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Formation of nitroethylene during selective catalytic reduction of NO_2 by C_2H_4 over H-ferrierite

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Nitroethylene, formed during the selective catalytic reduction (SCR) of NO_2 by C_2H_4 over H-ferrierite, was determined to be an intermediate in SCR due to its decomposition behavior in forming N_2.

In the selective catalytic reduction (SCR) of NO_x (NO and NO_2) by hydrocarbons, both spectroscopic observation and product analysis support the contention that HNCO and HCN are among the intermediates related to N_2 formation. However, the routes to the formation of these compounds are under discussion. Yokoyama and Misono[1] proposed that nitro compounds are precursors of HNCO and HCN, and Cowan *et al.*[2] speculated that $MeNO_2$ is an intermediate in the SCR of NO_x by CH_4 while Zuzaniuk *et al.* reported that HNCO is produced by nitromethane decomposition over Al_2O_3.[3] Joubert *et al.* also suggested that 2-nitropropane is an intermediate during SCR over a Pt-based catalyst.[4] In this study, we conducted a product analysis of the SCR of NO_2 by C_2H_4 over H-ferrierite, which shows activity for this reaction,[5] and attempted to elucidate the pathway of formation of the nitrogen-containing compounds.

The catalyst sample was obtained by wash-coating *ca.* 30 mg of H-ferrierite (Tosoh; HSZ-720HOA, SiO_2/Al_2O_3 = 17.0) onto a miniature cylindrical cordierite honeycomb (8 mm diameter × 9 mm length, 400 cells in^{-2}).[6] Catalytic activity tests were carried out under conventional flow reactor conditions at ambient pressure. The reactant gas for the SCR of NO_2 was composed of 1000 ppm NO_2, 1000 ppm C_2H_4 and 5% O_2 diluted in He. Products were analyzed with an FTIR spectrometer (Nicolet; Magna 560, resolution set at 0.5 cm^{-1}) equipped with a multi-reflection gas cell (Gemini Specialty Optics; optical path length = 2 m) and GC (Agilent; Micro GC).

Fig. 1(a) shows the gas-phase IR spectrum of the products of SCR at 473 K. To show the unknown band clearly, the absorption bands of coexisting NO_2 and C_2H_4 were subtracted from the original spectrum to an optimum extent. The absorption bands at 1562 and 1546 cm^{-1} were tentatively ascribed to nitro groups. To confirm this assumption, nitroethylene (NE), which was the most probable compound formed, was synthesized according to the literature,[7] and its gas-phase spectrum [Fig. 1(b)] was obtained. Characteristic bands appeared at 1562, 1546, 1384, 1377, 1365, 1355, 963, and 888 cm^{-1}. Comparison with the standard spectrum of 2-nitroethanol [Fig. 1(c)], used as a precursor for the synthesis, shows that this compound was not a contaminant in the synthesized NE. The unknown bands in Fig.1(a) agreed completely with those of NE. To our knowledge, this is the first report of the observation of a gas-phase NE IR spectrum. It is clear that NE is formed during the SCR of NO_2 by C_2H_4. As a comparison, the standard spectrum of nitromethane is shown in Fig. 1(d), which is clearly different from that observed during SCR.

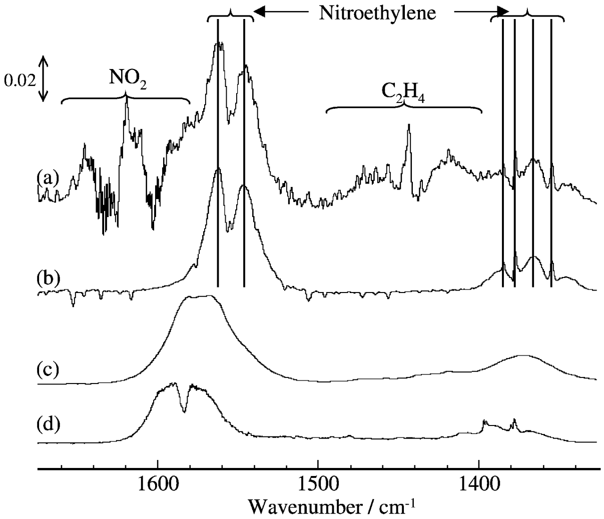

Fig. 1 Gas-phase IR spectra of (a) product gas of SCR of NO_2 by C_2H_4, (b) nitroethylene synthesized in this study, (c) standard 2-nitroethanol and (d) standard nitromethane.

