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Effect of $NaNO_3$ Addition on the Decomposition of $RuCl_3$ Supported on Alumina

INTRODUCTION

Ruthenium is one of the most active catalyst for hydrogenation of carbon oxides and for many other reactions (*1–4*). The Ru catalysts are sometime modified by the addition of alkali promoter, and catalyst performances of these alkali-promoted catalysts have been widely examined (*5–11*).

During the course of our study on the syngas conversion on alkali-promoted Ru catalysts (*12, 13*), we found that the performance of alkali-promoted Ru catalyst prepared from $NaNO_3$ and commercial "$RuCl_3 \cdot 3H_2O$" was strongly affected by its preparation conditions. Although detail investigation on the preparation of supported or unsupported Ru catalyst have appeared (*14–18*), preparation of alkali-promoted catalyst have not been dealt until quite recently where reduction of unsupported $RuCl_3$–$CsNO_3$ mixture was examined in some detail (*19*). Therefore, we examined the effects of $NaNO_3$ addition upon the thermal decomposition and reduction of alumina-supported Ru catalyst.

EXPERIMENTAL

Alumina-supported $RuCl_3$–$NaNO_3$ samples with varying $NaNO_3$ concentration (samples 1–10, Table 1) were prepared by impregnation of a predried alumina (2 g, γ-form, 82 m^2/g, 20–35 μm, obtained by 700°C calcination of well-crystallized boehmite (*20*)) with 2 ml of an aqueous solution of commercial "$RuCl_3 \cdot 3H_2O$" (Mitsuwa) and $NaNO_3$ followed by drying in air at room temperature with continuous stirring. The concentration of $RuCl_3$ was arbitrarily fixed to give 4% Ru in reduced catalysts.

RESULTS AND DISCUSSION

Thermal Decomposition

In a series of experiments, thermal decomposition up to 400°C was examined with the aid of a thermal analyzer (Shimazdu DTA-30), and the following observations were noted (Table 1). (a) When $NaNO_3$ and $RuCl_3$ were coimpregnated, two weight loss processes were detected, one at around 240°C, and the other at around 380°C (Fig. 1b). (b) The higher temperature weight loss took place at the similar temperature range as recorded for $RuCl_3/Al_2O_3$ (sample 1, see Fig. 1a). (c) The lower temperature weight loss process was an endothermic one which consumed significantly larger amounts of heat than the higher temperature weight loss process (Fig. 1). (d) The degree of weight loss at the lower temperature as well as the intensity of the associated endothermic peak increased with an increase in $NaNO_3$ loading until Na/Cl ratio became unity (i.e., $NaNO_3$ loading $\simeq$ 9.3%), and then attained a plateau level. (e) The degree of weight loss at higher temperature decreased with the increases in $NaNO_3$ loading, and this weight loss disappeared for the sample containing more than 9.3% $NaNO_3$ (Fig. 1c). (f) XRD patterns of the thermally treated sample showed presence of NaCl (Fig. 3a). The intensities of NaCl peaks were proportional to the $NaNO_3$ loading, but became constant when $NaNO_3$ loading exceeded 9.3% (Na/Cl $\simeq$ 1). (g) As-dried samples did not show NaCl peaks in XRD. They appeared at 250°C, slightly higher temperature than for the lower temperature weight loss process. (h) The $NaNO_3$ peaks could not be detected

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TABLE 1

Thermal Analysis of Alumina-Supported Mixture of $RuCl_3$ and $NaNO_3$

Sample No.	Sample composition[a]		Sample loaded (mg)	Weight loss at 140°C (mg)	Dry sample weight (mg)	TG				DTA[b]		
						Weight loss[c]		$(-dW/dT)_{max}$[d]		Decomposition of $RuCl_3$		Melt of $NaNO_3$
	$RuCl_3 \cdot 3H_2O$ (%)	$NaNO_3$ (%)				140–310°C (mg)	310–400°C (mg)	Lower (°C)	Higher (°C)	Temp. (°C)	Peak height (μV)	Peak height (μV)
1	9.82 (4.04)	0.00 (0.00)	33.20	1.14	32.06	0.26 (0.22)	0.60 (1.30)	—	350	(334)	(1.6)	—
2	9.77 (4.05)	1.13 (0.44)	32.50	1.24	31.31	0.59 (0.47)	0.53 (1.13)	267	387	—	—	—
3	9.63 (4.01)	2.11 (0.83)	33.60	1.12	32.48	0.56 (0.70)	0.41 (1.12)	239	388	230	0.5	—
4	9.64 (4.05)	3.28 (1.30)	33.40	0.92	32.48	0.85 (0.97)	0.35 (0.87)	248	385	241	3.0	—
5	9.36 (4.01)	6.33 (2.56)	32.95	1.16	31.79	1.54 (1.64)	0.31 (0.43)	255	380	250	6.0	—
6	9.31 (4.07)	9.29 (3.83)	33.25	1.65	31.60	1.88 (2.24)	0.26 (0.07)	225	—	220	5.5	0.6
7	8.99 (4.00)	12.1 (5.10)	32.75	1.32	31.43	2.18 (2.15)	0.29 (0.07)	285		238	6.0	3.8
			32.55	1.19	32.06	1.86 (2.18)	0.24 (0.07)	253	294	249	8.0	4.5
8	8.74 (4.08)	18.7 (8.21)	33.30	1.42	31.88	2.19 (2.11)	0.55 (0.07)	236	—	240	6.7	10.0
9	8.32 (4.12)	26.4 (12.3)	33.25	1.22	32.03	2.18 (2.00)	0.62 (0.06)	226	—	231	8.5	16.2
			33.50	1.18	32.32	2.12 (2.02)	0.59 (0.06)	232	—	232	7.2	15.8
10	7.47 (4.11)	39.6 (20.6)	33.00	1.08	31.92	1.80 (1.78)	0.48 (0.05)	235	—	241	8.0	31.0
Alumina	—	—	33.20	0.48	32.72	0.24	0.09	—	—	—	—	—

