

Article

# Ruthenium Modification on Mn and Zr-Modified Co/SiO<sub>2</sub> Catalysts for Slurry-Phase Fischer-Tropsch Synthesis

Tomohisa Miyazawa \*, Toshiaki Hanaoka, Katsuya Shimura and Satoshi Hirata

Biomass Refinery Research Center, Advanced Industrial Science and Technology (AIST); 3-11-32 Kagamiyama, Higashihiroshima, Hiroshima 737-0046, Japan; E-Mails: t.hanaoka@aist.go.jp (T.H.); katsuya-shimura@aist.go.jp (K.S.); satoshi.hirata@aist.go.jp (S.H.)

\* Author to whom correspondence should be addressed; E-Mail: tk-miyazawa@aist.go.jp; Tel./Fax: +81-82-420-8292.

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**Abstract:** The addition of Ru to Mn and Zr-modified Co/SiO<sub>2</sub> catalysts, while applying different preparation orders and loading amounts, was investigated as a means of enhancing the Fischer-Tropsch synthesis reaction. The coimpregnation of Zr/SiO<sub>2</sub> with Co, Mn and Ru gave the most attractive catalytic properties. This can be attributed to the higher dispersion of Co metal resulting from the coimpregnation of Co and Mn as well as enhanced reducibility due to the presence of Ru. The addition of a moderate amount of Ru together with the appropriate order of addition affected both the Co reducibility and the catalytic activity, primarily because of increased reducibility. The addition of even 0.1 wt.% Ru resulted in an obvious enhancement of Fischer-Tropsch synthesis activity.

Keywords: Fischer-Tropsch synthesis; cobalt catalyst; ruthenium; characterization

# 1. Introduction

Fischer-Tropsch (FT) synthesis is a useful means of producing liquid fuels and other chemicals from various carbon sources (such as coal, natural gas and biomass) via syngas [1,2]. Co-based catalysts are the most widely applied for this reaction since they exhibit higher activity and selectivity and thus are more economical [3,4]. It is generally accepted that the activity of Co catalysts for FT synthesis depends

on the presence of surface-exposed Co metal atoms [5,6], and therefore Co species should be both highly dispersed and reduced on the catalyst surface. For this reason, Co is generally deposited on high surface area supports such as SiO<sub>2</sub> [7–11], Al<sub>2</sub>O<sub>3</sub> [12,13] and TiO<sub>2</sub> [14,15], in order to increase the quantity of active Co metal species. However, strong interactions between Co atoms and the support material can decrease both the reducibility and the activity of a Co catalyst [7,8].

The support materials used for Co catalysts can significantly affect the state of Co on the catalyst surface, including factors such as particle size and reducibility. Our group is focused on the use of SiO<sub>2</sub> as a catalyst support and has investigated the modification of this support using both metals and oxide additives. It is well known that the addition of Zr to a Co/SiO<sub>2</sub> catalyst (Zr/Co/SiO<sub>2</sub>) increases the FT synthesis activity of the catalyst [9–11]. Furthermore, the addition of Mn to Zr/Co/SiO<sub>2</sub> enhances the catalyst stability during the FT synthesis reaction [16]. In a previous study, we found that the addition of moderate amounts of Mn and Zr affected both the reducibility of Co and the degree of Co dispersion. Various characterization results suggested that the enhanced FT synthesis activity observed following coimpregnation to produce a Mn+Zr+Co/SiO<sub>2</sub> catalyst can be attributed to the formation of highly dispersed Co metal particles interacting with Mn species [17].

However, on such modified catalysts, the degree of reduction of the Co component remains below 50%. Therefore, the goal of the present study was to increase the Co reducibility and the catalytic activity of Mn and Zr-modified Co/SiO<sub>2</sub> catalysts for the FT synthesis reaction. It has been demonstrated that the addition of noble metals to supported cobalt catalysts increases the Co reducibility [10,18–22] and so this project investigated the promotional effect of Ru on a Mn+Zr+Co/SiO<sub>2</sub> catalyst, in addition to the effects of reduction conditions.

