

Detection of Surface CN and NCO Species as Possible Reaction Intermediates in Catalytic Lean NO_x Reduction

Can Li, Kathleen A. Bethke, Harold H. Kung and Mayfair C. Kung*

Ipatieff Laboratory and Center for Catalysis and Surface Science, Northwestern University, Evanston, IL 60208, USA
E-mail address: M-Kung@NWU.Edu

Surface species characterized by IR bands at 2140 and 2190 cm⁻¹ and assigned to CN and NCO species are observed as possible reaction intermediates under reaction conditions for lean NO_x reduction by propene or ethanol over Cu-ZrO₂.

Lean NO_x catalysis is a chemically challenging problem as it requires the hydrocarbon reductant to react selectively with NO in the presence of a large excess of O₂. Cu-ZrO₂ and Cu-Ga₂O₃ are among the few catalysts that are active and selective for lean NO_x reduction at temperatures between 498–573 K.^{1–3} Until now, there has been little information on the mechanism of this reaction.

Various surface species containing carbon and nitrogen have been observed on different lean NO_x catalysts. Bell *et al.*⁴ observed Cu-(N_xO_y)_z, organic NCO and Cu-NCO species adsorbed on Cu-ZSM-5 under lean NO_x reaction conditions, but have not tested their reactivity in N₂ production. Ukisu *et al.* reported the formation of adsorbed isocyanate species on Cu-Al₂O₃ by adsorbing the reactant gases at low temperatures and heating in vacuum to 573 K.⁵ A flow of C₃H₆, O₂ and NO (within the usual range of lean NO_x feed mixture) was used by Hayes *et al.*⁶ to generate organic nitrile species over Cu-ZSM-5 catalyst, and by Misono and coworkers⁷ to generate nitro compounds and isocyanate species over Ce-ZSM-5 at temperatures lower than the steady-state reaction temperatures. All of these species reacted with NO_x at higher temperatures to produce N₂, but their roles as reaction intermediates have not been fully resolved as they were generated under conditions different from the steady-state reaction condition. It would be more desirable for assignment of surface species as reaction intermediates if they are observed under steady-state lean NO_x conditions found to produce N₂.

We had observed surface intermediates with *in situ* IR spectroscopy when a feed of 1000 ppm NO, 1000 ppm C₃H₆ and 4% O₂ was flowed over 7.4 mass% Cu-ZrO₂ at 498 K. Fig. 1 shows the IR absorption bands of these surface intermediates at 2140 and 2190 cm⁻¹ when ¹⁴NO was used in the feed. By making comparison with IR bands of inorganic compounds,^{8,9} the 2140 cm⁻¹ band was assigned to a CN species and the 2190 cm⁻¹ band to a NCO species. These assignments were supported by the fact that these bands shifted to 2106 and 2170 cm⁻¹ if ¹⁵NO was used. The frequency shift for the CN species agreed with the theoretical value for a simple harmonic oscillator of a diatomic molecule. These species were absent when only the inactive ZrO₂ support was used or when NO was omitted from the feed.

The same two IR bands assigned to CN and NCO species were also observed when ethanol was used in place of C₃H₆. Ethanol was also effective in the reduction of NO to N₂ in excess oxygen at low temperatures.¹⁰ Likewise, the position of the two peaks shifted exactly in the same manner when ¹⁴NO was replaced by ¹⁵NO in the feed. However, when ineffective reductants were used, such as methanol or CO,¹⁰ these two IR bands were not observed. These observations further support the conclusion that these surface species are possible reaction intermediates in the selective reduction of NO by C₃H₆ or ethanol.

The surface CN and NCO species formed with ethanol reductant were observed under a wide range of lean NO_x feed conditions: O₂ concentration 0.1–10%, NO 0.1–1% and EtOH 0.07–0.15%. The intensities of the two peaks and the CN:NCO ratio decreased with increasing O₂ concentration. They were observable up to 573 K, although at that temperature, their

intensities were significantly diminished, probably due to the enhanced reactivity of these species at the higher temperature.

Further confirmation of the role of these species in selective lean NO_x reduction was demonstrated by the production of N₂ upon their reaction with NO_x. The CN and NCO species on the Cu-ZrO₂ catalyst were first generated at reaction temperature under a lean NO_x feed mixture identical to the IR experiment using propene. Then the gas flow was switched to pure He, and known quantities of NO or NO₂ were pulsed over the catalyst and the N₂ production was monitored. Fig. 2 shows the percentage of the nitrogen atoms in the NO pulse being converted to N₂ as a function of the number of NO pulses at 498 and 543 K. The N₂ formed from the first few pulses was greater than the amount of N in the NO pulse, suggesting that N₂ was formed from both NO in the pulse and some N-containing species adsorbed on the surface. The total amount of N₂ formed from the NO pulses at 543 K was substantially lower than that from the 498 K experiment. This is in agreement with the IR results which showed that the intensities of the bands due to CN and NCO were lower at the higher temperature. Nitrogen dioxide was as effective as NO in the pulse reaction with the surface species to form N₂. Fig. 2 also shows the results of the control experiment in which NO was pulsed over Cu-ZrO₂ which had been pretreated in a flow of C₃H₆, O₂ and He (without NO). The level of N₂ production was much reduced and the amounts produced probably reflected the reaction of NO

