Triple Function Ru Catalysts for Low-Temperature CO Oxidation, VOC Combustion and SCR-DeNOx

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Introduction

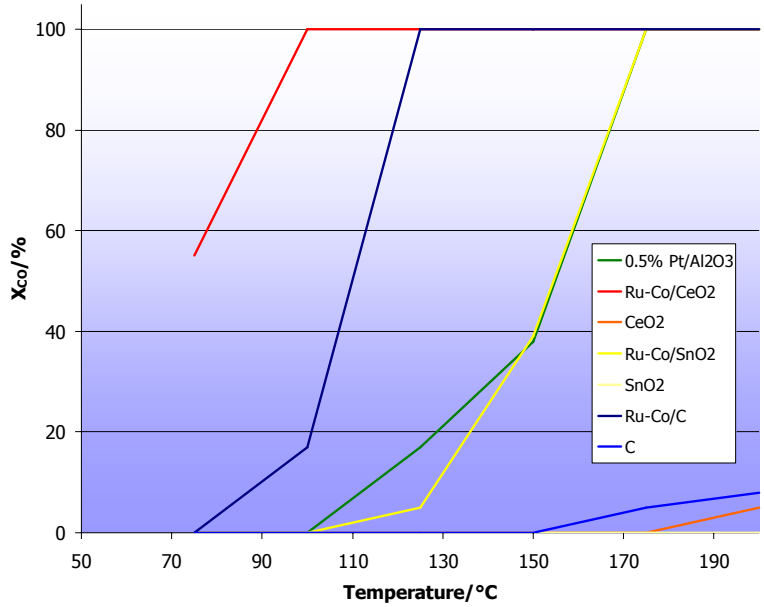
For emissions control of multicomponent exhaust gas streams, catalytic converters have to perform three functions: the catalytic oxidation of carbon monoxide to carbon dioxide, the destruction of Volatile Organic Carbon compounds (VOC's), and NOx abatement. State-of-art catalysts for CO oxidation are based on $CuMn_2O_4$ (hopcalite), for VOC combustion on Pt/alumina, and for DeNOx either supported noble metals (Rh, Pt, Pd) or redox metals (V, Mn) are commonly employed. Extensive research has focused on the improvement of catalytic activity at low temperatures. We have applied high-throughput and combinatorial approaches to the discovery of more efficient catalysts for low temperature CO oxidation, VOC combustion and DeNOx [1-5]. The screening approach was based on a hierarchy of qualitative and semi-quantitative primary screens for the discovery of hits, and quantitative secondary screens for hit confirmation, lead optimization and scale-up. Parallel IR thermography and fast serial scanning mass spectrometry were the primary screens for CO oxidation and SCR-DeNOx, respectively, using wafer-formatted libraries of 256 catalysts with CO/O2/N2 and sulfur- and water-free NH3/NO/O2/Ar model feeds. Multi-channel fixed bed reactors equipped with imaging reflection FTIR spectroscopy or GC were used for scale up as well as VOC screening using propylene/O2/N2 model feed.

CO oxidation and VOC combustion over Ru-based catalyst systems

Pt-free Ru-Co-Ce mixed oxide ternaries as well as ceria supported Ru-Co have been discovered and scaled up for further optimization [1-2]. The reactor consisted of 8 parallel fixed-beds with a flow-distributed feed, in which a stream selection valve selected one of the reactor effluents for rapid serial GC analysis. The feed consisted of 1% CO and/or 0.15% propylene in CDA at a space velocity of 25,000 1/hr. The reactor temperature was increased from 40°C to 200°C in 10-20°C increments in order to produce light-off curves for CO oxidation and propylene combustion both as pure components in CDA as well as a mixed CO-propylene-CDA feed. GC analysis used a TCD for quantitative detection of CO, CO_2, H_2O, propylene and O_2. Light off curves could be produced for the CO oxidation and VOC combustion analysis of all 8 candidate catalysts in ~12 hours, via automated Symyx' Impressionist® software control. Figure 1 shows representative light off curves for CO

oxidation. Ru-Co on ceria and active carbon are more active than the Pt/Al2O3 benchmark whereas Ru-Co on SnO2 lights off at comparable temperature.