# 2. Results and Discussion

#### 2.1. Effect of Noble Metal Addition and Impregnation Order

In a previous study [17], we prepared a Mn and Zr-modified  $Co/SiO_2$  catalyst and found that the coimpregnation method was preferable in terms of improving the catalytic activity of  $Co/SiO_2$  by Mn and Zr addition, and that the optimum loading amounts of Zr and Mn were 8 and 1 wt.%, respectively. The present study investigated the effect of adding a small amount of a noble metal to this Mn and Zr-modified  $Co/SiO_2$  catalyst. Table 1 summarizes the effect of noble metal addition and impregnation order on Mn and Zr-modified  $Co/SiO_2$  when applied to FT synthesis. Here STY indicates the space time yield of  $C_{5+}$  liquid products.

It is evident that the simple addition of a noble metal to the Co+Mn+Zr/SiO<sub>2</sub> catalyst following calcination was not effective, in the case of both Ru and Pt, since the CO conversion and C<sub>5+</sub> yield over the Ru and Pt-modified catalysts were lower than that over the Co+Mn+Zr/SiO<sub>2</sub> catalyst. It is believed that surface Co metal active sites on the Ru and Pt-treated catalysts were covered during the additional impregnation step thus decreasing their activity. In contrast, when Ru was added simultaneously with Co, the FT synthesis activity was enhanced in all cases. The effect of Ru addition was also found to be much more pronounced than that of Pt. Pt modification of the Co+Mn+Zr/SiO<sub>2</sub> catalyst was ineffective, whether accomplished by sequential or simultaneous impregnation. In addition, although details are not

provided here, it was determined that Ru+Mn+Zr/SiO<sub>2</sub> and Ru/SiO<sub>2</sub> catalysts without Co exhibited only very low activity during FT synthesis, with less than 5% CO conversion.

Catalyst	Conversion/%			Select	tivity/%		C ==============	STV/a/leash	
	CO	$H_2$	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> –C <sub>4</sub>	C <sub>5+</sub>	C <sub>5+</sub> yield/%	51 ¥/g/kg·n	
Co/SiO <sub>2</sub>	30.6	36.8	2.4	12.8	9.5	75.3	23.1	281.5	
Co+Ru/SiO <sub>2</sub>	31.9	38.0	1.1	9.9	3.8	85.2	27.2	310.7	
Co+Mn+Zr/SiO2	37.4	44.7	1.9	11.1	3.4	83.5	31.2	380.4	
Pt/Co+Mn+Zr/SiO2	34.2	42.8	2.4	17.3	6.3	74.1	25.3	308.9	
Pt+Co+Mn+Zr/SiO2	38.5	46.5	2.0	11.8	5.0	81.2	31.2	381.0	
Ru/Co+Mn+Zr/SiO2	36.9	45.3	1.7	14.3	5.0	79.1	29.2	355.6	
Ru+Co+Mn+Zr/SiO2	44.2	53.3	1.9	11.9	3.5	82.7	36.6	445.7	
Ru+Co/Mn+Zr/SiO2	45.0	54.0	2.1	12.1	3.5	82.3	37.1	452.0	
Ru+Co+Mn/Zr/SiO2	46.2	55.2	2.1	11.0	3.0	83.9	38.8	473.0	

Table 1. Effect of noble metal addition and addition order on FT synthesis over Co-Mn-Zr/SiO<sub>2</sub>.

Catalyst: 1.0 g, W/F: 4 g·h/mol, T=503 K, P=1.0 MPa; Co loading: 20 wt%, Mn loading 1 wt%, Zr loading 8 wt%, Ru or Pt loading 0.5 wt%

Figure 1 presents the H<sub>2</sub>-TPR profiles of Ru-Co-Mn-Zr/SiO<sub>2</sub> catalysts prepared using various orders of addition. As a reference, the profiles of Co+Mn+Zr/SiO<sub>2</sub> and Pt/Co+Mn+Zr/SiO<sub>2</sub> are also shown.



