School of Process, Environmental
& Materials Engineering

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Novel Application of Bio-char as a Catalyst in the Low Temperature SRC-deNO_x Process

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- SCR unit located up stream of air pre-heaters, FGD and particulate control devices to meet temperature requirements (300 – 400 ^{o}C).

- SCR unit aids in the conversion of SO_2 to SO_3 and the production of ammonia salts ($(NH_4)SO_4$ / $(NH_4)HSO_4$) known for their respective corrosive and fouling nature.

- SCR unit replacement costly and performed during an outage.

- Low temperature SCR (100 – 200 ^{o}C) down stream of air pre-heaters, FGD and particulate control devices.

- Low temperature SCR avoids conversion of SO_2 to SO_3 and the production of ammonia salts.

- Novel use of a waste derived SCR catalyst represents a way of combining waste disposal, energy recovery and pollution control (NO) in one process.

- Oxides of Manganese (Mn) and Ceruim (Ce) demonstrate excellent performance at low temperatures due to unique redox and acid-base properties.

Chemical Activation and Co-activation Processes
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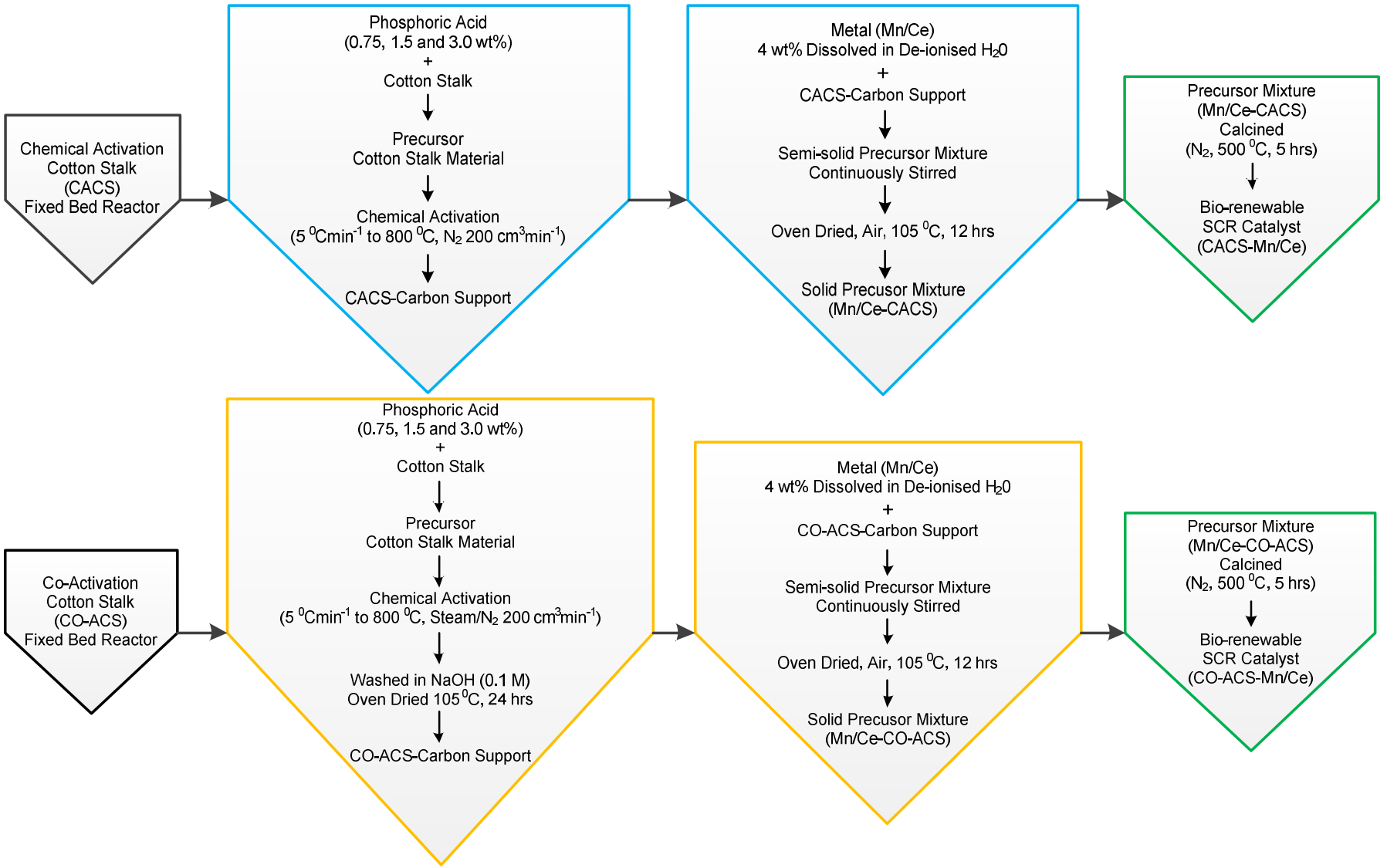