Figure 1: Light off curves (CO conversion versus reaction temperature) for Ru-Co leads in 8x1 multi channel fixed bed reactor.



We have then investigated the effect of yttrium doping. A library of Ru-Co-Ce-Y quaternaries has been synthesized by the modified Pechini method using Ce (III) nitrate, Co (II) nitrate, Y (III) nitrate and Ru (III) nitrosyl nitrate as precursors in aqueous glyoxylic acid as dispersant and calcining the solution according to the heat up protocol: 60C/2h ramp/120C/2h hold/1h ramp/200C/2h hold/1h ramp/350C/4h hold.

Glyoxylic acid 50% [ml]	Ce(NO3)3 1.5M [ml]	Co(NO3)2 1M [ml]	Y(NO3)3 2M [ml]	Ru(NO)(NO3)3 7% [ml]	Composition by weight	BET SA [m2g-1]
10	2.38	7.64	0	0.713	Ce0.5Co0.45Ru0.05	71
10	1.98	7.64	0.468	0.713	Ce0.42Y0.08Co0.45Ru0.05	89
10	1.59	7.64	0.937	0.713	Ce0.33Y0.17Co0.45Ru0.05	86
10	1.19	7.64	1.406	0.713	Ce0.25Y0.25Co0.45Ru0.05	67
10	0.79	7.64	1.874	0.713	Ce0.17Y0.33Co0.45Ru0.05	68

10	0.40	7.64	2.343	0.713	Ce0.08Y0.42Co0.45Ru0.05	71
10	0	7.64	2.812	0.713	Y0.5Co0.45Ru0.05	58

Figures 2-3 show the resulting light-off curves for both propylene and CO for the Ru-Co-Ce-Y library and the Pt/Al_2O_3 standard using a mixed propylene-CO-CDA feed. It can be seen from these plots that several catalysts reveal a lower light-off temperature for both CO and propylene as compared to the 0.5% Pt on alumina standard catalyst.

In addition to the synergistic RuCo and RuCoCe systems, RuSn and RuCu families of active hits were also discovered and optimized for CO oxidation [1] and the effect of doping was investigated for supported and bulk mixed oxide catalysts.

Figure 2: Light off curves (propylene conversion versus reaction temperature) for Ru-Co-Ce-Y leads in 8x1 multi channel fixed bed reactor using a mixed propylene-CO-CDA feed.

