Direct Synthesis of Propionamide and Propiononitrile from Ethylene, Carbon Monoxide, and Ammonia Using Supported Ru and Rh Catalysts

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Propionamide and propiononitrile were formed by passing the mixture of ethylene, carbon monoxide, and ammonia under atmospheric pressure over silica- or zeolite-supported Ru ammine complex catalyst. Rh ammine complex also promoted the reaction but the catalytic activity was low. It is inferred that propionamide is formed primarily and is dehydrated successively on the acidic site of the support.

Amide syntheses through carbonylation of amines with carbon monoxide and through amidation of alkenes or alkynes with carbon monoxide and amines are conducted generally in a liquid phase under high pressures using transition metal complexes as catalysts.[1] The amidation with ammonia instead of amines proceeds under similar reaction conditions as claimed by a few patents.[2] Iwashita and Sakuraba[3] synthesized imidazole derivatives from α-olefins, carbon monoxide, and ammonia at a carbon monoxide pressure of 250 kg/cm^2 using an aqueous methanol suspension of rhodium oxide, and found that propionamide was formed in the reaction of ethylene as a by-product (15% yield). Recently, we found a novel reaction to form propionamide or propiononitrile from ethylene, carbon monoxide, and ammonia under atmospheric pressure using supported Ru and Rh catalysts.

The catalysts were prepared by an ion exchange method. Silica gel (SiO_2) purchased from Fuji Silysia Chemical or NH_4^+-exchanged form of Y-zeolite (NH_4-Y) kindly supplied by Catalysts and Chemicals, was immersed in an aqueous solution of $[Ru(NH_3)_6]Cl_3$ or $[Rh(NH_3)_6]Cl_3$, washed well with distilled water, and dried at room temperature in a desiccator. The metal loading was 3 wt% for both catalysts. An amount of 1.0 g of the catalyst was loaded in a fixed bed flow reactor, pretreated in an Ar stream at reaction temperatures for 2 h, and then exposed to a feed (120 ml/min) composed of equimolar amounts of ethylene, carbon monoxide, and ammonia. Reaction products were trapped in two U-tubes which were dipped alternately in a dry ice-methanol bath at intervals of 1 h. The trapped products were identified with a GC-mass spectrometer and analyzed with a gas chromatograph using a 1 m column packed with Tenax GC.

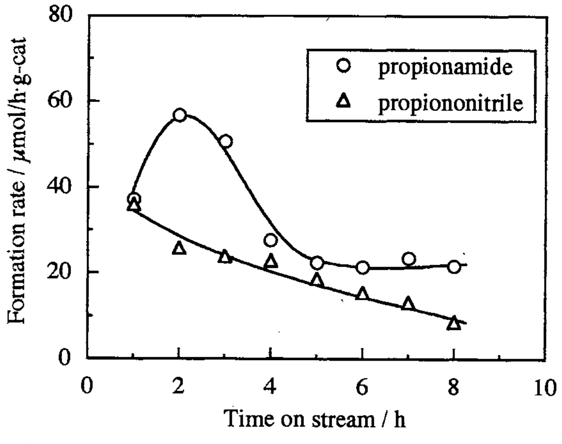

Figure 1. Time course of the rate of propionamide and propiononitrile formation over Ru/SiO_2 at 200 °C.

Both propionamide and propiononitrile were formed over the silica-supported Ru (Ru/SiO_2) catalyst. Results of the reaction at 200 °C are illustrated in figure 1, where the formation rate represents the amount of product trapped every an hour. Besides the products shown in the figure, only trace amounts of acetonitrile, propionic acid and carbon dioxide were detected. The rate of propiononitrile formation increased initially and then decreased to a steady rate, while the rate of propiononitrile formation decreased monotonously. Over the NH_4-Y-supported Ru catalyst (Ru/NH_4-Y), propiononitrile was formed selectively. The difference in the selectivity observed with the two catalysts suggests that the propiononitrile formation is directly affected by the acidic property of the support, and that propionamide is formed on the Ru entities and subsequently dehydrated to propiononitrile on the acid sites of the support. Some evidence for this reaction sequence has been obtained in supplemental studies. The reaction using a double layer catalyst in which the feed flows through Ru/SiO_2 layer and then silica-alumina layer proceeds at the same reaction rate as that using only Ru/SiO_2 catalyst, producing propiononitrile exclusively. The results indicate that the rate of amidation should be evaluated by the combined rate of propionamide and propiononitrile formation.