**Figure 1.** H<sub>2</sub>-TPR profiles of various catalysts: (**a**) Co+Mn+Zr/SiO<sub>2</sub>, (**b**) Pt/Co+Mn+Zr/SiO<sub>2</sub>; (**c**) Ru/Co+Mn+Zr/SiO<sub>2</sub>; (**d**) Ru+Co+Mn+Zr/SiO<sub>2</sub>; (**e**) Ru+Co+Mn/Zr/SiO<sub>2</sub>; (**f**) Ru+Co/Mn+Zr/SiO<sub>2</sub>.

It is evident that the reduction of Co species without noble metals has its onset at approximately 550 K and shows a maximum at around 640 K on the Co+Mn+Zr/SiO<sub>2</sub> catalyst. Reduction over the Co+Mn+Zr/SiO<sub>2</sub> catalyst during the 8 h hold proceeded slowly although a gradual reduction occurred and the extent of reduction eventually achieved is twice that calculated from the reduction below 673 K. In the case of the noble metal-modified catalysts, however, the reduction peaks are shifted to lower

temperatures and the reduction of Co species took place during the 8 h hold at 673 K. The Pt/Co+Mn+Zr/SiO<sub>2</sub> catalyst exhibited a startup temperature for the lower reduction peak in the vicinity of 470 K with a noticeably sharper and higher peak compared to the other Ru-modified catalysts. Similar behavior was observed for a Pt-modified Co/SiO<sub>2</sub> catalyst by Pirola et al. [23]. Based on these results, it appears that the addition of 0.5 wt.% Pt generates a cubic structure in the Pt-containing phase. In contrast, the same level of Ru addition produces a Ru-Co solid solution with a hexagonal close packed structure. This difference in the metal structures can be related to the differences in the TPR profiles. The sharp reduction peaks obtained from the Pt/Co+Mn+Zr/SiO<sub>2</sub> catalyst can be explained by the H<sub>2</sub> spillover effect from the cubic structure of Pt. Among the Ru-modified Ru+Co+Mn+Zr/SiO<sub>2</sub>, Ru+Co+Mn/Zr/SiO<sub>2</sub> and Ru+Co/Mn+Zr/SiO<sub>2</sub> catalysts, broad reduction peaks are seen at lower temperatures of approximately 440 K, although the peak heights are very low, while the main reduction peaks appear around 510 to 540 K. The peaks at lower temperatures are assigned to the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO, and the high temperature peaks are attributed to the reduction of CoO to Co metal. The Ru/Co+Mn+Zr/SiO<sub>2</sub> catalyst, compared with the other Ru-modified catalysts, has both its lower peak and its main peak at higher temperatures; the lower peak is situated at approximately 500 K and the main peak at 560 K. Table 2 summarizes the physical properties and CO conversions during FT synthesis reactions over these catalysts.

Catalyst	CO conv./%	H <sub>2</sub> consumption/mmol/g-cat	Reduction degree/% (at 673 K)	Reduction degree/% (after hold)	Dispersion/%
Co/SiO <sub>2</sub>	30.6	12.1	32	94	0.66
Co+Ru/SiO <sub>2</sub>	31.9	13.1	41	96	0.70
Co+Mn+Zr/SiO2	37.4	14.7	20	48	1.58
Pt/Co+Mn+Zr/SiO2	34.2	19.7	33	68	1.49
Pt+Co+Mn+Zr/SiO2	38.5	22.5	34	71	1.62
Ru/Co+Mn+Zr/SiO2	36.9	20.4	33	76	1.38
Ru+Co+Mn+Zr/SiO2	44.2	25.8	36	79	1.67
Ru+Co/Mn+Zr/SiO2	45.0	24.9	37	74	1.73
Ru+Co+Mn/Zr/SiO2	46.2	25.9	34	71	1.87

**Table 2.** Physical properties and CO conversions during Fischer-Tropsch (FT) synthesis reaction over various catalysts.

