

Amidation of ethylene with carbon monoxide and ammonia over supported Ru catalysts

Shu-Ping Zhao^{*}, Shu-Ichi Sassa, Hideaki Inoue, Masato Yamazaki, Hifumi Watanabe, Tohru Mori, Yutaka Morikawa

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

Abstract

The amidation of ethylene with carbon monoxide and ammonia over supported Ru ammine complex ion catalysts under atmospheric pressure has been investigated. The catalytic activity was affected remarkably by Ru precursors, supports and pretreatment temperature. The catalyst with highest activity was obtained using Ru ammine complex salts and by the pretreatment at 180–200°C. The selectivity to propionitrile formation increased with the acidity of the supports, indicating that propionamide was formed on Ru entities and was successively dehydrated to propionitrile on the acidic sites of the support. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Propionamide; Propionitrile; Amidation; Ru ammine complex; Heterogeneous catalysis

1. Introduction

Amide is an important intermediate for chemical industries and its 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 [1,2]. The amidation with ammonia instead of amines proceeds under similar reaction conditions as claimed by a few patents [3–6]. Iwashita and Sakuraba [7] synthesized imidazole derivatives from α -olefins, carbon monoxide, and am-

monia at a carbon monoxide pressure of 250 kg/cm² 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, ruthenium has received increasing interest because of its unique properties as a catalyst [8–11]. In the previous paper [12], we have reported that silica- and zeolite-supported Ru ammine complex catalysts promote a novel reaction to form propionamide and propionitrile from ethylene, carbon monoxide, and ammonia under atmospheric pressure. It is of interest that Ru is higher than Rh in catalytic activity, and Pd, Pt, and Co are almost inactive for this reaction.

In this study, we examined the effect of Ru precursors, supports, and the pretreatment temperature on the catalytic activity of Ru catalysts.

^{*} Corresponding author.

2. Experimental

Various commercial supports were used: silica gel (SiO_2 , Fuji Silysia Chemical), NH_4^+ or Na^+ -exchanged form of Y-zeolite ($\text{NH}_4\text{-Y}$, Na-Y, Catalysts and Chemicals), silica–alumina ($\text{SiO}_2\text{-Al}_2\text{O}_3$, Nikki Chemicals), and magnesia (MgO , Kanto Chemical). Ru precursors $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$, and RuCl_3 were commercially available reagent grade, and $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ was prepared by the method described in literatures [13,14].

To examine the effect of Ru precursors on the catalytic activities, silica gel was employed as a support. With $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ and $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$, catalysts were prepared by an ion exchange method. Prior to the ion exchange, silica gel was treated by 0.1 N ammonia solution at room temperature for 24 h and then washed well with distilled water. The ammonia-treated silica gel was immersed in an aqueous solution of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ or $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ at room temperature for 24 h, and then filtered. The exchanged sample was washed well with distilled water until Cl^- ions were no longer detectable in the washings by the addition of AgNO_3 solution, and dried at room temperature in a desiccator. With $\text{Ru}_3(\text{CO})_{12}$, $\text{Ru}(\text{acac})_3$, RuCl_3 , catalysts were prepared by an impregnation method. Silica gel as obtained was impregnated with a THF solution of $\text{Ru}_3(\text{CO})_{12}$ or $\text{Ru}(\text{acac})_3$ for 24 h and the solvent was evaporated at 60°C . In the impregnation of RuCl_3 , 0.01 N hydrochloric acid was used as a solvent.

Using $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ as the Ru precursor, Ru was supported on SiO_2 , $\text{NH}_4\text{-Y}$, Na-Y, or $\text{SiO}_2\text{-Al}_2\text{O}_3$ by the ion exchange method mentioned above. MgO -supported Ru catalyst was prepared by the impregnation method using the same precursor. The Ru loading of all catalysts prepared in this study was 3 wt.%.

An amount of 1.0 g of the catalyst was loaded in a fixed bed flow reactor, pretreated in an Ar stream at desired temperatures for 2 h, and then exposed to a feed (120 ml/min) com-

posed 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 (HITACHI M-80) and analyzed with a gas chromatograph (SHIMADZU GC-14B) using a 1-m column packed with Tenax GC.

Temperature-programmed decomposition (TPD) of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ was carried out in a He stream.

3. Results and discussion

3.1. Effect of Ru precursors

Fig. 1 shows the results of the reaction at 200°C over silica-supported catalysts prepared with various Ru precursors. The rate of amidation represents the combined rate of propionamide and propionitrile formation. Besides the two products, only trace amount of acetonitrile, propionic acid and carbon dioxide were detected.

