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Effect of Calcination Temperature on the Activity and Cobalt Crystallite Size of Fischer–Tropsch Co–Ru–Zr/SiO_2 Catalyst

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Abstract A series of Co–Ru–Zr/SiO_2 catalysts were prepared by the co-impregnation method in order to understand the effects of calcination temperature on their activity and stability. The crystallite size of cobalt obtained from H_2 chemisorption decreased up to a calcination temperature of 300 °C and then increased to reach a reasonably constant value. The activity for CO hydrogenation also increased upto this temperature and then decreased to be stabilized finally at a value smaller than the optimum one. The turn-over frequency values are not significantly altered on the catalysts calcined above 220 °C. It was observed that in the presence of chlorine released during the decomposition of the zirconium oxychloride precursor, the dispersion of cobalt crystallites was altered due to the different environment of chlorine and water evolved during the reduction step.

Keywords Rutheniu · Zirconium oxychloride · SiO_2 · Cobalt · Fischer–Tropsch synthesis · Calcination temperature

1 Introduction

The recent drastic increase in the price of crude oil and the demand for clean alternative fuels is forcing researchers to concentrate on the Fischer–Tropsch synthesis (FTS) for the manufacture of synthetic fuels. Supported cobalt-based catalysts have been widely investigated for this purpose due to its high selectivity for long chain linear paraffin and low selectivity to CO_2. The nature of support influences the dispersion, crystallite size and reducibility of the prepared cobalt species, and thereby alters the catalytic activity [1–6]. Addition of promoters such as Ru, Pt and Re to Co/Al_2O_3 catalysts is reported to give higher activity than Co/Al_2O_3 alone, as the promoters increase the reducibility of cobalt oxides, which is otherwise limited by the metal-support interaction [7–14]. SiO_2 is found to be a better support than Al_2O_3 for a fixed bed FTS reaction in this context. The role of zirconium in decreasing the formation of cobalt silicate has already been established [15].

The pretreatment conditions used during the preparation of cobalt-based catalysts can have a great influence on the surface states of cobalt species, thus determining the catalytic properties. A number of studies have been reported highlighting the effect of pretreatment conditions on the activity and selectivity of the catalysts [15–20]. According to the reports of Goodwin Jr. et al. [16] and Calleja et al. [17], the calcination or reduction temperature has a negligible effect on the catalytic activity. However, Rathousky et al. [18, 19] and Lira et al. [20] have shown that the pretreatment conditions affect the performance of Co/Al_2O_3 and Co/SiO_2 catalysts. The severe sintering phenomena has been reported on Co/SiO_2 with the increase of oxidation and(or) reduction temperature above 500 °C that resulted in forming cobalt silicates [21], however, the temperature at which cobalt silicates formed depend on the cobalt concentration and the nature of support. The presence of chlorine and water, Gjervan et al. [22] have shown that chlorine can apparently inhibit the mobility of metal components and bimetallic entity formation. However the added

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water can increase the mobility of metal oxide resulting in enhancing the bimetallic entity formation and enlarging the crystallite size. Furthermore, the oxychlorination condition during calcination step is mainly responsible for the re-dispersion of metal components by forming a mobile intermediate such as MO_xCl_y [23]. Although the CO conversion and product distribution on FTS is mainly affected by the cobalt cluster size and reduction degree [24, 25], the cluster size above 6–8 nm has trivial effect on enhancing the intrinsic turn-over frequency (TOF) values [26]. In general, many researchers have reported that zirconium generally affects to prevent the strong metal-support interaction and eventually suppress the formation of inactive cobalt species such as cobalt aluminate and cobalt silicate with an enhancement of the reducibility of cobalt oxide [25–27]. In the case of catalysts prepared using the chloride salts such as zirconium oxychloride precursor, the chlorine released during calcination or reduction can influence on the dispersion and in turn on the crystallite size. This aspect has not been thoroughly investigated, with respect to the effect of pretreatment conditions, particularly in zirconia containing cobalt-based FTS catalysts. In the present investigation, an effort is made to elucidate the role of chlorine released during the catalyst preparation on the FTS activity and selectivity with Co–Ru–Zr/SiO_2 catalysts.

