Catal Lett (2009) 128:343–348
DOI 10.1007/s10562-008-9751-7

Zr- and Li-Modified Ru/Sio$_2$ Catalysts for Fischer–Tropsch Synthesis

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Received: 22 August 2008 / Accepted: 21 October 2008 / Published online: 21 November 2008

Abstract We have found that Zr- and Li-modified Ru/SiO$_2$ catalysts (Q-15) are extremely stable and can be used in FT synthesis to maintain the conversion rate of CO constant even after 33 h. Modification of Ru/SiO$_2$ by Zr (5 wt%) and Li (0.1 wt%) resulted in a remarkable increase in the stability of the catalyst. Taking into account surface acidity and reducibility, we assumed that this remarkable stability is due to the cooperative effects of Ru, Zr, Li, and the SiO$_2$ support.

Keywords Ru/SiO$_2$ · Zr–SiO$_2$ support · Fischer–Tropsch · Li effect

1 Introduction

Biomass has recently received increased attention as a potential source of renewable energy [1]. The biomass to liquid (BTL) process is one of the most promising methods for conversion of biomass (from remote and/or local areas) to sulfur-free transportation fuels [2]. The development of high-performance catalysts for Fischer–Tropsch (FT) synthesis is essential for small-scale BTL processes that use ca. 10 t/d of biomass resources; this scale is approximately 1/1,000 that of a gas to liquid (GTL) process. The industrial output of Ru is ca.1/2,000 that of CO. Hence, from the viewpoint of catalyst regeneration, Ru-based BTL processes appear to be advantageous.

Ru catalysts were initially found to be effective for "polymethylene synthesis," [3] and later, it was reported that typical FT products could be obtained by using both unsupported and supported Ru catalysts [4–7] under moderate reaction conditions (pressure: ca.1–20 bar; temperature: 473–523 K). As opposed to Fe, Ru catalysts are not negatively affected by water, which is a byproduct in the FT synthesis [7–10], and hence, inactive ruthenium oxides are not formed. However, the exact mechanism of the Ru-catalyzed FT reaction appears to be similar to that of the co-catalyzed reaction [7].

Mn-modified Ru catalysts have attracted considerable attention over the last few decades because of their possible importance in the FT synthesis [12]. In our previous study, we found that Mn-containing γ-Al$_2$O$_3$ enhances the removal of chlorine from RuCl$_3$ to yield metallic Ru with a moderate particle size; Ru thus formed would be an active catalyst for the FT reaction [4]. On the contrary, even after addition of Mn, Ru/SiO$_2$ was found to be less effective than Ru/γ-Al$_2$O$_3$ for the FT reaction. Though unlike γ-Al$_2$O$_3$, SiO$_2$ is basic in nature [13], it has been reported to become slightly acidic after modification by zirconia [14]. Therefore, we explored the effect of zirconia addition on the FT activity of the Ru/SiO$_2$ catalyst. In this paper, we report the behavior of Zr-modified Ru/SiO$_2$ in the FT reaction.

2 Experimental

Mesoporous silicas such as Q-15 and Q-6 were provided by Fuji Silysia Co. Ltd. The Ru/SiO$_2$ catalyst used in this study was prepared by impregnation of SiO$_2$ granules with RuCl$_3$, followed by drying at 373 K and calcination for 5 h at 573 K. Ru–Zr/SiO$_2$ and Ru–Zr–Li/SiO$_2$ were prepared in the following manner: First, SiO$_2$ was impregnated with

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zirconyl nitrate in water, dried at 373 K, and calcined for 6 h at 773 K to obtain Zr/SiO_2. Then, to obtain $Ru–Zr/SiO_2$, Zr/SiO_2 was impregnated with $RuCl_3$ in water; the resulting granules were dried at 373 K and calcined for 5 h at 573 K. To obtain $Ru–Li–Zr/SiO_2$, Zr/SiO_2 was impregnated with lithium nitrate in water, and these impregnated granules were dried at 373 K and calcined for 5 h at 773 K to afford $Zr–Li/SiO_2$. This was impregnated with $RuCl_3$, dried at 373 K, and calcined for 5 h at 573 K to yield $Ru–Li–Zr/SiO_2$.

