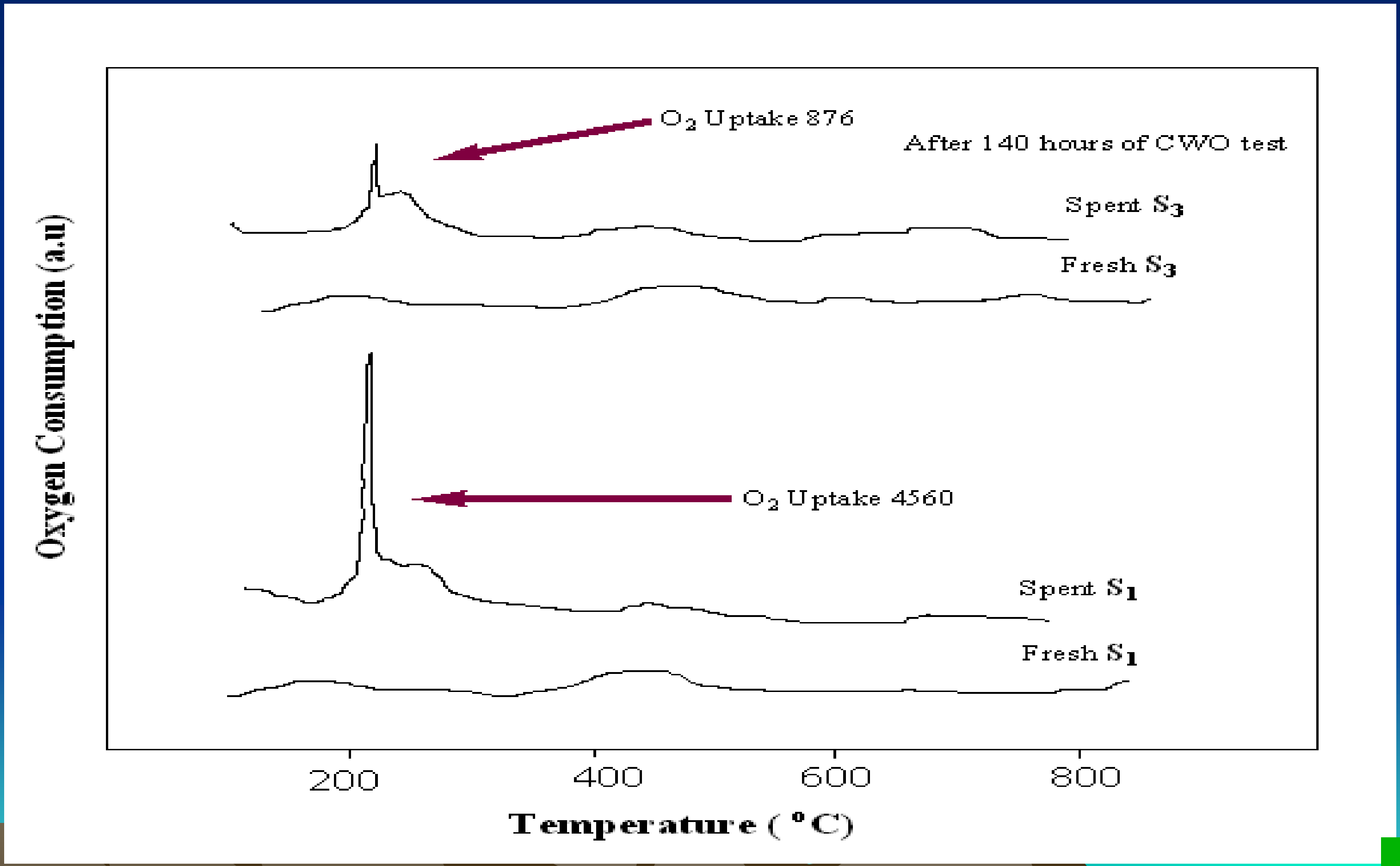
Effect of Zeolite addition on CWO reaction (catalyst Stability)



