Catalysis
Science &
Technology

PAPER

View Article Online
View Journal | View Issue

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

Cite this: *Catal. Sci. Technol.*, 2014, 4, 3099

Ruthenium promoted cobalt catalysts prepared by an autocombustion method directly used for Fischer–Tropsch synthesis without further reduction

Rungravee Phienluphon,[ab] Lei Shi,[bc] Jian Sun,[b] Wenqi Niu,[b] Peng Lu,[b] Pengfei Zhu,[b] Tharapong Vitidsant,*[a] Yoshiharu Yoneyama,[b] Qingjun Chen*[b] and Noritatsu Tsubaki*[b]

Ru promoted Co/SiO_2 Fischer–Tropsch synthesis (FTS) catalysts with high reduction levels were synthesized through an autocombustion method using citric acid (CA) as a reductant and nitrate ions as oxidants. The as-synthesized catalysts were used directly in FTS reaction without further reduction. The effects of the ruthenium promoter, citric acid contents and reductant types on the catalyst structures and FTS performance were systematically studied. Results indicated that the introduction of a small amount of Ru (1 wt%) improved the reduction and dispersion of cobalt during the autocombustion process, and significantly enhanced the FTS activity. The CO conversion of the catalyst increased rapidly from 0.8 to 41.4% after Ru promotion. The citric acid contents (molar ratio of citric acid to nitrates: CA/N) in the precursor also played an important role in controlling the structures and FTS performance of the catalysts. With the increase of CA/N, the metal reduction level increased and the Co crystalline size decreased but the activity of the catalyst first increased and then decreased with gradually increasing CA/N. An excessive amount of the reductant could result in more residual carbon species and decrease the activity of the catalyst. For different types of reductants (at the same molar ratio of reductants to nitrates), the catalyst prepared by citric acid exhibited the highest activity whereas the catalyst synthesized by oxalic acid showed the lowest methane selectivity. The Ru promoted cobalt catalysts prepared by the autocombustion method, which omits the complex and high energy consumption reduction process, can be used directly for highly efficient FTS and thus will be more promising in the future.

Received 31st March 2014,
Accepted 17th May 2014

DOI: 10.1039/c4cy00402g

www.rsc.org/catalysis

1. Introduction

Growing demand coupled with the possibility of running out of oil has significantly increased interest in the production of renewable and clean fuels. Fischer–Tropsch synthesis (FTS) has received more attention than ever since it is considered as an effective process to produce wide-range liquid hydrocarbon fuels and high-value added chemicals from relatively abundant resources, such as natural gas, coal and biomass, *via* synthetic gas (H_2 + CO).[1–3]

Due to high activities and selectivities to large molecular weight hydrocarbons, cobalt-based catalysts are widely used for FTS.[1–5] The high activity of cobalt catalysts requires both appropriate sizes of cobalt crystallines and high dispersion of cobalt active sites. The high dispersion of cobalt needs a large surface area of the support and a strong interaction between cobalt and the support[6] but a strong metal support interaction may decrease the reducibility and activity of the catalyst. Noble metals promotion (such as ruthenium), which can improve both the reduction and dispersion of cobalt, is an effective method to enhance the activity of the cobalt catalysts.[7–9] Besides, synergistic bimetallic interactions between cobalt and ruthenium can also increase the FTS activity and C_{5+} selectivity.[7–10] Even so, the conventional preparation of cobalt-based FTS catalysts involves impregnation, drying, calcination and reduction steps. Among these steps, the catalyst reduction is particularly important, but it increases the cost and complexity of FTS. Therefore, a promoted Co based catalyst with a high metal reduction level

---

[a] *Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand. E-mail: tharapong.v@chula.ac.th; Fax: +66 2 2185813; Tel: +66 2 2187517*
[b] *Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan. E-mail: tsubaki@eng.u-toyama.ac.jp, chenqingjunsh@gmail.com; Fax: +81 76 4456848; Tel: +81 76 4456846, +81 76 4456848*
[c] *Shenyang University of Chemical Technology, Shenyang, 110142, China*

This journal is © The Royal Society of Chemistry 2014

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

and no need for a reduction process will be more promising for FTS.

Autocombustion is a novel method to produce catalysts with high reduction levels.[11,12] In the autocombustion synthesis, a low temperature is required to start the combustion (exothermic decomposition of a redox mixture of metal salts and reductants), and then the combustion can continue without external energy supply. So this method has the advantages of low cost and high energy efficiency.[13] Furthermore, during the combustion process, the metal can be reduced by the released gases (such as H_2, CH_4, CO, and so on) from the pyrolysis of the reductant. Therefore, the as-prepared catalyst might be used directly for the FTS reaction without further reduction. However, the autocombustion process is very complex and usually occurs violently. It is more difficult to control the reduction level than the conventional H_2 reduction.

Many studies have been conducted to improve the metal reduction level during the autocombustion, which include varying the type of organic reductants,[13,14] the reductant contents,[15–19] and the pH value of the precursors.[20–22] But these methods cannot change the reduction temperature and the rate of cobalt essentially. A promoted autocombustion method by introducing a second metal Ru, which can decrease the reduction temperature of Co and increase the reduction rate by H_2 spillover, may obviously improve the reduction of Co and enhance the FTS activity. In addition, if combined with the optimization of types of organic reductants and the reductant contents, Ru promoted Co catalysts with high reduction levels and activities might be prepared by using this method.

In this work, Ru promoted Co/SiO_2 FTS catalysts with a high reduction level were developed by the autocombustion method. Catalyst characterization results indicated that the introduction of ruthenium significantly improved the reduction of cobalt during autocombustion and can help to achieve a high reduction level of cobalt at a very small amount of the reductant. The as-prepared catalyst without further reduction exhibited a high FTS activity comparable to the conventional H_2 reduced catalyst. The effects of the ruthenium promoter, citric acid contents and reductant types on the structures and FTS performance of the catalysts have been studied.