X-ray diffraction (XRD) patterns of the fresh catalysts were recorded on a Philips 1850 diffractometer (operated at 40 kV and 40 mA) using Cu radiation. The reducibility of the prepared $Ru–Zr/SiO_2$ catalysts was studied by H_2-temperature-programmed reduction (TPR). Before the analysis, 50 mg of the sample was placed in a quartz tube and purged with He at 473 K for 1 h in order to remove impurities from the catalyst surface. The sample was cooled to room temperature in flowing He; then, TPR was carried out using a 3% H_2/He (v/v) mixture (flow rate: of 30 mL/min) at a heating rate of 5 K min^{-1} from room temperature to 900 K, and the H_2 consumption was recorded with a thermal conductivity detector (TCD). NH_3 temperature-programmed desorption (TPD) experiments were carried out for $Ru–Zr/SiO_2$ and $Ru–Li–Zr/SiO_2$ on a special NH_3-TPD apparatus (BELCAT, Nippon Bell), which was connected to a Q-Mass analyzer (Pfeiffer Vacuum, Omnistar GCD301) for measuring the solid acidity of the supports and catalysts. After pretreatment under He flow at 773 K for 60 min, adsorption of NH_3 at 373 K for 90 min, and desorption of the weakly adsorbed NH_3 under He flow at 373 K for 30 min, TPD profiles were recorded under He flow between 373 K and 1,073 K (heating rate: 10 K min^{-1}).

The catalyst (0.5 g) was introduced into a 100 cm^3 autoclave-type reactor and pretreated by reduction with 2 MPa of H_2 at 443 K for 5 h. After the reduction, 20 cm^3 of hexadecane was introduced under an inert atmosphere, and a CO/H_2 mixture containing 12.6% N_2 was bubbled into the catalyst slurry with vigorous stirring. The reaction conditions were as follows: $H_2/CO = 2/1$, $T = 493$ K, $P = 2.0$ MPa. Gaseous analyses were performed by online gas chromatography (GC) every 3 h, and the CO conversion and C5+ selectivity were estimated. The liquid product formed in the reaction was collected and analyzed by offline flame ionization gas chromatography (FID-GC). The online gas chromatograph was equipped with Porapak Q and MS 5A columns for the TCD detector and a DB-1 capillary column for the FID detector for the analysis of C1–C10 hydrocarbons. In order to estimate the chain growth probability (α), the levels of C10+ hydrocarbons in the slurry were determined separately by offline FID-GC using an SE-30 column. The CO conversion and C5+ selectivity were estimated as follows:

$$\text{CO conv.} = \left(1 - \left([\text{CO}]_{\text{out}}/[\text{N}_2]_{\text{out}}\right)/\left([\text{CO}]_{\text{in}}/[\text{N}_2]_{\text{in}}\right)\right) \times 100$$

$$\text{C5} + \text{sel.} = 100 - -((\Sigma[\text{Cn}] * \text{n}\ (\text{n} = 1, 4))/([\text{CO}]_{\text{in}} \times ([\text{CO conversion}]/100))) \times 100,$$

where $[CO]_{in}$, $[CO]_{out}$, $[N_2]_{in}$, and $[N_2]_{out}$ denote the inlet and outlet gas compositions of CO and N_2, respectively. Cn denotes the concentration of hydrocarbons containing “n” carbon atoms. For example, C1 denotes the amount of CH_4. The value of C5+ selectivity obtained by online GC was in accordance with that obtained in the analysis of the liquid product formed in the reaction.

3 Results and Discussion

As shown in Fig. 1, the XRD patterns of the fresh Ru/SiO_2 and $RuZr/SiO_2$ catalysts after hydrogenation were similar to the diffraction pattern of metallic Ru at $2\theta = 44°$, while diffractions peaks corresponding to ruthenium and zirconia oxide were not detected; this showed that in addition to metallic Ru, both ZrO_2 and SiO_2 particles are highly dispersed.