2 Experimental

2.1 Catalyst Preparation

Ru promoted and Zr containing cobalt catalysts over SiO_2 were prepared, according to a designed weight ratio of (Ru:Co:Zr:SiO_2 = 0.5:20:5:100), by adopting the co-impregnation method. Precalcined SiO_2 (Sigma–Aldrich (Davisil 645 silicagel), surface area of 300 m^2/g and particle size of 120–140 μm after calcination) at 500 °C for 10 h was added to a well-mixed aqueous solution of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$), zirconium(IV) chloride oxide octahydrate ($ZrCl_2O \cdot 8H_2O$), and ruthenium(III) nitrosyl nitrate ($HN_4O_{10}Ru$). The pH of the mixed solution was close to 5. The resultant slurry was evacuated at 70 °C for 4 h, dried at 120 °C for 18 h. The prepared catalysts were calcined at different temperature for 6 h each under flowing air and they are represented as CRZS(*X*) in the present investigation. *X* denotes the calcination temperature, such as 128, 158, 220, 300, 350, 450, 500 and 600 °C.

2.2 Characterization

The differential thermogravimetric analysis (TGA) of the CRZS catalysts was carried out in flowing air at a heating rate of 1 °C/min using a DSC-TGA SDT 29S thermal analyzer. BET surface areas of the calcined catalysts were measured by nitrogen adsorption at −196 °C using Micromeritics ASAP 2020 adsorption apparatus. Prior to surface area measurement, the samples are pretreated under He flow at 300 °C for 4 h. Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/MAX-IIIB X-Ray diffractometer using Cu K_α radiation with a Ni filter. The average Co_3O_4 crystallite size was calculated using the Scherrer's equation from the most intense diffraction peak at $2\theta = 36.8°$. Temperature programmed reduction (TPR) of the catalysts was carried out in a quartz tubular reactor, fitted with a thermocouple for continuous temperature measurement. After a pretreatment with He flow at 300 °C for 4 h, 5% H_2/Ar was passed at 30 mL/min and the temperature was raised to 900 °C at a rate of 10 °C/min and held for 30 min. A thermal conductivity detector was used to determine the amount of H_2 consumed.

Hydrogen chemisorption measurements were also carried out using the Micromeritics ASAP 2020C. Before each measurement, the sample was dried in vacuum for 40 min at 400 °C and subsequently reduced at 400 °C in flowing H_2 for 6 h. After reduction the samples were evacuated for 2 h at the same temperature and the H_2 adsorption isotherms were measured at 100 °C. The H/Co ratio at zero pressure was found by extrapolation of the linear portion of the isotherm. Crystallite size estimations were made based on hemispherical geometry, according to reduction degree calculated from O_2 titration results and an H/Co adsorption stoichiometry of 1 [28]. O_2 titration was also carried out on the same instrument. The extent of cobalt reduction was determined by O_2 titration of the sample previously reduced at 400 °C. The extent of reduction was calculated by assuming that all the metallic Co was converted to Co_3O_4.

2.3 Activity Measurement

The FTS reaction was performed on these catalysts in a fixed bed tubular reactor (i.d. = 6 mm) at 2.0 MPa. The 300 mg of the calcined catalyst was loaded into the reactor and reduced under flowing hydrogen at 400 °C for 6 h. Subsequently, the reactor was cooled to 30 °C and reheated to the reaction temperature of 220 °C with a heating rate of 10 °C/min under the flow of syngas (molar ratio of H_2:CO:Ar = 31.6:63.2:5.2) with space velocity of 2,000 mL/g_{cat}/h. The pressure was increased to 2.0 MPa and maintained with a back-pressure regulator. The carbon monoxide conversion and the composition of gaseous products were determined every 2 h with an on-line gas chromatograph equipped with a Poraplot Q column (FID) and a Carbosphere column (TCD) using Ar as an internal standard. The collected liquid product and solid wax were analyzed on a GC equipped with HP-1 column (FID).

3 Results and Discussion

3.1 Physical Properties of CRZS Catalysts

The weight loss on CRZS catalysts during calcination step was estimated by a TG analysis of the dried catalyst in air flow and the results are shown in Fig. 1. About 30% of weight loss occurred below 128 °C, largely caused by water evolution and an additional 15% loss was observed after further heating to 200 °C. The catalyst did not show any further weight loss beyond this temperature.