[a] Hypothetical contents of Ru and Na_2O in the reduced catalysts are calculated assuming that $RuCl_3$ and $NaNO_3$ are converted into Ru^0 and Na_2O, respectively, and are given in parentheses.

[b] Platinum–platinum rhodium thermocouple and 30 mg of corundum were used for detector and reference, respectively.

[c] The values in parentheses represent the summation of calculated weight loss caused by dehydration of the support alumina and theoretical weight loss calculated based on the following equation: $RuCl_3 + NaNO_3 \rightarrow RuO_2 + NaCl$ for the lower temperature weight loss and $RuCl_3 \rightarrow RuO_2$ for the higher temperature weight loss.

[d] Temperature for the maximum rate of weight loss.

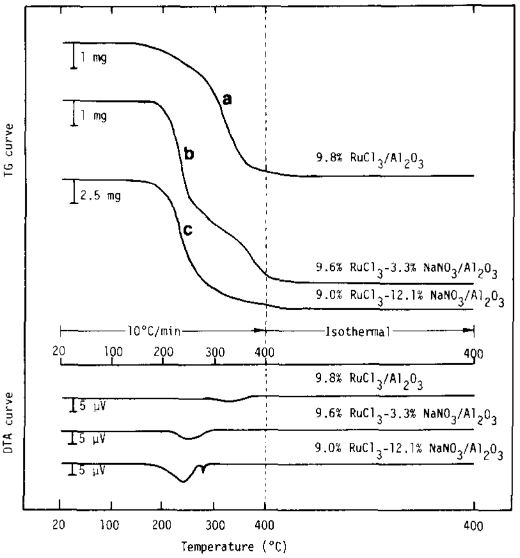

FIG. 1. Typical TG-TDA profiles.

for the thermally treated samples of low $NaNO_3$ loading; when $NaNO_3$ loading exceeded 9.3%, $NaNO_3$ peaks were detected and the intensity of the peaks increased with the increase in $NaNO_3$ loading.

These results suggest that $RuCl_3$ is decomposed by the following two reactions:

$$\text{``}RuCl_3\text{''} + NaNO_3 \xrightarrow[\sim 240°C]{\text{process } \mathbf{a}} RuO_2 + NaCl \quad (1)$$

$$\text{``}RuCl_3\text{''} \xrightarrow[\sim 380°C]{\text{process } \mathbf{b}} RuO_2 \quad (2)$$

The theoretical weight loss calculated based on Eq. (1) was in good agreement with observed degree of weight loss at the lower temperature. The theoretical amount of undecomposed $NaNO_3$ remained after process **a** was proportional to the intensity of the endothermic peak for melt of $NaNO_3$ detected by DTA at around 295°C for high $NaNO_3$ loading samples (Table 1).

Since commercial "$RuCl_3 \cdot 3H_2O$" is a complex mixture of polynuclear Ru(IV) oxychloro species (*21*), detail mechanism for process **a** is not clear. However, it must be noted that whenever alkali-promoted Ru catalyst was prepared by impregnation of commercial "$RuCl_3 \cdot 3H_2O$" and alkali or alkaline earth nitrate followed by thermal treatment and reduction, a process similar to process **a** produced alkali or alkaline earth chloride which cannot be removed by reduction, and that remaining chloride ion severely affects the catalyst performance (*22*).