The general reduction of ruthenium oxide can be written as $RuO_x + xH_2 \rightarrow Ru + xH_2O$, where x indicates different oxides. Figure 2 reports the results of the TPR analysis on 5% Ru supported on Zr-modified silica. The results indicate that the well-defined peak at $T = 468$ K is attributable to the first reduction of RuO_2 (x = 2) [15],

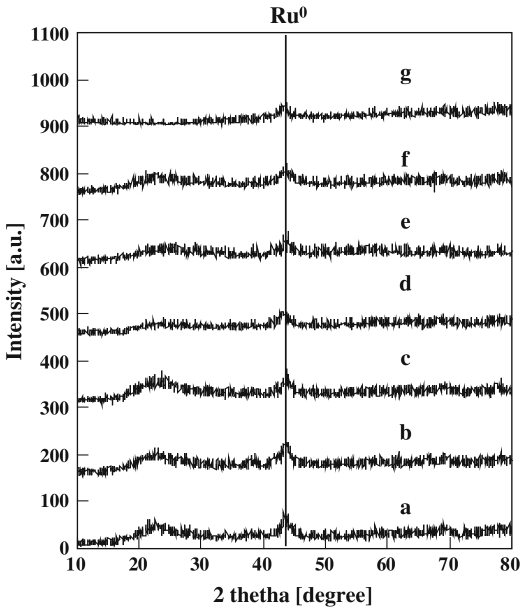

Fig. 1 XRD patterns of **a** Ru/Q-15, **b** Ru–2.5Zr/Q-15, **c** Ru–5Zr/Q-15, **d** Ru–10Zr/Q-15, **e** Ru–20Zr/Q-15, **f** Ru–0.1Li–5Zr/Q15 and **g** Ru–0.1Ca–5Zr/Q-15 after H_2 pretreatment at 473 K

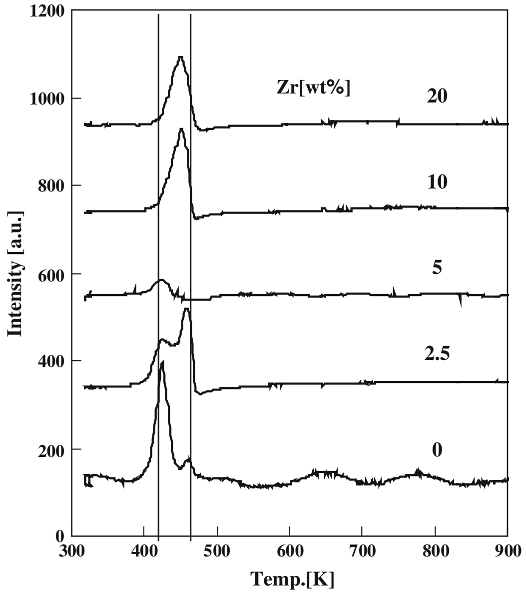

Fig. 2 TPR plots of 5 wt%Ru–xwt%Zr/SiO2(Q-15)

while the second peak at $T = 422$ K is due to the reduction of the well-dispersed RuO_x species [16]. The small broad peak between 600 K and 800 K is attributed to the reduction of SiO_2 supports [17]. The intensity of the peak at 468 K decreased and that of the peak at 422 K increased with an increase in the Zr content; however, the peak obtained for 5 wt% Zr remained unaffected. These results indicate that the concentration of the surface RuO_2 species increases after modification by Zr. As shown in Fig. 3 (Ru–Li/Q-15), the addition of Li brought about a decrease in the intensity of the peak at 422 K and an increase in the intensity of the broad peak at 468 K. In the case of Ru–Li–Zr/Q-15, the peak at 468 K appeared to be more intense than that at 422 K, whereas the reverse trend was observed for Ru–Li–Zr/Q-50.