The BET surface area (around 215 m^2/g) of the support (Table 1) is found to change insignificantly (within 3%) with the variation of calcination temperature. The pore volume and pore diameter also varied within 5% of 0.75 cm^3/g and 14 nm, respectively, indicating that there is no pore blocking. The XRD patterns of the CRZS catalysts as shown in Fig. 2 displayed presence of the characteristic diffraction peaks of Co_3O_4 after calcination. No peaks due to Ru or Zr crystalline oxides were observed, possibly due to their low contents and high dispersion. The average crystallite size (dp, nm) as shown in Table 2, was estimated by the Scherrer's equation from the most intense Co_3O_4 peak. The crystallite size of Co_3O_4 is varied in the range of 30.8–38.2 nm with an inverse volcano shape as a function of the calcination temperature and it is minimum at the calcination temperature of 300 °C.

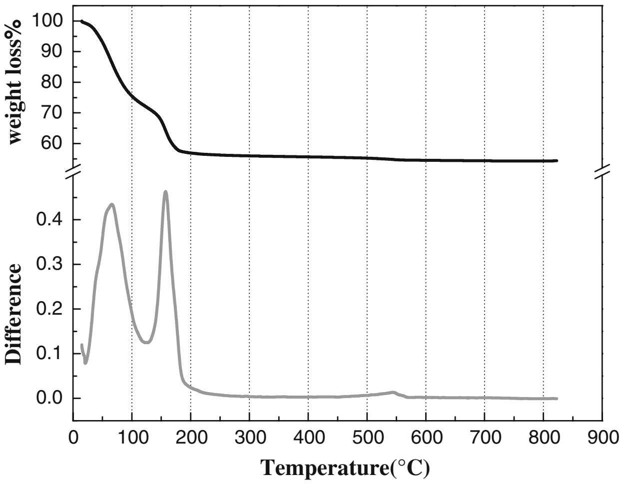

Fig. 1 TGA pattern of just oven-dried CRZS catalyst

Table 1 Effect of calcination temperature of CRZS catalysts on the surface area, pore volume and pore diameter

Notation[a]	Calcination Temperature (°C)	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
CRZS(128)	128	215.8	0.739	14.0
CRZS(158)	158	214.4	0.742	14.1
CRZS(220)	220	218.1	0.742	14.2
CRZS(300)	300	216.2	0.742	14.0
CRZS(350)	350	216.3	0.761	14.4
CRZS(450)	450	215.5	0.763	14.5
CRZS(500)	500	215.2	0.766	14.5
CRZS(600)	600	212.2	0.755	14.2

[a] The catalysts notation of CRZS(*X*) stand for the co-impregnated Co–Ru–Zr on SiO_2 support at different calcination temperature (*X*) at 128, 158, 220, 300, 350, 450, 500 and 600 °C

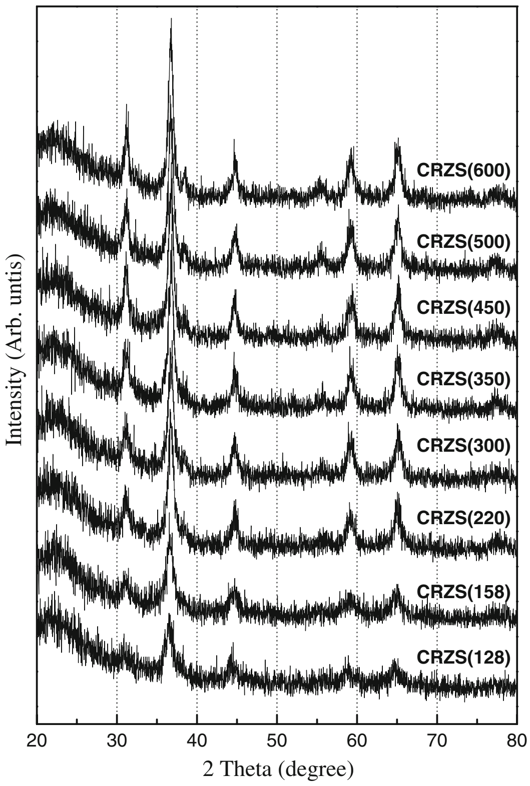

Fig. 2 Power XRD patterns of CRZS catalysts

Table 2 Effect of calcination temperature on the crystallite size of Co_3O_4 in CRZS catalysts calculated from XRD and on the chlorine content from XRF analysis