It is clear that the degree of reduction of Co was significantly enhanced by noble metal addition in all cases. However, the activities during FT synthesis of both Ru/Co+Mn+Zr/SiO<sub>2</sub> and Pt/Co+Mn+Zr/SiO<sub>2</sub> were decreased compared to that of Co+Mn+Zr/SiO<sub>2</sub>. From the H<sub>2</sub> chemisorption results, the dispersion of Co metal was decreased during the Ru or Pt modification by simple sequential impregnation of Co+Mn+Zr/SiO<sub>2</sub>. This likely resulted in spite of the enhanced reducibility because coverage of the Co metal particles by the sequential impregnation decreases the Co dispersion and hence the FT synthesis activity. In contrast, the catalyst that had been simultaneously impregnated with Ru and Co exhibited higher Co reducibility and FT synthesis activity compared to the Co+Mn+Zr/SiO<sub>2</sub>. From these results, it can be expected that Ru-Co solid solutions were formed during the coimpregnation process, leading to a greater degree of Co reducibility. The H<sub>2</sub>-TPR profiles and catalytic properties are similar among these Ru and Co coimpregnation catalysts, and the differences in their FT synthesis activities are minor,

although Ru+Co+Mn/Zr/SiO<sub>2</sub> exhibited the highest activity. Ru+Co+Mn/Zr/SiO<sub>2</sub> also showed the highest level of metal dispersion and this can be related to its superior catalytic activity. In addition, the catalytic activity normalized to the level of dispersion was almost constant among all the Ru-modified catalysts. This result indicates that the site-time yields over the Co catalysts were independent of the metal dispersion, and that the nature of the active sites on the catalysts is likely unchanged, which is also consistent with the findings of Iglesia *et al.* [6]. Our previous work [17] suggested that, during the coimpregnation catalyst preparation process, the interaction between Co and Mn species enhances Co dispersion and therefore FT synthesis activity. Hence, it is thought that the higher dispersion of Co metal results from coimpregnation of the Co and Mn while the higher reducibility is due to the presence of Ru, and these two effects combine such that Ru+Co+Mn/Zr/SiO<sub>2</sub> shows the highest activity among the Ru-modified catalysts.

#### 2.2. Effects of Ru Quantity on Ru+Co+Mn/Zr/SiO2

In the previous section, it was shown that the addition of Ru clearly enhances the catalytic activity of Ru+Co+Mn/Zr/SiO<sub>2</sub>. However, Ru is a less than ideal additive due to its high cost and limited availability. Therefore, the variations in the catalytic activity of the Ru+Co+Mn/Zr/SiO<sub>2</sub> catalyst with Ru content were evaluated. Figure 2 shows the H<sub>2</sub>-TPR profiles of Ru+Co+Mn+Zr/SiO<sub>2</sub> catalysts with different Ru amounts. The preparation and reaction procedures applied in these trials were the same as those described above. (wt.%).



**Figure 2.** H<sub>2</sub>-TPR profiles of Ru+Co+Mn/Zr/SiO<sub>2</sub> catalysts with different Ru amounts. Numbers in brackets indicate the Ru loading amounts. (**a**) Without Ru; (**b**) 0.1 wt%; (**c**) 0.3wt%; (**d**) 0.5wt%; (**e**) 1.0wt%

It is evident that higher concentrations of Ru allow the Co to be reduced more readily. Without Ru addition, the reduction of Co species starts around 550 K and the reduction peak is centered at approximately 640 K. Even 0.1 wt.% Ru decreases the peak temperature to 590 K and 0.3 wt.% lowers

the peak temperature still further, to 550 K. At more than 0.3 wt.% Ru, however, the enhancement effect appears to plateau: the difference in the peak temperatures between 0.3 and 1.0 wt.% is only 20 K. Figure 3 summarizes the effect of Ru concentration on the FT synthesis activity.



**Figure 3.** Ru amount dependence of the FT synthesis activity over the Ru+Co+Mn/Zr/SiO<sub>2</sub> catalyst. Catalyst: 1.0 g, W/F: 4 g·h/mol, Co loading: 20 wt%, Pressure: 1.0–4.0 MPa, Temperature: 503 K.

Both the CO conversion and STY were increased by addition of 0.1 wt.% Ru, although the selectivity was not as dependent on the Ru amount. In addition, the effects of increasing the Ru concentration on the CO conversion and STY were also not overly significant above 0.1 wt.%. Table 3 summarizes the physical properties and CO conversions during the FT synthesis reaction over these catalysts.