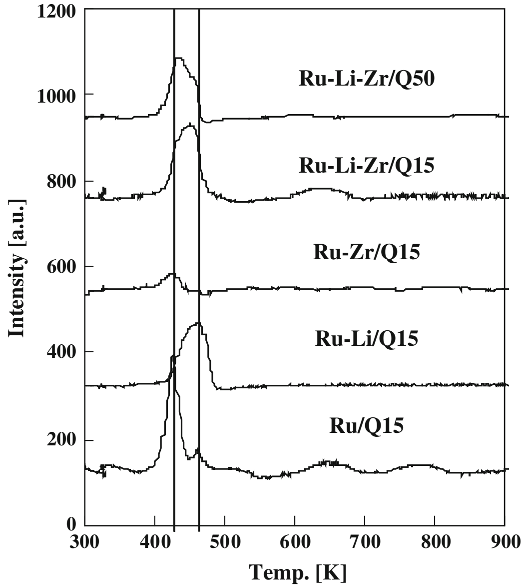

Fig. 3 TPR plots of Zr- and Li-modified Ru/SiO_2 catalysts

The NH_3-TPD profiles of Zr-modified SiO_2 catalysts are shown in Fig. 4a. Ru/SiO_2 (a) showed a desorption peak at approximately 420 K and a weak peak at 475 K. The intensity of the peak at 420 K increased with the Zr content, and concomitantly, the peak at 474 K became more intense and appeared as a large, broad peak made of several small peaks. As shown in Fig. 4b, the amount of NH_3 adsorbed on the catalyst surface between 350 K and 650 K is linearly correlated with the Zr content in Ru/Q-15. This possibly indicates that the addition of Zr to SiO_2 enhances the acidic nature of Ru/Q-15 [6].

The effects of Zr addition to Ru/SiO_2 (Q-15) on the FT reaction were studied using the initial activity observed after 3 h; these results are summarized in Table 1. The CO conversion initially increased with an increase in the Zr content from 2.5 wt% to 5.0 wt%, and then decreased with a further increase in the Zr content. The C5+ selectivities were almost constant for 0–5 wt% Zr, but gradually decreased when the Zr content exceeded 5 wt%. On the other hand, the CH_4 selectivities remained constant upto 5 wt% Zr, and subsequently showed a gradual increase with the Zr concentration. α remained unchanged for the entire range of Zr concentrations in this study. Figure 5 shows the effect of time-on-stream on the catalytic activity of Zr-modified Ru/SiO_2(Q-15). The activities were found to decrease as the reaction proceeded. At 5 wt% Zr, the CO conversion was 65.4% initially, but it rapidly decreased to 25.2% after 33 h. Similarly, for Zr contents of 2.5, 7.0, and 10 wt%, the CO conversion reduced from 47.7% to 27.8%, from 53.8% to 40.2%, and from 35.2% to 27.6%, respectively. At 5 wt% Zr, the second NH_3-TPD peak at 474 K was not observed, as can be seen from Fig. 4a; furthermore, the TPR peak of Ru was diminished (Fig. 2). Thus, SiO_2 modified by 5 wt% Zr appears to have a specific surface acidity, because of which it enhances the catalytic activity, although the amount of NH_3 absorbed between 350 K and 650 K increases linearly with the Zr content (Fig. 4b).

In order to improve the stability of the Ru–Zr/SiO_2 (Q-15) catalyst, effects of addition of alkali and alkali-earth metals were explored. As shown in Table 2, addition of these metals resulted in a decrease in the initial CO conversion, although other parameters such as C5+ and CH_4 selectivities and α were almost constant. Then, the effect of time-on-stream on the catalysts was investigated for a reaction time of 33 h. The addition of Li (0.1 wt%) was found to result in an improvement in the catalyst stability. As shown in Fig. 6, the CO conversion observed for Ru–Li–Zr/SiO_2 (Q-15) remained constant at ca.48% after

