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Focus Event:
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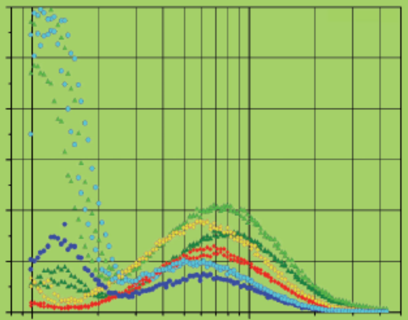

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Effects of Catalyst Particle Structure on Soot Oxidation Kinetics

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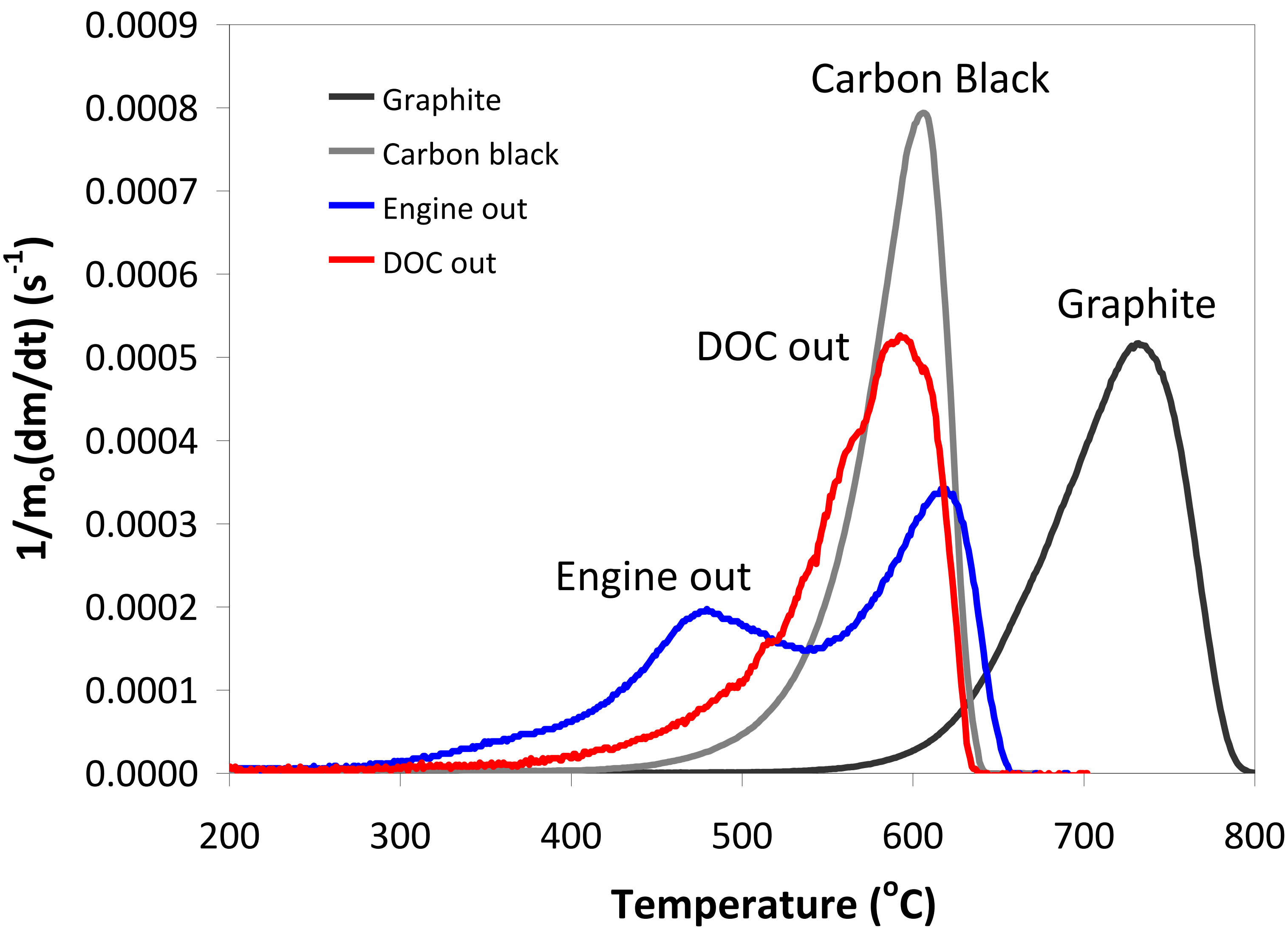
Outline

- **Motivation**
  - Soot **reactivity** and the factors that influence it
  - Develop **better models of catalytic soot oxidation**

    (Influence of catalyst particle **morphological** characteristics)
- **Goal**
  - Effect on soot oxidation of **same catalyst chemistry** with different morphological characteristics
    - → Particle size
    - → Surface area
    - → Pore size/Porosity
    - → Crystallite size
- **Experimental procedure**
  - Catalyst powder milling (**Micron sized**)
  - **Nanoparticle** Catalyst synthesis (by Aerosol and Sol-gel methods)
  - Thermogravimetric analysis of catalyst-soot mixtures

Oxidation of soot and carbonaceous materials



Soot Oxidation: Multi-population Model

Different populations of soot each with its own oxidation rate

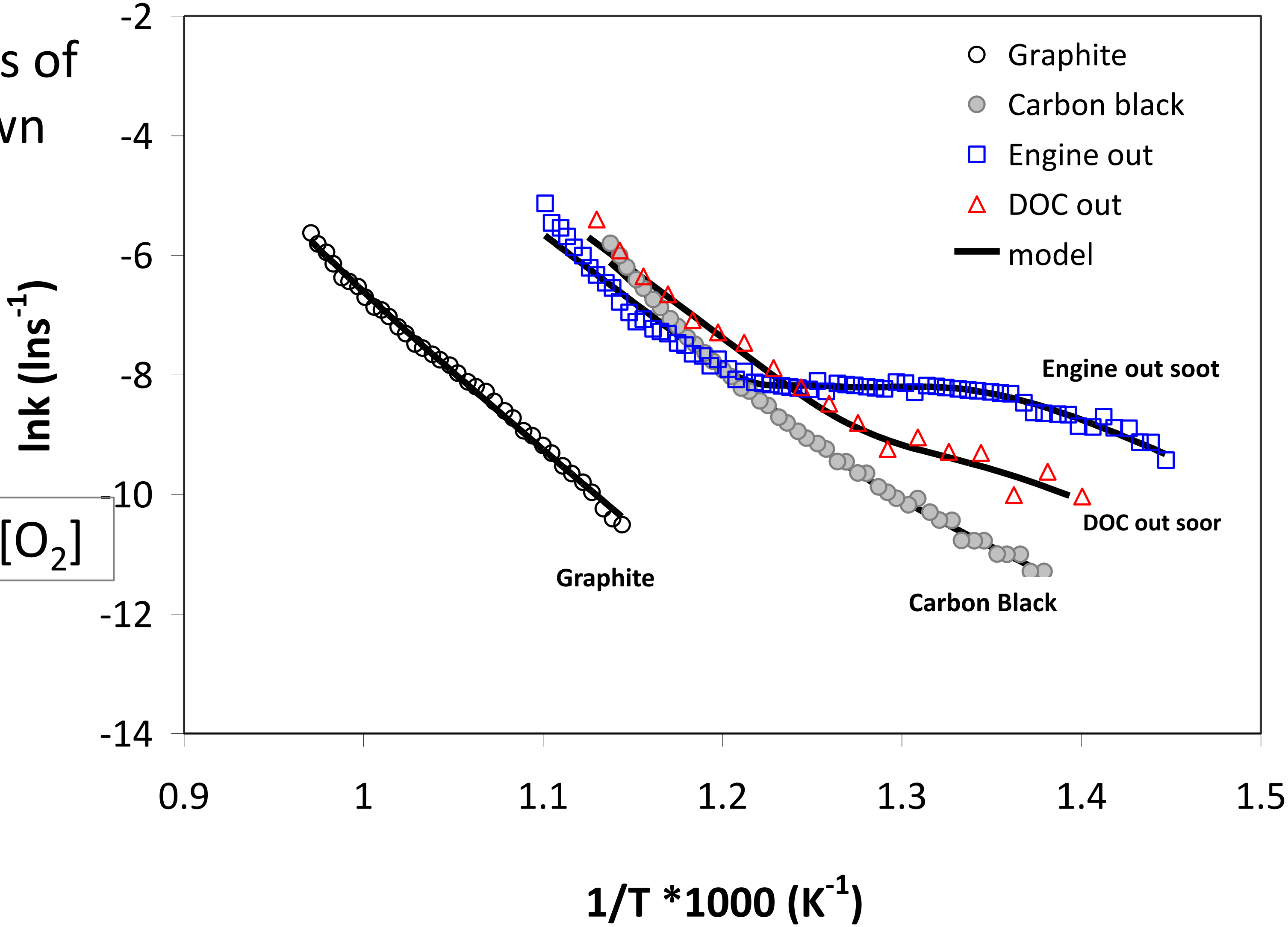
$$\left(\frac{dm_i}{dt}\right)_{ox} = -k_i m_i$$

for i=1 to n, $k_i > k_{i+1}$

$$k_i = k_{oi}\, T \exp(-E_i/RT)\, [O_2]$$

Initial condition

$$m_{i,0} = \varphi_i m_0$$
$$\sum_i \varphi_i = 1$$



Konstandopoulos A.G., Kostoglou M., Lorentzou S., Vlachos N. (2012), *Catalysis Today*, 188 (1), pp. 2-13.