Notation	Crystallite size of Co_3O_4 by XRD (nm)	Molar ratio of Cl/Zr by XRF
CRZS(128)	35.5	0.26
CRZS(158)	35.0	0.26
CRZS(220)	34.9	0.25
CRZS(300)	30.8	0.26
CRZS(350)	38.2	0.22
CRZS(450)	33.9	0.16
CRZS(500)	33.8	0.16
CRZS(600)	34.5	0.17

Increase of calcination temperature normally brings about changes in structural as well as textural properties. The textural change should be visible in terms of change in surface area and/or pore size distribution. However, as revealed by the data provided in Table 1, there was no significant change in surface area or pore size distribution. Therefore, it is prudent to conclude that there are only marginal variations of physical properties of the cobalt-based CRZS catalysts as a function of calcination temperature. The XRD patterns shown in Fig. 2 did not display significantly any trend in the basic features of the active component, Co_3O_4. The effect of Zr on Co/SiO_2 catalyst is known to be the prevention of Co–Si interaction and eventually suppressing the cobalt silicate formation. However, the type of Zr also influences the dispersion of cobalt crystallites during the catalyst preparation. Interestingly, when the zirconium oxychloride was employed to prepare catalysts, the oxychlorination conditions could be realized during the calcination step and it could enhance the dispersion of cobalt crystallites by the formation of a mobile MO*x*Cl*y* species [23]. Furthermore, the possibility of oxychlorination could be substantiated in the Cl content as shown in Table 2. Although the mole ratio of Cl/Zr is not much altered upto 350 °C, its ratio decreased above 350 °C during calcination step. Since the re-dispersion of cobalt species on CRZS catalysts during calcination step was not predominant at low calcination temperature below 600 °C, additional characterizations by using the H_2 chemisorption and TPR were simultaneously carried out to further understand the its redispersion and aggregation of cobalt crystallite as a function of calcination temperature and eventually it affects on the catalytic activity and stability.

3.2 Reducibility and Measurement of Cobalt Crystallite Size

The TPR profiles of the CRZS catalysts calcined at different temperature are presented in Fig. 3. The calcined catalysts at low temperature of 128 and 158 °C show distinctly different reduction maxima than the catalysts calcined at higher temperature. The reduction peaks at low temperature represent the decomposition of the cobalt and zirconium salts/hydroxides together with the reduction of cobalt oxides. It is expected that at low calcination temperature, the salt exists in a non-interactive state with the support. Essentially it can be considered as a bulk cobalt oxide, reducing in a single step with a maximum for the peak (T_{max}) at around 300 °C. The TPR profiles of the catalysts calcined above 220 °C basically exhibit two reduction maxima in the temperature regions of 200–250 and 350–450 °C, respectively. The cobalt oxide reduction occurs either by reduction of a single cobalt phase in a two-step mechanism or reduction of two phases with different reducibility [15–20]. Based on the present data it is difficult to point out in which way it occurs. Although T_{max} of the first peak almost remained constant, the second peak was broadened with the increase of calcination temperature and T_{max} is shifted to higher temperature, which indicates a stronger metal-support interaction. It has been reported in the literature that cobalt can be present on the catalyst surface as individual oxides, CoO or Co_3O_4, or as surface compounds with the support, with the amounts depending upon the nature of the support and on the calcination temperature [29, 30]. At low calcination temperature upto 158 °C, the cobalt species on the surface exists as bulk species. With increase in calcination temperature, it gets dispersed on the support. The extent of dispersion and variation of cobalt crystallite size will be further examined by the H_2 chemisorption studies.