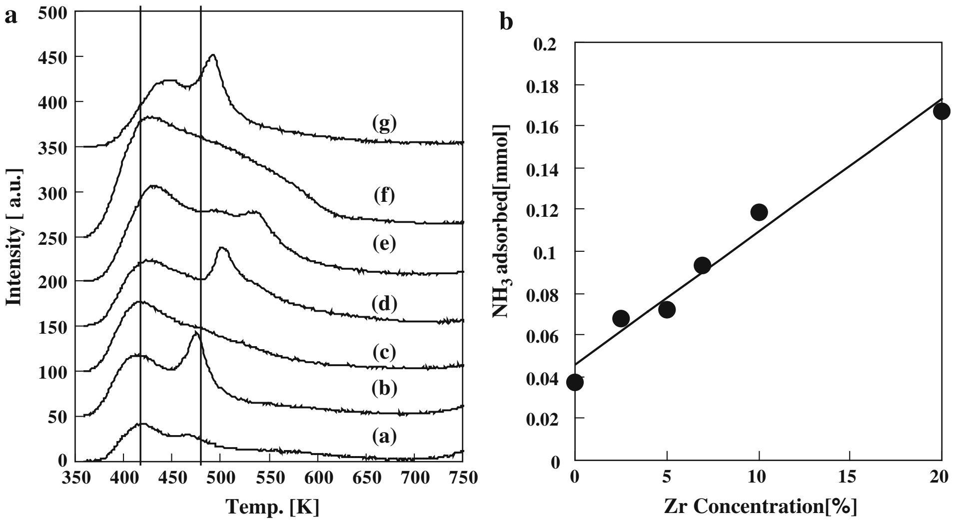

Fig. 4 NH_3-TPD profiles of Zr- and Li-modified 5 wt%Ru/SiO_2 (Q-15) catalysts. **a**: NH3-TPD data (Zr (wt%)): (a) 0, (b) 2.5, (c) 5, (d) 7, (e) 10, (f) 20, (g) 5 + 0.1 wt% Li. **b** Correlation between Zr concentration and total amount of NH_3 adsorbed at 350–650 K

Table 1 Effect of Zr additive on initial FT activity[a]

Zr[b] (wt%)	CO Conv. (%)	C5+ Sel.[c] (%)	CH_4 Sel.[c] (%)	STY C5-g/kg-cat./h	α[d]
0	47.6	91.0	1.64	33.4	0.88
2.5	53.6	95.9	0.92	39.6	0.86
5.0	62.5	93.2	1.26	44.9	0.85
7.0	51.4	85.3	3.64	33.8	0.86
10	43.5	90.3	2.42	30.2	0.88
20	39.3	83.8	8.16	28.0	0.85

[a] Conditions: 5 wt%Ru/Zr/SiO_2 (Q-15), 0.5 g; hexadecane, 20 mL, $T = 493$ K, 3 h, P = 2.0 MPa, $H_2/CO/N_2 = 60/30/10$. Pretreatment: calcination at 573 K for 5 h, followed by reduction at 443 K and 2 MPa for 4 h. [b] Zirconium nitrate was used. [c] C5 + Selectivity = 100−sum of (C1–C4) selectivities. [d] Chain growth probability

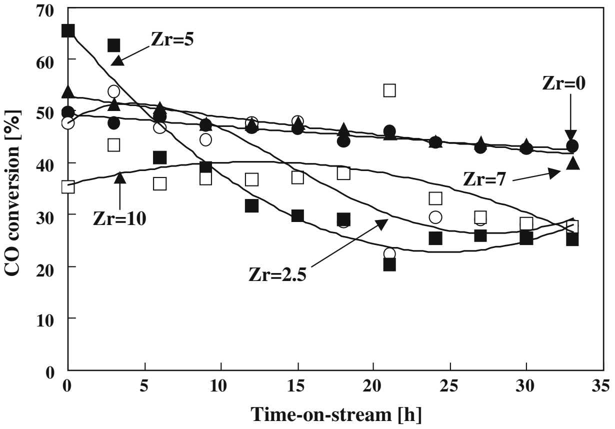

Fig. 5 Effect of Zr concentration on activity in FT reaction. Conditions: catalyst, 0.5 g; hexadecane, 20 mL; N_2, 12.6 (vol%); $H_2/CO = 2/1$; total pressure, 2 MPa; temperature, 493 K, and W/F = 6.84 g-cat. h/mol