Fixed Bed Reactor Chemical Activation
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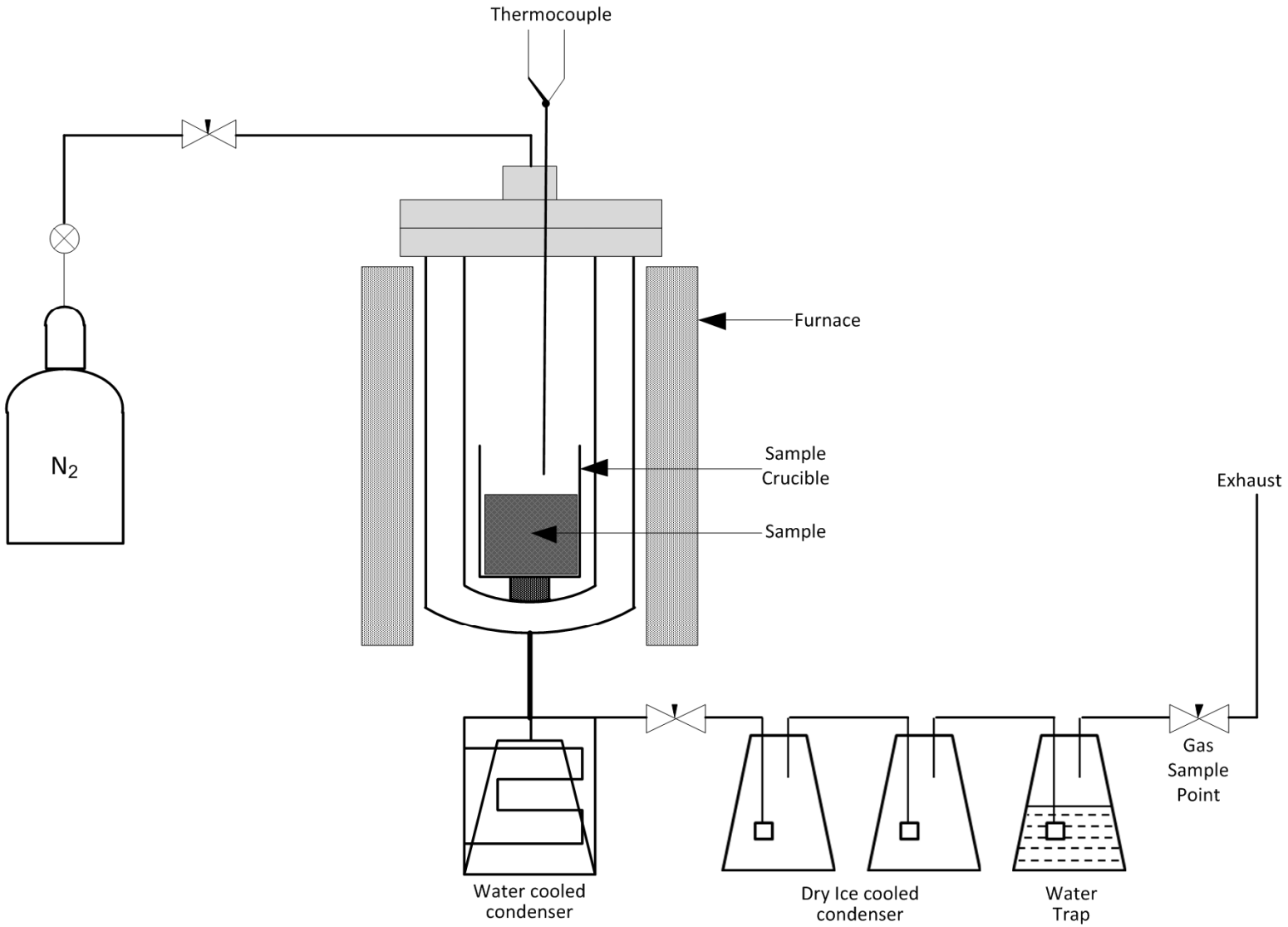