2. Experiment

2.1 Preparation of the catalysts

Ru promoted Co/SiO_2 FTS catalysts were synthesized through the autocombustion method using citric acid (CA) as a reductant and nitrate ions as oxidants. The contents of cobalt and ruthenium in the catalysts are fixed at 10 wt% and 1 wt%, respectively. The nitrate compounds ($Co(NO_3)_2$ and $Ru(NO_3)_3$) are denoted as N and citric acid is denoted as CA. First, the cobalt nitrate, ruthenium nitrate and CA were dissolved in 100 ml of distilled water based on the different molar ratios of citric acid to nitrates (CA/N) of 0.15, 0.2, 0.25, 0.3, 0.35 and 0.4. The solution's pH was adjusted using 28 wt% of ammonia solution to obtain a value of 7. Then, the solution was stirred and refluxed at 80 °C for 2 h. Subsequently, the neutralized solution was evaporated and condensed at 70 °C on a hot plate with continuous stirring to obtain 20 ml of solution. Next, the obtained solution was impregnated over 5 g of silica (Q-50, Fuji Silysia Co.; surface area: 79 m^2 g^{-1}, pore volume: 1.1 cm^3 g^{-1}). After the impregnation, the sample was dried in air at 120 °C for 12 h and then calcined in argon at 400 °C for 3 h to obtain the Ru promoted Co/SiO_2 FTS catalyst. The catalyst was subsequently passivated by 1% oxygen in argon at room temperature for 4 h. The preparation procedure of ruthenium promoted catalysts by the autocombustion method was shown in Fig. 1. The obtained catalysts with different CA/N values are denoted as 0.15RuCo, 0.2RuCo, 0.25RuCo, 0.3RuCo, 0.35RuCo and 0.4RuCo. Different types of reductants (formic acid and oxalic acid) with the molar ratio of reductant to oxidants of 0.3 were also used to prepare the catalysts under the same preparation conditions as citric acid. Monometal (cobalt/ruthenium) catalysts with the CA/N of 0.3 were also prepared by the same autocombustion method and were denoted as 0.3Co and 0.3Ru, respectively.

As a reference catalyst, the air combustion–reduction catalyst $M_{\text{air-reduction}}$ refers to the catalyst prepared by the similar autocombustion method with M metal salt and citric acid (M is Co, Ru or RuCo). The differences are that the catalysts were obtained by calcination in air at 400 °C for 3 h and then reduction at 400 °C for 10 h in H_2. For comparison, conventional impregnated catalysts (denoted as M_N, where M was the loaded metal Co, Ru or RuCo) with 10 wt% cobalt and/or 1 wt% ruthenium were also prepared. The catalysts were calcined in air at 400 °C for 3 h and then reduced in H_2 at 400 °C for 10 h. All of the catalysts were passivated by 1% oxygen in argon at room temperature for 4 h.

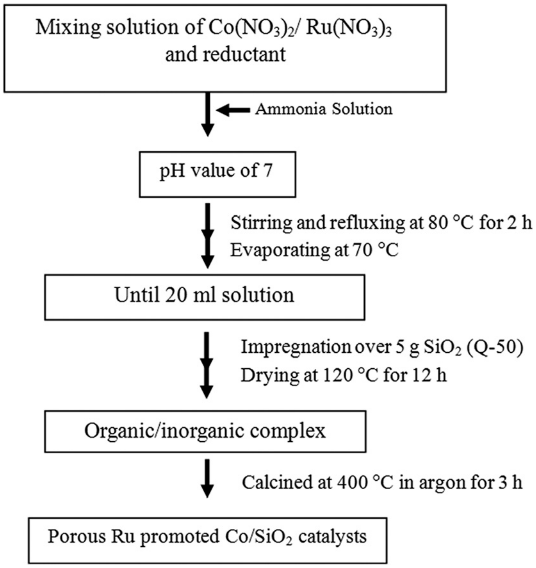

Fig. 1 Schematic flow chart of the catalysts preparation by the autocombustion method.

This journal is © The Royal Society of Chemistry 2014

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

2.2 Characterization of the catalysts

The behavior of the autocombustion process was characterized by thermogravimetic and differential thermal analyses (DTA/TGA-60, Shimadzu) at a heating rate of 10 °C min^{-1} from room temperature to 800 °C in a nitrogen atmosphere.

X-ray diffraction (XRD) patterns of the prepared catalysts were measured using a Rigaku RINT 2200 X-ray powder diffractometer with a monochromatic Cu Kα radiation source at 40 kV and 40 mA in the 2θ range of 10–80 degrees. The average crystalline sizes of the powders were calculated by the Scherrer equation. The pore structures of the catalysts were determined by N_2 physisorption using a NOVA 2200e apparatus. The samples were degassed at 200 °C for 2 h before the analysis. The specific surface area (S) was obtained by the BET method. The total pore volume (V) was calculated by the single point method and the average pore size was achieved by $4V/S$. The determination of the metal content in the catalyst was carried out using a scanning electron microscope equipped with an energy-diffusive X-ray (EDX) spectroscopy attachment (SEM-EDS, JEOL JSM-6360LV).

The reduction behaviors were studied by hydrogen temperature-programmed reduction (H_2-TPR) (BELCAT-B-TT). Before reduction, the catalysts were heated at 150 °C for 2 h in argon flow. After that, the temperature was cooled down to 50 °C. Then, 5% H_2–Ar mixture gas with a flow rate of 30 cm^3 min^{-1} was passed through the catalysts. The temperature was linearly raised from 50 °C to 800 °C at a heating rate of 5.0 °C min^{-1}. The effluent gas was analyzed using a thermal conductivity detector (TCD).