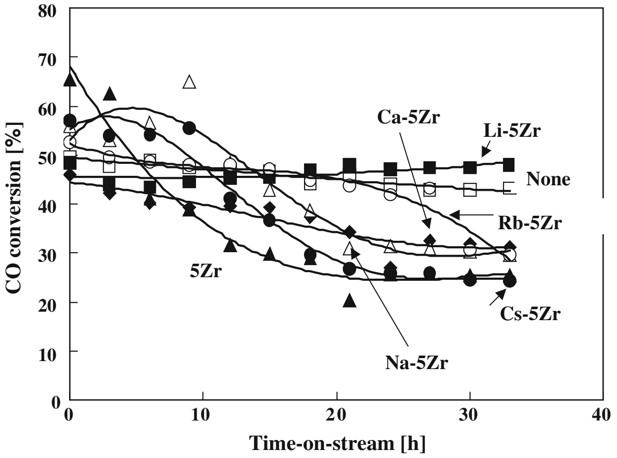

Fig. 6 Effect of second additives on FT activity. Conditions are identical to those shown in Fig. 5

33 h. Activity tests performed until 150 h revealed a decrease in CO conversion to within 3%. On the contrary, in the case of the unstable Ru/SiO_2 catalyst, the CO conversion decreased to less than 3% after 33 h. The stability of this catalyst could not be improved even after the addition of other alkali metal additives such as Na, Ca, Cs, and Rb. Figure 7 summarizes the observation results of the Li-modified catalysts. The CO conversion rate after 33 h

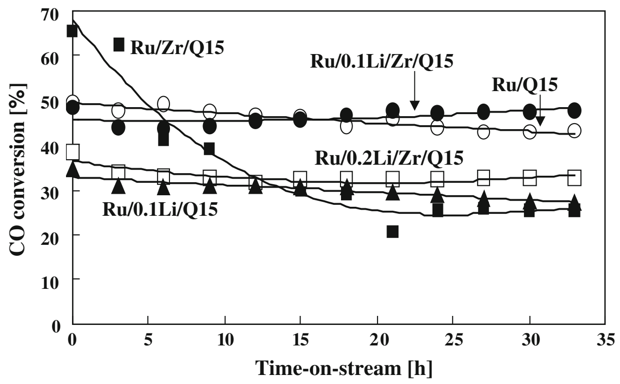

Fig. 7 Comparison of Zr- and Li-modified Ru/SiO_2 catalysts. Conditions are identical to those shown in Fig. 5

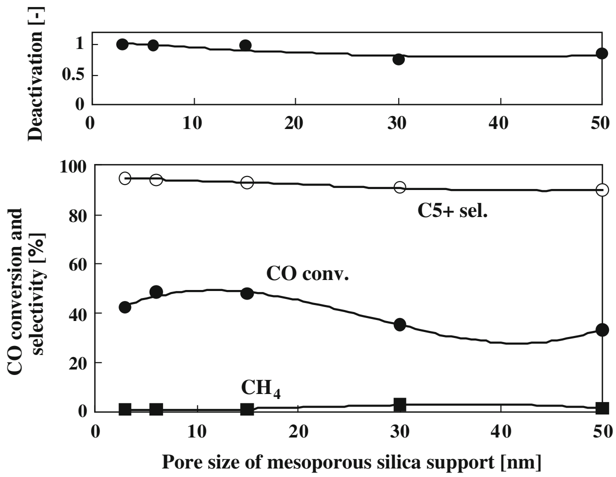

Fig. 8 Effect of meso-pore size of SiO_2 support. Catalyst: 5 wt%Ru–5 wt%Zr–0.1 wt%Li/silica. Deactivation denotes the ratio of initial (3 h) and final (33 h) CO conversion. Conditions are identical to those shown in Fig. 5

