Investigation of surfaced-catalyzed NO decomposition

Benefits at a glance

- Real-time, *in situ*, non-invasive analysis of catalysts on the molecular level
- Strong signal from active materials without interference from support
- Accurate measurement above 600°C

Introduction

Nitric oxide (NO) is a major pollutant present in combustion emissions from both automobiles and industrial sources. It leads to smog formation in the lower atmosphere and contributes to ozone depletion in the upper atmosphere. In spite of much research, current methods of destruction of NO still have significant limitations. In automobiles, for example, most of the NO is removed along with Carbon Monoxide (CO) and unburned hydrocarbons using so-called three-way catalysts. One problem with these commercial catalysts is that they only function efficiently over a narrow fuel/oxygen range. This has hampered the development of leaner-burning engines with reduced fuel consumption.

In many power plants, oxygen and a reducing agent such as ammonia are often added to allow catalytic reduction of NO:

$4NH_3 + 2NO + 2O_2 \rightarrow 6H_2O + 3N_2$ (1)

But the ideal reaction, particularly for automotive use, is direct catalytic dissociation of NO:

$2NO \rightarrow N_2 + O_2$ (2)

Unfortunately, no one has yet developed a catalyst for this dissociation reaction with high enough activity at reasonable operating temperatures (catalytic activity is measured in moles per gram catalyst per second, and usually scales with increasing temperature).

This work uses Raman spectroscopy to explore the use of barium oxide supported on magnesium oxide for NO dissociation. Under certain reaction conditions, highly unusual behavior has been observed in this system. Specifically, when the barium loading is ≥11 mol%, the catalytic activity rises rapidly with temperature, before sharply falling off.[1] Further, this fall-off temperature is dependent on the partial pressures of NO and added O_2. At higher temperatures (>750°C), catalytic reactivity begins to recover, but the marked difference in slope (temperature dependence) indicates that a different mechanism is involved in the two temperature regimes (Figure 1). Much work has been devoted to understanding this behavior in terms of surface phases and surface chemistry.

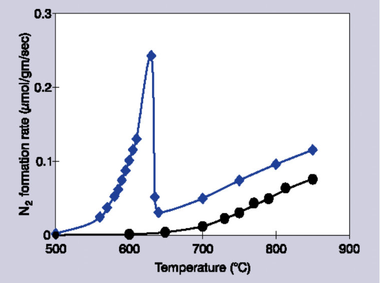

Figure 1: Decomposition rates of 1% NO/He over Ba/MgO catalysts. Circles indicate 1 mol% Ba/MgO, diamonds indicate 14 mol% Ba/MgO.

Analysis methods

In principle, both FTIR and Raman could be used to identify the various barium species that might be involved in this process. However, the interesting chemistry occurs at temperatures between 600°C and 700°C, and FTIR cannot be easily employed above 500°C because of excessive blackbody emission from the samples.

Experimental

In situ Raman measurements were made using a Raman analyzer with 532 nm incident radiation. The analyzer's high sensitivity is important because surface concentrations of active species are likely to be small, and low laser powers (a few mW) must be used to avoid excessive sample heating of this thermally sensitive reactive system. Since the samples do not fluoresce with

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

visible excitation, a short wavelength is preferred because Raman signal intensity is proportional to $1/\lambda^4$. Using short wavelengths also prevents blackbody emission.

Laser excitation and signal collection were performed using a Raman probe with a working distance of 50mm. The high sensitivity of this setup allowed spectra to be obtained with only 2.5 mW of laser light on the sample. Tests with thermocouples indicated that this produces local temperature increases of <5°C.

In each experiment, 50 mg of the catalyst was supported on a fused-quartz frit through which the gases (NO, O_2, He) flowed. This was enclosed in a low-volume (10 ml) cell to facilitate rapid re-equilibration after changes in operating temperature or gas mixture.

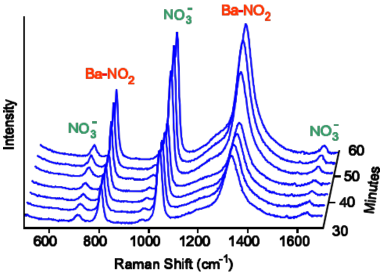

Figure 2: At 550°C a barium-nitro species builds up, corresponding to an increase in catalytic activity.

Results and discussion

Depending on operating conditions, Raman spectra could be observed for several different "BaNO" species, including barium nitrate $Ba(NO_3)_2$, barium nitrite $Ba(NO_2)_2$, and a barium-nitro species—barium oxide with a nitro (NO_2) ligand attached to the barium (Figure 2). Parameters such as gas partial pressures and operating temperature were varied around the activity peak so as to move from the high-activity regime to the low-activity regime. Spectral intensities for all the "BaNO" species varied, but only the nitro species intensity closely correlated with measured catalytic activity across the entire range of operating conditions. These results indicate that the barium nitro species is the active intermediate responsible for this peak in catalytic activity.

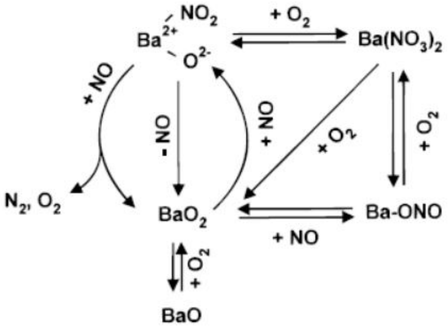

Figure 3: The catalytic reaction scheme. A barium-nitro reaction intermediate is formed by reaction of NO with barium peroxide (BaO_2).

By monitoring the Raman bands due to the nitrate and those assigned to crystalline barium peroxide, the observed complex dependency on O_2 pressure could also be interpreted and incorporated into an overall reaction scheme. Oxygen plays a dual role (Figure 3). It produces barium peroxide, which gives rise to the nitro species. On the other hand, excessive O_2 converts the active nitro species to the inactive nitrate.

The role of catalyst surface morphology is being investigated. It appears that the active barium-nitro phase is not a monolayer but rather behaves as though it consists of microcrystals. Raman spectroscopy is being used to study the chemistry of interaction between each of the phases.

Conclusion

In situ Raman spectroscopy has proven to be an invaluable tool to understand a new catalytic mechanism for NO elimination. While this type of Ba/MgO catalyst in itself does not appear to exhibit sufficiently high activity for ultimate commercial use, this study has provided important detailed insight into the type and structure of catalytic intermediates that can cause NO decomposition.

References

1. Xie, S.; Mestl, G.; Rosynek, M.P.; and Lunsford, J.H., "Decomposition of Nitric Oxide over Barium Oxide Supported on Magnesium Oxide. 1. Catalytic Results and *In Situ* Raman Spectroscopic Evidence for a Barium–Nitro Intermediate." *Journal of the American Chemical Society,* Vol. 119, **1997**, 10186.