2.3 Fischer–Tropsch synthesis tests

The FTS performance of the catalysts was tested in a semibatch slurry-phase reactor with an inner volume of 80 ml. 1 g of passivated catalyst was ground to fine particles in 20 ml of *n*-hexadecane, and then the mixture was transferred into the reactor. Syngas with a H_2/CO molar ratio of 2 was used as a reactant and 3% Ar was used as an inner standard. During the reaction, the effluent gas from the reactor was analyzed by online gas chromatography. A thermal conductivity detector (TCD) was used to analyze the gaseous products (CO, CO_2, and CH_4). Light hydrocarbons (C_1–C_5) were online analyzed using a flame ionization detector (FID) with a Porapak-Q column. The liquid products collected in a dry-ice trap and hydrocarbons dissolved in the solvent were combined and all of them were analyzed using a FID with a silicone SE-30 column. The FTS reaction conditions were: H_2/CO = 2, T = 240 °C, P (total) = 1.0 MPa, and W/F = 10 gh mol^{-1}, where W is the weight of the catalyst and F is total syngas flow rate (including H_2, CO and 3% Ar).

3. Results and discussion

3.1 Evolution of Ru promoted Co/SiO_2 catalysts during the autocombustion process

In this work, Ru promoted Co/SiO_2 FTS catalysts were prepared by the autocombustion method using cobalt and ruthenium nitrates as the oxidants and citric acid as the reductant. After the impregnation of the precursors over SiO_2 (Q-50, shown in Fig. 1), the dried samples were characterized by thermal analysis to elucidate the evolution of the Ru promoted Co/SiO_2 catalyst during the autocombustion process. The TG/DTA results of the dried samples prepared with different reductant contents (molar ratio of citric acid to nitrates: CA/N) are shown in Fig. 2.

The DTA curves of the samples exhibited one endothermic peak and two exothermic peaks. The endothermic peak below 100 °C could be assigned to the removal of adsorbed water. The two exothermal peaks at about 200 and 270 °C were ascribed to the redox reaction of nitrates with citric acid, meanwhile the TG curves decreased deeply. During this process, nitrates and citric acid were decomposed, forming cobalt and ruthenium oxides. Large amounts of gases such as H_2, CO, H_2O, CH_4, NO, CO_2, NH_3 and NO_2 were released. During this process, the formed H_2, CO and CH_4 acted as the reductants to reduce the metal oxides to metallic Co and Ru. Ru might be firstly reduced due to the low reduction temperature. The reduced Ru could act as a promoter to improve the Co reduction. When the temperature was higher than 300 °C, the weight losses of the catalysts were very small.

For the catalysts with different reductant contents, it is clear that the decomposition and redox reaction of nitrates and citric acid took place in a low rate at low CA/N (0.15–0.3). With the increase of CA/N, the intensity of the exothermic peak increased, indicating that the combustion process occurred more severely. At the same time, the weight loss in the temperature region of 180–250 °C increased with increasing CA/N. It needs to be noted that the weight losses in 0.35RuCo and 0.4RuCo are much smaller than that in 0.3RuCo. This is because an excessive amount of citric acid might result in obvious carbon deposition over the catalysts. The deposition of carbon species could decrease the weight loss of the catalysts.

3.2 Physical and chemical properties of Ru promoted catalysts synthesized by the autocombustion method

3.2.1 Crystal phase analysis of the as-synthesized catalysts. The XRD patterns of Ru promoted Co/SiO_2 catalysts prepared by different methods are presented in Fig. 3a. The XRD patterns of Co and Ru monometal catalysts were also measured and the results were shown in Fig. 3b and c, respectively. It can be seen that the catalyst prepared by the Ru promoted autocombustion method (0.3RuCo) exhibited weak peaks for metallic Co and SiO_2. No diffraction peaks for cobalt oxides were identified in this catalyst. This finding indicated that most of the cobalt oxides were reduced to metallic Co and the formed Co was well dispersed. For Ru promoted catalysts prepared by air combustion–reduction (0.3RuCo$_{\text{air-reduction}}$) and conventional (RuCo$_N$) methods, both SiO_2 and metallic Co crystals were identified, but the intensity of Co crystalline peaks was much higher than that of the autocombustion catalyst. It can be concluded that the catalysts prepared by the

