

Tailoring the Crystallite Size of $\text{Co}_3\text{O}_4/\text{SiO}_2$ Catalyst Using Organic-Metal Matrix Method

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Abstract

In this work, a series of SiO_2 supported Co catalyst have been prepared by adding urea or ruthenium to the cobalt precursor solution compared with the catalysts prepared without using urea. The characterization results show that cobalt is present as Co_3O_4 over the silica supports. The addition of urea to the catalyst precursor helps to generate smaller crystallite even at very high cobalt loading, while impregnation without using urea results in larger crystallite size as Co loading increases. Likewise, the addition of Ru to the catalyst precursor leads to a more uniform crystallite of Co_3O_4 , and can help to lower the Co_3O_4 crystallite size to some extent, which has the similar effect on the catalyst prepared with urea. We have also shown that the support pore size and volume do have significant effect on the crystallite size of the cobalt oxide. The catalytic performances of the Co/SiO_2 catalysts prepared with and without adding urea have been evaluated for Fischer Tropsch synthesis and the catalyst prepared using urea demonstrates significantly improved catalyst activity as well as selectivity to C_5^+ .

Key words: Organic matrix method, crystallite size, Fischer Tropsch synthesis, Co/SiO_2

Introduction

Heterogeneous catalyst preparation has many different protocols with a multitude of possible preparation schemes, especially those composing of different supports and active components. Preparation involves a sequence of several complex processes, many of them have not been completely understood [1]. Supported catalyst often consists of a support mostly with high surface area and some active nano-particles as the active components or their precursors. For example, low temperature Fischer Tropsch synthesis catalysts are mostly supported cobalt catalysts, where cobalt nano-particles are dispersed onto the inert supports such as TiO_2 , SiO_2 or

Al_2O_3 et.al, and it has been shown that the cobalt particle size has strong influence on catalyst activity and selectivity .[2-6]

Due to the increasing demand for clean and renewable energy, there has been lots of research on the preparation of Fischer Tropsch catalysts [2, 3, 7, 8]. Fischer Tropsch catalysts have a very high catalyst sensitivity index [9], so the improvement of the catalyst performance is especially important in the process. So far, in the preparation of supported cobalt catalyst, the most often used methods are wet impregnation method, sol-gel , mechanical milling method, and precipitation method [10-12]. The wet impregnation method often leads to the formation of inert phase CoSiO_3 or a lower dispersion when used with higher metal loading. Recently, a novel preparation method has been developed, which is to use organic-metal matrix (OMX) solution to impregnate with the dried support, the catalyst showed very high activity and stability in Fischer Tropsch synthesis [4, 13-16]. The method is hereafter named as OMX method, which is in fact somewhat similar to the combustion method [7, 17-19], but the maximum temperature reached is much lower than the combustion method, and it is conducted in static air or inert atmosphere conditions, however the mechanism of the organic effect on the catalyst is not clear. It has shown that even trace amount of noble metal has significant effect on Fischer-Tropsch catalysts, but there have been few studies about the noble metal addition on the catalyst preparation step, e.g., the effect of noble metal on the cobalt crystallite dispersion. Sometimes to get highly active catalyst, high metal loading is often desired, but the dispersion and atomic efficiency is always an issue in the conventional catalyst preparation, especially as the metal oxide crystallite size may grow larger with the increase of the metal loading.

To control the particle size of the active component whilst increasing the metal loading, lots of research has examined combustion synthesis, which is to use organic-metal solution and combusted at high temperature in air [7, 14, 19]. This method has been effective for the synthesis of nanoscale materials and has been used in the production of various ceramic powders for a variety of advanced applications. [20, 21].

In this research, we have prepared a series of silica supported cobalt catalyst using organic-metal matrix solution and the precursor combustion temperature is set as low as possible for the process to be controllable. The purpose of this experiment is to explore the mechanism of effects of organic compounds and noble metal for the supported catalyst preparation, namely, the effect of urea addition to the cobalt impregnation solution, noble metal addition on the cobalt crystallite size and dispersion has been studied.