Subsequent Reduction

In another series of experiments, samples were thermally treated at 400°C in the thermal analyzer and subsequent TPR profiles were examined on the same instrument. Maximum rates for the reduction of samples 1–6 were observed at about 160°C. This reduction temperature is slightly lower than reported temperature for bulk RuO_2 (203°C, (*14*)) or RuO_2/SiO_2 (180°C, (*16*)). A higher loading of $NaNO_3$ caused both a drastic rise in the reduction temperature and an increase in the intensity of the exothermic peak in DTA. Because the reduction temperature remained essentially constant unless $NaNO_3$ loading in the original sample exceeded 9.3% (i.e., $Na/Cl \simeq 1$), increase in the reduction temperature for high $NaNO_3$-loading samples seems to be caused by the remaining $NaNO_3$ undecomposed by process **a**.

The XRD patterns for the reduced samples showed Ru metal peaks, and NaCl peaks were also seen in Na-containing samples (Figs. 2b and 3b). The peaks of $NaNO_3$ which could be observed for the thermally treated samples of high $NaNO_3$ loading disappeared in the reduced samples. However, sodium salts other than NaCl could not be detected by XRD except β-$NaAlO_4$ (*23*) found in samples 9 and 10.

The XRD peak height of Ru metal varied with Na content. This result was not caused by the presence of Ru species other than Ru metal, because the degree of weight loss at the reduction stage was essentially constant when $NaNO_3$ loading is less than 9.3%. Therefore, the peak height of Ru seems to reflect the particle size of Ru metal crystallites. To discuss the Ru particle size, the half-height width must be measured. However, as Ru peaks overlapped with alumina peaks, accurate half-height width could not be obtained even after subtraction of alumina peaks from XRD patterns of the sample. Therefore, Ru peak height was determined instead of the half-height width. Relative peak height of Ru(101) to γ-Al_2O_3(440) was then calculated, and thus experimental variance in determining XRD was eliminated. As can be seen in Fig. 4, relative peak height of Ru metal decreased with the increase in Na/Cl ratio, and relative peak height of Ru metal reached minimum at Na/Cl = 1. In order to elucidate the effect of alkaline component on the particle size of Ru, the following experiments were carried out.

1. The sample 1 (9.8% $RuCl_3/Al_2O_3$) was heated at 250°C. A part of this sample was reduced with hydrogen on the thermal analyzer at 400°C. To the remaining part of the heated sample, NaCl was impregnated. The concentration of NaCl was adjusted to give the same concentration as sample 6. After drying in air, the sample was thermally treated in air at 400°C and reduced with hydrogen at 400°C.

2. The sample 6 (9.3% $RuCl_3$–9.3% $NaNO_3/Al_2O_3$) was heated at 250°C. Using a part of this, TPR profile was examined and then XRD of the reduced sample was examined. The remaining part of the heated sample was washed with water repeatedly until no more chloride ions were detected in the supernatant. The sample was then dried in air. Thermal decomposition behaviour and subsequent TPR profile were examined.

Relative peak height of Ru became higher in the following order (sample No., thermal

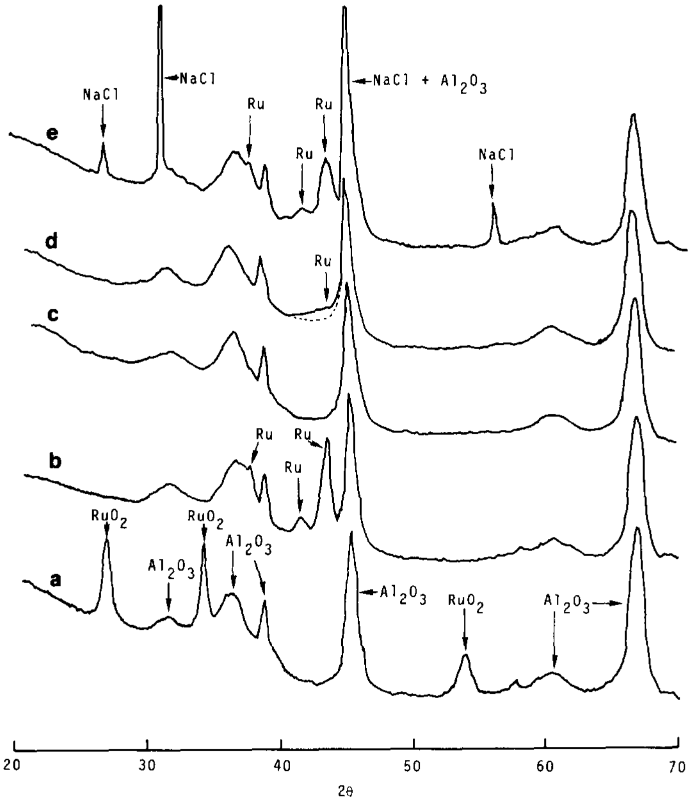

FIG. 2. XRD profiles of the samples derived from 9.8% $RuCl_3/Al_2O_3$ (Sample 1). They were prepared by (a) thermal treatment at 400°C; (b) thermal treatment at 400°C followed by reduction at 400°C; (c) heating at 250°C; (d) heating at 250°C followed by reduction at 400°C; (e) heating at 250°C, impregnation of NaCl, thermal treatment at 400°C, and subsequent reduction at 400°C.