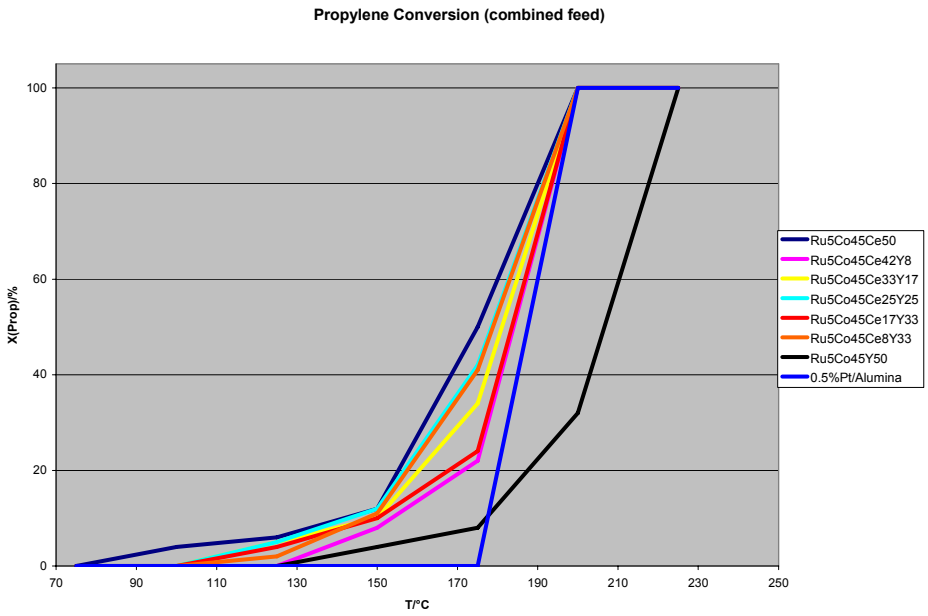
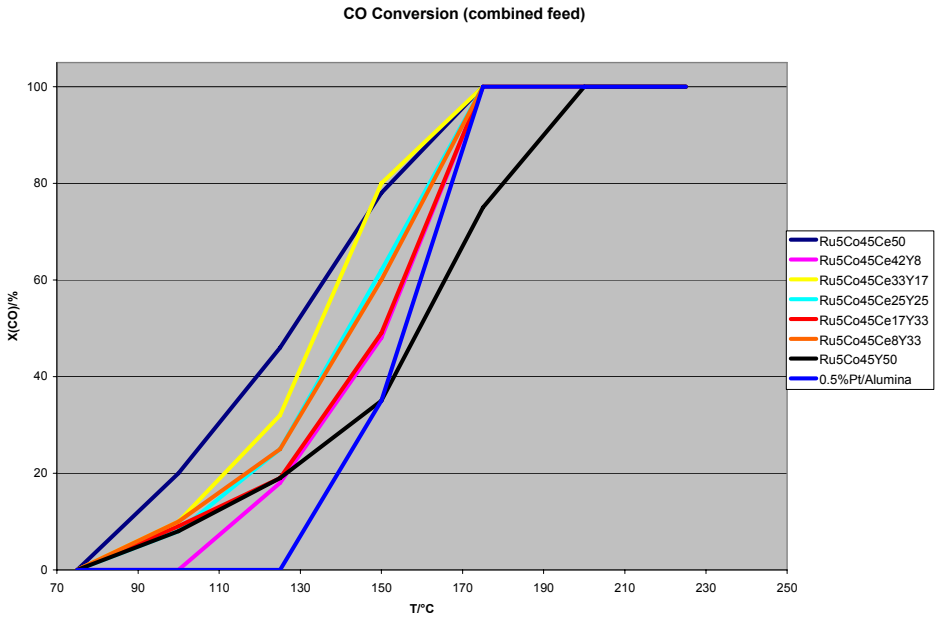


Figure 3: Light off curves (CO conversion versus reaction temperature) for Ru-Co-Ce-Y leads in 8x1 multi channel fixed bed reactor using a mixed propylene-CO-CDA feed.



SCR-DeNOx over Ru-based compositions

NO_x abatement by selective catalytic reduction (SCR) with injected ammonia (4 NO + 4 NH_3 + O_2 → 4 N_2 + 6 H_2O) has been extensively studied. The commercial honeycomb catalyst for NH_3-SCR Stack $DeNO_x$ used in the clean up of exhaust gas streams in stationary power plants at low to medium temperatures basically consists of $V_2O_5/WO_3/TiO_2$ and allows up to 90% NO_x removal to be achieved with less than about 5ppm ammonia slip. We have targeted approximately an order of magnitude more active SCR Stack DeNOx catalysts operating in a broad temperature window in the range of 200-300°C.

We have initiated a broad screening program encompassing supported redox, noble and base metal catalysts for LT-SCR-DeNOx in high-throughput scanning mass spectrometers [3]. The aim was to discover novel compositions with drastically enhanced activity or a broader dynamic temperature window, provide an activity ranking of catalyst compositions and identify general trends. A large number of catalyst libraries consisting of binary, ternary, and quaternary catalyst compositions were synthesized and screened.