As seen in Fig. 1, the rate of amidation increased in the initial stage of reaction over every catalyst and then decreased through maximum. The catalysts prepared with $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ showed al-

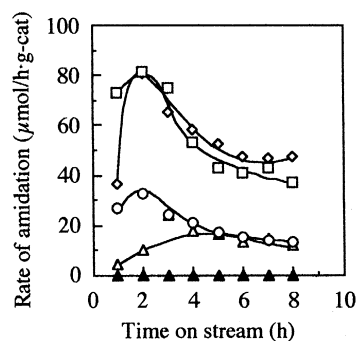


Fig. 1. Rate of amidation (propionamide and propionitrile formation) at 200°C over silica-supported Ru catalysts prepared with various Ru precursors. □, $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$; ◇, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$; ○, $\text{Ru}_3(\text{CO})_{12}$; △, $\text{Ru}(\text{acac})_3$; ▲, RuCl_3 .

most the same activity, giving the maximum values of amidation rate 79.5 and 81.7 $\mu\text{mol/h}$ g-cat, respectively. The catalyst prepared with RuCl_3 showed no activity.

The maximum rates of amidation and the values of selectivity to propionamide and propionitrile are summarized in Table 1. The catalytic activities of the catalysts prepared by the impregnation method with $\text{Ru}_3(\text{CO})_{12}$ and $\text{Ru}(\text{acac})_3$ were half and one-third lower than those prepared by the ion exchange method. Although the reason why the difference in the catalytic activity comes from, that is, from the presence of ammonia ligands or from the preparation method, is not clear yet, it should be noted that the values of selectivity to propionamide (31–37%) and propionitrile (63–69%) are about the same among the catalysts examined in this study.

3.2. Effect of supports

The reaction was conducted at 200°C using the Ru catalysts prepared with various supports. $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ was employed as the Ru precursor, which lead to the highest activity as shown in Table 1. The results are summarized in Table 2, where the maximum rates of amidation and the values of selectivity to propionamide and propionitrile are listed. By using Na-Y and $\text{NH}_4\text{-Y}$ instead of SiO_2 , the catalytic activity increased as high as two-fold and four-fold, respectively.

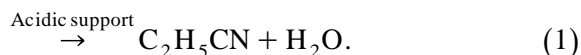
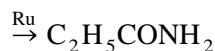
The selectivity of the catalysts differed remarkably by the supports. The catalysts prepared with the acidic supports, $\text{NH}_4\text{-Y}$, Na-Y,

Table 2

Rate of amidation and selectivity at 200°C over supported Ru catalysts

Support	Rate of amidation ($\mu\text{mol/h}$ g-cat)	Selectivity (%)	
		Propionamide	Propionitrile
$\text{NH}_4\text{-Y}$	360.8	2.4	97.6
Na-Y	181.7	9.2	90.8
SiO_2 –	113.1	2.7	97.3
Al_2O_3			
SiO_2	79.5	62.9	37.1
MgO	10.0	100.0	0.0

and $\text{SiO}_2\text{-Al}_2\text{O}_3$, gave propionitrile at high selectivity (90–98%), while the catalyst prepared with the basic support MgO gave propionamide selectivity (at 100% selectivity). The difference in the selectivity observed with the various supports suggests that the propionitrile formation is directly affected by the acidic property of the support, and that propionamide is formed on the Ru entities and subsequently dehydrated to propionitrile on the acidic sites of the support, i.e.:



To elucidate this reaction sequence, we carried out the reaction using a double layer catalyst in which the feed flows through Ru/ SiO_2 layer and then silica–alumina layer. The results are shown in Fig. 2. The dashed line stands for the summation of the rates of propionamide and propionitrile formation over the single layer catalyst (Ru/ SiO_2). The reaction with the dou-

Table 1

Rate of amidation and selectivity at 200°C over silica-supported Ru catalysts prepared with various Ru precursors

Ru precursor	Method	Selectivity (%)		Rate of amidation ($\mu\text{mol/h}$ g-cat)
		Propionamide	Propionitrile	
$[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$	Ion exchange	69.4	30.6	81.7
$[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$	Ion exchange	62.9	37.1	79.5
$\text{Ru}_3(\text{CO})_{12}$	Impregnation	68.7	31.3	32.6
$\text{Ru}(\text{acac})_3$	Impregnation	66.0	34.0	24.6
RuCl_3	Impregnation	0.0	0.0	0.0