SAE 2013-01-0524, SAE 2012-01-1288

Experimental

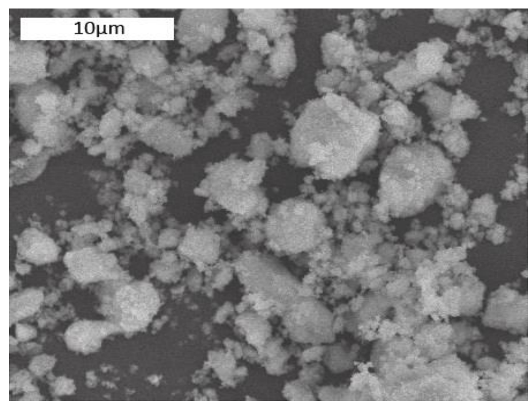
Catalyst Powder Milling

Mixed Ceria-Zirconia powder, ball milling

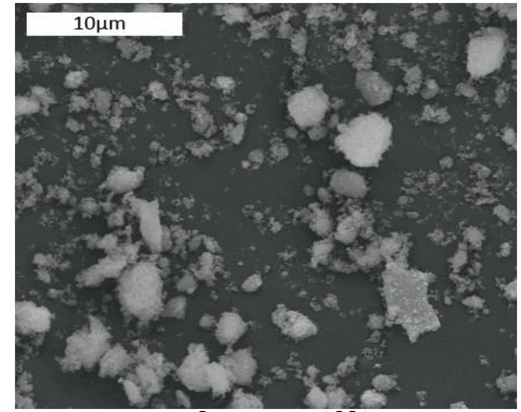
→ **Ceria-rich** : 0, 6, 12, 40, 72 hrs

→ **Zirconia-rich** : 0, 6, 12, 40 hrs

Ce-rich sample



Raw



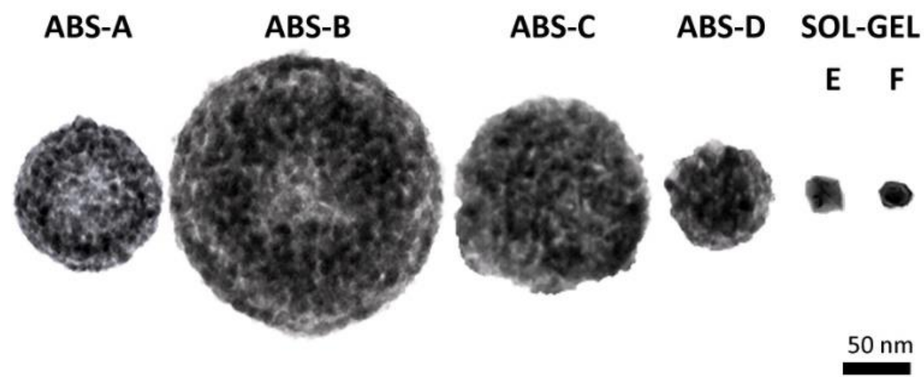
40 hrs milling

Catalyst Nanoparticle Synthesis

Cerium Oxide (CeO_2) from pre-cursor solutions

→ **Aerosol based synthesis, (ABS)*** :
4 CeO_2 catalysts (A, B, C, D)

→ **Sol-gel synthesis**: 2 CeO_2 catalysts (E, F)



*K. Karadimitra, G. Macheridou, E. Papaioannou, A. G. Konstandopoulos, *PARTEC 2001*

Lorentzou S., Kastrinaki G., Pagkoura C., Konstandopoulos A.G., *Nanoscience and Nanotechnology Letters*, 3 (5), pp. 697-704(8), 2011

Experimental

- **Physical and morphological characterization**

  - → Particle size
  - → Surface area
  - → Pore size/Porosity
  - → Crystallite size

  X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Particle Size Distribution (PSD) and BET analysis.

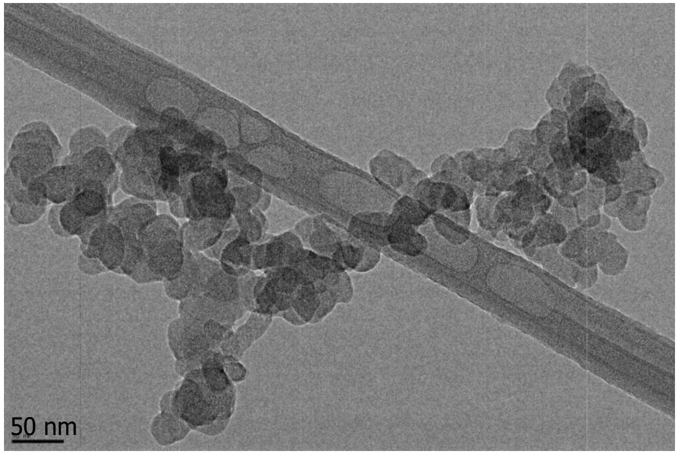
*K. Karadimitra, G. Macheridou, E. Papaioannou, A. G. Konstandopoulos, *PARTEC 2001*

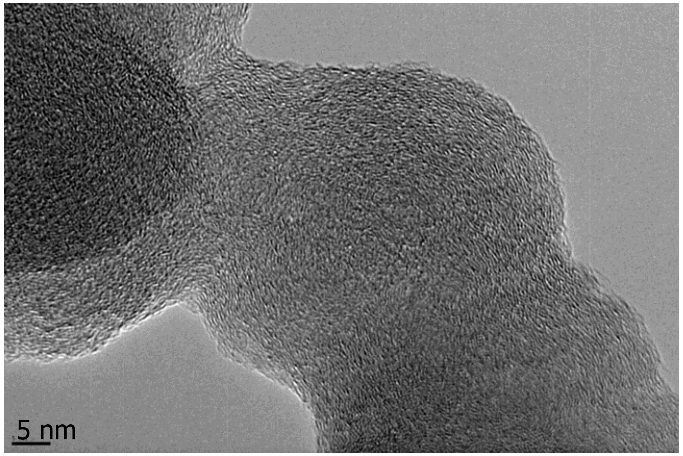
Lorentzou S., Kastrinaki G., Pagkoura C., Konstandopoulos A.G., *Nanoscience and Nanotechnology Letters*, 3 (5), pp. 697-704(8), 2011

Experimental

Catalytic Soot Oxidation

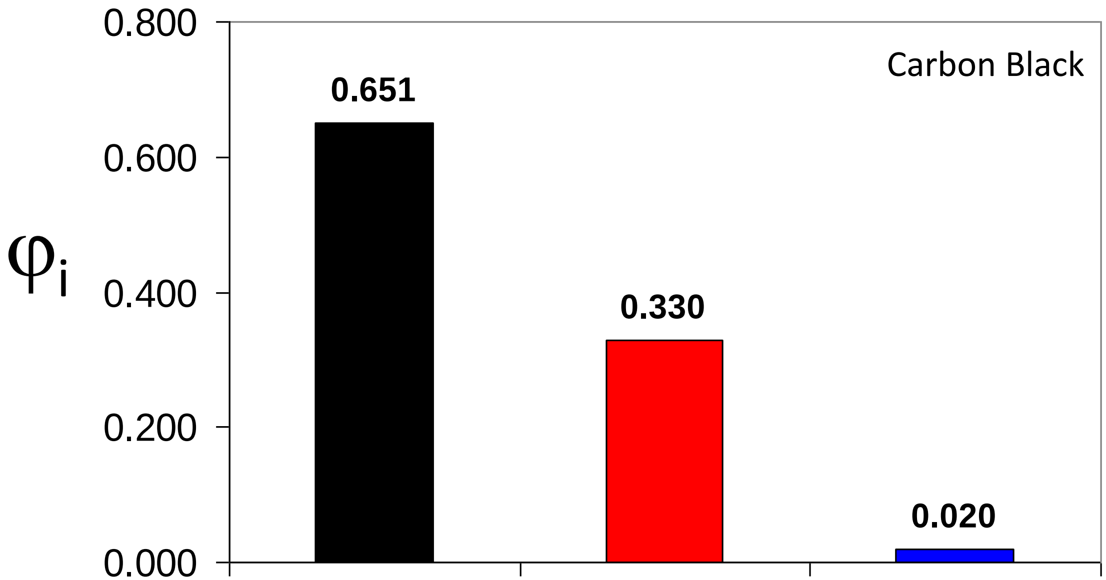
A flame-generated Carbon Black (N330) was employed to warrant absence of inorganic ashes and false catalytic activity





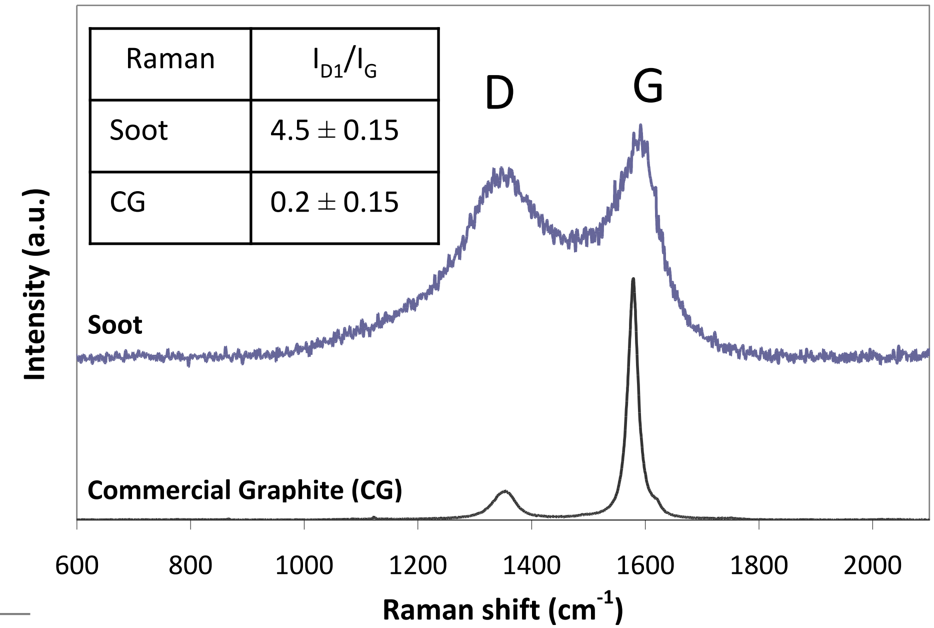
- ➔ Aggregates are composed of near-spherical primary particles (~26 nm) and have a 74.2 m^2/g surface area.
- ➔ Mixing with catalyst in a mortar at a catalyst-soot ratio 2:1
- ➔ Oxidation in a Thermogravimetric Analyzer, under a stream of 20% O_2 in N_2 with a temperature increase rate of 3°C/min from 150 to 700°C.