Modified Fixed Bed Reactor Co-activation
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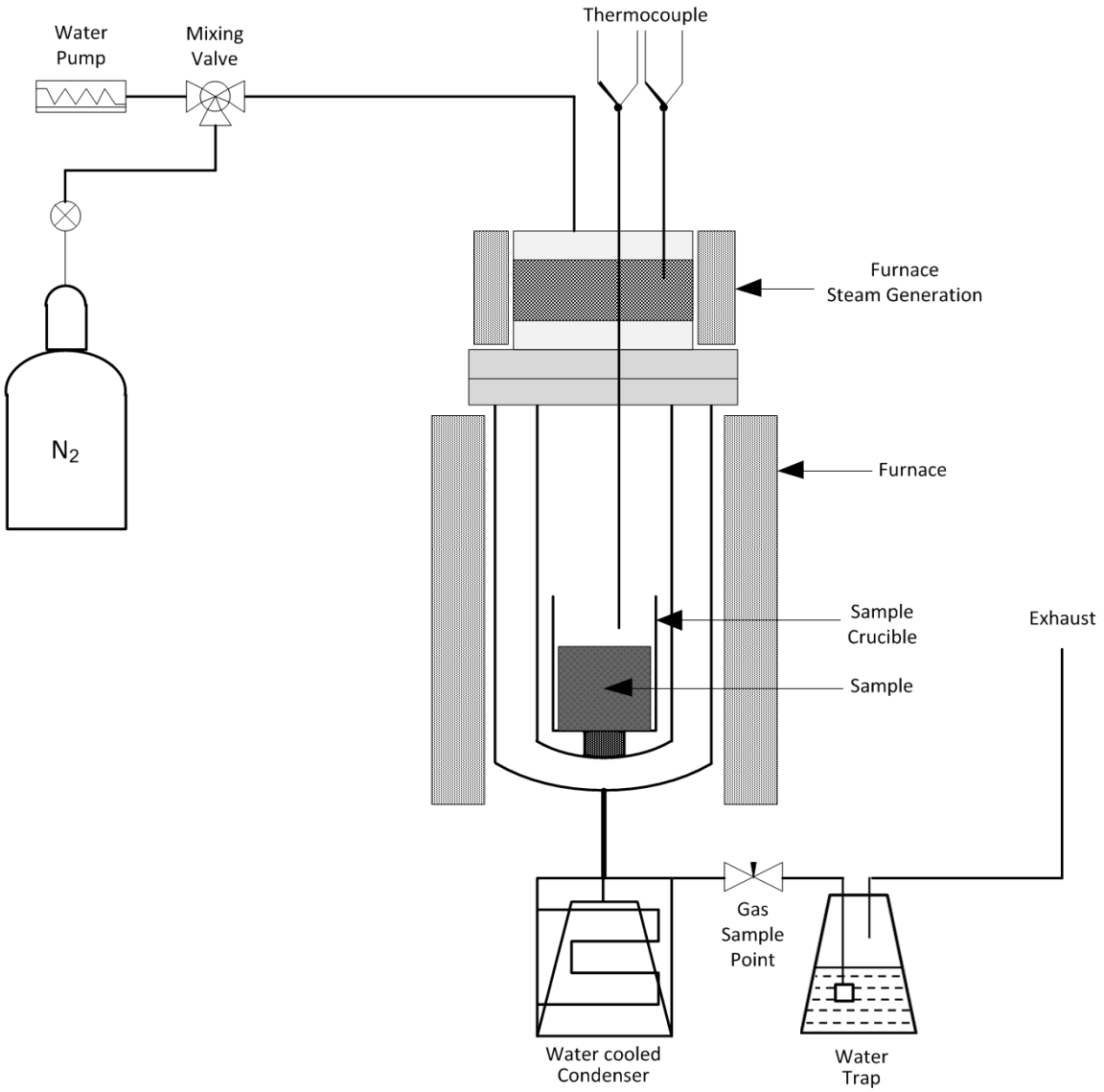