Table 3.	Physical	properties	and CO	) conversi	ons during	the F	T synthesis	reaction	over
Ru-modif	fied cataly	/sts.							

Ru amount/wt%	CO conv./%	H <sub>2</sub> consumption/mmol/g-cat	Reduction degree/% (at 673 K)	Reduction degree/% (after hold)	Dispersion/%
0.0	38.0	14.6	20	47	1.60
0.1	44.3	21.1	24	61	1.77
0.3	45.0	25.2	42	71	1.84
0.5	46.2	25.9	34	71	1.87
1.0	45.4	25.7	41	73	1.81

These data clearly show that the degree of reduction of Co after H<sub>2</sub>-TPR is increased by the Ru addition and that this increase was almost saturated at 0.3 wt.% Ru addition. In addition, in accordance with increasing reduction degree, the H<sub>2</sub> consumption also increased. Therefore, the increased quantity of active Co metal sites on the Ru-modified Ru+Co+Mn/Zr/SiO<sub>2</sub> may be attributed to the enhanced reducibility of the Co resulting from its interaction with the Ru. However, an overly high Ru concentration actually decreases both the metal dispersion and catalytic activity. As an example, the material with 0.5 wt.% Ru exhibited the highest FT synthesis activity, due to the segregation of Ru [21].

From these results, it can be said that moderate amounts of Ru addition to the Ru+Co+Mn/Zr/SiO<sub>2</sub> catalysts enhance the FT synthesis activity primarily due to the increasing reducibility. Even 0.1 wt.% Ru addition generated an obvious enhancement of the catalytic activity and reducibility.

#### 2.3. Effect of H<sub>2</sub> Reduction Conditions on the Ru+Co+Mn/Zr/SiO<sub>2</sub>

As discussed in the previous section, Ru addition improved the catalyst reducibility under 1.0 MPa pressure. To confirm this improvement, the FT activity of Ru+Co+Mn/Zr/SiO<sub>2</sub> under various H<sub>2</sub> reduction conditions was evaluated. The H<sub>2</sub> reduction temperature was varied from 573 to 773 K and the pressure was varied between ambient and 1.0 MPa. In each trial, the same temperature increase rate (10 K/min) and reduction time (8 h hold at the desired temperature) were applied. Table 4 summarizes the variations in the FT reaction with changing reduction conditions.

Table 4. Effects of reduction conditions on the performance of Ru+Co+Mn+Zr/SiO<sub>2</sub> catalysts.

<b>Reduction Condition</b>	Reduction Condition Conversion/%			Select	tivity/%	C			
Temperature, Pressure	CO	H <sub>2</sub>	CO <sub>2</sub>	CH4	C2-C4	C5+	C <sub>5+</sub> yield/%	51 1/g/kg·li	
673 K, 1.0 MPa	41.4	48.7	1.9	11.1	3.4	83.5	34.5	421.1	
573 K, 0.1 MPa	46.1	54.9	2.2	11.8	3.4	82.6	38.1	464.3	
673 K, 0.1 MPa	46.2	55.2	2.1	11.0	3.0	83.9	38.8	473.0	
773 K, 0.1 MPa	43.4	51.8	1.5	12.8	4.5	81.2	35.2	429.7	

Catalyst: 1.0 g, W/F: 4 g h/mol, T=503 K, P=1.0 MPa; Co loading: 20 wt%, Mn loading 1 wt%, Zr loading 8 wt%, Ru 0.5 wt%

It can be seen that reduction with this catalyst at 1.0 MPa generates less activity than reduction at ambient pressure (0.1 MPa), thus H<sub>2</sub> reduction at 1.0 MPa is not suitable for this catalyst. It is thought that reduction at higher pressures decreases both the metal dispersion and the catalytic activity. In addition, H<sub>2</sub> reduction at 773 K also lowers the FT activity compared to the reaction at lower temperatures, although the difference between the catalytic activities at 573 and 673 K was minimal. As discussed in Section 2.1, the addition of Ru to the catalyst enables sufficient Co reduction at 573 K and generates almost the same level of FT synthesis activity. It can be expected that the energy input required for H<sub>2</sub> reduction would be decreased by the lowering of the reduction temperature from 673 K to 573 K.