Kinetic Parameters of Thermal Oxidation



E_i (kJ/mol)	240.00	180.00	120.00
k_{0i} (1/sK)	5.0E+08	1.0E+05	257

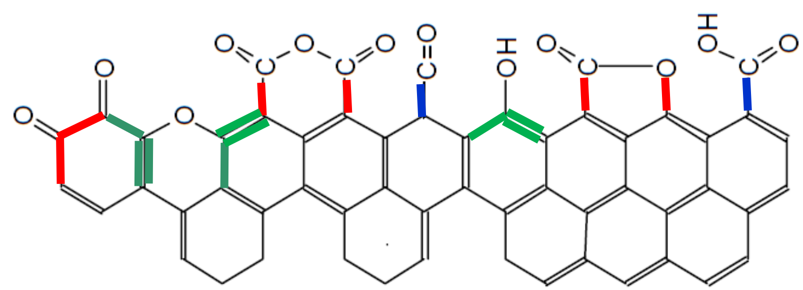
Raman Spectrum: At least two populations



Raman	I_{D1}/I_G
Soot	4.5 ± 0.15
CG	0.2 ± 0.15

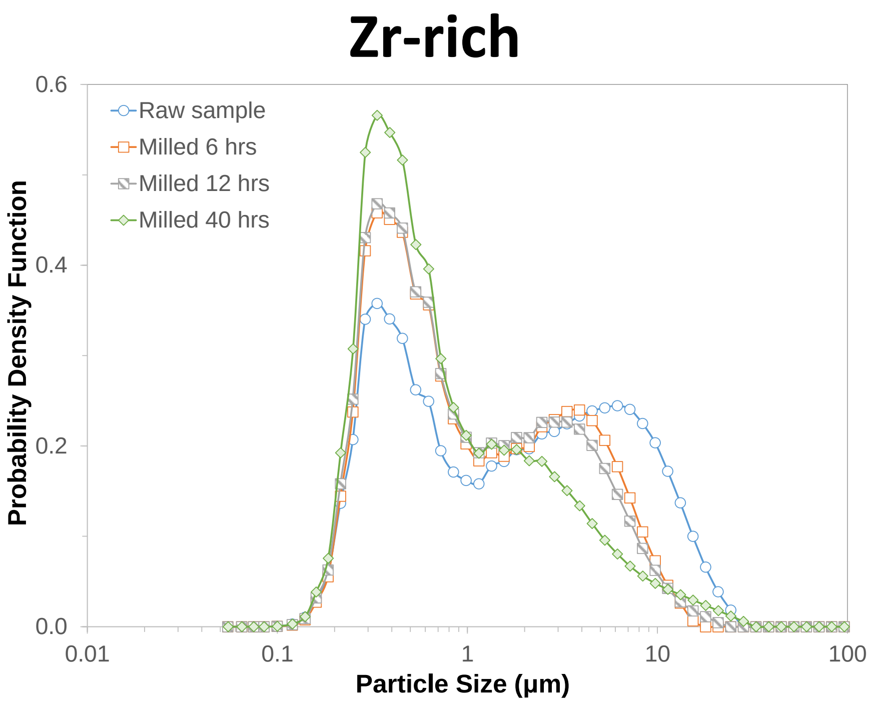
Different Surface Oxygen Complexes

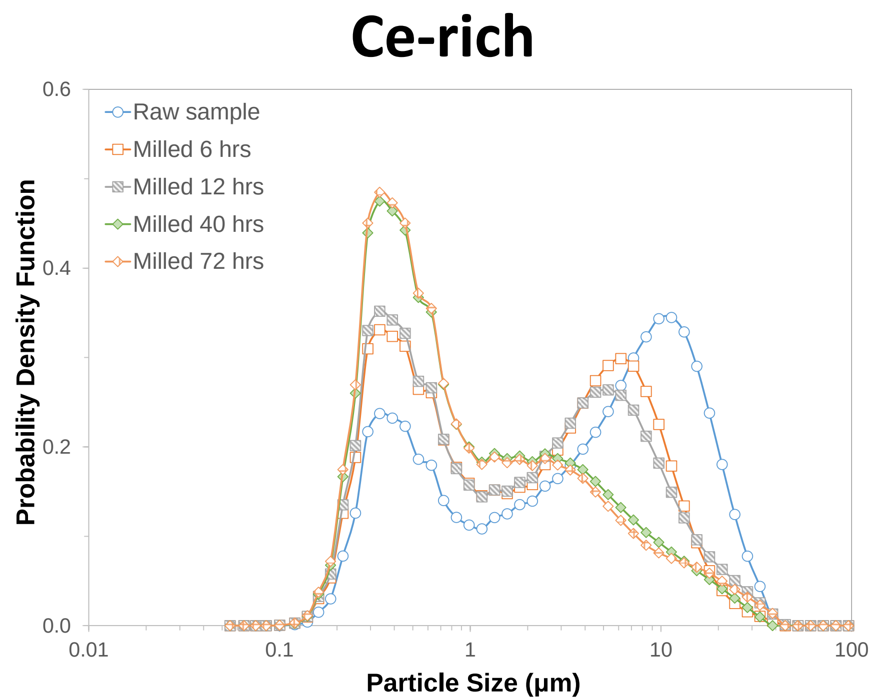
1, 2 or 3 bonds need to brake for gasification of a SOC



Ordered and Disordered Domains

Particle Size Distribution

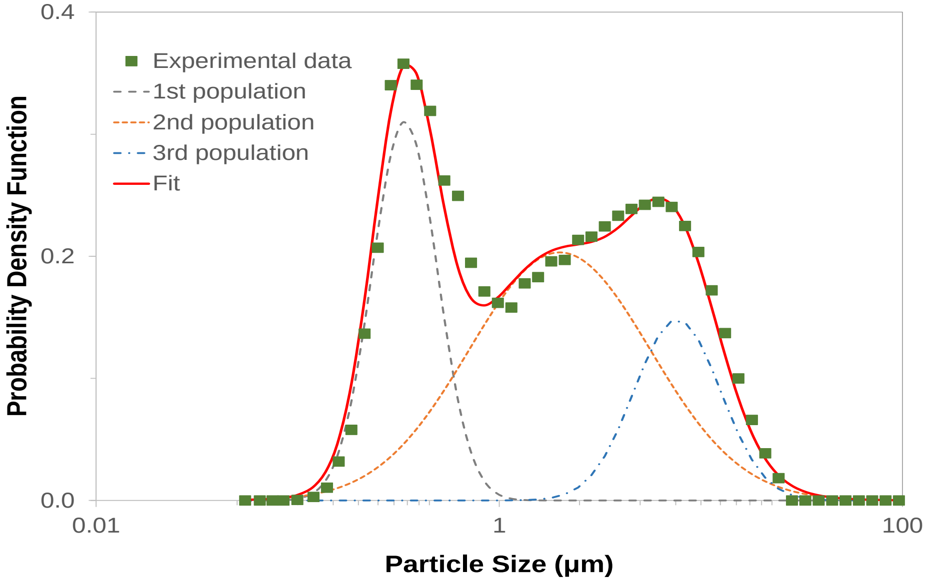




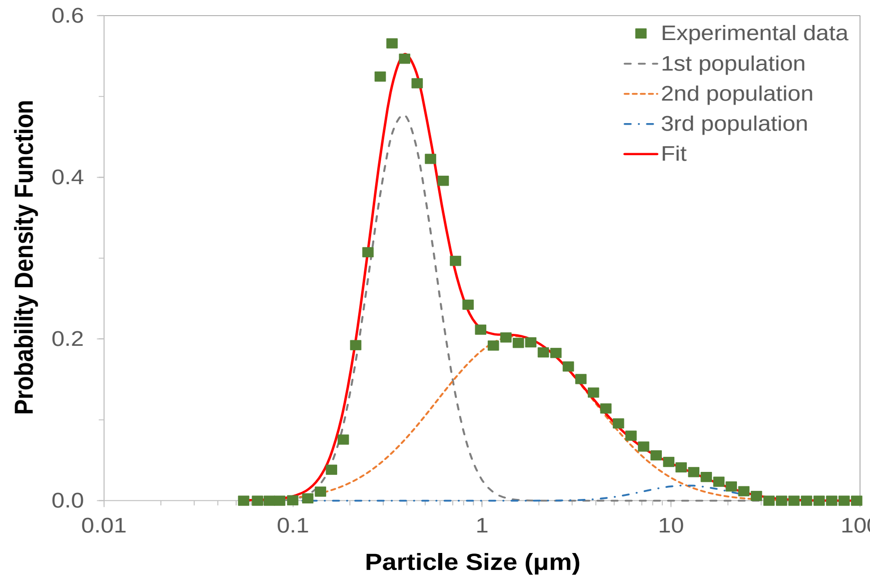
- Decrease of large size particles with milling duration for both samples
- Characteristic size $d_{3,2}$ (Sauter Mean Diameter)