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

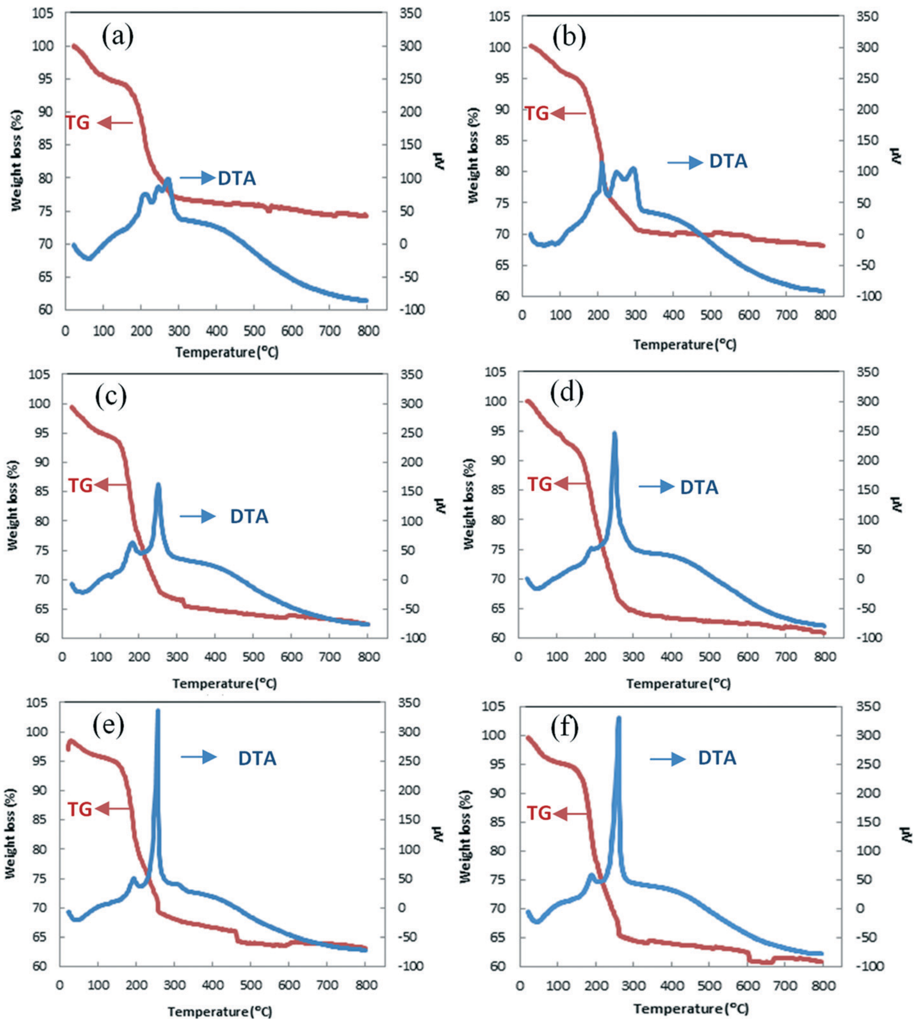

Fig. 2 TG/DTA curves of Ru-promoted Co catalysts with different CA/N values: (a) 0.15RuCo, (b) 0.2RuCo, (c) 0.25RuCo, (d) 0.3RuCo, (e) 0.35RuCo and (f) 0.4RuCo.

autocombustion method exhibited a higher dispersion of cobalt than those prepared by the air combustion–reduction and conventional methods.

In the case of the cobalt catalyst (0.3Co, Fig. 3b) prepared by the autocombustion method without Ru promotion, weak diffraction peaks for metallic cobalt crystalline were identified but the peak intensity of Co crystalline in 0.3Co is weaker than that in 0.3RuCo. Furthermore, CoO crystalline was also observed in the 0.3Co catalyst. These results indicated that only part of cobalt was reduced at a low reduction content (CA/N = 0.3) without ruthenium promotion. Therefore, ruthenium played an important role in the reduction of cobalt during the autocombustion process. No obvious diffraction peaks except for SiO_2 were found in the 0.3Ru catalyst. This result was probably due to the low content and well dispersion of Ru in the catalyst.

The effect of CA/N on the reduction and dispersion of cobalt was also studied by XRD, and the results are presented in Fig. 4 and Table 1. The narrow and intense diffraction peaks of 0.15RuCo are indexed to the CoO phase, showing that the major phase of this catalyst is CoO. It meant that the amount of citric acid was not enough to reduce Co_3O_4 completely and some CoO was left. With the increase of CA/N in the precursors, the diffraction peaks of CoO gradually decreased while the diffraction peaks of metallic Co became stronger. When CA/N increased to 0.3, pure metallic Co was obtained. However, further increasing CA/N to 0.4, small and board peaks of metallic Co were detected. This result indicated that the metallic Co sites were relative small and well-dispersed at a high reductant content.

During the autocombustion process, citric acid was decomposed into a large amount of gases such as H_2, H_2O, CO, CH_4 and CO_2, which could reduce the cobalt oxides to metallic Co.[23–25] With the increase of the citric acid content, more H_2, CO and CH_4 were formed, and thus more cobalt oxides were reduced to metallic Co. In our previous work,[15] the Co/SiO_2 catalyst was synthesized by an autocombustion method using citric acid as a reductant and burnt in argon, but the highest activity was achieved at a very high reductant content (CA/N = 1). In this work, a small amount of reductant

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

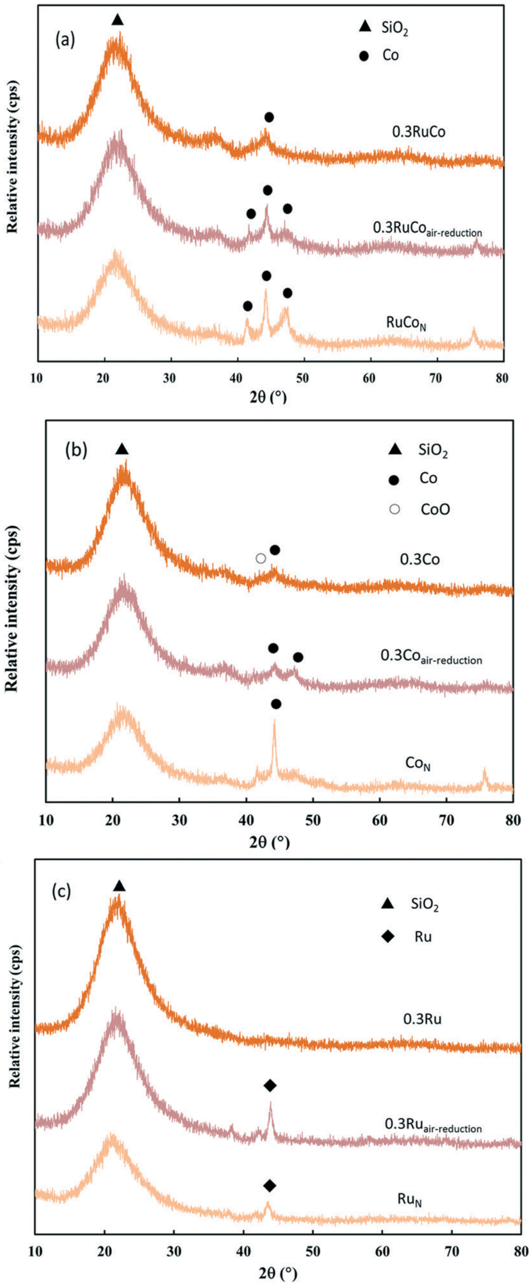

Fig. 3 X-ray diffraction patterns of the catalysts prepared by different methods (a: Ru promoted Co catalysts, b: Co catalysts, c: Ru catalysts).