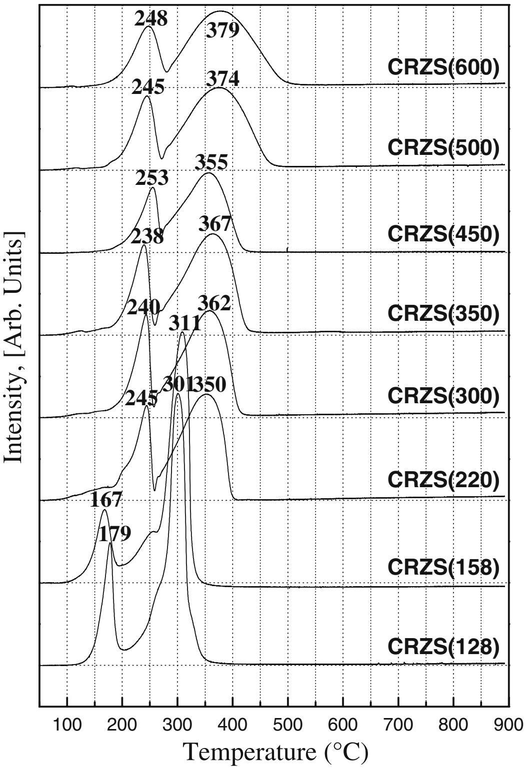

Fig. 3 TPR profiles of CRZS catalysts

The hydrogen uptake and the crystallite size of cobalt metal in the reduced catalysts were estimated by H_2 chemisorption method. The values were first calculated based on the total cobalt metal loading, and then they were corrected taking the degree of reduction into consideration. The O_2 titration method was used to measure the degree of reduction of the catalysts. The degree of reduction was defined as the percentage of cobalt reduced upto 400 °C, (the temperature at which the catalysts were subjected to reduction before activity evaluation). The corresponding results on crystallite size and dispersion are summarized in Table 3. In the case of catalysts with calcination temperature below 220 °C, the average crystallite size obtained

Table 3 Effect of calcination temperature on the cobalt crystallite size and dispersion calculated from H_2 chemisorption and reduction degree from O_2 titration

Notation	O_2 titration		H_2 chemisorption		
	O_2 consumption ($mmol/g_{cat.}$)	Reduction degree (%)	Chemisorbed H_2 ($mmol/g_{cat.}$)	Dispersion (%)	Crystallite size (nm)
CRZS(128)	1.643	95.7	0.0079	0.60	153.6
CRZS(158)	1.609	93.8	0.0088	0.65	136.6
CRZS(220)	1.599	93.1	0.0276	2.01	43.2
CRZS(300)	1.565	91.2	0.0413	2.95	28.3
CRZS(350)	1.622	94.5	0.0233	1.72	52.0
CRZS(450)	1.694	98.7	0.0334	2.58	37.8
CRZS(500)	1.658	96.6	0.0318	2.41	38.8
CRZS(600)	1.640	95.5	0.0304	2.27	40.3

was about three times larger than that of the catalysts calcined above 220 °C. Appearance of larger crystallites after reduction might be explained as due to the agglomeration of cobalt crystallites or the inhibition of H_2 chemisorption on cobalt atoms due to the presence of chlorine residue. Increase in calcination temperature led to dispersion of cobalt and decreasing in the cobalt crystallite size. The decreasing trend of cobalt crystallite size continued upto 300 °C, however, there was an increasing trend slightly above 350 °C. As shown in Table 3, the reduction degree is very high for the catalyst calcined at low temperature and it decreases with increasing calcination temperature till 300 °C. Above a calcination temperature of 350 °C, the reduction degree again increased and sustained its high value above 95%.

3.3 Fischer–Tropsch Synthesis Activity and its Relation to Cobalt Crystallite Size

It is necessary to understand how the crystallite size decreased up to the calcination temperature of 300 °C and then slightly increased. In the presence of chlorine, the formation of mobile intermediate MO_xCl_y occurs by oxy-chlorination condition and it increase in number of smaller metal crystallites on the surface [23]. Of noble metals, this is well known phenomena in Pt-based catalysts that are used in catalytic reforming of naphtha. Such a phenomenon may also be expected in the case of cobalt catalysts as well. During the calcination process on our CRZS catalysts, there is a trivial effect of chlorine on cobalt re-dispersion (crystallite size of Co_3O_4 from XRD) upto 600 °C due to the somewhat lower oxychlorination temperature. However, above 350 °C, smaller cobalt crystallite size was observed during calcination step. Therefore, the variation of cobalt crystallite size mainly occurred at reduction step on our CRZS catalysts instead of calcination step as shown in Table 3. As reported by other previous research groups [21, 22], the existence of chlorine could inhibit the mobility of metal oxides resulting in increase of the dispersion (smaller crystallite size). However, the generated water during reduction step increased the cobalt crystallite size by enhancing the mobility of metal oxides as well. In our CRZS catalysts, the crystallite size of cobalt decreased upto 300 °C due to the evolution of chlorine from Zr precursor and the slow rate of water formation at low reduction temperature. Above 350 °C, the fast evolution of water could be the reason for the slight sintering of cobalt crystallites, however, this is still inhibited due to the existence of chlorine. A close look at the degree of reduction reported in Table 3 also supports this explanation. As the crystallite size decreased, the degree of reduction decreased upto a calcination temperature of 300 °C beyond which the larger crystallites with reduced salt-support interaction showed increase in reducibility.

