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A Study of the Thermal Decomposition of Ruthenium Ammine Zeolites

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Synopsis. Treatment of Ru(II) ammine-NaY under nitrogen at 100 and 300 °C leads to formation of $[Ru(NH_3)_5N_2]^{2+}$-NaY and metallic Ru-N_2, respectively. The effect of atmosphere and the type of Ru ammine complexes and zeolites on the decomposition behavior is discussed.

Metal ions can be introduced into zeolites by cation exchange. This ion exchange procedure is expected to give metal catalysts with a highly dispersed metal phase with superior properties to catalysts prepared by impregnation with simple metal halide salts.[1] Recently much attention is being devoted to the catalytic activity of zeolite-supported Ru,[2–5] since Ru has been shown to be one of the best catalysts for the hydrogenation of CO.[10] The preparation of Ru-containing zeolites *via* ammine complexes has been successful and shows promise as an advantageous route to industrially important catalysts.[4–9] Ruthenium is also known to be a highly effective metal for the activation of nitrogen and adsorbs a significant amount of nitrogen during ammonia synthesis, when K is added. Adsorbed or coordinated nitrogen is infrared active in the $\approx 2000\,cm^{-1}$ region of the spectrum.[11] In this paper we describe the IR results of zeolite-supported Ru ammine complexes during heating processes under a nitrogen atmosphere.

Experimental

$[Ru(NH_3)_6]Cl_2$ was prepared by the method of Allen and Senoff.[12] $[Ru(NH_3)_6]Cl_3$ was purchased from Strem Chemicals. The $[Ru(NH_3)_6]^{2+}$ cation was exchanged into the zeolite NaY (Ru content *ca.* 4 wt%) in deoxygenated water under a nitrogen atmosphere. The pH of the exchanged solution was adjusted to 4.5 by the addition of hydrochloric acid. $[Ru(NH_3)_6]^{3+}$ cation was exchanged into the NaY or HY zeolite (Ru *ca.* 4 wt%). In this case no attempt was made to control the pH of the solution. The zeolites were filtered, washed with water and then with ethanol, and dried under vacuum at room temperature for 2 d. Samples for IR investigations were prepared in the form of wafers having a diameter of 20 mm and weights between 25 and 35 mg. IR spectra were recorded on a Nihon Bunko IRA-2 grating spectrophotometer. The wafers were heated to desired temperature in a stream of nitrogen or helium, maintained at that temperature for 30 min, and then subjected to IR analysis at room temperature.

Results and Discussion

The ammine complex $[Ru(NH_3)_6]^{2+}$ was exchanged into the Na-Y zeolite and the zeolite obtained was degassed for 2 d at room temperature. The IR spectrum of the fresh zeolite sample (Fig. 1a) showed three significant bands assigned as follows: $1640\,cm^{-1}$ (very strong, $\delta_d(NH_3)$ in conjunction with adsorbed water), $1450\,cm^{-1}$ (weak, $\delta_d(NH_4)$) and $1320\,cm^{-1}$ (strong, $\delta_s(NH_3)$). The $\delta_s(NH_3)$ band at $1220\,cm^{-1}$ which is characteristic of the original $[Ru(NH_3)_6]Cl_2$ complex,[12] has been shifted by $100\,cm^{-1}$ to higher wavenumber upon exchange into the zeolite. When the pale yellow $[Ru(NH_3)_6]^{2+}$-NaY zeolite sample was kept for a few days under an inert atmosphere, the zeolite turned purple and the band at $1450\,cm^{-1}$ increased in intensity, while the band at $1320\,cm^{-1}$ was shifted to $1340\,cm^{-1}$ and weakened (Fig. 1b). This finding indicates a part of Ru(II) ions has undergone the hydrolysis as follows:

$$[Ru^{II}(NH_3)_6]^{2+}\text{-NaY} + H_2O \longrightarrow [Ru^{III}(NH_3)_5OH]^{2+}\text{-NaY} + NH_4^+.$$

This reaction is closely similar to that proposed by Laing *et al.* to account for the color change of $[Ru(NH_3)_5N_2]^{2+}$-NaY upon storage.[8] This purple zeolite designated as RuNaY was used for the subsequent experiment.

As shown in Fig. 2a, the IR spectrum of the freshly prepared $[Ru(NH_3)_6]^{3+}$-HY sample displayed two intense bands at $1640\,cm^{-1}$ ($\delta_d(NH_3)$ plus $\delta_d(H_2O)$) and $1440\,cm^{-1}$ ($\delta_d(NH_4)$). The band around $1350\,cm^{-1}$ which is typical of deformation band of coordinated NH_3 of $[Ru(NH_3)_6]^{3+}$ was not observed.[12] This fact suggest that the NH_3 ligands which had been present in the coordination sphere of Ru migrated to Brϕnsted acid site of the zeolite. This is contrasted with the results obtained with the fresh $[Ru(NH_3)_6]^{3+}$-NaY zeolite, which showed an intense band at $1340\,cm^{-1}$ ($\delta_s(NH_3)$) and a very weak NH_4 deformation band.[9]

Figure 1c shows the IR spectrum of RuNaY when

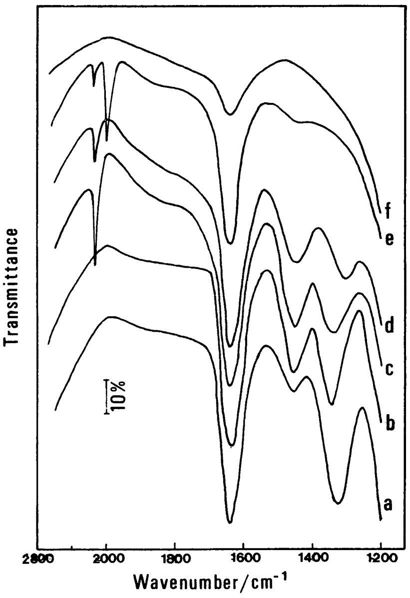

Fig. 1. Variation of infrared spectra of $[Ru(NH_3)_6]^{2+}$-NaY under N_2.
a): Fresh, b): on storage under N_2 for 2 weeks, c): 100 °C, d): 200 °C, e) 300 °C, f): 350 °C.