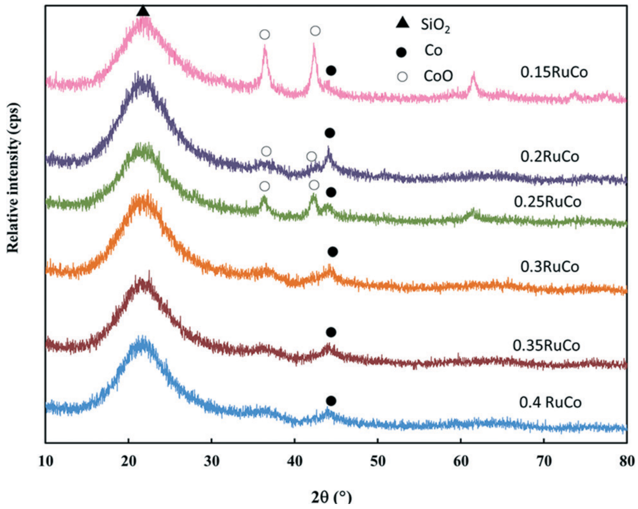

Fig. 4 The X-ray diffraction patterns of the as-synthesized catalysts with different contents of the reductant.

(CA/N = 0.3) could reduce the cobalt oxides completely. This result further proved that the adding of Ru promoted the reduction of cobalt. In addition, Ru also acted as a structural promoter to increase the dispersion of cobalt particles and decrease the average cobalt cluster sizes.[8,25]

3.2.2 Pore structure and elemental composition analysis. The pore structure parameters of the as-synthesized catalysts are also shown in Table 1. The BET surface area of the support silica (Q-50) was 79 $m^2 g^{-1}$, whereas the surface area of the as-synthesized catalyst 0.3RuCo was 90 $m^2 g^{-1}$. The increase of BET surface area after autocombustion was mainly derived from some Co nanoparticles loaded in the pores of the support. With the increase of reductant content, the BET surface area of the as-synthesized catalyst first increased, reached a maximum at 0.3RuCo, and then decreased. This is because a higher amount of the reductant led to smaller Co particle sizes, which could improve the BET surface area. However, an excessive amount of the reductant could result in the oversupply of the carbonic residues, and cause the decrease of the surface areas. For the 0.4RuCo catalyst, although it had the smallest Co crystalline size, its surface area was limited to 74 $m^2 g^{-1}$ due to the accumulation of excessive carbonic residues.

The metal contents of the catalysts prepared by autocombustion and conventional impregnation methods were measured by scanning electron microscopy with EDS, and the results are collected in Table 1. The contents of Ru and Co prepared by the autocombustion method are close to the desired values but the content of Co in the conventionally prepared catalyst is much higher, which might be attributed to the fact that more Co was impregnated on the external surface of the catalysts.

3.2.3 Reduction properties of the as-synthesized catalysts. The reduction properties of Ru promoted Co/SiO_2 catalysts prepared by the autocombustion method were characterized by H_2 temperature programmed reduction (TPR). For comparison, TPR curves of the monometal catalysts and the catalysts prepared by the conventional impregnated method were also measured. The TPR results of different catalysts are shown in Fig. 5. The reduction of the calcined catalyst Co_N can be assigned to a two-step reduction of Co_3O_4 to CoO and then to metallic Co. The presence of Ru resulted in a decrease in the reduction temperature of cobalt in the calcined $RuCo_N$ catalyst. The reduction of RuO_2 to metallic Ru usually takes place at a lower temperature than the reduction of Co_3O_4.[26–28] It did not exhibit a separate peak in the calcined $RuCo_N$ catalyst and was probably overlapped with the first reduction peak (180 °C) of Co_3O_4. The peak at 250 °C is

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

Table 1 Physical and chemical parameters of the catalysts

					EDS (wt%)	
Catalysts	Surface areas[a] (m^2 g^{-1})	Pore volume[a] (cm^3 g^{-1})	Pore diameter[a] (nm)	Crystallite size[b] (nm)	Co	Ru
0.15RuCo	80	0.68	21	11.3[c]	11.0	1.2
0.2RuCo	79	0.91	20	10.0	9.9	0.7
0.25RuCo	77	1.32	21	9.1	9.3	0.7
0.3RuCo	90	1.19	37	6.7	10.6	1.3
0.35RuCo	81	0.95	32	6.0	10.3	1.0
0.4RuCo	74	1.05	21	5.0	10.2	1.3
$RuCo_N$	74	1.08	21	15.5	12.1	0.9
Co_N	83	0.70	21	13.7	12.8	—

[a] Determined by the N_2 adsorption method. [b] Calculated by the Scherrer formula, using the peak at $2\theta = 44.05°$. [c] CoO crystalline size.

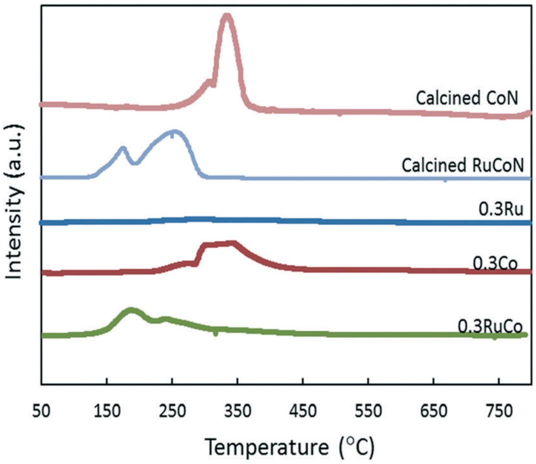

Fig. 5 TPR profiles of the catalysts prepared by different methods.