EXPERIMENTAL

Catalyst preparation

The catalysts were prepared using Organic-Metal matrix (OMX) method. The details of the preparation process are as follows. The cobalt precursor is from cobalt nitrate hexahydrate (Alfa, Analytical Grade), and quantitatively mixed with urea at urea/Co mole ratio of 2, with minimum water added at ambient temperature to form a pink solution. A shaped SiO₂ support (from Silica, Japan) is dried at temperature of 450°C and is maintained at this temperature for 10 hours prior to its impregnation. It is impregnated with the cobalt solution using incipient wetness method, and placed in static air for 24 hours, then drying/calcination after each impregnation at the following temperature program in static air 2°C/100°/9h; 0.1°C/140°/5h; 0.1°C/160°/3h; 0.1°C/170°/3h; 0.1°C/180°/2h; 2°C/350°/3h. The resultant catalysts became black with the support almost no changes in its size and strength. To increase the amount of the cobalt loading, the calcined cobalt oxide containing silica is impregnated with cobalt-urea solution and the drying and calcination are kept under the same conditions.

In preparing the Ru containing CoO_x/SiO₂ catalyst, the Ru (III) nitrosyl nitrate solution (Sigma-Aldrich, containing 1.5 wt% Ru in the solution) was added to the Co(NO₃)₂·6H₂O-urea solution according to the required amount, then co-impregnated with the dried silica support. The drying and calcination conditions were kept all the same as the previous CoO_x/SiO₂ catalysts.

XRD characterization

The X-ray diffraction (XRD) analysis is carried out using a fully automated Siemens D5000 theta/theta powder diffractometer employing copper K α radiation ($\lambda=0.15406\text{nm}$) and a secondary monochromator. The samples are continuously spun during data collection and were scanned using a step size of 2θ at 0.04° between the range of $5-70^\circ$.

The peak of 2θ from $30-45^\circ$ is assigned to plane 311 of Co₃O₄, which is used to calculate the crystallite size from XRD line broadening (measuring the full width at half

maximum intensity [FWHM]) using the method developed by Scherrer in 1918, which uses the following equation:

$$D_v = K\lambda / (\beta \cos\theta)$$

where D_v = Crystallite size weighted by volume, K = Scherrer constant (0.9), λ = wavelength of radiation, and β = integral breadth of peak (in radians 2θ) located at angle θ . This approach does, however, neglect the effect that strain can have on crystallite size and for this reason the minimum crystallite size is quoted. The observed diffraction peak is stripped of the alpha 2 component using the Rachinger method and the alpha 2 stripped value for the FWHM used for the Scherrer calculation. No provision has been made for the instrumental broadening. The peak selected for analysis is the (311) reflection at approximately 36.8° of 2θ .

TEM analysis of the catalyst:

Experiments were carried out on a JEOL 2010 analytical TEM, which has a LaB_6 electron gun and can be operated between 80 and 200kV. This instrument has a resolution of 0.19nm, an electron probe size down to 0.5nm and a maximum specimen tilt of ± 10 degrees along both axes. The instrument is equipped with an Oxford Instruments LZ5 windowless energy dispersive X-ray spectrometer (EDS) controlled by INCA. It has facilities for point analysis as well as mapping and line scanning through the SemiStem controller. For elemental mapping, EDX mapping was carried out with a nominally 1 nm probe at three different magnifications, imaging small and large particle aggregates. Areas were mapped for approx. 5-10 minutes. Drift and contamination problems prevented longer counting times.

Laser Raman spectra are recorded with a Perkin-Elmer Raman Station 400F Raman Spectrometer. The powder sample is pressed onto of clean glass slide for scanning from 200cm^{-1} to 2000cm^{-1} .