Particle Size Distributions

Raw sample



40 hrs milling

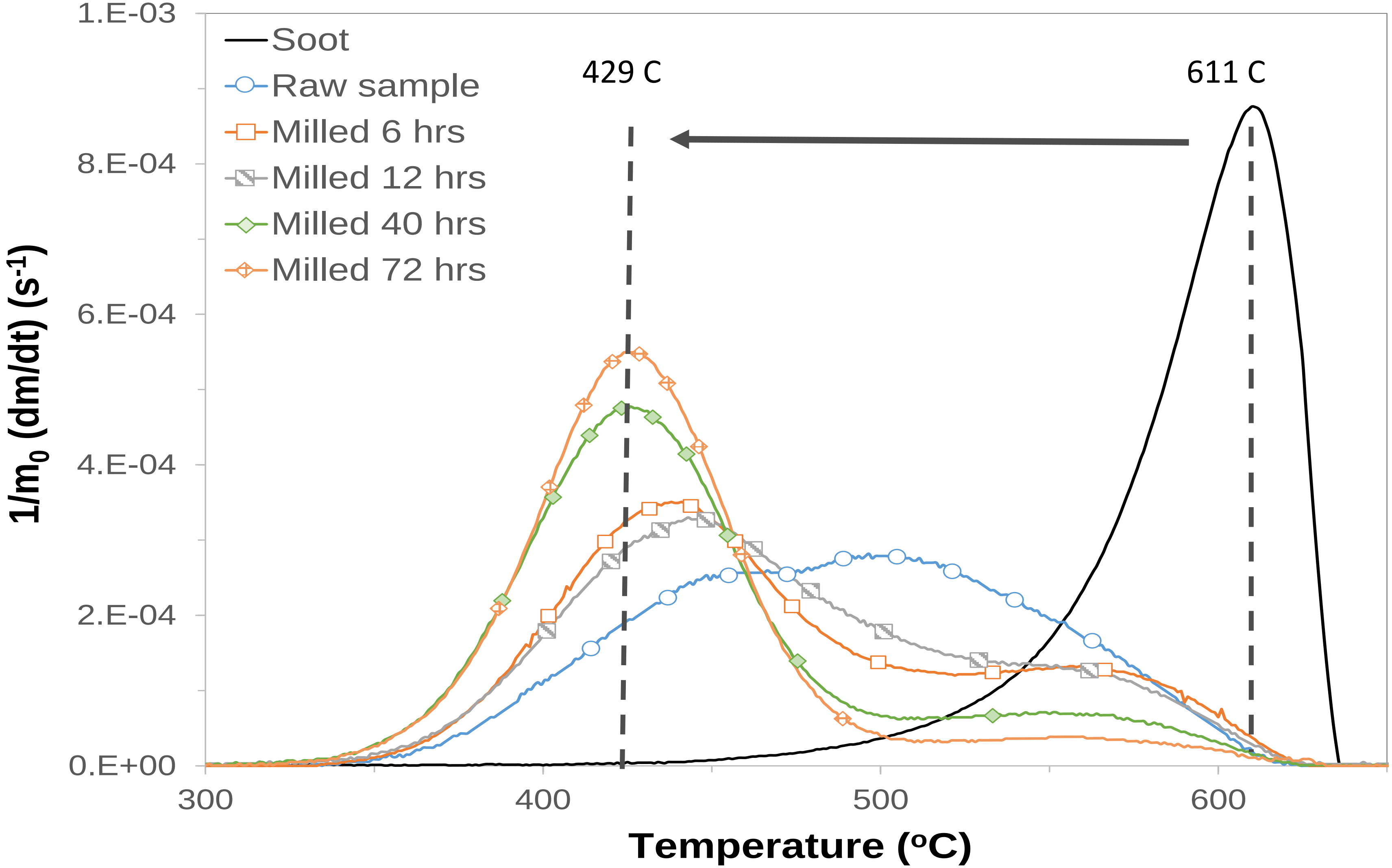


	Milling duration (hrs)	Population 1			Population 2			Population 3		
		d_M (µm)	σ_g	Fraction	d_M (µm)	σ_g	Fraction	d_M (µm)	σ_g	Fraction
Zr-rich catalyst	0	0.37	1.51	0.33	**1.99**	2.41	0.43	7.63	1.71	0.24
	6	0.37	1.46	0.34	**0.77**	1.79	0.29	3.70	1.83	0.36
	12	0.36	1.46	0.35	**0.73**	1.32	0.27	3.33	1.46	0.38
	40	0.38	1.49	0.48	**1.50**	2.60	0.49	12.00	1.68	0.02
Ce-rich catalyst	0	0.40	1.53	0.24	**2.92**	2.52	0.37	11.37	1.69	0.38
	6	0.37	1.51	0.27	**1.02**	2.10	0.27	6.12	1.86	0.45
	12	0.34	1.41	0.20	**0.60**	1.71	0.25	4.89	2.31	0.55
	40	0.30	1.26	0.10	**0.44**	1.47	0.33	2.21	3.22	0.57
	72	0.39	1.53	0.45	**2.05**	2.84	0.51	16.68	1.59	0.04

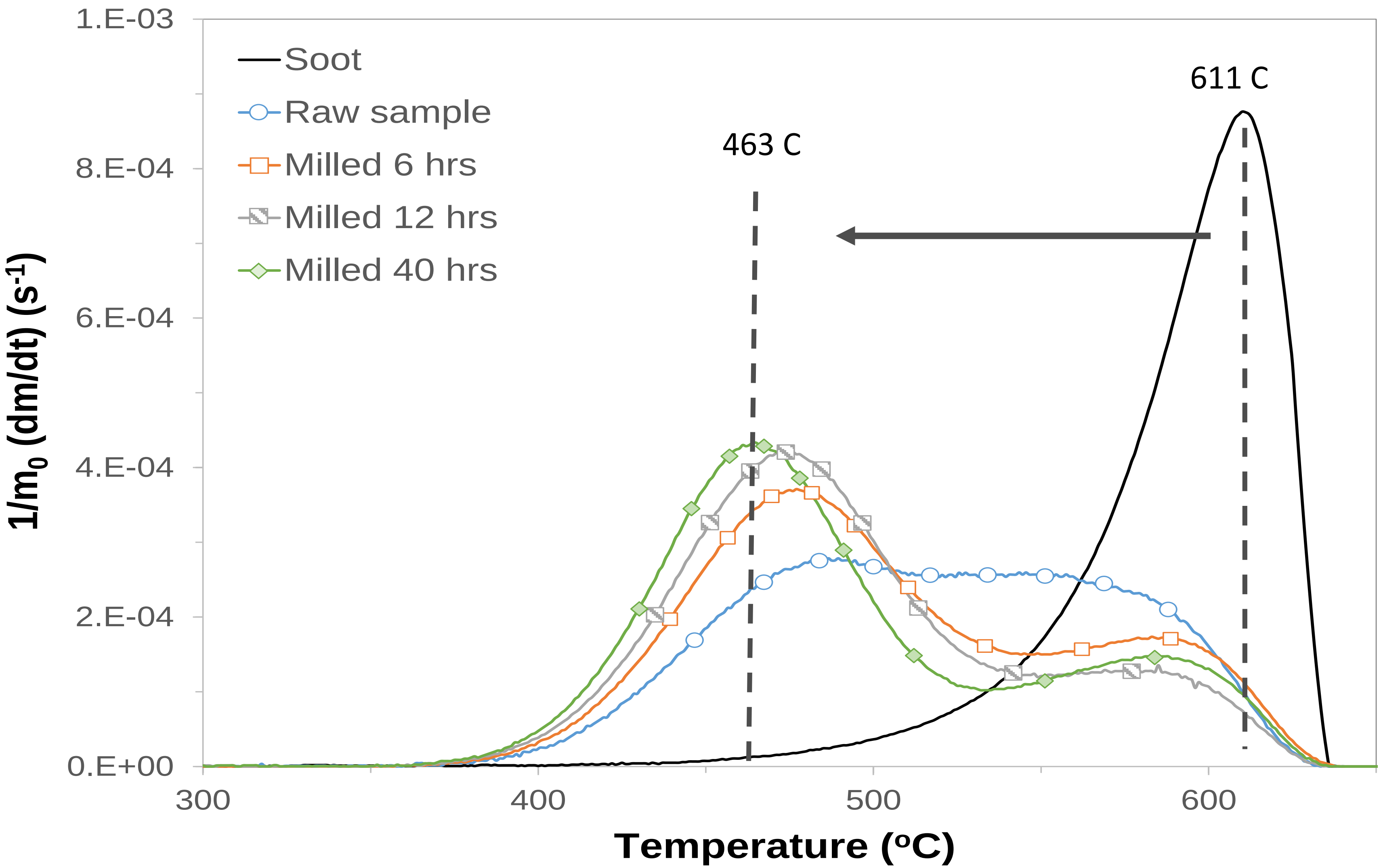
Summary of Catalyst Structural Characteristics

	Milling duration (hrs)	$d_{3,2}$ (µm)	Surface area (m^2/gr)	Crystallite size (nm)
Zr-rich catalyst	0	0.77	70.58	59
	6	0.64	71.64	57
	12	0.62	68.93	58
	40	0.54	66.99	59
Ce-rich catalyst	0	1.14	77.30	59
	6	0.82	75.27	58
	12	0.78	72.85	59
	40	0.62	73.32	57
	72	0.61	73.29	58