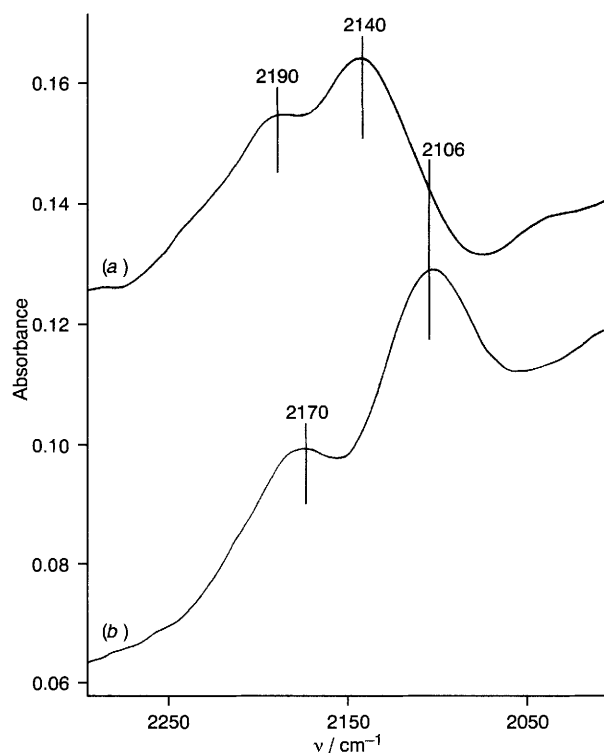


Fig. 1 IR spectra recorded at 498 K in a flow of 1000 ppm C₃H₆, 1000 ppm NO and 4% O₂ over Cu-ZrO₂; (a) ¹⁴NO and (b) ¹⁵NO

with surface carbonaceous deposits. Similar low levels of N_2 production were observed for the pulse reaction of NO_2 with the surface carbonaceous deposits.

In conclusion, this work extends the earlier observations of organic nitrile species by Hayes *et al.*,⁶ and nitro and isocyanate species by Misono and coworkers⁷ as possible reaction

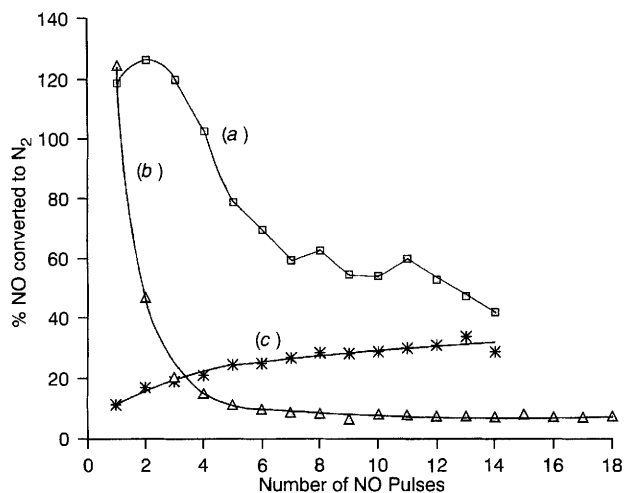


Fig. 2 N_2 production, as % of nitrogen in a NO pulse (0.5 ml of 1% NO), when the pulse was passed over 0.25 g of 7.4 mass% Cu-ZrO₂ catalyst pretreated for 1 h in a 150 ml min⁻¹ flow of (a) 1000 ppm NO, 1000 ppm C₃H₆ and 4% O₂ at 498 K; (b) 1000 ppm NO, 1000 ppm C₃H₆ and 4% O₂ at 543 K; (c) 1000 ppm C₃H₆ and 4% O₂ at 498 K. The temperatures of NO pulses were the same as the pretreatment temperature.

intermediates in the selective reduction of NO by hydrocarbons. Using IR spectroscopy under lean NO_x reduction conditions, the formation of surface CN and NCO species was detected if reductants effective in NO_x reduction, such as propene and ethanol, were used. The roles of these species as possible reaction intermediates are demonstrated with (a) the failure of their formation when non-selective reductants were used, and (b) N_2 production when they reacted with NO or NO₂.

This research was supported by the US Department of Energy, Basic Energy Sciences and GM Corporation.

Received, 6th January 1994; Com. 5/00116A

References

- 1 K. A. Bethke, D. Alt and M. C. Kung, *Catal. Lett.*, 1994, **25**, 37.
- 2 M. C. Kung, K. A. Bethke and H. H. Kung, *Preprints Am. Chem. Soc. Div. Petrol. Chem.*, 1994, **39**(1), 154.
- 3 M. C. Kung, K. A. Bethke, D. Alt, B. Yang and H. H. Kung, *ACS Symp. Ser.*, 1994, in the press.
- 4 V. A. Bell, J. S. Feeley, M. Deeba and R. J. Farrauto, *Catal. Lett.*, 1994, **29**, 15.
- 5 Y. Ukisu, S. Sato, G. Muramatsu and K. Yoshida, *Catal. Lett.*, 1992, **16**, 11.
- 6 N. W. Hayes, W. Grunert, G. J. Hutchings, R. W. Joyner and E. S. Shpiro, *J. Chem. Soc., Chem. Commun.*, 1994, 531.
- 7 H. Yasuda, T. Miyamoto and M. Misono, *Preprints Am. Chem. Soc. Div. Petrol. Chem.*, 1994, **39**(1), 99.
- 8 K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1986.
- 9 P. Gans, J. B. Gill and L. H. Johnson, *J. Chem. Soc., Dalton Trans.*, 1987, 673.
- 10 B. L. Yang, M. C. Kung, H. H. Kung, B. W. Jang and J. J. Spivey, paper 83e presented in the 1994 AIChE Annual Meeting, San Francisco, November 1994.