Catalyst activity test

The as-prepared catalyst samples were activated and tested in a fixed bed micro-reactor high-pressure gas-phase reactor system including a cylindrical stainless reactor (9-mm i.d., 400 mm long). Each time, 0.10 g of the catalyst was loaded into the reactor, activated with flowing H₂ at 1°C/min to 400 °C for 6 hours and then cooled to 100 °C. The flowing H₂ was switched to pressurized mixture of H₂ and CO with a molar ratio of 2:1, and heating to target temperature at 5.0 °C/hour. In the syngas gas mixture 5.0% of N₂ is contained as an internal standard being included in the mixed gas, each catalyst test lasted more than 10 days and the activity and selectivity data were taken after the reaction reach steady state. The volume space velocity of syngas was adjusted to be about 6000h⁻¹, and the reactor pressure of 2.0 MPa, and the reaction temperature at 200 °C, the temperature was controlled and measured with a thermocouple inserted into the catalyst bed. The product stream after catalyst bed flows through a cold trap to separate water and heavy hydrocarbons in the effluent, and the gaseous products were analyzed using an on-line GC.

Results and Discussion

In this study, silica supports with various pore sizes are used, and their properties are shown in Table 1.

Table 1 Physical properties of the SiO₂ supports

sample	BET (m ² /g)	Pore volume (cm ³ /g)	Adsorption average pore width (Å)
Small pore sized SiO ₂ -10	304.6	1.049	137.7
Meso-pore sized SiO ₂ -30	131.4	1.085	330.4

The surface areas of the two supports have significant difference, the sample with bigger pore size (pore width, 330.4 Å) has only surface area of 131.3 m²/g, which is marked as SiO₂-30, while the sample with pore width of 137.7 Å has surface area of 304.6 m²/g. Although the pore volumes of the two supports are very close to each other, suggesting that the SiO₂-30

supports has a very shallow depth of the pore, whose internal surface area would be much less than the SiO₂-10, which has higher surface area, but smaller and longer pore in the support.

After cobalt nitrate and urea solution is loaded over the supports and calcined finally at temperature of 350°C, the supports become black, and the adopted calcination in static air, the support did not breakdown and the strength of the support was not affected. The XRD results of the catalyst prepared without urea, with urea and with urea and Ru containing 36% of Co₃O₄ over SiO₂-10 are shown in Figure 1. It can be seen that only Co₃O₄ spinel is present as crystalline phase in the resulting composite, with the main peaks at 2θ of 37.01, and the small diffraction peaks at 2θ of 31 and 44, which can be assigned to the Co₃O₄ crystalline plane of 220, 311 and 400 planes. There are no shift of diffraction peaks observed with respect to conventional Co₃O₄ spinel (PDF-2 entry 42-1467), and also no extra peaks showing that there is no cobalt silicate formed, also indicating that no silicon-containing solid solution was formed. The relatively broad and weak diffraction peaks show that the catalysts have particularly small crystallite sizes, even with 36.0 wt% of Co₃O₄ loading. The (311) peak selected for analysis is quite close to the (222) peak, which is very weak, so it would not exert marked influence on the measurement of the (311) peak,

The laser Raman spectra of the SiO₂-10 supported Co₃O₄ catalysts prepared with and without urea or Ru are given in Figure 2. An intense Raman band at 686 cm⁻¹ accompanied with a weak one between 482, 518 and 596 cm⁻¹ arises in the spectrum of the prepared catalysts, which can be assigned to the Co=O bond vibration A_{1g} and E_g of the Co₃O₄. [22, 23] There are no significant difference resonance frequencies of the Raman bands, and even the peak intensity, suggesting that the Co₃O₄ are present in almost the same status over the silica support. It is interesting to see that there are no clear Raman band for SiO₂, which can be explained by the fully coverage of the Co₃O₄ over the support, as the Co₃O₄ loading is more than 26.0 wt% over the catalyst.