Figure 4 displays the variation in crystallite size of cobalt and CO conversion according to the calcination temperature. Whereas the reduction degree showed a minimum value at 300 °C, the crystallite size of cobalt decreased upto this temperature and then on increased as

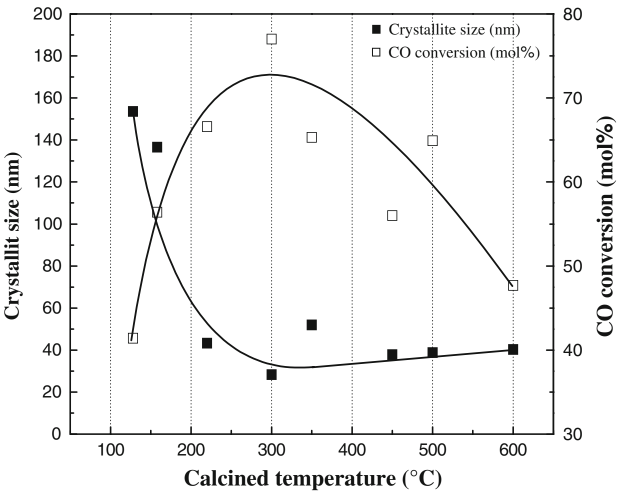

Fig. 4 Correlation between cobalt crystallite size on CRZS catalysts and CO conversion

explained above. CO conversion on CRZS catalysts obtained after calcination at various temperature was maximum on CRZS(300) which is showing smallest cobalt crystallite size. A comparison of the crystallite size and activity data presented in Fig. 4 reveals that as the calcination temperature increased upto 300 °C, the crystallite size decreased to the lowest value of 28.3 nm with a proportionate increase in the CO conversion from 41.4% on catalyst calcined at 128 °C to 77.0% on the one at 300 °C. Beyond 300 °C, the crystallite size increased to 40.3 nm and the CO conversion decreased to 47.7% which is lower than the maximum value.

A comparison of the product distribution in terms of $C_{2–4}$ and C_{5+} showed similar responses as shown in Table 4. The C_{5+}selectivity decreased slightly with increase in calcination temperature, the selectivity started increasing, showing a positive response with that of the crystallite size. What is interesting is a continuous increase in olefin selectivity in $C_{2–4}$ range upto the calcination temperature of 300 °C and a drastic decrease with further increase in the temperature. Lower olefin selectivity in the case of the CRZS catalysts calcined at higher temperature can be a manifestation of decreased hydrogen uptake as compared with that calcined at lower temperature. Therefore, higher C_{5+} yield was obtained on properly calcined CRZS catalyst at around 300 °C due to the existence of well reduced small cobalt crystallites. Furthermore, the value of TOF is not significantly altered on the CRZS catalysts calcined above 220 °C and is found to be in the range of 0.061–0.115 converted CO molecules/surface Co atom/s. The relatively larger TOF values of above 0.213 observed on CRZS(128) and CRZS(158) is probably attributed to the presence of different active hexagonal phase of cobalt crystallite or the presence of amorphous hexagonal cobalt phase [31, 32] at low calcination temperature below 220 °C which is also confirmed in our samples by XRD analysis showing a lower intensity at $2\theta = 36.8°$ (Fig. 2).