Fixed Bed SCR Reactor
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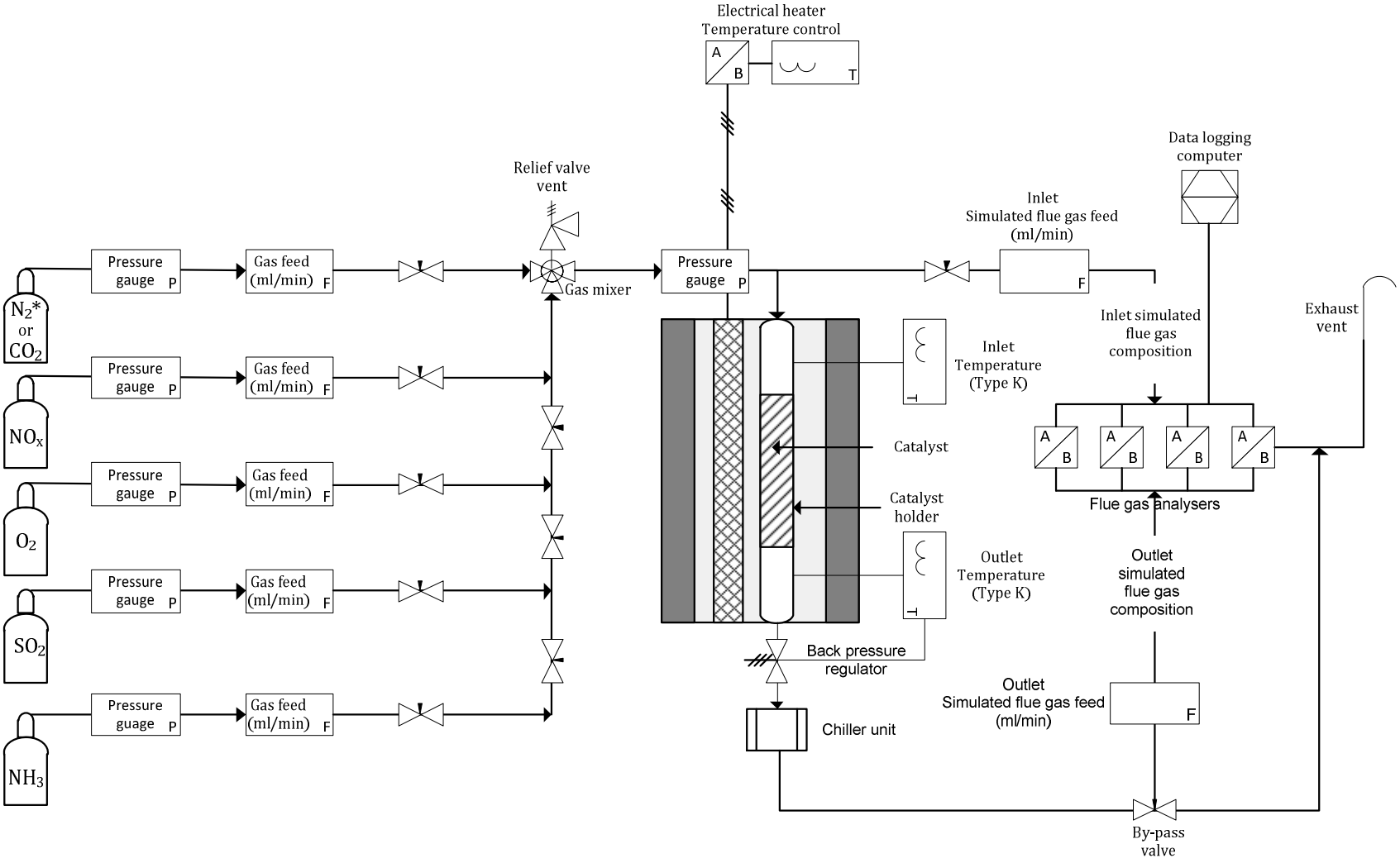