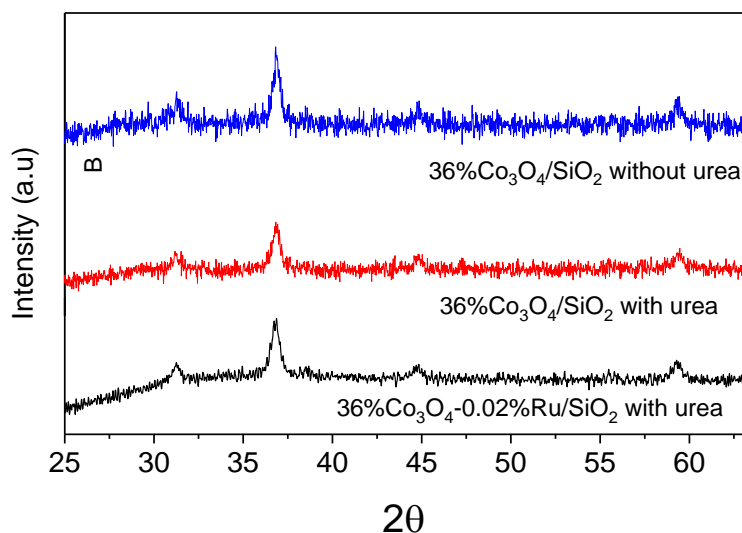


Figure 1. XRD patterns of the typical $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalyst

From the above XRD and Laser Raman results, it is shown that cobalt exists mostly in Co_3O_4 over the silica support, and the crystallite size might be different. So in the next part, we will calculate the Co_3O_4 crystallite size with various prepared methods and Co loadings. Given the main diffraction at 311 plane is sharp and high signal to noise ratio, we compare samples with similar Co_3O_4 loading, but with organic or Ru addition. It seems that there are some peaks width differences among the catalyst samples. The one without urea seems to have sharper diffraction peaks at 2θ of 37. Based on these results, we have measured the prepared samples with various loading of Co_3O_4 with and without urea of Ru added and the crystallite size of the samples have been measured, we have used the Sherrer Equation to obtain the results, which are summarized in Figures 3-6.

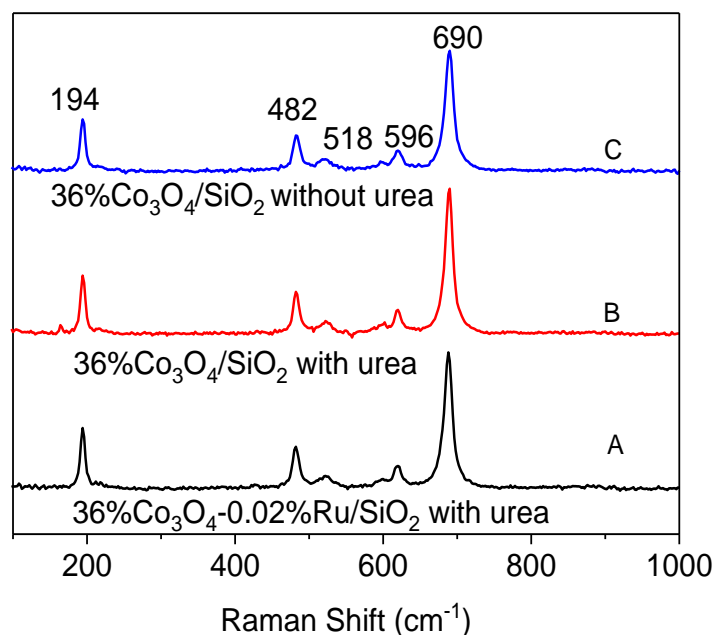


Figure 2 Laser Raman spectra of the $\text{Co}_3\text{O}_4/\text{SiO}_2$ prepared with A) urea and Ru addition, b) with urea, and C) no urea or Ru addition.