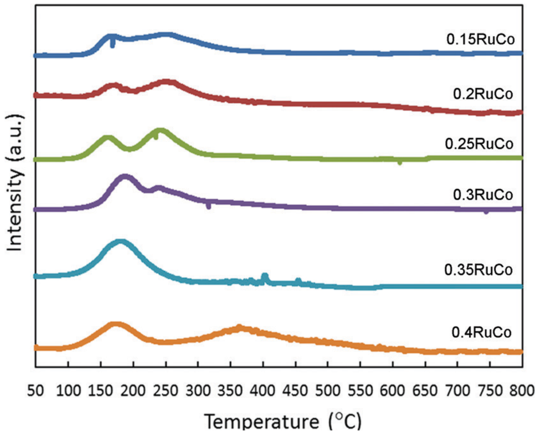

Fig. 6 TPR profiles of the catalysts with different reductant contents.

due to the reduction of Co_3O_4, which is promoted by Ru *via* hydrogen spillover.[29] For the catalysts prepared by the autocombustion method, there were nearly no reduction peaks in 0.3Ru. This result was probably attributed to the fact that the amount of Ru was very low (1 wt%) and most of the Ru was reduced during the autocombustion process. However, for the monometal catalyst 0.3Co, a relative high reduction temperature and a large amount of H_2 consumption are observed. This phenomenon suggested that the reduction of cobalt was more difficult and most of the cobalt was not reduced in 0.3Co. In the case of 0.3RuCo, the reduction temperature of cobalt was much lower and the H_2 consumption was much smaller than those of $RuCo_N$ and 0.3Co, demonstrating that most of the cobalt in 0.3RuCo was reduced during the autocombustion process. These results confirmed that Ru promoted the cobalt reduction during the autocombustion process.

TPR profiles of Ru promoted Co catalysts with different reductant contents are compared in Fig. 6. With the increase of reductant content, the peak for cobalt reduction (250 °C) decreased gradually and even disappeared at the CA/N ratio of 0.35. This result indicated that the reduction level of cobalt increased with the reductant content. However, an excessive amount of the reductant could result in severe residual carbon species in the catalyst. The broad peak at about 350–450 °C in the 0.4RuCo catalyst was assigned to the hydrogenation of residual amorphous carbon.

3.3 FTS performance of Ru promoted catalysts prepared by the autocombustion method

3.3.1 Effect of Ru promotion on the FTS performance of the catalysts. The FTS catalytic activities of the catalysts prepared by different methods were measured in a slurry bed reactor under the reaction conditions of 240 °C, 1.0 MPa and $H_2/CO = 2$. The activity curves and product selectivities are shown in Fig. 7 and Table 2. In this work, the reaction time is five hours and the measured activities were the initial activities. Generally, the initial activity may not correlate well with the steady-state activity. Fortunately, the initial activities of the catalysts are relative stable as shown in Fig. 7, so we can make the correlation between the structures and performance of the catalysts.

The FTS activities of monometal catalysts prepared by the autocombustion method are very low. The CO conversions of 0.3Co and 0.3Ru were only 0.8 and 1.7%, respectively. The low activity of 0.3Co is mainly due to most of the cobalt not being reduced during the autocombustion (Fig. 3 and 5). Although most of Ru was reduced in the 0.3Ru catalyst, the small loading amount and the high dispersion of Ru might

This journal is © The Royal Society of Chemistry 2014

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

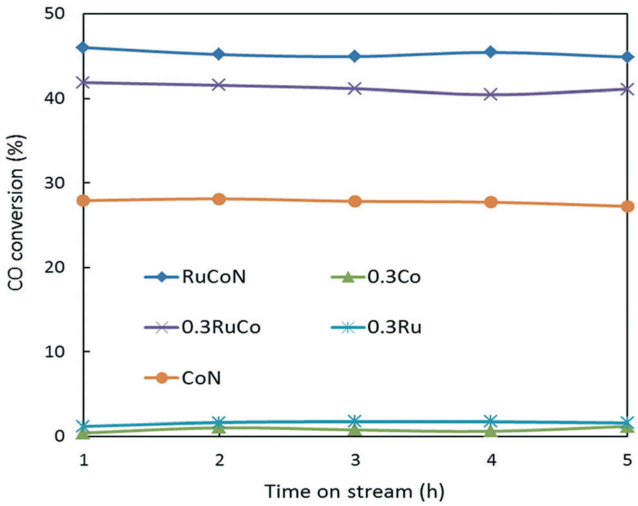

Fig. 7 Activity curves of the catalysts prepared by different methods (FTS reaction conditions: $H_2/CO = 2$, 240 °C, 1 MPa, *W*/*F* (CO, H_2 and 3% Ar) = 10 gh mol^{-1}).

Table 2 The FTS[a] performance of the catalysts prepared by different methods

Catalysts	Conversion of CO (%)	Selectivity (%)			
		CO_2	CH_4	C_{5+}	α
0.3RuCo	41.4	3.5	21.1	59.8	0.83
0.3Co	0.8	—	—	—	—
0.3Ru	1.7	—	—	—	—
$0.3RuCo_{air\text{-}reduction}$	60.4	8.5	21.1	64.1	0.82
$0.3Co_{air\text{-}reduction}$	26.5	4.1	14.4	68.3	0.81
$RuCo_N$	45.1	3.4	19.7	60.6	0.77
Co_N	27.7	3.0	25.4	50.4	0.76
Ru_N	8.0	—	—	—	—

[a] The reactions were carried out under the conditions of $H_2/CO = 2$, 240 °C, 1 MPa, *W*/*F* (CO, H_2 and 3% Ar) = 10 gh mol^{-1}, and reaction time of 5 h.

result in the low activity (Fig. 3 and 5). The Ru promoted Co catalyst prepared by the autocombustion method (0.3RuCo) exhibited a high FTS activity with the CO conversion of 41.1%. Furthermore, there was no obvious activity loss in the five hours of reaction time on stream, indicating a high stability of this catalyst (Fig. 7). It is believed that the promotion of Ru on the reduction and dispersion of Co (Table 2 and Fig. 5) played important roles in the high activity of 0.3RuCo. Ru itself in the 0.3RuCo catalyst may also contribute significantly to the high FTS activity by improving the nature of Co as an effective promoter, as demonstrated by other authors.[7–10]

The improvements in the FTS activity by Ru were also found for the catalysts prepared by air combustion–reduction ($0.3RuCo_{air\text{-}reduction}$) and conventional impregnated ($RuCo_N$) methods. It is worth noting that the CO conversion and hydrocarbon selectivity of 0.3RuCo are similar to those of $RuCo_N$. It can be concluded that the Ru promoted catalyst prepared by the autocombustion method may not undergo the complex and high energy consumption reduction process, and achieved the similar activity and selectivity to the catalyst prepared by the conventional method.