#### 2.4. FT Synthesis Reaction under High Pressure Conditions

As noted above, Ru addition improved the FT synthesis activity of the Mn and Zr-modified Co/SiO<sub>2</sub> catalysts under a pressure of 1.0 MPa. This reaction pressure is sufficiently low so as to avoid any restrictions associated with the Japanese High-Pressure Gas Safety Law. However, on an industrial scale, the FT synthesis reaction is typically performed under higher pressure conditions, such as 2.0–5.0 MPa [7]. Hence the catalytic FT synthesis reactivity at 4.0 MPa was also investigated and compared with the results obtained at 1.0 MPa. Table 5 presents the effect of reaction pressure on the Co/SiO<sub>2</sub>, Co+Mn+Zr/SiO<sub>2</sub> and Ru+Co+Mn/Zr/SiO<sub>2</sub> catalysts during FT synthesis. The activity order of these catalysts was: Ru+Co+Mn/Zr/SiO<sub>2</sub> > Co+Mn+Zr/SiO<sub>2</sub> at both pressures. The Ru/Co+Mn/Zr/SiO<sub>2</sub> produced greater CO and H<sub>2</sub> conversions, and exhibited higher C<sub>5+</sub> selectivity

and chain growth probability ( $\alpha$ ), compared to Co+Mn+Zr/SiO<sub>2</sub> and Co/SiO<sub>2</sub>. The results also indicated that, at higher reaction pressures, higher conversions, C<sub>5+</sub> selectivity and  $\alpha$  values were achieved in the case of all catalysts. In addition, CH<sub>4</sub> selectivity was drastically reduced at higher pressures, leading to greater C<sub>5+</sub> selectivity, particularly with the Ru/Co+Mn/Zr/SiO<sub>2</sub> catalyst. In this research, the raw material synthesis gas included 5.0 vol% CH<sub>4</sub> and so CH<sub>4</sub> selectivity was calculated by subtracting the CH<sub>4</sub> from the raw synthesis gas, possibly generating artificially low values for the CH<sub>4</sub> selectivity. Despite this potential source of error in the selectivity estimations, we are confident that the general selectivity trends identified here are correct. Although both CO conversion and STY were seen to increase with pressure, these parameters increased at rates lower than the pressure elevation rates; when the reaction pressure was quadrupled from 1 to 4 MPa, the CO conversions and STY increased by only approximately 50%. It was determined that the Ru/Co+Mn/Zr/SiO<sub>2</sub> catalyst exhibited the highest FT synthesis activity compared to the Co/SiO<sub>2</sub> and Co+Mn+Zr/SiO<sub>2</sub>.

Catalyst Pressu	D (MD	Conversion/%			Selectivities/%			C <sub>5+</sub>		STY/g/	Dispersion	Reduction
	Pressure/wiPa	СО	$H_2$	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> –C <sub>4</sub>	C <sub>5+</sub>	yield/%	u	kg∙h	degree <sup>b</sup> /%	degree °/%
0.10.0	1.0	30.6	36.8	2.4	12.8	9.5	75.3	23.1	0.86	281	0.66	94
Co/SiO <sub>2</sub> 4.0	4.0	44.4	53.4	0.7	2.7	8.0	88.5	39.3	0.87	427		
Co+Mn+Zr/	1.0	37.4	44.7	1.9	11.1	3.4	83.5	31.2	0.86	380	1.57	48
SiO <sub>2</sub>	4.0	53.6	58.7	0.5	1.6	5.9	92.0	49.3	0.90	601		
Ru+Co+Mn/	1.0	46.2	55.2	2.1	11.0	3.0	83.9	38.8	0.86	473		71
Zr/SiO <sub>2</sub>	4.0	70.5	77.8	1.4	1.3	3.4	93.9	66.2	0.90	758	1.87	

Table 5. Effect of reaction pressure on FT synthesis. <sup>a</sup>

<sup>a</sup> Catalyst: 1.0 g, W/F: 4.0 g h/mol, Pressure: 1.0-4.0 MPa, T=503 K; <sup>b</sup> Determined by H<sub>2</sub> chemisorption at 373 K; <sup>c</sup> Reduction percentage of Co<sub>3</sub>O<sub>4</sub> to Co<sup>0</sup>, mesured by TPR at 673 K.