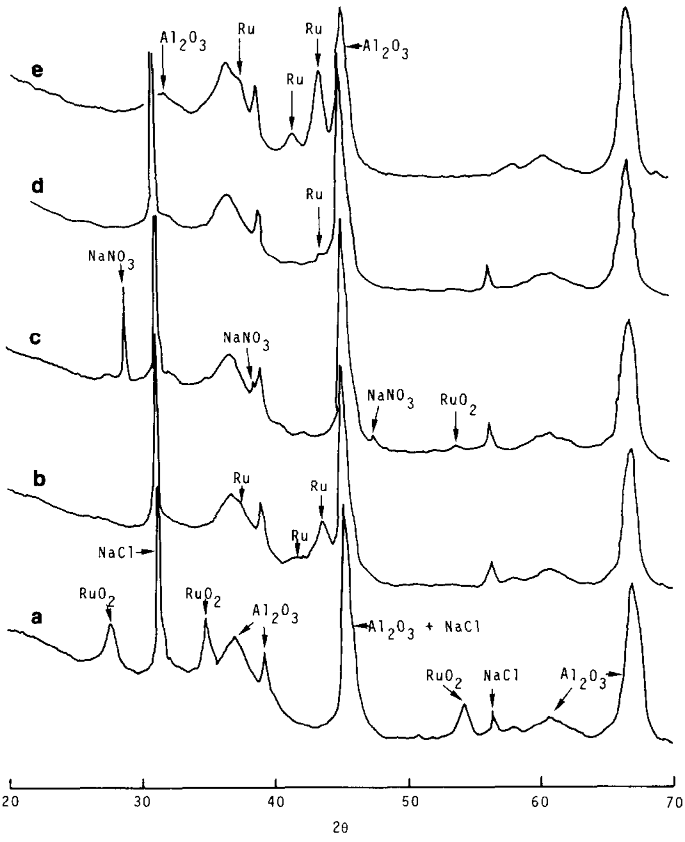

FIG. 3. XRD profiles of the samples derived from 9.3% $RuCl_3$–9.3% $NaNO_3/Al_2O_3$ (Sample 6). They were prepared by (a) thermal treatment at 400°C; (b) thermal treatment at 400°C followed by reduction at 400°C; (c) heating at 250°C; (d) heating at 250°C followed by reduction at 400°C; (e) heating at 250°C, removal of NaCl by washing with water, thermal treatment at 400°C, and subsequent reduction at 400°C.

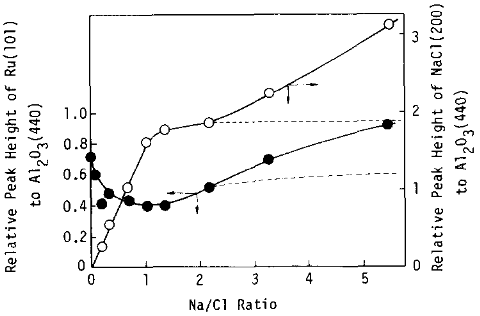

FIG. 4. Relation between Na/Cl ratio and relative peak heights of Ru(101) and NaCl(200) to Al_2O_3(440) found in the XRD profiles of reduced $RuCl_3$–$NaNO_3$/Al_2O_3 samples. Broken lines indicate peak heights corrected by taking into account of formation of $NaAlO_2$ from Al_2O_3.

treatment temperature, and figure No. are given in this order; all samples were reduced at 400°C; other treatment was specified in parentheses):

1,250,2d < 6,250,3d < 6,400,3b < 1,(addition of NaCl),400,2e < 6,(removal of NaCl),400,3e < 1,400,2b.

When two samples prepared by the thermal treatment at 400 and 250°C are compared, Ru peak height of the former is much higher than the latter. This result indicates that during the thermal treatment sintering of RuO_2 particles occurs via the formation of volatile higher oxides of Ru (*24, 25*), and that sintering of Ru metal particles during reduction stage can be neglected under our reduction conditions.

As the heating temperature 250°C is above the temperature for process **a**, $RuCl_3$ and $NaNO_3$ in sample 6 had been decomposed into RuO_2 and NaCl. Removal of NaCl from this sample promoted the aggregation of Ru particles. On the other hand, addition of NaCl to sample 1 prevented the aggregation of Ru particles. Therefore, we concluded that NaCl has a retarding effect on the sintering of RuO_2 during the thermal treatment stage. Consequently, the effect of $NaNO_3$ addition on the peak height of Ru (Fig. 4) can be explained along the same line because of the formation of NaCl by process **a**.

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