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CN-COMPOUNDS FORMATION OVER Al_2O_3 SUPPORTED Pt AND Rh CATALYSTS IN THE REDUCTION OF NO WITH PROPYLENE AND H_2-CO

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Large amounts of hydrogen cyanide (HCN), acetonitrile, acrylonitrile, and propionitrile were formed in the reduction of NO with propylene and H_2-CO over Al_2O_3 supported Pt and Rh catalysts. Rh was more active in both the reduction of NO and the formation of HCN and nitriles than Pt. Propylene employed as a reducing agent was more reactive in the conversion of NO into HCN than H_2-CO.

Air pollutants of NO_x, CO, and hydrocarbons emitted from automotive vehicles have decreased remarkably, owing to recent progress in emission control techniques such as engine modification and catalytic systems. Research on catalytic systems for exhaust-gas treatment has now been extended to other pollutants emitted as a result of catalytic treatment of the three major pollutants (NO_x, CO, and hydrocarbons). Hydrogen cyanide (HCN) was recently found in exhaust gas, which was emitted under conditions of fuel-rich combustion from vehicles equipped with three-way catalysts containing Pt and Rh.[1-3] HCN formation took place in the reduction of NO with H_2-CO over various noble-metal supported catalysts.[4-7] We studied the reduction of NO with propylene (C_3H_6) as a hydrocarbon over Al_2O_3 supported Pt and/or Rh catalysts for automotive exhaust-gas treatment, and found that organic nitriles as well as HCN were formed in the system. In addition, the reduction of NO with H_2-CO was also carried out to elucidate the mechanism for the formation of HCN and organic nitriles.

Three kinds of catalysts (Pt-Rh/Al_2O_3, Pt/Al_2O_3, and Rh/Al_2O_3) were prepared by impregnation of γ-Al_2O_3 (Sumitomo Chemical Co. Ltd., type X-7; 2–3 mmϕ, BET surface area 170 m^2/g) with aqueous solutions of H_2PtCl_6 and $RhCl_3$, followed by calcination at 600°C for 3 h, prior to the reaction at 300–600°C. Contents of Pt and Rh were 0.05 and 0.002%, respectively. The reaction was studied in a conventional fixed-bed reactor (13 mmϕ i.d., quartz glass). A reactant mixture of NO-C_3H_6 or NO-H_2-CO diluted with N_2 was fed continuously to ca. 3 ml (1.5 ± 0.1 g) of each catalyst. Space velocity of 50,000 h^{-1} was employed in all experiments. NO was analyzed by a chemiluminescent NO_x analyzer (Thermoelectron Model 10A). CN-compounds (HCN and organic nitriles) and C_3H_6 were separated with a 2 m-glass column of Chromosorb 101, and analyzed by a flame thermionic detector (Shimadzu Model FTD-7), which can selectively detect materials containing both C and N atoms such as acetonitrile and pyridine. The calibration of the detector with respect to CN-compounds was carried out in the same way as described in the literature.[8] H_2, CO, and CH_4 were

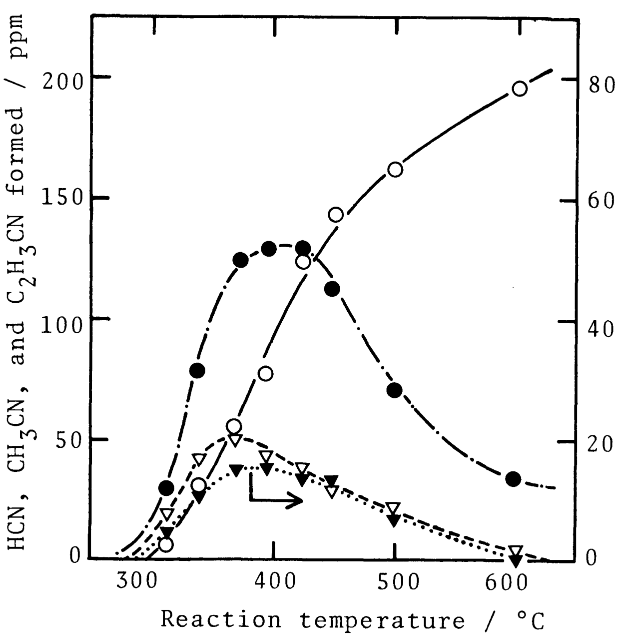

Fig. 1 Temperature dependence of the formation of HCN (—○—), CH_3CN (--●--), C_2H_3CN (--▽--), and C_2H_5CN (····▼····) in the reduction of NO (3,000 ppm) with propylene (3,000 ppm) over Pt-Rh/Al_2O_3.

