Ammoxidation Catalysis for NO$_x$ Control in Partial Combustion FCC

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Introduction

Environmental regulations are pressuring petroleum refiners to reduce CO and NO$_x$ emissions from the catalyst regenerator of the fluidized catalytic cracking (FCC) unit. In the case of most FCC units, CO emissions are controlled using Pt-group CO oxidation catalysts. The present work concerns the remaining one-third of the ~440 FCC units world-wide that often operate with heavier residual feeds that deposit higher levels of coke and other contaminants on the catalyst. These units instead operate under partial combustion conditions because the additional exotherm from concurrent CO oxidation is undesirable; the CO-laden flue gas is instead passed to a furnace downstream for heat recovery.

NO$_x$ emissions are inadvertently increased by coincidental catalysis in both the full and partial CO combustion modes. HCN, formed via the pyrolysis of the nitrogen in coke, might initially be hydrolyzed to NH$_3$, but either HCN or NH$_3$ can be oxidized to NO$_x$ by CO oxidation catalysts in full or an intermediate mode of combustion. Antimony, often added to suppress the activity of Ni contaminants for forming additional coke in residual feed operations, has also recently been found to increase NO$_x$ emissions. Finally, unconverted HCN and NH$_3$ passed to the downstream combustion furnace are likely to form at least a portion of NO$_x$ during homogeneous combustion. In order to minimize NO$_x$ emissions under partial FCC combustion conditions then, a catalyst is desired that will selectively, partially oxidize HCN and NH$_3$ to H$_2$O, CO and N$_2$, without making CO$_2$ or NO$_x$.

Materials and Methods

Fe$_1$Sb$_{2.5}$M$_n$O$_x$ (M=Cu, Mo, Sn, Ni, V, Bi, Zn, Ce; n=0.2 – 2) ammoxidation catalyst [1] additives were prepared by co-precipitating mixed metal nitrate and SbCl$_3$ solutions with ammonium hydroxide within the pores of a pre-formed microspheroidal zirconia-stabilized precipitated silica and clay support [2]. Impregnations to incipient wetness with intermediate washing and drying steps were repeated until 10 wt% loading was reached. The samples were then calcined 24 h at 427° C and then 8 h at 760° C. Deactivations were done at 816° C by fluidizing in 100% steam additives diluted to 20% in REUSY FCC catalyst. The proprietary lambda sweep test method [3] for FCC regenerator simulation was employed in the reaction studies after further dilution to 1% fresh and 1% steamed additive in steamed FCC catalyst.

Gibbs free energy hypothesis. Based on the Mars-van Krevelen mechanism, we had proposed earlier [4] to rank the catalytic activity and selectivity of NH$_3$ oxidation to form NO$_x$ with the ΔG° at 718° C for the stoichiometric reaction with the corresponding metal oxides. This leads to what amounts to a lattice oxygen activity ranking of Pt>>Cu>Sb>Fe.

Ammoxidation analogy. Mixed base metal oxide ammoxidation catalysts activate NH$_3$ and build C≡N bonds with hydrocarbons under combustion conditions. The reverse reaction must also be catalyzed. We therefore hypothesized that ammoxidation catalysts might be useful in hydrolyzing H-C≡N back to NH$_3$ and CO. The Gibbs free energy hypothesis further suggested that the resulting activated ammonia would be able to form N$_2$, but unable to form NO$_x$, if we used appropriate base metal oxides in the ammoxidation catalysts.

Results and Discussion

Our catalysts were not tested for their effectiveness in ammoxidation, however repeated lambda sweep testing of fresh/steamed blends of FeSbMO$_x$ additives in partial combustion mode confirmed that some ammoxidation formulations were quite effective at converting HCN-NH$_3$-NO$_x$ mixtures in CO$_2$-CO-O$_2$-H$_2$O-SO$_x$ to N$_2$ under both lean and rich conditions. Cu was the most effective promoter found with Fe$_1$Sb$_{2.5}$Cu$_1$ achieving 94% yield of N$_2$, independent of the lambda value. The same composition was effective using alumina, clay or FCC catalyst as a support, but a W/TiO$_2$ support led to high HCN and NH$_3$ conversion to NO$_x$ [2]. Studies on the effect of the Fe/Sb/Cu atomic ratios and the role of the individual elements then showed Sb$_{2.5}$Cu$_1$ was similarly high in activity and NO$_x$ selectivity. Fe$_1$Cu$_1$ gave 115 µmol 2*N$_2$ with low NO$_x$ but FeSb$_n$ formulations were lower in activity.

Table 1. Lambda sweep [3] partial combustion mode results [2] for FeSbMO$_x$/ZrO$_2$-SiO$_2$. Integrated yields (µmol, rich + lean) for 3 cycles at 704° C and GHSV=100,000 h^{-1}.

Catalyst additive	FCC Blank	+Fe$_1$Sb$_{2.5}$ Cu$_1$	+Fe$_1$Sb$_{2.5}$ Sn$_{0.35}$	+Pt/ Al$_2$O$_3$	+CuCe/ Al$_2$O$_3$	+CeV/ MgAl$_2$O$_4$
CO	1494	1139	1033	652	368	1137
HCN	14.2	0.1	5.9	3.2	0.9	5.8
NH$_3$	22.6	1.0	1.8	2.8	9.5	6.1
NO$_x$	3.1	5.5	8.7	26.0	12.7	9.9
2*N$_2$	91	124	107	100	107	109
k$_{CO}$	---	0.07	0.12	3.69	---	0.09

Activity and selectivity in selective catalytic oxidation are determined by the oxidizing power of lattice oxygen, which is controlled by the strength of the M$_1$-O-M$_2$ bonds, which in turn are determined by the identities of M$_1$ and M$_2$ and the lattice structure. Base metals are generally more selective but changes in M$_2$ or the lattice via the support, preparation method, or gas composition can induce significant structural and therefore selectivity changes.

Significance

Selective oxidation by mixed metal oxides and ammoxidation catalysts are new approaches in FCC NO$_x$ reduction catalysis. If the FeSbCu/ZrO$_2$-SiO$_2$ composition were stable in activity and selectivity while in use, this would be the first successful NO$_x$ reduction additive strategy for partial combustion units, which might otherwise employ NCSR or add on an SCR unit.

References

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