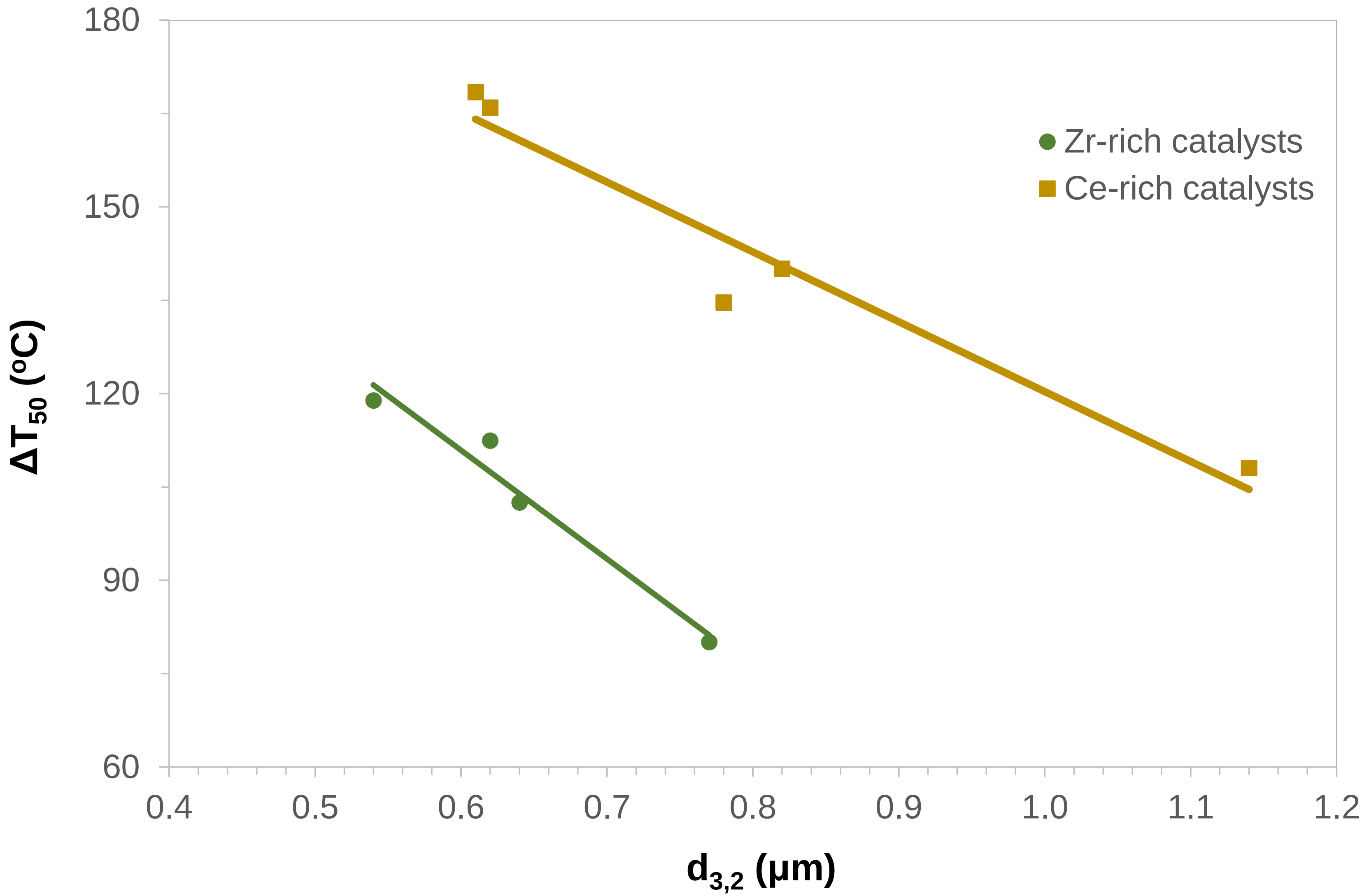
Soot oxidation rate- Ce-rich



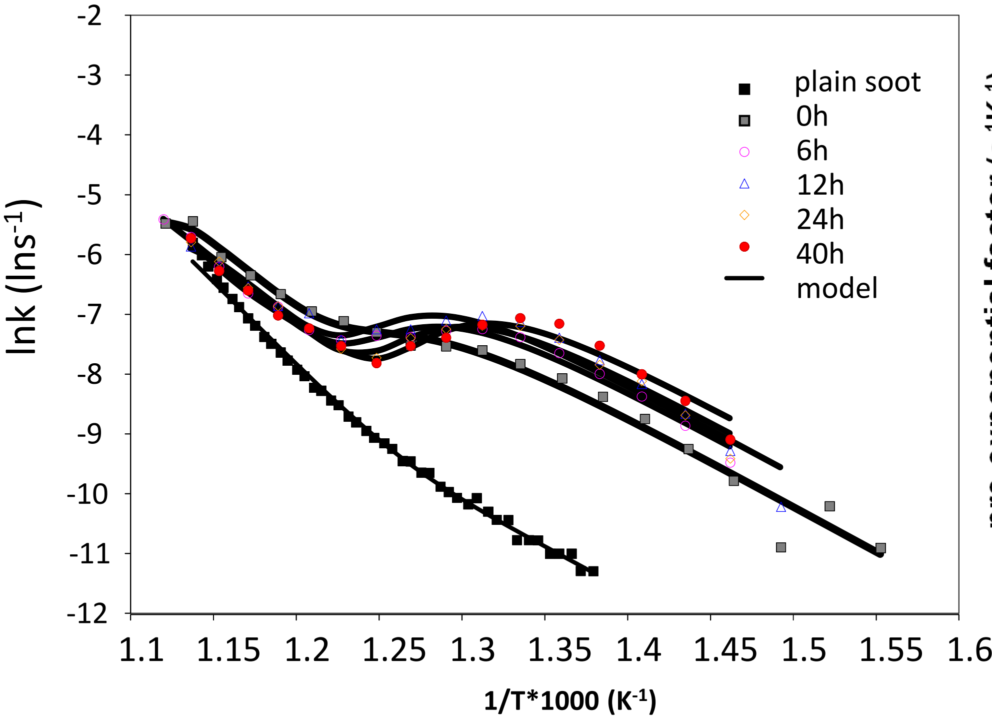
Soot oxidation rate- Zr-rich

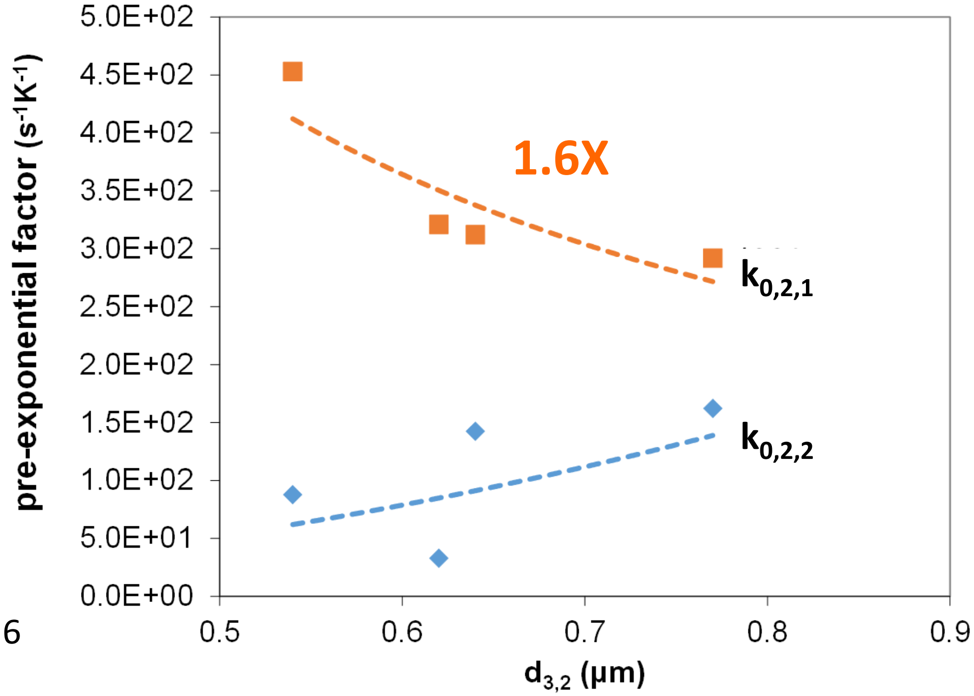


Correlation of Soot Oxidation to $d_{3,2}$



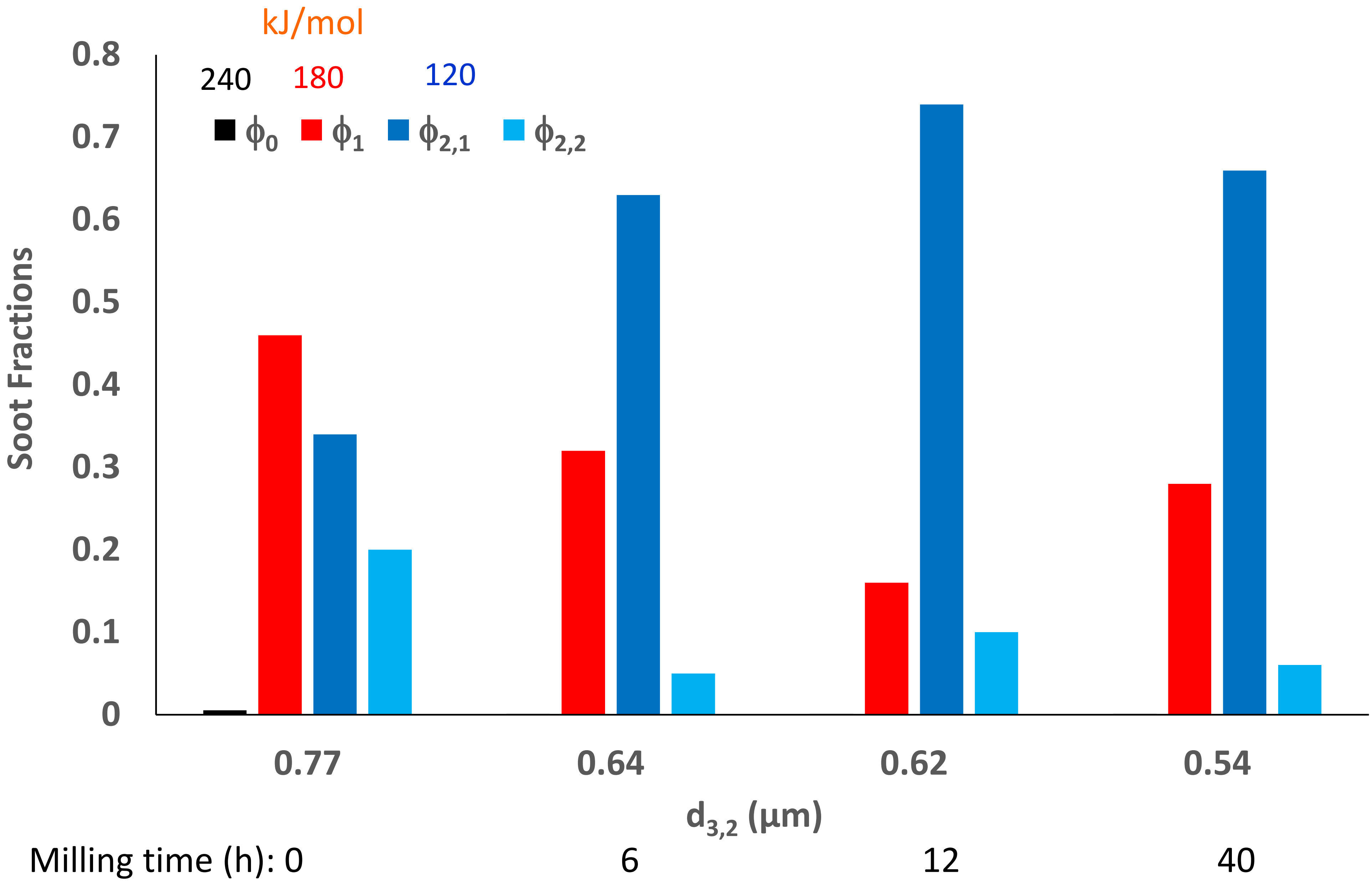
Kinetics Zr-rich



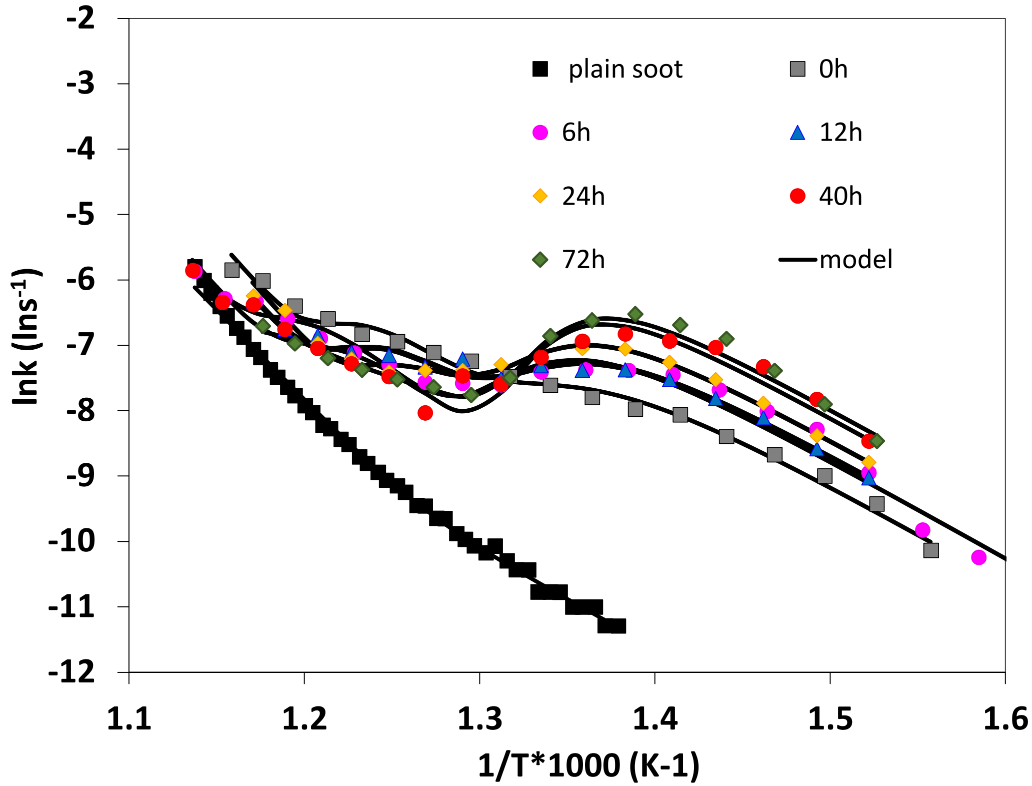


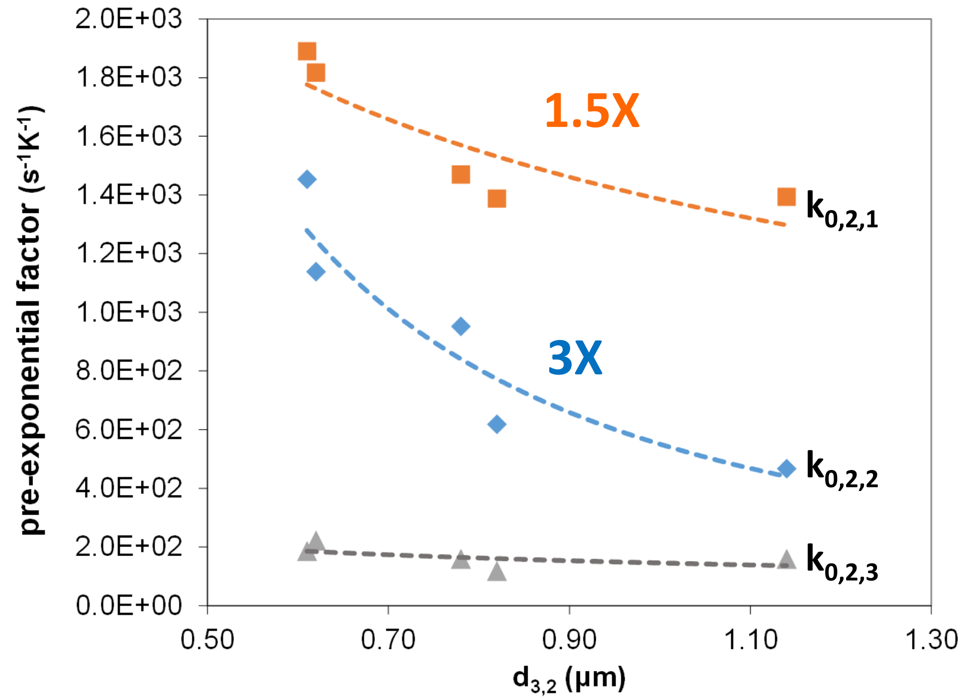
Zr-rich catalyst	$d_{3,2}$	E_0:240 kJ/mol	E_1:180 kJ/mol	E_2:120 kJ/mol	
milling (h)	µm	$k_{0,0}$	$k_{0,1}$	$k_{0,2,1}$	$k_{0,2,2}$
0	0.77	3.00E+05	1.89E+05	2.92E+02	1.62E+02
6	0.64	3.00E+05	1.73E+05	3.12E+02	1.42E+02
12	0.62	3.00E+05	2.03E+05	3.21E+02	3.28E+01