was in the order: Ru–Li(0.1)–Zr/SiO_2 > Ru/SiO_2 > Ru–Li(0.2)–Zr/SiO_2 > Ru–Li(0.1)/SiO_2 > Ru–Zr/SiO_2. The catalytic activity and stability of Ru–Li(0.1)–Zr/SiO_2 (1) were comparable to those of CO–Ir/SiO_2 (2). The C5+ selectivity of (1) was higher than that of (2), while the CH_4 selectivity of (1) was lower than that of (2) [18] [See Table 2 in ref.[18]. The amount of NH_3 adsorbed on Ru–Li(0.1)–Zr/SiO_2 was approximately equal to that of NH_3 adsorbed on Ru–Zr/SiO_2 (Fig. 4g); the TPR results obtained for Ru–Li(0.1)–Zr/SiO_2 were similar to those obtained for Ru–Li(0.1)/SiO_2 (Fig. 3). Thus, the synergistic effect of Zr and Li appears to play an important role in improving the catalyst stability. Figure 8 shows the effects of the pore size of SiO_2 on the activity of the catalyst in the FT reaction. The initial CO conversion increased with an increase in the pore size from 3 nm to 15 nm, and then decreased with when the pore size was further increased to 50 nm. The C5+ selectivities gradually decreased in the pore size range of 3–50 nm, while the CH_4 selectivity gradually increased. The deactivation factor, which was estimated from the ratio of CO conversions after 3 h and 33 h, was constant in the pore size range of 3–15 nm, but decreased with a further increase in the pore size. Thus, among all the supports analyzed, Q-6 and Q-15 appeared to be the most effective for FT reactions catalyzed by Ru–Zr–Li/SiO_2. The stability of the Ru–Mn/γ–Al_2O_3 catalyst could be associated with the particle size of metallic Ru and resistance to the formation of inactive ruthenium oxides [12]. Therefore, the stability of Ru–Li(0.1)–Zr/SiO_2 was also probably due to improvement in the stability of the active metallic Ru caused by the use of SiO_2 of suitable pore size (Q-6 and Q-15) and modification of the surface acidity by Li and Zr [19]. Further research on elucidation of the mechanism underlying the action of these catalysts and extension of catalyst life in progress.

4 Conclusion

In this study, Zr- and Li-modified Ru catalysts supported on SiO_2 (Q-15) have been found to be more stable and

Table 2 Effect of additives on initial FT activity of Ru–Zr/SiO_2^a

Additive (wt%)[b]	CO Conv. (%)	C5+ Sel.[c] %	CH_4 Sel (%)	STY C5-g/kg-cat./h	α[c]
0	62.5	93.2	1.26	44.9	0.85
Na(0.1)	53.2	89.2	2.42	33.2	0.88
Rb(0.1)	49.3	87.3	2.96	33.2	0.88
Cs(0.1)	53.8	87.0	2.86	36.1	0.87
Li(0.1)	43.9	89.9	1.68	30.4	0.88
Li(0.1)d	30.8	89.2	2.11	23.2	0.89
Li(0.2)	33.9	88.0	1.96	22.9	0.85
Ca(0.1)	42.2	88.6	2.54	28.8	0.87
La(0.1)	57.9	89.6	2.50	39.9	0.88

[a] Conditions: 5 wt%Ru/Zr/SiO_2 (Q-15), 0.5 g; hexadecane, 20 mL; $T = 493$ K; 3 h; $P = 2.0$ MPa; $H_2/CO/N_2 = 60/30/10$. Pretreatment: calcination at 573 K for 5 h, followed by reduction at 443 K and 2 MPa for 4 h. [b] Metal nitrate was used. [c] See Table 1. [d] Without Zr

effective than unmodified Ru/silica for the FT synthesis. The addition of Zr (5 wt%) and Li (0.1 wt%) afforded the most stable catalyst, the CO conversion of which was constant after 33 h. Taking both surface acid character and reducibility into account, it is assumed that the high stability of the catalyst is a result of the cooperative effects of Ru, Zr, Li, and the SiO_2 support.

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