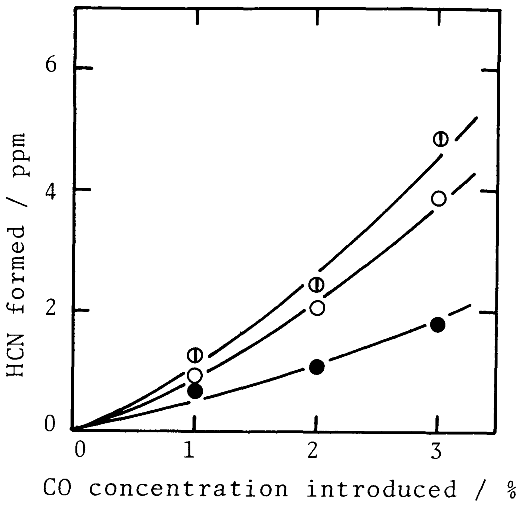

Fig. 2 HCN concentration formed in the reduction of NO with mixtures of H_2 (1%) and CO over Pt-Rh/Al_2O_3 (⦶), Pt/Al_2O_3 (●), and Rh/Al_2O_3 (○) at 500°C as a function of CO concentration introduced.

separated with a 1 m-column of molecular sieve 5A, and analyzed by a TCD and a FID.

Reduction of NO with C_3H_6 Considerable amounts of acetonitrile (CH_3CN), acrylonitrile (C_2H_3CN), and propionitrile (C_2H_5CN) together with HCN were formed in the reduction of NO with C_3H_6 over Pt-Rh/Al_2O_3, as shown in Fig. 1. Organic nitriles (CH_3CN, C_2H_3CN, and C_2H_5CN) were formed mainly at lower temperatures. At progressively higher temperatures, the amounts of organic nitriles formed decreased while the amount of HCN increased. For instance, the amounts of HCN, CH_3CN, C_2H_3CN, and C_2H_5CN formed at 350°C were 30, 80, 42, and 11 ppm, while those formed at 600°C were 200, 35, 5, and 1 ppm, respectively. The conversion of NO and C_3H_6 reached 70–80% at 400°C. The amounts of CN-compounds formed over Pt-Rh/Al_2O_3, Pt/Al_2O_3, and Rh/Al_2O_3 at 400°C and apparent activation energies for their formation are summarized in Table 1. The apparent activation energies were obtained for Pt-Rh/Al_2O_3 and Rh/Al_2O_3 at 300–350°C and for Pt/Al_2O_3 at 450–600°C. The amounts of CN-compounds formed over Rh/Al_2O_3 and their activation energies were similar to those over Pt-Rh/Al_2O_3. On the contrary, the amounts of them formed over Pt/Al_2O_3 were much smaller than those over Pt-Rh/Al_2O_3 and Rh/Al_2O_3. The conversion of NO and C_3H_6 over Pt/Al_2O_3 was less than 30% at all the temperatures studied. These indicate that Pt/Al_2O_3 was less active in both the reduction of NO with C_3H_6 and the formation of CN-compounds from them. Moreover, the activation energies obtained for Pt/Al_2O_3 were different from those for the other two catalysts. These results

Table 1 Amounts of CN-compounds formed over Pt and Rh supported catalysts and their apparent activation energies[a)]

CN-compound	metal supported on Al_2O_3		
	Pt-Rh	Rh	Pt
HCN	78[b)] (32)[c)]	145 (34)	9 (24)
CH_3CN	128 (31)	138 (32)	5 (14)
C_2H_3CN	43 (29)	56 (32)	2 (14)
C_2H_5CN	15 (29)	20 (32)	1 (15)

a) reactant gas; NO 3,000 ppm, C_3H_6 3,000 ppm
b) amount of CN-compound formed at 400°C, ppm
c) apparent activation energy for the formation, kcal/mol

lead us to conclude that Rh metal supported on Al_2O_3 plays an important role in the formation of CN-compounds.

Reduction of NO with H_2-CO It is necessary to compare the reactivity of C_3H_6 with that of H_2-CO in the conversion of NO into CN-compounds, because automotive exhausts contain H_2 and CO along with hydrocarbons as reducing agents. Only HCN was found as a CN-compound in the reduction with H_2-CO over the three catalysts. The amounts of HCN formed increased with increasing H_2 and CO concentrations introduced. Fig. 2 shows HCN formed at 500°C as a function of CO concentration. In contrast with the results using C_3H_6, the amount of HCN formed from a mixture containing 1% of H_2 and 3% of CO was as low as 5 ppm, indicating that a mixture of H_2-CO was less reactive than C_3H_6 in the conversion of NO into HCN.

The mechanism for the formation of C_2H_3CN, CH_3CN, and HCN in ammoxidation of C_3H_6 has been widely discussed in many literatures. NO formed from oxidation of NH_3 may react with allyl or further dehydrogenated species formed from C_3H_6.[9,10)] It is well known that a H_2-CO mixture is converted into CH_4 over Pt and Rh supported Al_2O_3, and that CHOH species is postulated as an intermediate.[11)] In our system, it was confirmed that 3 ppm of CH_4 was produced from a mixture of H_2 (1%) and CO (3%) in the absence of NO. However, the amount of CH_4 decreased to 0.5 ppm and HCN was formed from the mixture in the presence of NO. It is, therefore, considered that HCN may be formed through the reaction of NO with CH_xO species formed over the surface from H_2 and CO.

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