## **3. Experimental Section**

#### 3.1. Catalyst Preparation

SiO<sub>2</sub> Q-10 used as support material for the Co catalysts (average pore size: 10 nm, surface area: 300 m<sup>2</sup>/g) was purchased from the Fuji Silysia Chemical Co., Ltd. (Kasugai, Japan). The Co loading was 20 wt.% on each catalyst and supports were impregnated using an aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. Attempts were made to improve the catalytic activity, stability and reducibility by modification with Mn, Zr and Ru or Pt. The loading amounts of Mn and Zr was 1 and 8 wt.%, respectively, while Ru was added in the concentration range of 0.1 to 1.0 wt.%. Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Nacalai Tesque, Inc., Kyoto, Japan), ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd., Osaka, Japan) and RuCl<sub>3</sub>·nH<sub>2</sub>O (SOEKAWA chemical Co., Ltd., Tokyo, Japan assay: 41%) or H<sub>2</sub>PtCl<sub>6</sub>·2H<sub>2</sub>O (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used as precursors. The purities of these chemical reagents were 99%. SiO<sub>2</sub> supports were impregnated with Co, Mn, Zr and Ru or Pt using aqueous solutions of the above precursors, followed by drying and calcination. In this impregnation process, some catalysts were impregnated twice. A typical procedure, used to fabricate Ru/Co+Mn+Zr/SiO<sub>2</sub>, was as follows. The SiO<sub>2</sub> support was first impregnated with Co, Mn and Zr using aqueous solutions of the above precursors, followed by drying and calcination. In this impregnated with Ru using an aqueous solution of RuCl<sub>3</sub>·nH<sub>2</sub>O

and again subjected to drying and calcination. In the catalyst nomenclature applied herein, the "/" symbol indicates that the material to the right of the slash was impregnated with the components shown on the left. To evaluate the effect of Ru addition and the addition order, Co+Mn+Zr/SiO<sub>2</sub>, Ru/Co+Mn+Zr/SiO<sub>2</sub>, Ru+Co+Mn+Zr/SiO<sub>2</sub> and Ru+Co/Mn+Zr/SiO<sub>2</sub> were prepared. In addition, Co/SiO<sub>2</sub>, Co+Ru/SiO<sub>2</sub>, Pt/Co+Mn+Zr/SiO<sub>2</sub> and Pt+Co+Mn+Zr/SiO<sub>2</sub> were fabricated as reference catalysts. In all cases, drying conditions were 383 K for 12 h, and calcination condition conditions were 673 K for 3 h (temperature increase rate: 10 K/min).

#### 3.2. Characterization

Hydrogen temperature-programmed reduction (H2-TPR) and hydrogen chemisorption were carried out using a BELCAT-B automatic instrument equipped with a thermal conductivity detector (TCD) and a mass spectrometer detector. During the H<sub>2</sub>-TPR measurements, each calcined sample (ca. 0.10 g) was flushed with Ar at room temperature while held in a guartz tubular reactor, after which a 5% H<sub>2</sub>/Ar mixture was introduced at a flow rate of 30 mL/min. The temperature was increased at a rate of 10 K/min from ambient to 673 K and the sample was held at the final temperature for 3 h. In hydrogen chemisorption trials, prior to the adsorption of H<sub>2</sub>, the catalysts were treated in a 5% H<sub>2</sub>/Ar flow at 673 K for 8 h, followed by Ar purging during cool down. Hydrogen chemisorption was carried out at 373 K. The Co metal surface area and hydrogen consumption were calculated according to a method reported in the literature [24-26]. In this work, catalysts loaded with both Co and a noble metal (Ru or Pt) were characterized and so it was difficult to differentiate the hydrogen consumption resulting from Co compared to that resulting from Ru or Pt. However, the amounts of noble metals added were much smaller than the quantity of Co present (a ratio of approximately 1:40 by weight), and so the contributions of the noble metals to the total chemisorption amount can be regarded as minimal. The dispersion values in this paper were calculated by subtracting the chemisorption of the noble metals assuming full reduction.

