

The Effect of CO₂ and H₂O on the Kinetics of NO Reduction by CH₄ over a La₂O₃/γ-Al₂O₃ Catalyst

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Abstract

The kinetic behavior of NO reduction by CH₄ over a 40% La₂O₃/γ-Al₂O₃ catalyst in the absence and presence of O₂ in the feed was studied, and the addition of either CO₂ or H₂O to the feed produced a reversible inhibitory effect on the rate similar to that observed with unsupported La₂O₃; however, the extent of rate inhibition was considerably smaller compared to unsupported La₂O₃. At 973K, either CO₂ (9%) or H₂O (2%) in the feed decreased activity by about 35% in the absence of O₂ and by only 20% with excess O₂ in the feed. In the absence of O₂, a reaction mechanism previously proposed for La₂O₃ described the kinetic behavior very well regarding all components after competitive CO₂ and H₂O adsorption was incorporated into the model to give the following rate expression:

$$r_{\text{N}_2} = \frac{(LkK_{\text{NO}}K_{\text{CH}_4})P_{\text{NO}}P_{\text{CH}_4}}{(1 + K_{\text{NO}}P_{\text{NO}} + K_{\text{CH}_4}P_{\text{CH}_4} + K_{\text{CO}_2}P_{\text{CO}_2} + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}})^2}$$

This equation fit the data well, had apparent activation energies of 14-25 kcal/mole, and gave thermodynamically consistent enthalpies and entropies of adsorption.

Stable rates at 973K with O₂ and either CO₂ or H₂O in the feed were between 0.94 and 0.99 μmol N₂/s/g catalyst. In the presence of excess O₂, when H₂O was also added to the feed a rate equation proposed earlier for La₂O₃ again provided a good fit of the data with thermodynamically consistent parameters determined under integral reaction operation. However, with both excess O₂ and CO₂ in the feed, this rate expression could not provide thermodynamically meaningful parameters from the fitting constants even though it fit the data well. This was attributed to a major contribution from the alumina to the overall rate because CO₂ had no significant effect on NO reduction on alumina, yet it inhibited it on La₂O₃. To satisfactorily account for this contribution from the Al₂O₃ support, this reaction model was altered by assuming that NO₂, rather than NO, was the principal N-containing surface intermediate on alumina. This led to the following rate expression for total CH₄ disappearance due to both combustion and NO reduction over γ-Al₂O₃:

$$(r_{\text{CH}_4})_{\text{T}} = \frac{k'_{\text{com}}P_{\text{CH}_4}P_{\text{O}_2}^{0.5} + k'_{\text{NO}}P_{\text{NO}}P_{\text{CH}_4}P_{\text{O}_2}^{0.5}}{(1 + K'_{\text{NO}_2}P_{\text{NO}}P_{\text{O}_2}^{0.5} + K_{\text{CH}_4}P_{\text{CH}_4} + K_{\text{O}_2}^{0.5}P_{\text{O}_2}^{0.5} + K_{\text{CO}_2}P_{\text{CO}_2} + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}})^2},$$

which gave satisfactory fits to the data and thermodynamically consistent parameters. The second term in this equation, which represents the rate of N₂ formation, was then combined with the rate equation describing NO reduction on pure La₂O₃ in the presence of O₂ to determine overall reaction performance, and the data were fit well assuming that La₂O₃ comprised 6.8% of the total surface area, a value in good agreement with that of 6.1% which was obtained from XRD line-broadening calculations.