A representative library containing 24 metals supported on a gamma alumina carrier is shown in figures 4-6 (library design, NO conversion plotted versus N2 production and versus wafer column). Note that different precursors have been used for some metals. Gamma-alumina is identified as active carrier. High N2O production is found for Mn > Co > Mo (already indicated by the deviation from the NO-N2 mass balance). For 300°C, the activity ranking is Ru > Co ~ Cu > V ~ Fe > Mn. Ru is

less active at low temperatures but highly active at medium and high temperatures. NiO is inactive but Co oxide is active.

Figure 4: Library design for discovery wafer containing 24 metals (30 different metal precursors) on gamma alumina carrier (Catalox SBa150). 8- and 7-point vertical gradients of metal loading. Calcination at 450C.

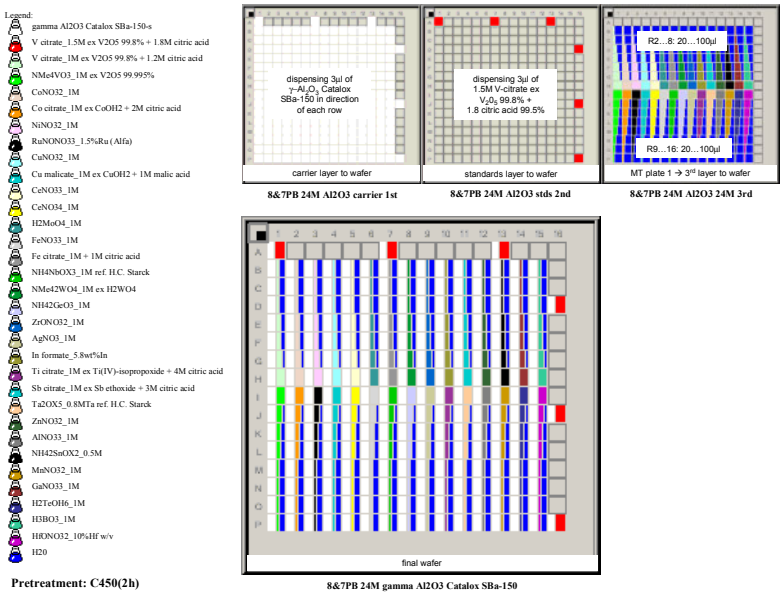


Figure 5: Screening data: NO conversion versus N2 production

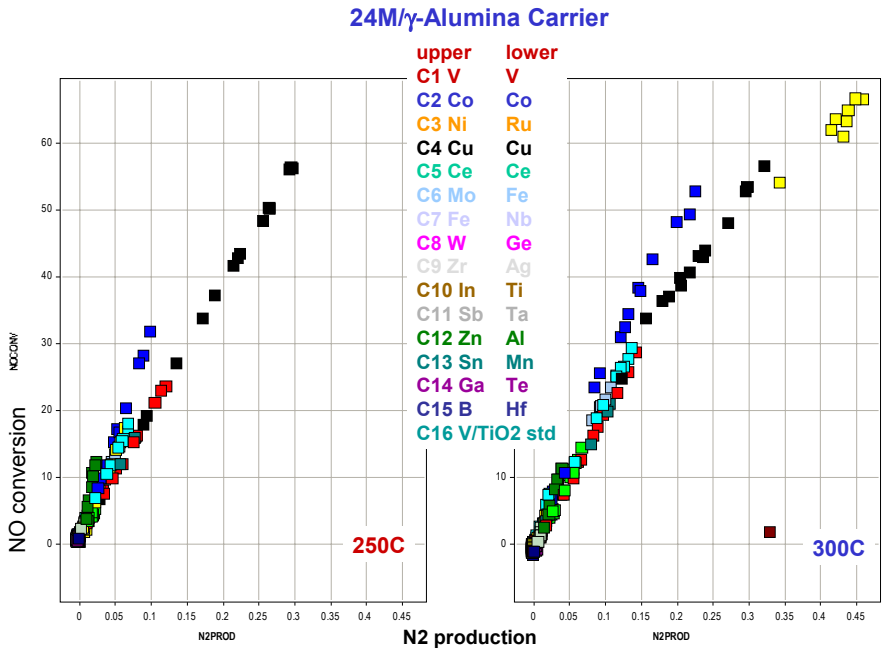
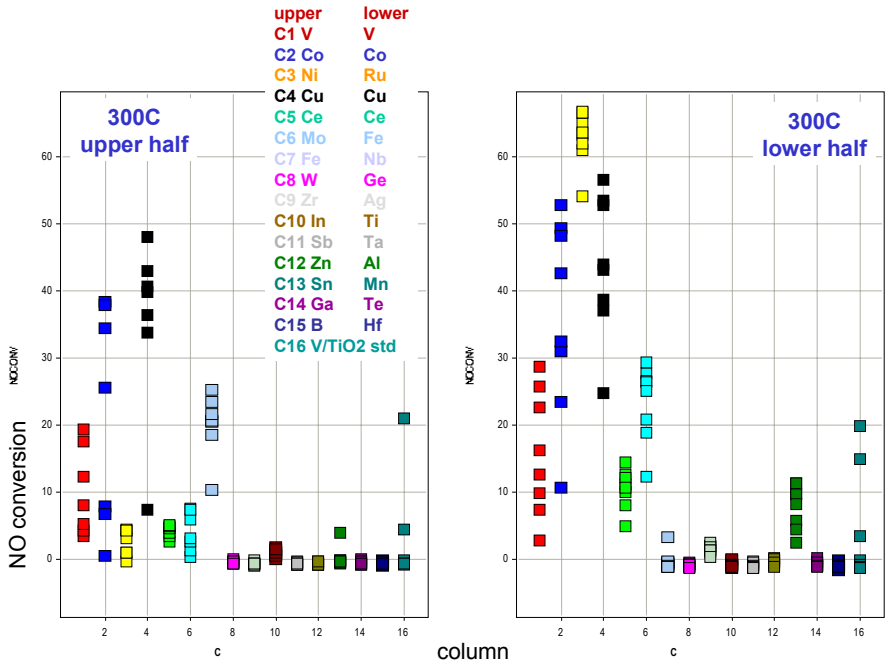


Figure 6: Screening data: NO conversion versus wafer column at 300C



Conclusions

By applying high throughput screening methodologies in microreactors in combination with scale up and further optimization of leads in parallel fixed bed reactors we have classified and ranked metals with respect to their catalytic function for CO oxidation, VOC destruction (propylene combustion) and