It needs to be noted that the chain growth factors (alpha value) of the catalysts prepared by the autocombustion method are in the region of 0.81–0.83, which is much smaller than the traditional cobalt catalysts (about 0.88).[30,31] There are two possible reasons for these results. One is that the cobalt crystalline sizes prepared by the autocombustion method were much smaller and the finely dispersed metallic crystallines were not suitable for carbon chain growth reaction. The other is that the relative high reaction temperature (240 °C) resulted in more methane and less long chain hydrocarbon formation.

3.3.2 Effect of citric acid contents on the FTS performance. FTS catalytic activities and selectivities of Ru-promoted catalysts with different CA/N values are presented in Fig. 8 and Table 3. All of the catalysts prepared by the autocombustion method exhibited highly stable initial activities for the FTS as shown in Fig. 8. It is clear that the 0.15RuCo catalyst exhibited a limited CO conversion as low as 21.4%, which is mainly restricted by its unreduced CoO (as shown in Fig. 4 and Table 1). With the increase of CA/N, the content of reduced cobalt increased and the CO conversion generally increased but the oversupplied of CA (0.4RuCo) resulted in the decrease of CO conversion. The small sizes of cobalt crystallines and a lot of carbonic residues accumulated on their surfaces resulted in the low CO conversion. For the 0.4RuCo catalyst, the methane selectivity was high, which may be also due to the small sizes of cobalt crystallines. The finely dispersed metallic crystallines are not suitable for carbon chain growth but enhance the formation of methane.[15]

3.3.3 Effect of reductant types on the FTS performance. In this work, Ru promoted catalysts with different types of organic reductants were also prepared and tested for the FTS performance. For all of the catalysts, the molar ratio of the reductant to nitrates is fixed at 0.3. The FTS activities and selectivities of these catalysts are listed in Table 4. It can be found that the organic reductant types showed a remarkable

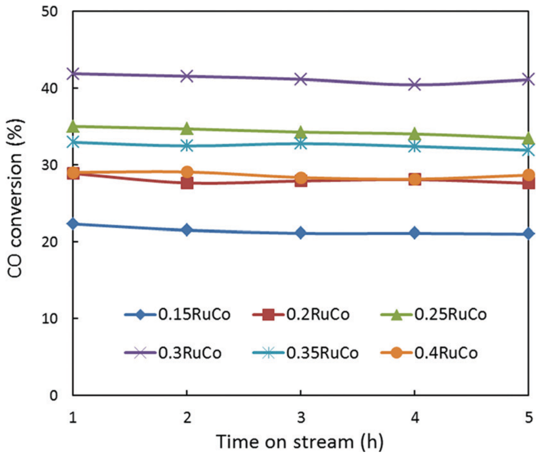

Fig. 8 Activity curves of the catalysts with different reductant contents (FTS reaction conditions: $H_2/CO = 2$, 240 °C, 1 MPa, *W*/*F* (CO, H_2 and 3% Ar) = 10 gh mol^{-1}).

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

Table 3 The FTS[a] performance of the catalysts with different contents of reductant

Catalysts	Conversion of CO (%)	Selectivity (%) CO_2	CH_4	C_{5+}	α
0.15RuCo	21.4	2.8	14.1	72.4	0.89
0.2RuCo	28.1	2.8	17.1	66.6	0.87
0.25RuCo	34.1	2.9	17.3	65.7	0.87
0.3RuCo	41.4	3.5	20.5	59.8	0.83
0.35RuCo	32.7	3.3	20.1	58	0.77
0.4RuCo	28.7	3.2	23.0	57.4	0.77

[a] The reactions were carried out under the conditions of $H_2/CO = 2$, 240 °C, 1 MPa, W/F (CO, H_2 and 3% Ar) = 10 gh mol^{-1}, and reaction time of 5 h.

Table 4 The FTS[a] performance of the catalysts prepared using different organic reductants

Reductant	Conversion of CO (%)	Selectivity (%) CO_2	CH_4	C_{5+}	α
Formic acid	38.7	2.2	19.4	65.0	0.81
Oxalic acid	32.8	1.7	15.7	67.9	0.79
Citric acid	41.4	3.5	20.5	59.8	0.83

[a] The reactions were carried out under the conditions of $H_2/CO = 2$, 240 °C, 1 MPa, W/F (CO, H_2 and 3% Ar) = 10 gh mol^{-1}, and reaction time of 5 h.

influence on the FTS performance. When citric acid was used as the reductant, the maximum catalytic activity was achieved. The high activity might be due to the high amount of C, H, and O atoms in the citric acid molecule, which can release more reducing gases during the autocombustion and improve the reduction of the metals. The sequence of catalytic activity followed the order of citric acid > formic acid > oxalic acid. Although the catalyst prepared by oxalic acid showed the lowest activity, the lowest methane and highest C_{5+} selectivities were achieved in this catalyst.