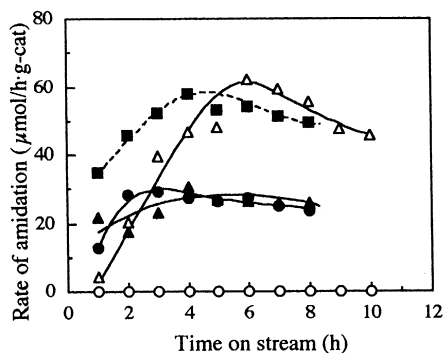


Fig. 2. Time courses of amidation rate at 200°C over Ru/SiO₂ in the absence and presence of SiO₂-Al₂O₃ downstream. Pretreatment condition: in Ar at reaction temperature for 2 h. Circle, triangle and square symbols represent the formation rates of propionamide, propionitrile and the summation of them, respectively. Solid and open symbols represent the absence and presence of SiO₂-Al₂O₃, respectively.

ble layer catalyst produced propionitrile selectively and proceeded at the same reaction rate as the combined formation rate over the single layer catalyst. The facts indicate that propionamide is readily dehydrated to propionitrile over acidic supports.

As seen in Fig. 2, the rate of amidation over Ru/SiO₂ attained its maximum at the time on stream 4 h, while the maximum rate is achieved after 6 h of reaction over the double layer catalyst. The difference between the two time courses of amidation rate might be caused by the adsorption of product on the additional SiO₂-Al₂O₃. The adsorption prevents the amidation products from eluting in the effluent gas and from being trapped for the quantitative analysis. This suggests that the phenomenon like an induction period, namely, the initial increase in the amidation observed with all catalysts, is caused by the adsorption of products over the supports of catalysts.

3.3. Zeolite-supported Ru catalyst

3.3.1. Effect of reaction temperature

The reaction was conducted at 180, 190, and 200°C using Ru/NH₄-Y. The reaction produced

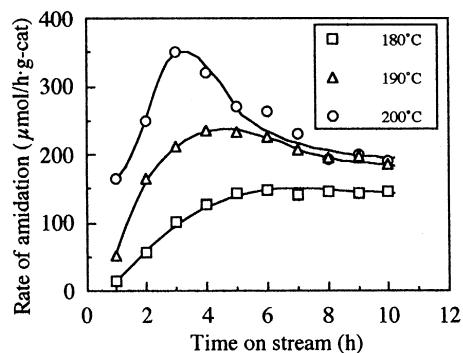


Fig. 3. Time courses of the rate of propionitrile formation over Ru/NH₄-Y at different temperatures. Pretreatment condition: in Ar at reaction temperature for 2 h.

only propionitrile at every temperature. Fig. 3 illustrates the time courses of the rate of propionitrile formation. The initial increase in the formation rate was observed at all temperatures. The rate decreased through maxima at 190 and 200°C, indicating the catalytic activity declined at higher temperatures. At the lowest temperature 180°C, the deactivation was not observed.

3.3.2. Effect of pretreatment

Considering the results of Fig. 3, the reaction was carried out at 180°C using Ru/NH₄-Y after the pretreatment at different temperatures. The results were shown in Fig. 4. The catalytic activity changed by the pretreatment tempera-

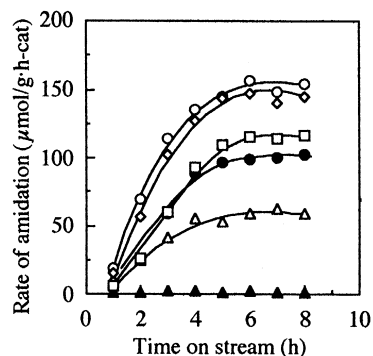


Fig. 4. Effect of pretreatment on the catalytic activity of Ru/NH₄-Y. Pretreatment condition: in Ar at □, 150°C; ◇, 180°C; ○, 200°C; △, 250°C; ▲, 300°C for 2 h, or ●, heated to 180°C in reaction gas. Reaction temperature: 180°C.

