

Enhanced Mass Transfer Substrates: Results with a Preferential Oxidation (PROX) Pt/Al₂O₃ catalyst.

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Introduction

A highly active catalytic material is always required to meet the conversion requirements under the expectant reaction conditions but often the lowest level of contaminant achievable cannot be attained due to bulk mass transfer limitations. This is especially the case for conventional parallel channel catalyzed monoliths currently used worldwide for environmental applications such as passenger cars, truck, high-flying aircraft, and motorcycle catalytic converters, as well as abatement of emissions from power plants, chemical facilities, and restaurants. To enhance conversion efficiencies in a mass transfer limited system a short contact time (SCT) substrate can be used, which possess attributes that position them more favorably for these applications. The extremely short channel length and tortuosity of these substrates avoids boundary layer buildup observed in conventional parallel channel monoliths. The heat and mass transfer coefficients also depend on the boundary layer thickness.

To begin to understand the effect of SCT on trace contaminant cleanup, PROX reactors were tested to oxidize CO in a simulated reformat mixture for a PEM fuel cell application. A two-stage PROX reactor set up was operated over a range of O₂-to-CO (λ) ratios to achieve less than 10 ppm CO effluent. Testing was conducted over a range of GHSV from 88,000 to 176,000 h⁻¹ and inlet temperatures from 140°C to 160°C. The following reactor tests have been conducted: *i*) Single PROX: the effects of space velocity, steam flow rate, O₂-to-CO ratio and inlet temperature on conversion and reaction temperatures; *ii*) combined PROX 1 & 2 train parametric study: The PROX train was tested for the effects of steam-to-carbon ratio between 1.5-2.5 and oxygen-to-carbon ratio between 0.75-1.25 all at 90,000 hr⁻¹. A resulting H₂ stream of 35% outlet concentration was generated for a 0.21kW system. The results of the testing revealed that there were multiple steady-states and an unexpected water-oxygen synergy present in the system. This presentation will show the results of the testing and provide a likely explanation for them.

Materials and Methods

The reactor setup consisted of a gas delivery manifold, using N₂ (UHP grade), H₂ (High Purity), CO (UHP), CO₂ (UHP) and Air (Industrial Grade) via mass flow controllers (Aalborg GFC-17) mixed to generate the simulated reformat feed. An inlet and outlet gas sample port was installed and coupled directly to an on-line gas chromatograph (Agilent MicroGC-3000) for analysis. A syringe pump (Razel) was used to generate the desired amounts of steam assisted by a N₂ sweep gas. The PROX reactors consisted of short contact time (SCT) elements obtained from Precision Combustion Inc. The SCT was coated with a Pt/ γ -Al₂O₃ washcoat. Reactor temperatures were maintained via insulated trace tape (Omega) controlled by variable resistors (Variat) and externally attached E-type thermocouples (Omega). Inlet and outlet gas temperatures were taken by a separate set of E-type thermocouples (Omega) installed in the gas path.

Results and Discussion

Figure 1 shows the results of hysteresis and multiple steady operation for a range of CO conversion and catalyst exit temperature vs. λ . Between lambda of 1.8 to 2.2, the catalyst displays an expected hysteresis, whereas at lower lambda there are different CO conversions

for the same lambda and temperature. The conversion as a function of λ is most sensitive near

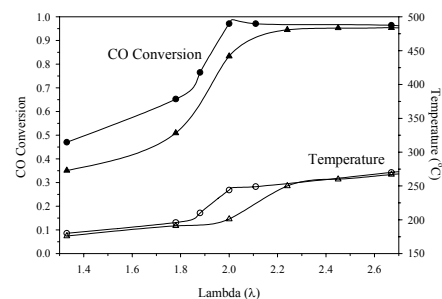


Figure 1: CO conversion and exit temperature hysteresis in single PROX

To provide insight into the operational modes of the conversion/selectivity performance, two PROX reactors were tested in series over a range of operating conditions. Figure 2 shows the conversion versus selectivity of the combined PROX reactor system. A maximum selectivity (~52%) is achieved for two conversion levels. This is tied to the multiple steady state performance. The operational trends for a S/C ratio of 1.5 to 2.5 highlight interesting behavior. As O/C increases for the S/C=1.5 condition, the conversion and selectivity increase, yet, as the O/C increases for the S/C=2.5 case, the conversion and selectivity decrease. This is currently still under investigation.

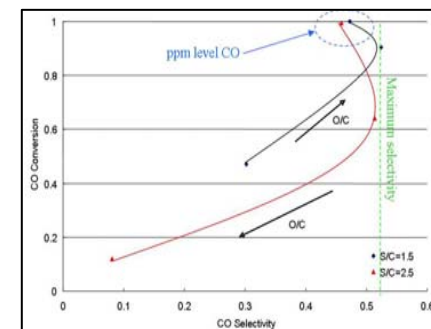


Figure 2: CO conversion vs. selectivity for S:C=1.5, 2.5 & O:C=0.75-1.25 @ 90,000 hr⁻¹

Finally evidence of a water-oxygen synergy was observed during operation by progressively decreasing the water feed to zero. Interestingly, the CO conversion did not decrease and the temperature remained practically constant. Conversely, cooling the reactor and feeding the same dry composition results in a lower CO conversion.

Significance

The observed multiple steady state, hysteresis, conversion-selectivity and water-oxygen synergy behavior is a function of transport and kinetic rate competition. In designing reactors to achieve very low levels of contaminant output, i.e. high conversion for low concentrations, the transport implications must be considered. The data presented will show how transport can both enhance and reduce reactor performance and efficiency.

[1] Kahlich, M.J., H.A. Gasteiger, and R.J. Behm, Kinetics of the Selective CO Oxidation in H₂-Rich Gas on Pt/Al₂O₃. *Journal of Catalysis*, 1997. 171(1): p. 93-105.