NH3-SCR-DeNOx. We have identified Ru based building blocks as highly active for combined CO oxidation and propylene combustion in mixed CO-C3-O2 feed and developed synergistic Ru-Co, Ru-Cu and Ru-Sn compositions, preferably doped with or supported on ceria, that are competitive to state-of-art Pt catalysts [4-5]. Independently, when executing a combinatorial screening program on SCR-DeNOx over supported metals (using NH3 as reductant) we found Ru and Cu to be the most active metals, and moreover form a synergistic pair. Therefore, Ru based compositions such as Ru-Co and Ru-Cu systems could lead to novel multi-functional classes of catalysts suitable for 3-way catalytic converters.

[1] S. Cypes et al., "High Throughput Screening of Low Temperature CO Oxidation Catalysts in IR Thermography Reactor", in: Special Issue of "High Throughput Screening and Combinatorial Chemistry", Ed. Jozsef Margitfalvi, 2006 (submitted).
[2] A. Hagemeyer et al., "Novel Ru-Co Catalysts for Combined Low Temperature CO Oxidation/VOC Combustion", ACS Spring National Meeting, Atlanta, GA, March 26-30, 2006.
[3] G. Streukens et al., "Discovery of Novel Catalytic Materials for Emissions Control using High Throughput Scanning Mass Spectrometry", 4th International Conference on Environmental Catalysis, Heidelberg, Germany, June 5-8, 2005.
[4] H. Weinberg et al., Irsee III Symposium on Selective Oxidation, Irsee, Germany, June 10-11, 2005; Topics in Catalysis (2006), in press.
[5] Patent pending.