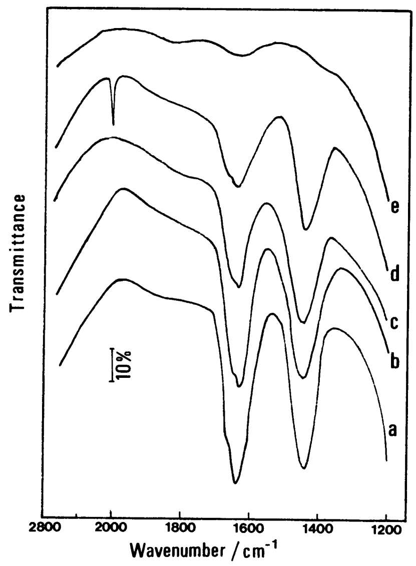

Fig. 2. Variation of infrared spectra of $[Ru(NH_3)_6]^{3+}$-HY under N_2.
a): Fresh, b): 100 °C, c): 200 °C, d): 300 °C, e) 400 °C.

heated under N_2 at 100 °C. The band at 1340 cm^{-1} was attenuated and the strong band developed at 2135 cm^{-1}. The latter may be assigned to the stretching frequency of a coordinated nitrogen molecule and suggested the formation of $[Ru(NH_3)_5N_2]^{2+}$-NaY which was first prepared by Laing *et al.* by the addition of hydrazine to $[Ru(NH_3)_5NO]^{3+}$-NaY.[8] Atmospheric nitrogen seems to have substituted one NH_3 ligand from the residual $[Ru(NH_3)_6]^{2+}$ ion in RuNaY, although this type of simple displacement reaction in solution has not been reported. A similar treatment of RuNaY under helium at 100 °C resulting in the spectrum lacking the band around 2135 cm^{-1}. Recently Aika *et al.* found that N_2 is adsorbed on a support with K[13] or a basic support such as CaO and MgO_2.[14] Thus the band at 2135 cm^{-1} might be due to a N_2 species adsorbed on the NaY support. No band corresponding to the adsorbed N_2 species was found over NaY. It is well known that transition metals which bind nitrogen molecules are in low oxidation states;[15,16] no nitrogen complex of Ru(III) has been reported. As we would expect, treatment of $[Ru(NH_3)_6]^{3+}$-NaY or HY with N_2 at 100 °C afforded a spectrum with no N-N band. From these results we assumed that N_2 is coordinated to a Ru(II) species encaged in NaY.

When RuNaY was subsequently heated at 200 °C, the band at 2135 cm^{-1} was weakened and the band at 1340 cm^{-1} was shifted to 1295 cm^{-1} (Fig. 1d). Subsequent heating at 300 °C resulted in a new band at 2000 cm^{-1} (Fig. 1e). Since its frequency is too low to regard as that arising from ionic Ru species,[15,16] the band is attributable to ν(NN) of a nitrogen molecule chemisorbed to Ru(0) (presumably metallic ruthenium in view of the absence of the band at 1295 cm^{-1}). An almost identical spectrum resulted from the treatment of $[Ru(NH_3)_6]^{3+}$-NaY with N_2 at 300 °C. Heating the samples at 350 °C resulted in the removal of the bands at 2000 and 1450 cm^{-1}, as shown in Fig. 1f. It should be noted that Laing *et al.* have observed a band at 2000 cm^{-1} on the reaction of $[Ru(NH_3)_x(NO)]Y$ with NH_3 at 150 °C.[8] Treatment of RuNaY under helium at 300 °C resulted in only a weak band at 2000 cm^{-1}; the presence of N_2 greatly enhanced the intensity of the ν(NN) band. The nitrogen molecule observed in the case of the treatment under a helium flow is ascribed to the decompsition of the NH_3 ligands. Verdonck *et al.* have shown that on degassing $[Ru(NH_3)_6]^{3+}$-NaY the complex is reduced to the metallic state accompanied by the liberation of N_2.[6]

Treatment of $[Ru(NH_3)_6]^{3+}$-HY with N_2 at 300 °C yielded a band at 2025 cm^{-1}, as shown in Fig. 2d. The difference in wavenumber between the ν(NN) bands in the two zeolites should be accounted for in terms of electron defficiency in the metal on HY. The electron-acceptor strength of the zeolite is expected to increase in the direction NaY<HY. The electron concentration in the metal would decrease accordingly, thus decreasing electron donation to N_2. The bands might be due to N_2 species adsorbed on the zeolite supports but they were observed for neither NaY nor HY without Ru. The acidic property of the HY zeolite is also responsible for the persistence of the $\delta_d(NH_4)$ band during the heating process (Fig. 2d). After the treatment at 300 °C, the $\delta_d(NH_4)$ band was scarcely observed with the RuNaY zeolite, while the $[Ru(NH_3)_6]^{3+}$-HY sample still retained 40—50% of its NH_4^+ (as estimated from the intensity of $\delta_d(NH_4)$).

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