Experimental Conditions
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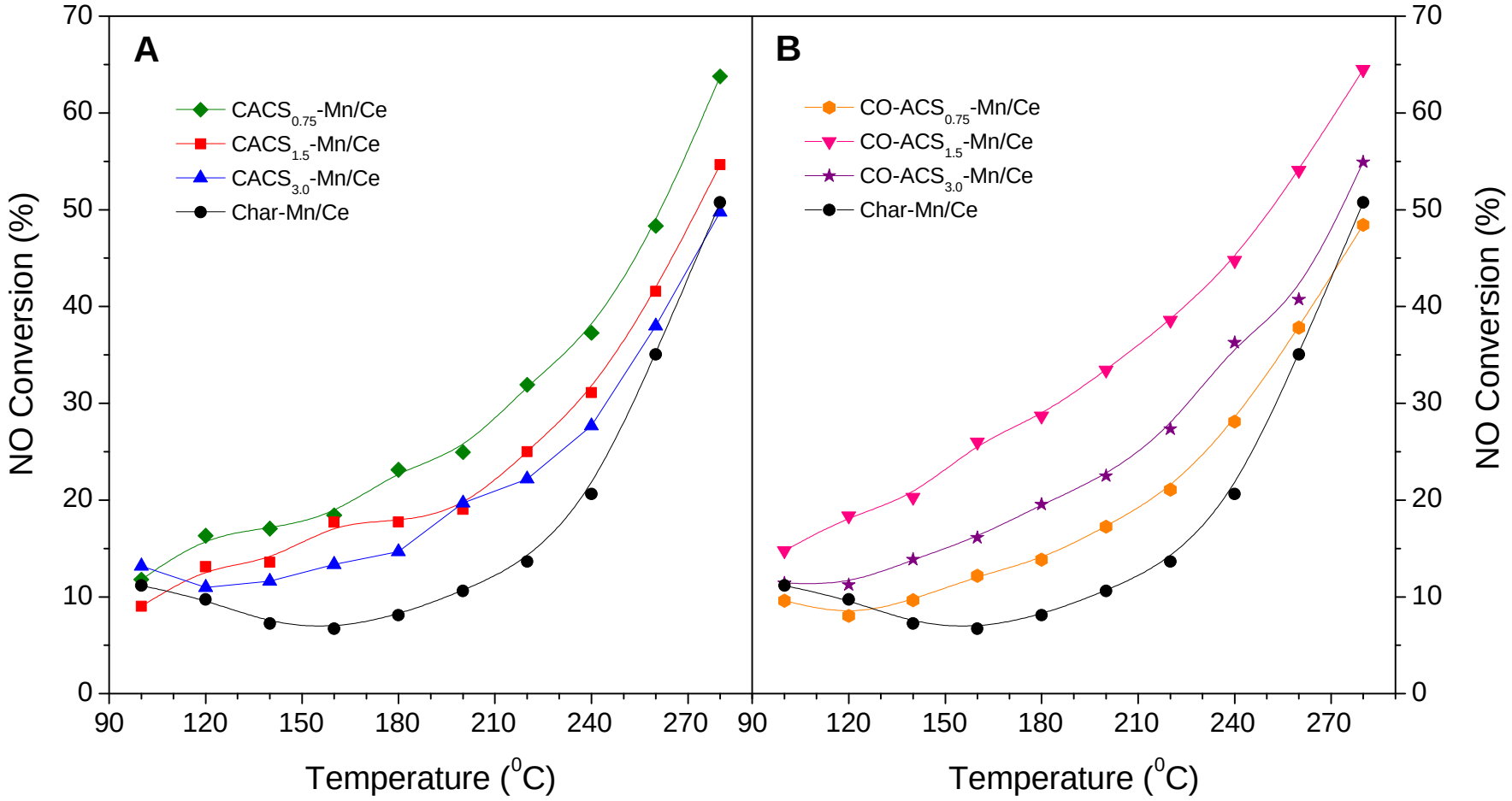
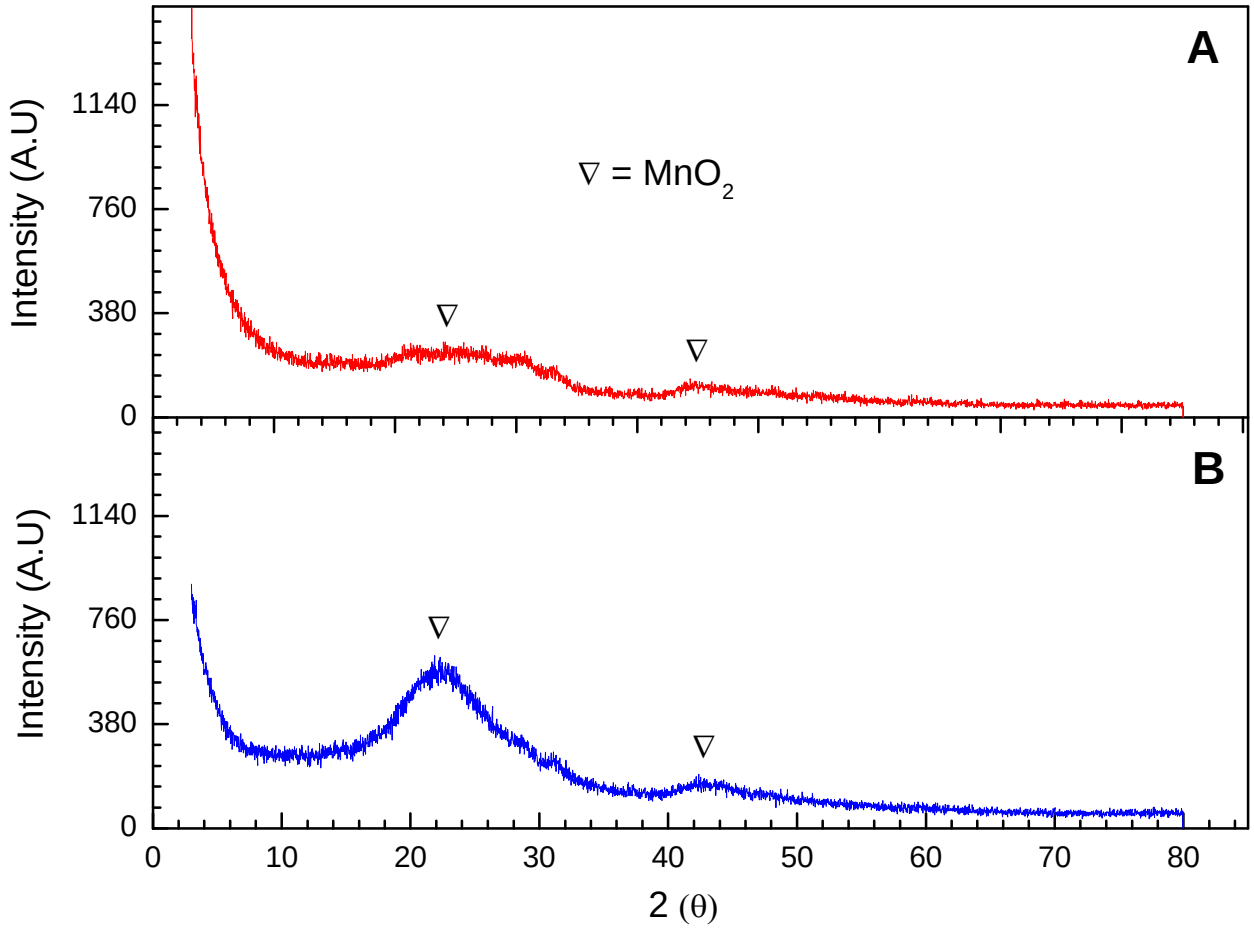
SCR-deNO$_x$ Catalyst	Ce/Mn (Molar Ratio)	Temperature (^{0}C)	H_3PO_4 (wt% Ratio)	Hold Time (Hrs)	Atmosphere	BET Surface Area ($m^2\ g^{-1}$)	Pore Diameter (nm)
Chemical Activation							
$CACS_{0.75}$-Mn/Ce	1:2	800	0.75:1	2	N_2	826.95	2.74
$CACS_{1.5}$-Mn/Ce	1:2	800	1.5:1	2	N_2	1100.63	3.79
$CACS_{3.0}$-Mn/Ce	1:2	800	3.0:1	2	N_2	1184.83	5.26
Co- Activation							
CO-$ACS_{0.75}$-Mn/Ce	1:2	800	0.75:1	2	N_2/Steam	1293.90	2.46
CO-$ACS_{1.5}$-Mn/Ce	1:2	800	1.5:1	2	N_2/Steam	1613.63	3.45
CO-$ACS_{1.5}$-Mn/Ce	1:2	800	3.0:1	2	N_2/Steam	1541.00	4.61