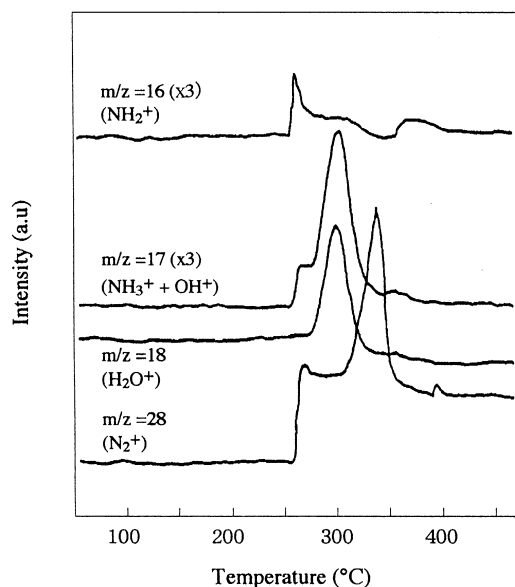


Fig. 5. TPD spectra of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$.

tures. The catalysts pretreated at 180 and 200°C showed the highest and almost the same activity, ca. 150 $\mu\text{mol}/\text{h g-cat}$. The catalysts not pretreated, that is, 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 and 300°C, the catalytic activity fell down to one-third of the highest activity and was lost completely, respectively.

TPD of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ was carried out using a mass spectrometer to detect evolving gases. During heating at a rate of 10°C/min, the signal intensities of $m/z = 16$ (NH_2^+), 17 ($\text{NH}_3^+ + \text{OH}^+$), 18 (H_2O^+), and 28 (N_2^+) were continuously monitored. The results are illustrated in Fig. 5. The spectrum of $m/z = 16$ signal reveals that $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ is not deammoniated below 250°C. The increase in the signal intensity of $m/z = 28$ suggests that NH_3 evolved from the complex is decomposed over Ru metal formed by the deammoniation. Although the results show that the catalyst precursor

$[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ is not deammoniated at the pretreatment temperatures, it is possible that $[\text{Ru}(\text{NH}_3)_6]^{3+}$ exchanged on the supports transforms as prepared or by the pretreatment as revealed by the infrared study on the decomposition of the same Ru complex ion exchanged into the supercages of Y-zeolite [15]. It is assumed that $[\text{Ru}(\text{NH}_3)_6]^{3+}$ ions on the supports change to catalytic species by the pretreatment releasing some ammonia ligands and is decomposed to inactive entities at relatively high temperatures.

4. Conclusion

The amidation of ethylene with carbon monoxide and ammonia proceeded over supported Ru catalysts under atmospheric pressure to form propionamide and/or propionitrile. The catalyst with the highest activity was obtained using $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ or $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{Cl}_2$ as a Ru precursor. The selectivity of catalyst depended on the acid–base properties of the support. Propionamide was formed selectively over the catalyst prepared with MgO support, while propionitrile did at high selectivity over those prepared with acidic support. The reaction and the pretreatment of catalysts should be conducted below 200°C to keep the high catalytic activity.

References

- [1] J. Falbe, in: Carbon monoxide in Organic Synthesis, Springer-Verlag, Berlin, 1970, p. 78, Chap. 2.
- [2] A. Mullen, in: New Synthesis with Carbon monoxide, Springer-Verlag, Berlin, 1980, p. 243, Chap. 3.
- [3] H.J. Nienburg, E. Keunecke, German Patent (1953) 863799.
- [4] H.J. Nienburg, E. Keunecke, Chem. Abstr. 48 (1954) 1427.
- [5] J.J. Lin, U.S. Patent, 1989, 4866177.
- [6] H.J. Nienburg, E. Keunecke, Chem. Abstr. 112 (1990) 757.
- [7] Y. Iwashita, M. Sakuraba, J. Org. Chem. 36 (1971) 3927.
- [8] K. Aika, A. Ohya, A. Ozaka, Y. Inoue, I. Yasumori, J. Catal. 92 (1985) 305.

- [9] P. Ferreira-Aparicio, C. Márquez-Alvarez, I. Rodríguez-Ramos, Y. Schuurman, A. Guerrero-Ruiz, C. Mirodatos, *J. Catal.* 184 (1999) 202.
- [10] C.L. Bianchi, V. Ragaini, *J. Catal.* 168 (1997) 70.
- [11] H.C. Long, M.L. Turner, D. Fornasiero, J. Kaspar, M. Graziani, P.M. Maitlis, *J. Catal.* 167 (1997) 172.
- [12] S.P. Zhao, S.I. Sassa, H. Inoue, M. Yamazaki, T. Mori, M. Kobayashi, Y. Morikawa, *Chem. Lett.* 1 (1999) 77.
- [13] G.W. Parshall, *Inorg. Synth.* 12 (1968) 1.
- [14] A.D. Allen, F. Bottomley, R.O. Harris, V.P. Reinsalu, C.V. Senoff, *J. Am. Chem. Soc.* 89 (1967) 5595.
- [15] S.P. Sheu, H.G. Karge, R. Schlögl, *J. Catal.* 168 (1997) 278.