4. Conclusion

Ru promoted cobalt catalysts with high reduction levels were successfully synthesized by the autocombustion method using citric acid as a reductant and nitrate ions as oxidants. The as-synthesized catalysts were used directly in the Fischer–Tropsch synthesis without further reduction. The effects of the ruthenium promoter, citric acid contents, and reductant types in the precursors on the catalyst structures and FTS performance were studied. It was found that the introduction of Ru (1 wt%) in the precursor notably improved the reduction and dispersion of Co during the autocombustion process. With the increase of the citric acid content, the metal reduction level increased and the Co crystalline size decreased but the catalyst exhibited the maximum activity at a moderate citric acid content (ratio of citric acid to metal was 0.3). An excessive amount of citric acid caused more residual carbon species, which covered part of the active sites and decrease the activity of the catalysts. Reductant types also had a remarkable influence on the FTS performance. The maximum catalytic activity was achieved when citric acid was used as the reductant. The Ru promoted cobalt catalysts prepared by the autocombustion method, which omits the complex and high energy consumption reduction process, can be used directly for high efficiency FTS and thus will be more promising in the future.

Acknowledgements

This work was supported by co-funding of the Thailand Research Fund (through the Royal Golden Jubilee Ph.D. Program) and Chulalongkorn University (grant no. PHD/0010/2553), the Higher Education Research Promotion and the National Research University Project of Thailand, the Office of the Higher Education Commission (EN 272 A), the Ratchadaphiseksomphot Endowment Fund (CU-CLUSTER-FUND), the Research Program on Materials for Future Energy and the Center of Excellence on Petrochemical and Materials Technology.

References

1 Q. Zhang, J. Kang and Y. Wang, *ChemCatChem*, 2010, **2**, 1030–1058.
2 R. Luque, A. Osa, J. M. Campelo, A. A. Romero, J. L. Valverdeb and P. Sanchezb, *Energy Environ. Sci.*, 2012, **5**, 5186–5202.
3 E. Iglesia, *Appl. Catal., A*, 1997, **161**, 59–78.
4 C. Ngamcharussrivichai, X. Liu, X. Li, T. Vitidsant and K. Fujimoto, *Fuel*, 2007, **86**, 50–59.
5 M. P. Anderssona, T. Bligaarda, A. Kustovb, K. E. Larsenc, J. Greeleya, T. Johannessenc, C. H. Christensenb and J. K. Nørskova, *J. Catal.*, 2006, **239**, 501–506.
6 S. Sun, N. Tsubaki and K. Fujimoto, *Appl. Catal., A*, 2000, **202**, 121–131.
7 N. Tsubaki, S. L. Sun and K. Fujimoto, *J. Catal.*, 2001, **199**, 236–246.
8 M. Trépaniera, A. Tavasolia, A. Dalaia and N. Abatzoglouc, *Appl. Catal., A*, 2009, **353**, 193–202.
9 S. A. Hosseini, A. Taeb and F. Feyzi, *Catal. Commun.*, 2005, **6**, 233–240.
10 N. Escalona, C. Medina, R. García and P. Reyes, *Catal. Today*, 2009, **143**, 76–79.
11 L. Shi, C. Y. Zeng, Y. Z. Jin, T. J. Wang and N. Tsubaki, *Catal. Sci. Technol.*, 2012, **2**, 2569–2577.
12 Z. Hua, Z. Cao, Y. Deng, Y. Jiang and S. Yang, *Mater. Chem. Phys.*, 2011, **126**, 542–545.
13 J. Chandradass, B. Jun and D. Bae, *J. Non-Cryst. Solids*, 2008, **354**, 3085–3087.
14 F. Li, K. Hu, J. Li, D. Zhang and G. Chen, *J. Nucl. Mater.*, 2002, **300**, 82–88.
15 L. Shi, K. Tao, T. Kawabata, T. Shimamura, X. J. Zhang and N. Tsubaki, *ACS Catal.*, 2011, **1**, 1225–1233.
16 W. Chen, F. Li and J. Yu, *Mater. Lett.*, 2006, **60**, 57–62.
17 M. Marins, K. Zupan and J. Mae, *J. Power Sources*, 2002, **106**, 178–188.

This journal is © The Royal Society of Chemistry 2014

Published on 19 May 2014. Downloaded by University of Notre Dame on 26/08/2014 11:14:43.

18 A. Chakroborty, A. Sharma, B. Maiti and H. Maiti, *Mater. Lett.*, 2002, **57**, 862–867.

19 S. Hosseini, H. R. Madaah and Z. A. Nemati, *J. Alloys Compd.*, 2007, **430**, 339–343.

20 T. Peng, X. Liu, K. Dai, J. Xiao and H. Song, *Mater. Res. Bull.*, 2006, **41**, 1638–1645.

21 G. Xu, H. Ma, M. Zhong, J. Zhou, Y. Yue and Z. He, *J. Magn. Magn. Mater.*, 2006, **301**, 383–388.

22 Z. Yue, W. Guo, J. Zhou and L. Li, *J. Magn. Magn. Mater.*, 2004, **270**, 216–223.

23 Y. Jiang, S. Yang, Z. Hua and H. Huang, *Angew. Chem., Int. Ed.*, 2009, **48**, 8529–8531.

24 J. G. Huang, H. R. Zhuang and W. Li, *Mater. Res. Bull.*, 2003, **38**, 149–159.

25 D. Bahadur, S. Rajakumar and A. Kumar, *J. Chem. Sci.*, 2006, **118**, 15–21.

26 T. Ahmad, M. Yadollah, K. Abbas Ali and M. Mohammad Ali, *Iran. J. Chem. Chem. Eng.*, 2005, **24**, 9–17.

27 J. Panpranot, J. Goodwin and A. Sayari, *Catal. Today*, 2002, 77, 269–284.

28 J. Sun, X. Li, A. Taguchi, T. Abe, W. Niu, P. Lu, Y. Yoneyama and N. Tsubaki, *ACS Catal.*, 2014, **4**, 1–8.

29 M. Kraum and M. Baerns, *Appl. Catal., A*, 1999, **186**, 189–200.

30 L. S. Yu, X. H. Liu, Y. Y. Fang, C. L. Wang and Y. H. Sun, *Fuel*, 2013, **112**, 483–488.

31 B. Ernst, S. Libs, P. Chaumette and A. Kiennemann, *Appl. Catal., A*, 1999, **186**, 145–168.

This journal is © The Royal Society of Chemistry 2014