The rate of amidation (propionamide and propiononitrile formation) changed through a maximum over every catalyst which was active for this reaction. The maximum values observed with Ru and Rh catalysts at 200 °C are summarized in Table 1. Ru/NH_4-Y shows more than three times the activity of Ru/SiO_2. Rh/NH_4-Y catalyzes this reaction but Rh/SiO_2 shows no activity. Although Rh catalysts are known to be active for carbon monoxide insertion,[1] the activity of Rh/NH_4-Y is one third as low as that of Ru/NH_4-Y. We prepared SiO_2 or NH_4-Y-

Table 1. Rate of Amidation and Selectivity over Supported Ru and Rh Catalysts (3 wt%) at 200 °C

Catalyst	Rate of Amidation μmol/h·g-cat	Selectivity /% Propionamide	Selectivity /% Propiononitrile
Ru/SiO_2	93.5	62.9	37.1
Ru/NH_4-Y	360.8	2.4	97.6
Rh/SiO_2	0	0	0
Rh/NH_4-Y	124.0	6.7	93.3

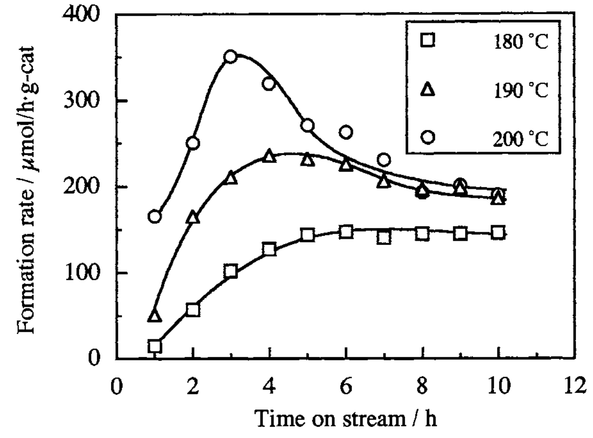

Figure 2. Time courses of the rate of propiononitrile formation over Ru/NH_4-Y at different temperatures. Pretreatment condition : in Ar at reaction temperature for 2 h.

supported Co, Pd and Pt catalysts in the same way as described above using their ammine complex chloride. Pd/SiO_2 and Pt/NH_4-Y showed faint activity producing a detectable amount of propionamide or propiononitrile and the others showed no activity. We also prepared SiO_2-supported Ru catalysts using different Ru precursors. The catalyst prepared with $[Ru(NH_3)_5N_2]Cl_2$ obtained from $RuCl_3$[4,5] showed the same activity as Ru/SiO_2. The SiO_2-supported Ru catalysts prepared by an impregnation method with $Ru(CO)_{12}$ and $Ru(acac)_3$ showed one fourth the activity of Ru/SiO_2 and that with $RuCl_3$ did no activity.

Figure 2 illustrates the time courses of the rate of propiononitrile formation over Ru/NH_4-Y at different reaction temperatures. An initial increase in the formation rate was observed at every temperature. The results suggest that the reaction has an induction period in which the catalyst precursor might transform into active species. After the induction period, the catalytic activity decreased at temperatures 190 and 200 °C, and the rate of propiononitrile formation fell to the same value 180 μmol/h·g-cat in 8 h. At the lowest temperature 180 °C, the deactivation was not observed.

Considering the results of Figure 2 , the reaction was carried out at 180 °C after the pretreatment at different temperatures. The result are shown in Figure 3. The catalytic activity changed by the pretreatment temperatures and similar induction periods were observed for the formation rate with all catalysts. The catalysts pretreated at 180 °C and 200 °C showed the highest and the same activity 150 μmol/h·g-cat. The catalysts not pretreated, heated from room temperature to 180 °C in the reaction feed , and pretreated at 150 °C were, respectively, four fifths and two thirds as low as the most active catalysts in activity. When the pretreatment temperature was raised to 250 °C and 300 °C, the catalytic activity, respectively, fell down to one third of the highest activity and was lost completely. These results suggest that ruthenium ammine complex ion supported on Y-zeolite changes to catalytic species by the heat treatment releasing some ammonia ligands and is decomposed to inactive entities at relatively high temperatures.

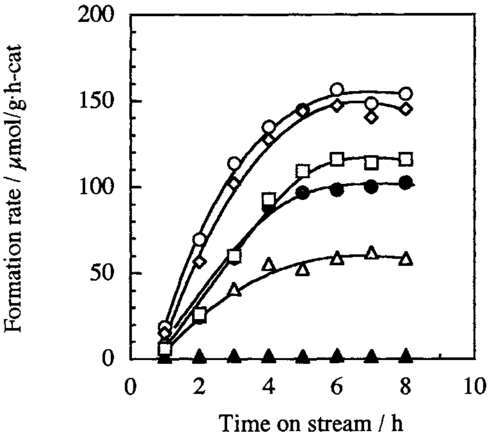

Figure 3. Effect of pretreatment on the catalytic activity of Ru/NH_4-Y. Pretreatment condition : in Ar at □, 150 °C; ◇, 180 °C; ○, 200 °C; △, 250 °C; ▲, 300 °C for 2 h, or ●, heated to 200 °C in reaction gas. Reaction temperature : 200 °C .

We conducted the reaction at 200 °C for 20 h to examine Ru/NH_4-Y for durability. A turn over number attained to 14 and the steady activity, 120 μmol/h·g-cat, still lasted. Our investigations are now centered on the preparation and characterization of Ru or Rh catalyst to develop more active and stable catalysts.

References

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