40	0.54	3.00E+05	1.33E+05	4.53E+02	8.77E+01

Soot fractions φ_i vs Zr-rich milling time / $d_{3,2}$



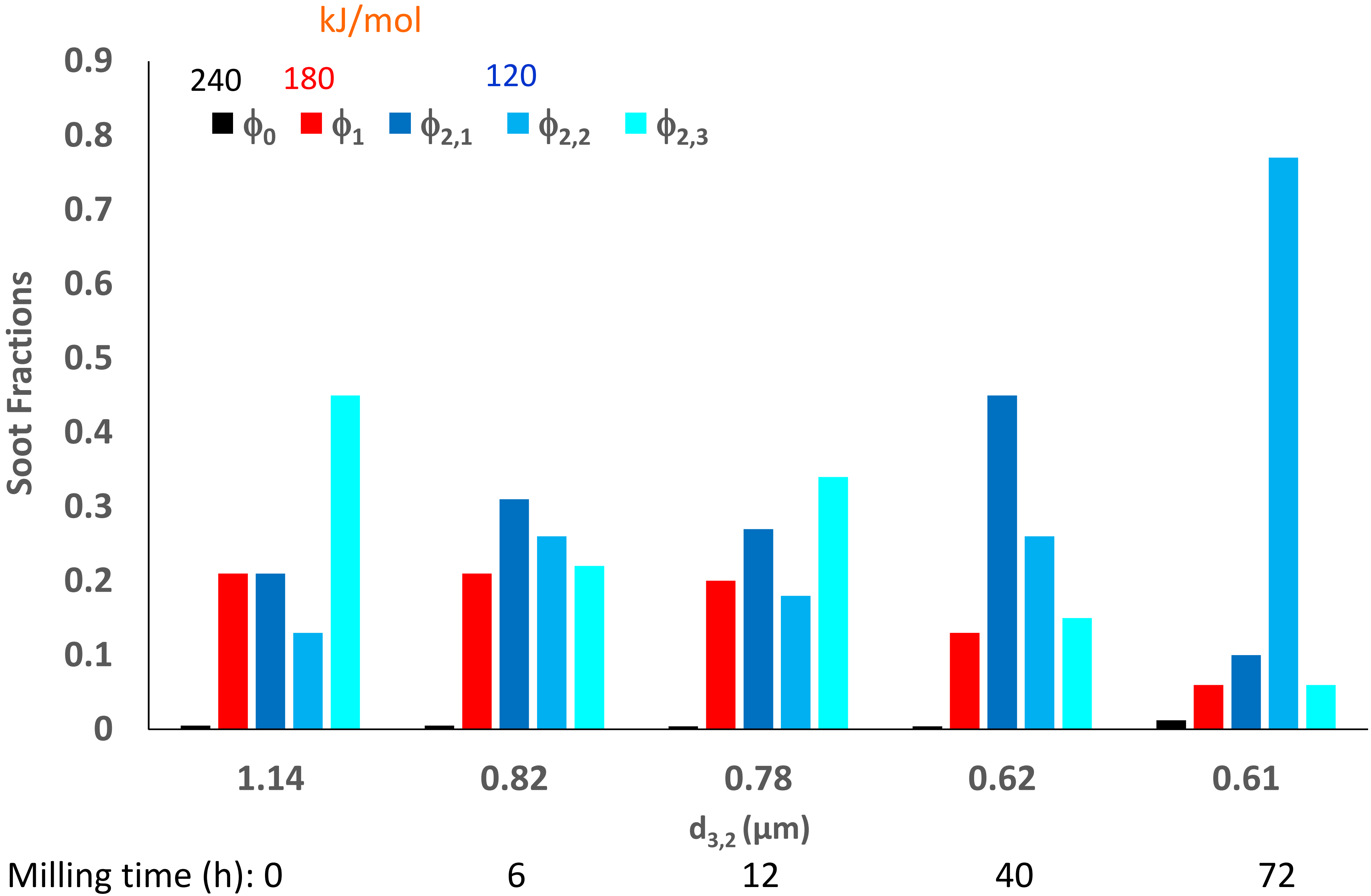
Kinetics Ce-rich





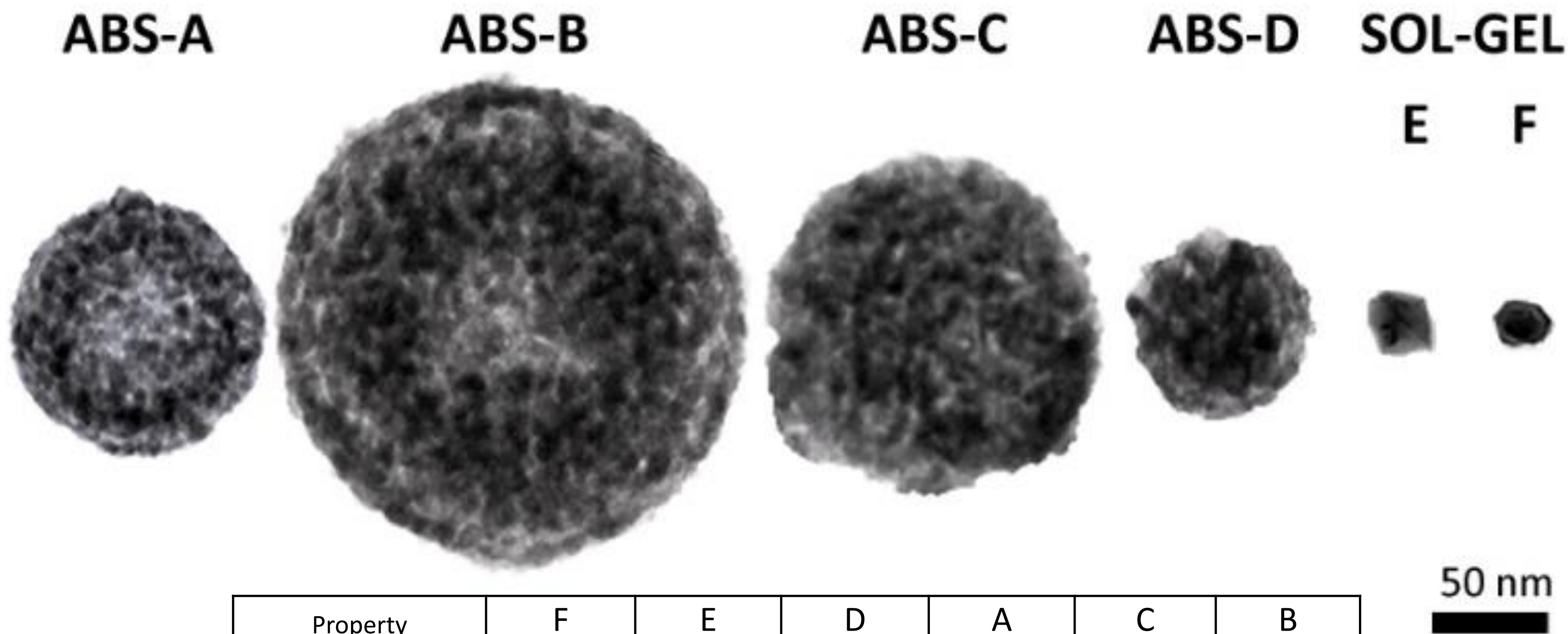
Ce-rich catalyst	$d_{3,2}$	E_0:240 kJ/mol	E_1:180 kJ/mol	E_2:120 kJ/mol		
milling (h)	μm	$k_{0,0}$	$k_{0,1}$	$k_{0,2,1}$	$k_{0,2,2}$	$k_{0,2,3}$
0.00	1.14	4.93E+05	2.24E+05	1.39E+03	4.67E+02	1.59E+02
6.00	0.82	4.93E+05	2.24E+05	1.39E+03	6.19E+02	1.17E+02
12.00	0.78	2.77E+05	1.88E+05	1.47E+03	9.52E+02	1.59E+02
40.00	0.62	2.77E+05	2.00E+05	1.82E+03	1.14E+03	2.22E+02
72.00	0.61	3.00E+05	3.00E+05	1.89E+03	1.45E+03	1.86E+02