## 3.3. Syngas Preparation

The syngas used during FT synthesis trials in this research was produced and stored using a bench-scale BTL plant installed at the Biomass Refinery Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan. In this apparatus, syngas produced from a gasifier was purified by passing through a scrubber and desulfization towers [27]. The final compressed gas composition employed for FT synthesis was (in vol%):  $H_2 = 59.9$ , CO = 29.8,  $CH_4 = 5.0$ ,  $N_2 = 4.9$ ,  $CO_2 = 0.4$ .

## 3.4. FT Reaction

FT synthesis was carried out using a continuous stirred tank reactor system equipped with a 0.13 L volume reactor. Each catalyst (100–200 mesh) was set in the reactor and reduced *in situ* under an atmospheric pressure H<sub>2</sub> flow at 673 K for 8 h before reaction. After cooling down the reactor, 50 mL of n-hexadecane was added into the reactor as a solvent by pumping through a valve without introducing any of the external atmosphere. The FT synthesis reaction was typically carried out at 503 K and 1.0 MPa for

8 h, during which time the syngas feed rate was controlled at a W/F ratio of 4.0 g·h/mol. During the reaction, the gaseous products were continuously analyzed by two on-line gas chromatographs (GCs) in order to calculate CO conversion. Inorganic gases (N<sub>2</sub>, H<sub>2</sub>, CO and CO<sub>2</sub>) were analyzed using a Shimadzu GC-2014 equipped with a TCD and a Porapak-Q column. Light hydrocarbons (C<sub>1-4</sub>) were analyzed with a Shimadzu GC-2014 equipped with a flame ionization detector (FID) and an RT-QPLOT capillary column. No obvious deactivation was observed over the course of an 8 h reaction with almost all of the catalysts. After each reaction, the gasoline-range hydrocarbons (C<sub>5-10</sub>) collected in the trap and the heavy hydrocarbons (C<sub>11+</sub>) dissolved in the solvent were analyzed and quantified using an Agilent 6890 N GC equipped with an FID and a UA-DX30 capillary column.

#### 4. Conclusions

The effects of small amounts of noble metal addition on the performance of a Mn-Zr-Co/SiO<sub>2</sub> catalyst were investigated. Simultaneously impregnation of Ru with Co gave much higher reactivity than simple sequential addition and this effect was much more remarkable when adding Ru compared to Pt. In H<sub>2</sub>-TPR measurements, reduction peaks were shifted to lower temperatures and the extent of reduction of Co was shown to be significantly enhanced by the Ru addition. The combination of higher dispersion of Co metal obtained via the coimpregnation of Co and Mn and higher reducibility due to the presence of Ru generated the highest activity in the case of the Ru+Co+Mn/Zr/SiO<sub>2</sub> among the Ru-modified catalysts.

The effect of Ru concentration on the Ru+Co+Mn/Zr/SiO<sub>2</sub> catalyst showing the highest FT synthesis activity was also examined. Ru addition clearly enhanced the Co reducibility and FT synthesis activity. However, more than 0.3 wt.% Ru gave no further enhancement of the reducibility. A moderate amount of Ru addition enhances the catalytic activity mainly due to the increasing reducibility, and as little as 0.1 wt.% Ru generated an obvious enhancement of catalytic activity and reducibility.

The Ru+Co+Mn/Zr/SiO<sub>2</sub> catalyst exhibited superior catalytic properties under various FT synthesis conditions. These results demonstrate that the addition of a small amount of Ru using coimpregnation is an effective means of improving the performance of Mn-Zr-Co/SiO<sub>2</sub> catalysts.

## **Author Contributions**

T.M. carried out the catalyst preparation and hydrocracking behavior studies and drafted the manuscript. T.H., K.S. and S.H. participated in the design of the study and assisted in drafting the manuscript. All authors read and approved the final manuscript.

### **Conflicts of Interest**

The authors declare no conflict of interest.

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