Fig. 2 shows the effect of contact time with a reactant gas on the formation of NE and N_2 at 523 K. The concentration of NE in the product gas decreased drastically at contact times > 0.15 s, becoming negligible at contact times > 0.3 s; on the other hand, the N_2 concentration increased with increasing contact time. This result suggests that NE is an intermediate in the production of N_2. In similar experiments at 623 and 723 K, NE formation was not observed at any contact time, indicating that NE decomposition or a secondary NE reaction is very fast at higher temperatures.

Using the synthesized NE, we further investigated its reactivity over H-ferrierite. In the presence of 5% O_2, decomposition of diluted NE (*ca.* 230 ppm) became prominent above 600 K; CO_2 CO, NH_3 HCN and trace amounts of HNCO and N_2 were observed as the products. The formation of HCN and HNCO is in accord with theoretical calculation results for the thermal decomposition of NE through a four-membered-

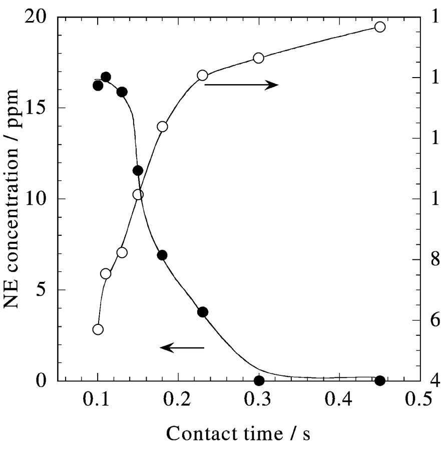

Fig. 2 Effect of contact time on NE and N_2 formation. Symbols indicate the concentration of NE (●) and N_2 (○) in the product gas.

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ring structure (4*H*-oxazete *N*-oxide).[8] NH_3 is speculated to be produced by catalytic hydrolysis of HCN[9] and HNCO,[10] which simultaneously form CO and CO_2, respectively.

The formation of NH_3 led us to invoke successive occurrence of the conventional SCR reaction, *i.e.*, selective reaction of NO_x with NH_3 to form N_2 in the presence of excess O_2, over this proton-type zeolite catalyst.[9] Incidentally, under most reaction conditions, the product gas of the SCR of NO_2 with C_2H_4 contains more NO than NO_2; partial reduction of NO_2 to NO by C_2H_4 must have occurred, in addition to the total reduction process. To confirm the above possible role of NH_3 we conducted NE (230 ppm) decomposition over H-ferrierite in the presence of 1000 ppm NO and 5% O_2, as shown in Fig. 3. Conversions in this figure were defined as follows:

NO_x and NE conversion = (Inlet concentration – Outlet concentration)/(Inlet concentration) × 100 (%)

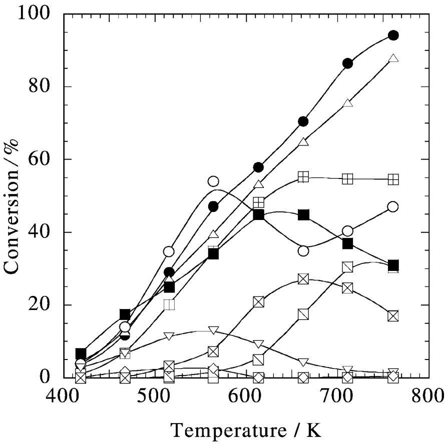

Fig. 3 Behavior of NE decomposition over H-ferrierite. The feed gas was composed of 230 ppm NE, 5% O_2 and 1000 ppm NO. The total flow rate was 160 ml min^{-1}, corresponding to 21 000 h^{-1}. Symbols indicate NE (●) and NO_x conversion (■), and conversion to CO_2 (△), NH_3 (□), N_2 (⊞), CO (○), HNCO (◇), N_2O (▽), HCN (⧅) and HCHO (⊠).

Conversion to products = (Product concentration)/(NE inlet concentration) × 100 (%)

In the presence of NO + O_2, NE decomposition became prominent above 425 K, and the conversion increased with increasing temperature. It is noteworthy that both the NO_x conversion and conversion to N_2 were almost equal to the NE conversion below 623 K. This result strongly suggests that both NE and NO_x molecules supplied, respectively, one nitrogen atom to form one N_2 molecule. The rather high conversion to CO at lower temperatures, amost equal to the NE conversion, might be produced by the decomposition of HCO_2H. We confirmed that HCO_2H is easily produced by the oxidation of HCHO with NO_2 and also decomposed to CO and H_2O over H-ferrierite under conditions similar to that for the present SCR reaction. Formaldehyde should be formed by NE decomposition, simultaneously with HNCO.[8]

To summarize these results, we conclude that the NE we detected is not merely a byproduct in HC-SCR but is very probably an intermediate in the formation of N_2, through conversion to HNCO or HCN followed by formation of NH_3.

Notes and references

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