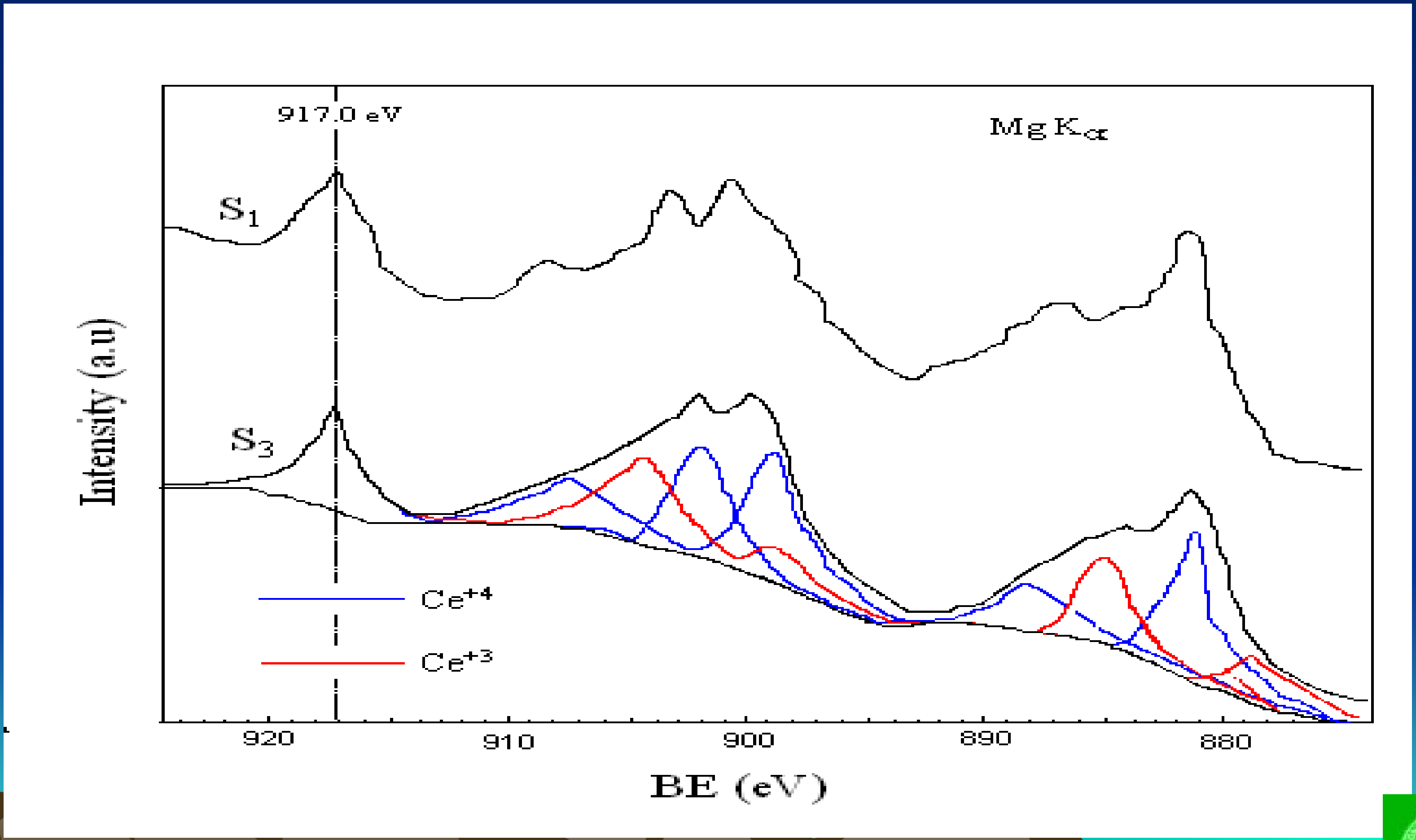
CO_2 yield (%) on Zeolite supported and unsupported CWO catalysts



TPO Study of CWO catalyst



XPS analysis of CWO Catalysts



CONCLUDING REMARKS

*Phenol & TOC removal is fast during CWO @ mild T & P over Mn/Ce
Deactivating carbonaceous deposits on catalyst surface.
<< K >> addition drastically reduces the carbonaceous deposits.
* Zeolite supportes CWO catalyst increases the catalyst life.
* Phenol CWO kinetics treated using the LHHW approach for deactivating systems.
*Successful description by LHHW approach of the 4 lumped species
(CD;TIC; TOC; Solid C).
*Enhanced selectivity to CO_2 with M/zeolite-promoted Mn/Ce;
*CWO effective removal Cl-guaiacol (Mn/Ce > Pt/Al_2O_3 > Co/Bi);
*Fast destruction Cl-guaiacol & formation of recalcitrant interm. which can be used as polymers.