Soot fractions φ_i vs Ce-rich milling time / $d_{3,2}$



Synthesized Catalyst Nanoparticles

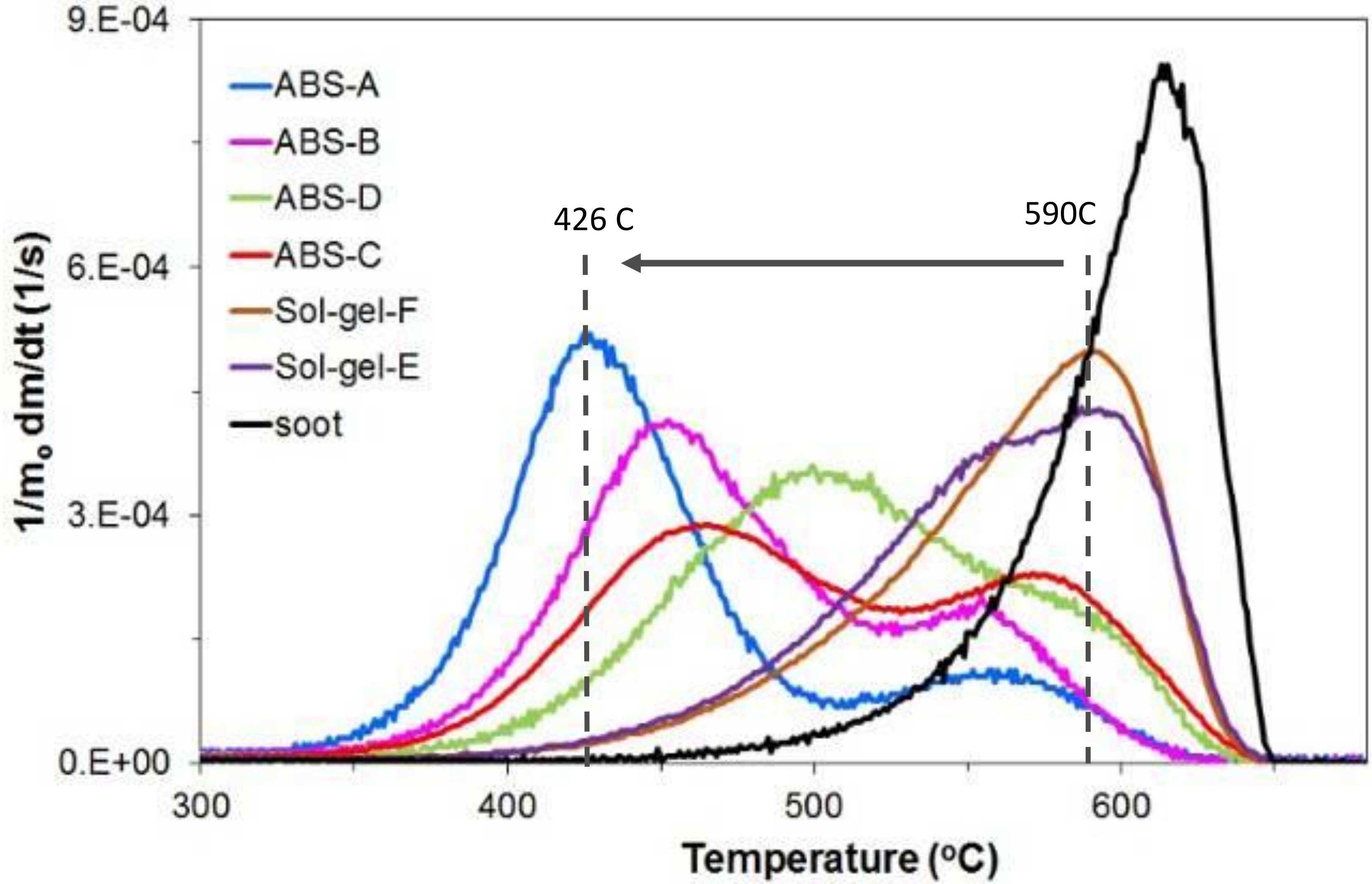
CeO_2



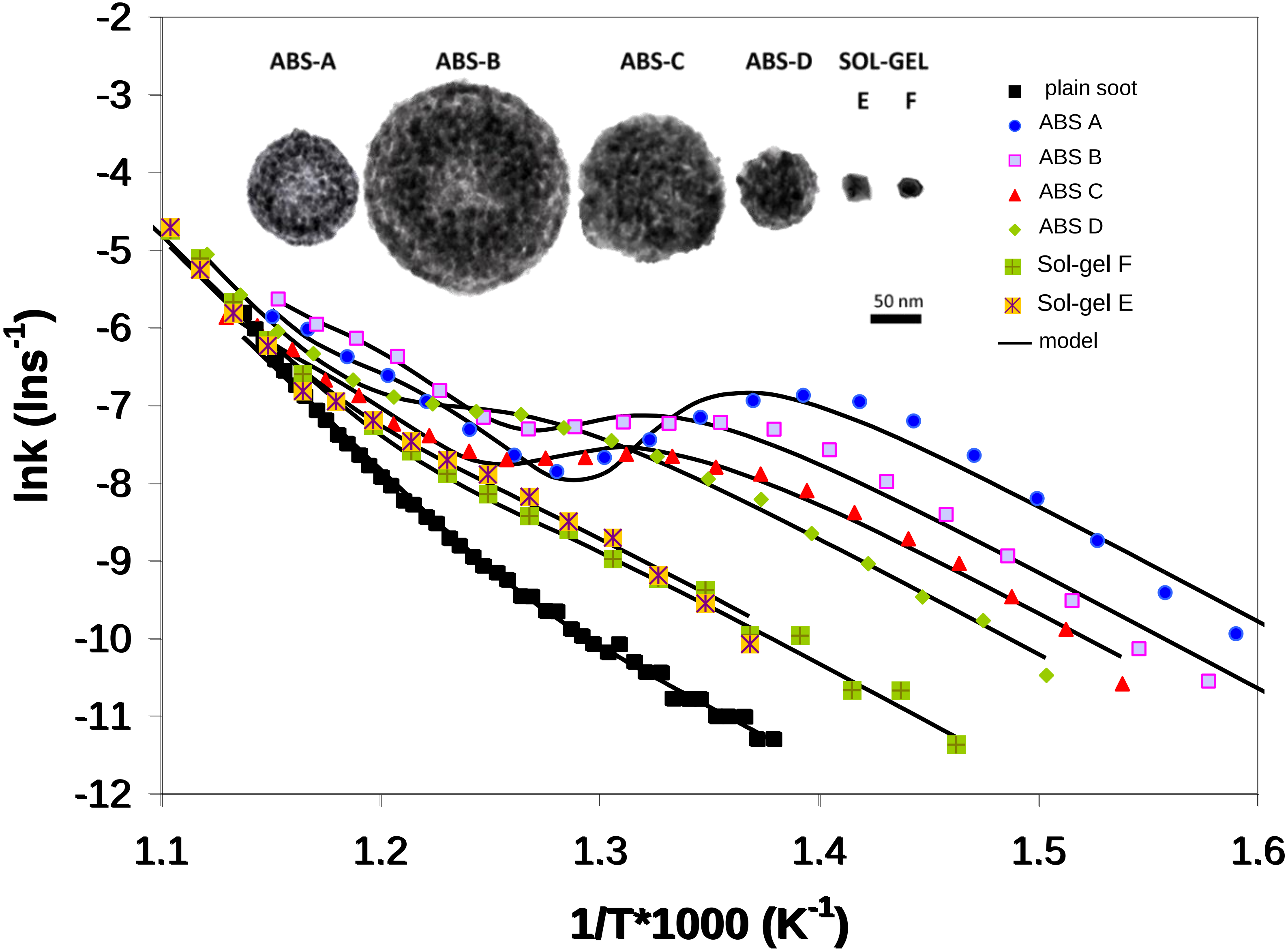
Property	F	E	D	A	C	B
Particle size (nm)	**28**	**32**	**90**	**121**	**161**	**222**
surface area (m2/g)	12	5	8	59	35	37
crystallite size (nm)	18	29	25	9	18	25
pore size (nm)	-	-	13.7	12.4	20.7	10.5
porosity	-	-	0.451	0.674	0.633	0.387

Emission Control Sci. & Tech1(3):247-253, 2015

Soot oxidation rate



Effect of Catalyst Nanostructure on Soot Oxidation



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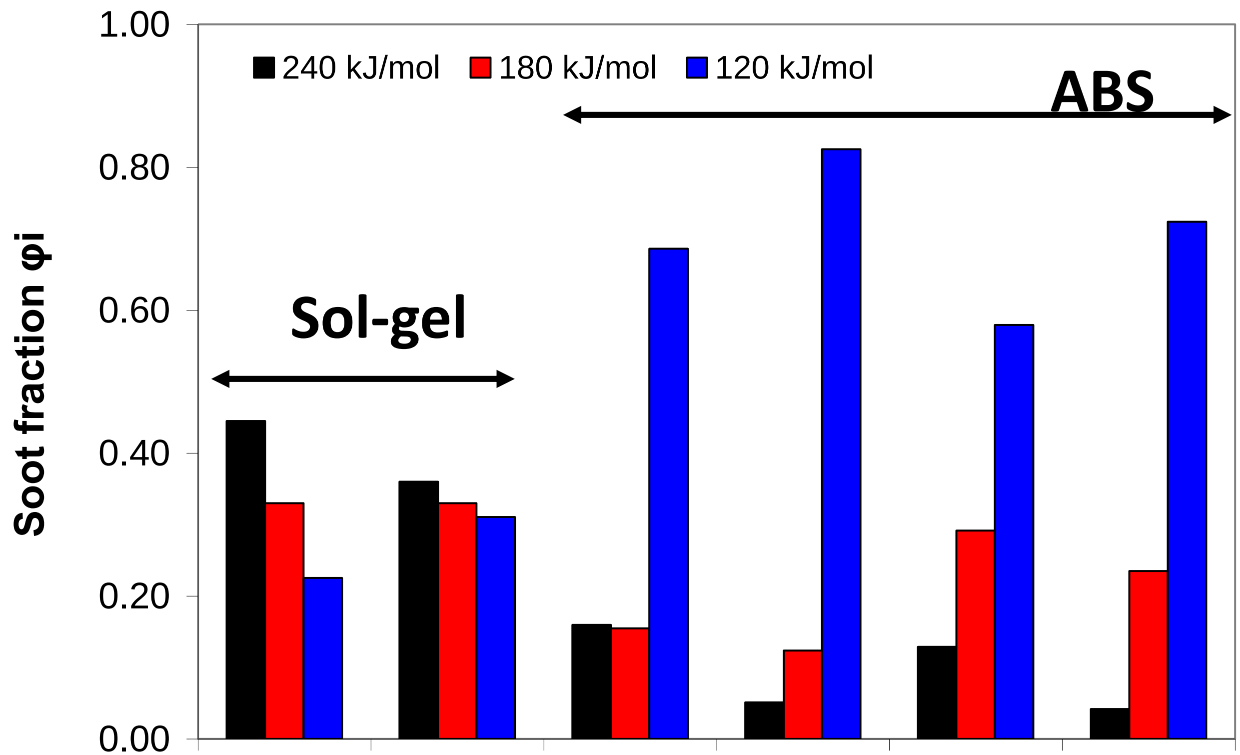
Soot fractions φ_i