Experimental conditions employed to chemically activate (CACS) and co-activate (CO-ACS) cotton stalk impregnated with Ce/Mn.



NO conversion (%) of chemically activated ($CACS_x$-Mn/Ce) and co-activated (CO-ACS_x-Mn/Ce) cotton stalk derived SCR-deNO_x catalysts impregnated with Mn/Ce. A = $CACS_x$-Mn/Ce, B= CO-ACS_x-Mn/Ce.



X-ray diffraction patterns of chemically activated ($CACS_x$-Mn/Ce) and co-activated ($CO\text{-}ACS_x$-Mn/Ce) cotton stalk derived SCR-deNO_x catalysts impregnated with Mn/Ce. A = $CACS_{1.5}$-Mn/Ce, B = $CO\text{-}ACS_{1.5}$-Mn/Ce.

- NO conversion efficiencies were seen to range from ~48 % to 68 % for both $CACS_x$-Mn/Ce and CO-ACS_x-Mn/Ce.

- The catalysts ability to oxidize NO to NO_2 is crucial for the overall conversion of NO to N_2:

$$NH_3(aq) + O\,(aq) \rightarrow NH_2\,(aq) + OH\,(aq) \qquad \text{RQ-1}$$

$$2NO\,(g) + 2O_2\,(g) \rightarrow 2NO_2\,(aq) \qquad \text{RQ-2}$$

$$NH_2\,(aq) + NO\,(g) \rightarrow NH_2NO\,(aq) \rightarrow N_2\,(g) + H_2O\,(g) \qquad \text{RQ-3}$$

$$OH\,(aq) + NO_2\,(aq) \rightarrow O\,(aq) + HNO_2\,(aq) \qquad \text{RQ-4}$$

$$NH_3\,(aq) + HNO_2\,(aq) \rightarrow NH_4NO_2(aq) \rightarrow NH_2NO\,(aq) + H_2O\,(g) \rightarrow N_2\,(g) + 2H_2O\,(g) \qquad \text{RQ-5}$$

- The required excess of O_2 for reactions 1 and 2 to occur is significantly reduced impacting on reactions 3 to 5.

- The redox potential of the catalysts is dependent on the transition metals (valency) ability to maximize reaction rates between NO and NH_3 in the presence of O_2 on their respective active sites.

- Saturation of the active sites is suggested to occur rapidly allowing for an increased excess of NH_3 and NO to pass un-reacted over the catalyst.

- The low metal loading of 4 wt% is thought to be mainly responsible for the conservative NO reductions.

- Historical literature has demonstrated NO reductions >95% for metal loadings ranging from 10 - 30 wt% at temperatures between 150 and 230 ^{0}C.

- The raw cotton stalk and pyrolysed char have shown a potential for possible application in the low temperature SCR-deNO_x process.
- NO reduction far more dependent on the wt% of the metal loading than the physical parameters such as the pore size, pore structure and surface area.
- The addition of phosphoric acid significantly increased the BET surface area (m^2g^{-1}) for $CACS_x$-Mn/Ce and CO-ACS_x-Mn/Ce catalysts.
- Higher NO reductions can be realised by an increase in the metal loadings of Mn/Ce.

- The influence of the activation methods in conjunction with H_3PO_4 on NO reduction are complex and require further investigation.
- Investigate the highest NO reductions associated with metal loading (4 wt% - 30 wt%).
- SCR experiments using a variety of other waste materials as a catalytic support (MSW, waste plastics and waste tyres).
- SCR experiments to be conducted in a synthesised flue gas containing both particulates, SO_2 and H_2O as well as Hg.
- Investigate application of low temperature catalyst in NO emission control from heavy duty vehicle engines.

Acknowledgements

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