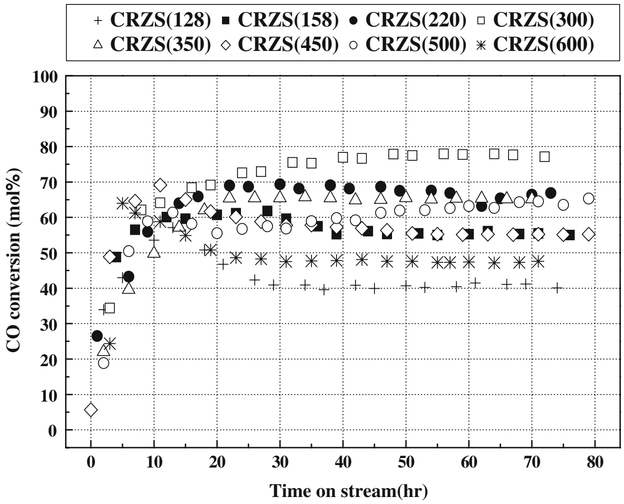

Fig. 5 Variation of CO conversion with time on stream (h) on CRZS catalysts.Reaction conditions: $T = 220$ °C; $P = 2.0$ MPa; molar ratio of H_2:CO:Ar = 31.6:63.2:5.2 with SV = 2,000 mL/$g_{cat.}$/h

The catalytic stabilities are shown in Fig. 5 with time on stream upto 80 h on stream. All CRZS catalysts calcined above 300 °C which are characterized by cobalt crystallite size above 28 nm (Table 3) with a complete removal of nitrate precursor of cobalt (Fig. 1) show stable catalytic activity, showing a different CO conversion and product distribution as a function of cobalt crystallite size. However, CRZS catalysts calcined below 220 °C show a low activity at steady-state with a fast initial deactivation due to possible formation of coke on the amorphous cobalt crystallite and the defect sites. The initially high active cobalt crystallites

Table 4 Effect of calcination temperature of CRZS catalysts on FTS activity in a fixed bed reactor

Notation	Conversion (C-mol%)		Hydrocarbon distribution (C-mol%)			Olefin selectivity[a] (C-mol%)	TOF ($\times 10^{-2}$)[b]
	Of CO	To CO_2	C_1	$C_{2–4}$	C_{5+}		
CRZS(128)	41.4	0.5	3.3	2.9	93.8	30.0	21.3
CRZS(158)	56.4	0.7	4.1	3.8	92.1	32.8	26.3
CRZS(220)	66.6	1.8	4.2	4.1	91.7	34.2	9.9
CRZS(300)	77.0	2.0	4.8	5.1	90.1	35.2	8.4
CRZS(350)	65.3	0.8	3.9	7.5	88.6	20.0	11.5
CRZS(450)	56.0	0.6	3.7	6.7	89.6	15.9	6.9
CRZS(500)	64.9	0.9	3.3	3.4	93.3	38.5	8.4
CRZS(600)	47.7	0.7	7.5	5.1	87.4	26.5	6.1

The averaged values in CO conversion and hydrocarbon distribution are obtained after stabilization of activity around 30 h on stream at the following reaction conditions: $P = 2.0$ MPa, SV = 2,000 mL/$g_{cat.}$/h and $T = 220$ °C

[a] The olefin selectivity is calculated in the range of $C_{2–4}$ hydrocarbons (olefin selectivity = mole of olefins in $C_{2–4}$/moles of total hydrocarbons in $C_{2–4}$)

[b] The unit of turn-over frequency is the converted CO molecules/surface CO atom/s

on CRZS(128) and CRZS(158) which is possibly possessing an amorphous hexagonal phase exhibiting fast catalyst deactivation, however, the well-defined small cobalt crystallites obtained on catalysts calcined at around 300 °C without precursor residue are showing a stable catalytic activity with high CO conversion.

4 Conclusion

The present investigation reveals correlation of calcination temperature with cobalt crystallite size in the presence of zirconium oxychloride precursor to find out proper pretreatment conditions to obtain a high FTS activity and stability. The reduction treatment extensively affects the amount of chlorine and water release which again influences the cobalt dispersion, compared to the calcination treatment on CRZS catalysts. Lower crystallite size and better catalytic activity during FTS could be achieved with catalysts calcined at lower temperature around 300 °C in the presence of chlorine originated from zirconium oxychloride precursor. The evolution of chlorine and water during reduction step competitively affect the cobalt dispersion by changing the mobility of cobalt species. The optimum calcination temperature on CRZS catalysts seems to be around 300 °C at a fixed reduction temperature of 400 °C.

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