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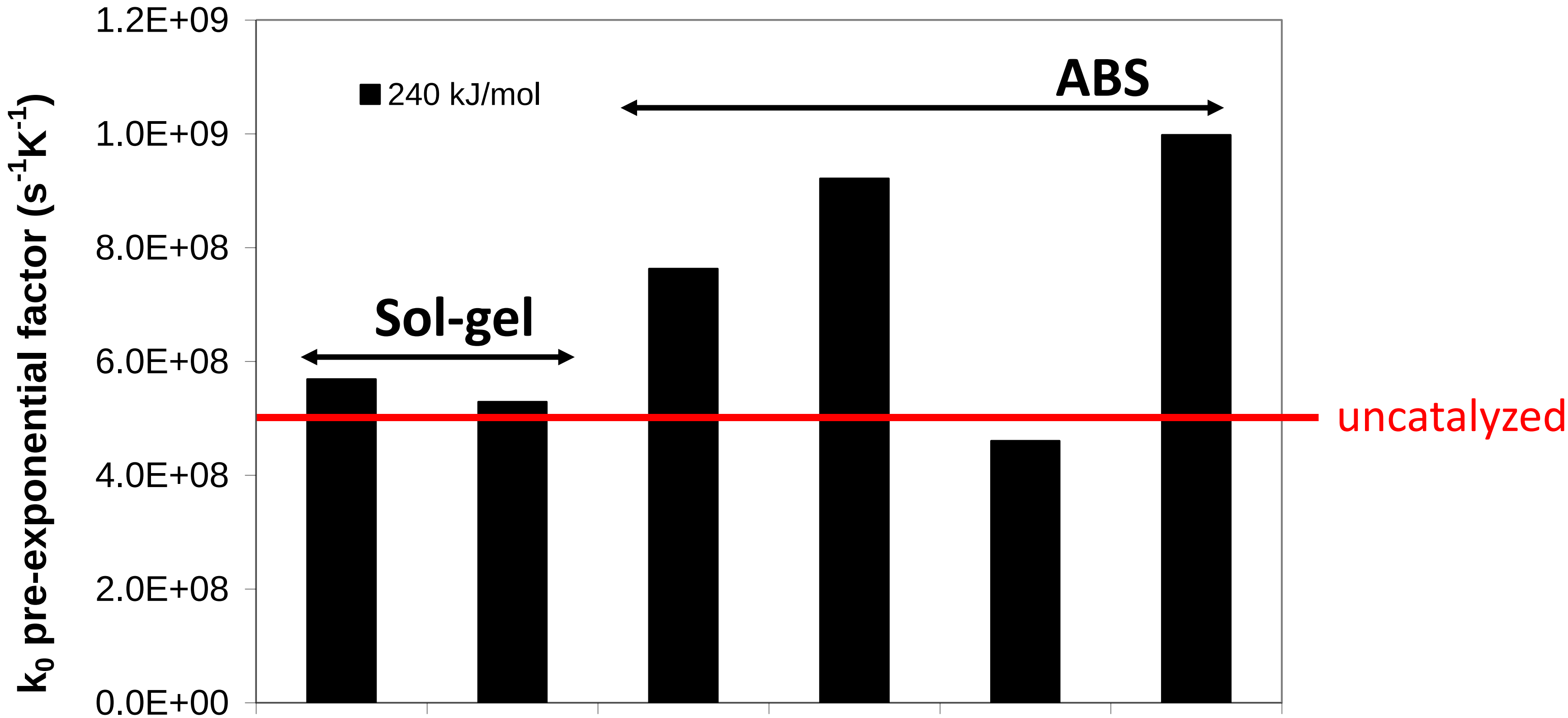
$k_{0,0}$ of 240 kJ/mol vs Catalyst Morphology



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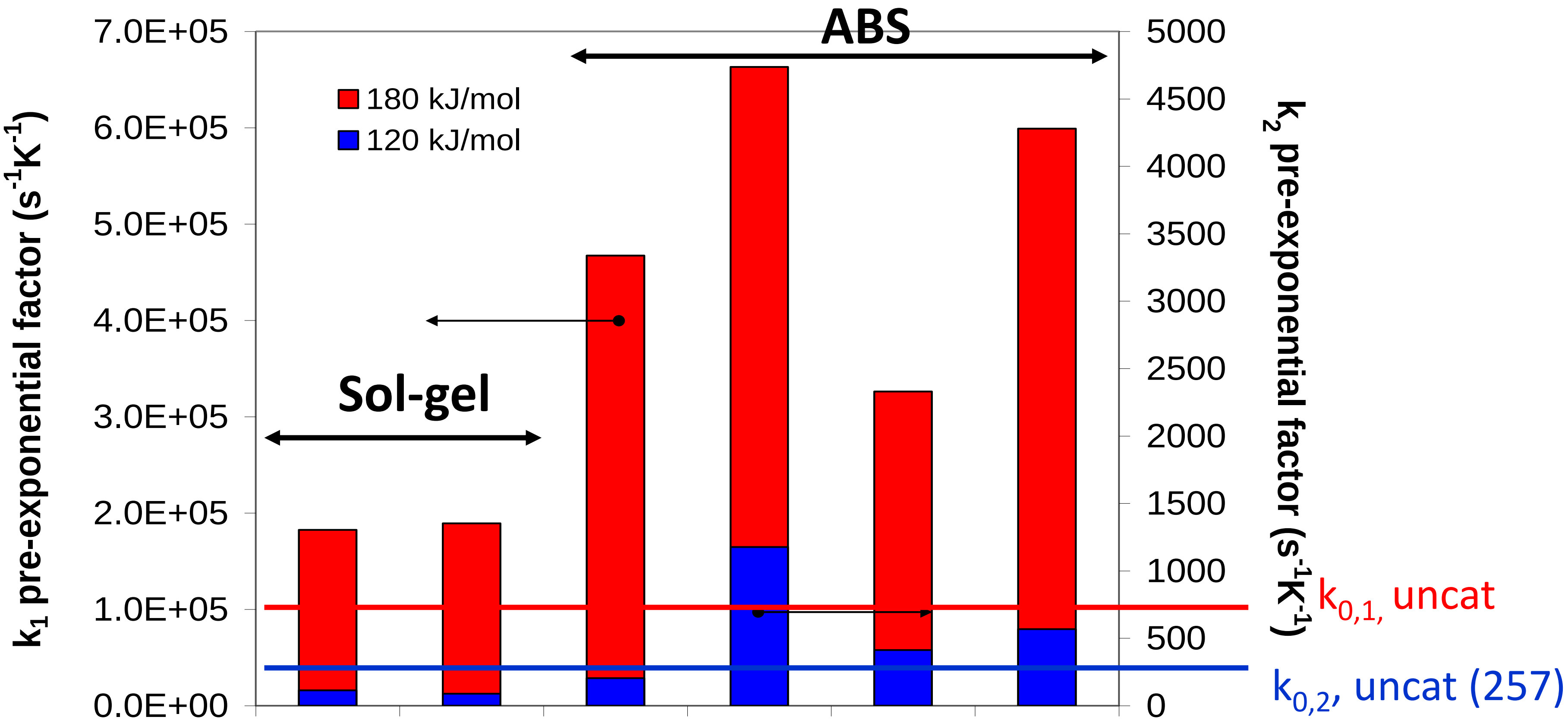
pore size (nm)	-	-	13.7	12.4	20.7	10.5
porosity	-	-	0.451	0.674	0.633	0.387

$k_{0,1}$ and $k_{0,2}$ (180 & 120 kJ/mol) vs Catalyst Morphology



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porosity	-	-	0.451	0.674	0.633	0.387

Conclusions

- Soot reactivity requires **a multi-population approach for its accurate description**. Based on our current and past research we can identify **3 populations** (fractions) of (diesel and carbon black) soot with activation energies 120, 180 and 240 kJ/mol, most likely **reflecting differences in surface oxygen complexes that are formed on each**.
- The pre-exponentials of all populations have been characterized and **correlated to catalyst particle size, surface area, crystallite size, pore size and porosity**.
- **Micron-sized powder Ceria-Zirconia** based catalyst activity is shown to correlate with the **Sauter Mean Diameter ($d_{3,2}$)** of the Powder Size Distribution.
- **Ceria-nanoparticles oxidize catalytically** all three populations of soot with an order of magnitude higher pre-exponential factors, reflecting the **high capacity of the catalyst to generate respective surface-oxygen-complexes.**
- **Ceria-nanoparticle** catalyst activity is shown to correlate to a morphological metric combining **particle size, surface area, crystallite size, and porosity**.
- These results provide more **accurate descriptions of soot reactivity and are readily incorporated into our DPF simulation codes.**

Thank you for your attention!

Acknowledgments

- **The European Commission for supporting our research in combustion engines, emissions, hydrogen and solar fuels** through >45 projects over the last 20 years, including current projects APT-STEP and ARMOS
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- **Past and Current Industrial Partners** with special thanks to Molycorp, Tenneco, Ibiden, Honda, CR Fiat, AVL and CERTAM.
- **My colleagues at APTL**

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