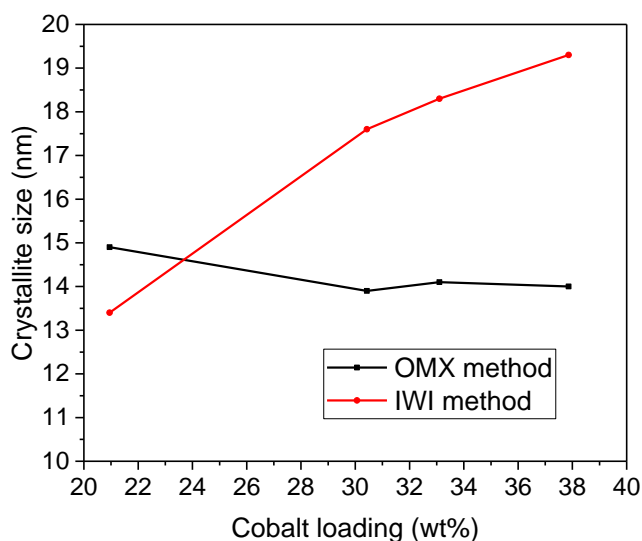


Figure 3 The changes of Co_3O_4 crystallite size with the Co loading over SiO_2 -10 support

Cobalt oxide crystallite size was measured using XRD in the SiO_2 supported Co catalysts, focusing the scanning from 36-38 of 2 θ . The changes in crystallite size of Co_3O_4 with its cobalt oxide loadings over the SiO_2 -10 supports are shown in Figure 3. It can be seen at relatively lower loading, 20.6 wt % of Co_3O_4 (determined by ICP and weight gain after the impregnation), the $\text{Co}_3\text{O}_4/\text{SiO}_2$ -10 catalyst prepared with adding urea has crystallite size of 14.8 nm, while the one prepared without urea addition has crystallite size of 13.4 nm. When

increasing Co_3O_4 loading to 30.1 wt% over the catalyst, the Co_3O_4 crystallite size in the catalyst prepared without urea increases to 17.9 nm. But the one prepared in the presence of urea has 13.9 nm, slightly smaller than the lower loading catalyst. Further increasing Co content in the catalyst by one more impregnation gives Co_3O_4 crystallite size about 14.0 nm for the catalyst prepared with urea added to the Co precursor solution. Meanwhile the Co_3O_4 crystallite size further increases to 18.2 nm in the catalyst prepared without adding urea, and further grows to 19.2 nm when cobalt loading is increased to 38.0 wt. %. In contrast, the $\text{Co}_3\text{O}_4/\text{SiO}_2\text{-10}$ prepared with urea added in the cobalt nitrate solution the Co_3O_4 crystallite size remains at 14.0 nm even when Co_3O_4 loading increased to 38.0 wt. %.

The above results show that the addition of urea does have a significant effect on the crystallite size of Co_3O_4 in the incipient wetness preparation of the catalyst. This may be due to the coordination effect of urea, which can form complex with cobalt nitrate, with a certain size of cluster, and will not aggregate during the calcination. Another reason for the smaller crystallite size of Co_3O_4 may lie in the significant amount of gases produced during the decomposition of the urea, which may depress the growth of the crystallite. Overall, it is observed that no matter whether or not urea is added to the cobalt precursor solution, the resultant catalyst oxide Co_3O_4 crystallite size is bigger than the pore size of the $\text{SiO}_2\text{-10}$ support (11.3 nm), suggesting that a fair amount of Co_3O_4 crystallite extend outside of the pore and outgrown above the catalyst surface. Especially for the catalyst prepared without urea added, Co_3O_4 crystallizes continuously grows bigger with Co increased loading, as the catalysts were prepared using sequential incipient wetness impregnation method to increase the cobalt loading, the later impregnated cobalt formed crystallite linked to the previous impregnated Co_3O_4 . However, the addition of urea did not enhance the growth of Co_3O_4 crystallite size, but just formed extra number of Co_3O_4 crystallites on top of the previous catalyst. This is a very interesting phenomenon, which may be useful to explain the sol-gel methods, which can give uniform particle size of the catalyst [2, 5, 24, 25].

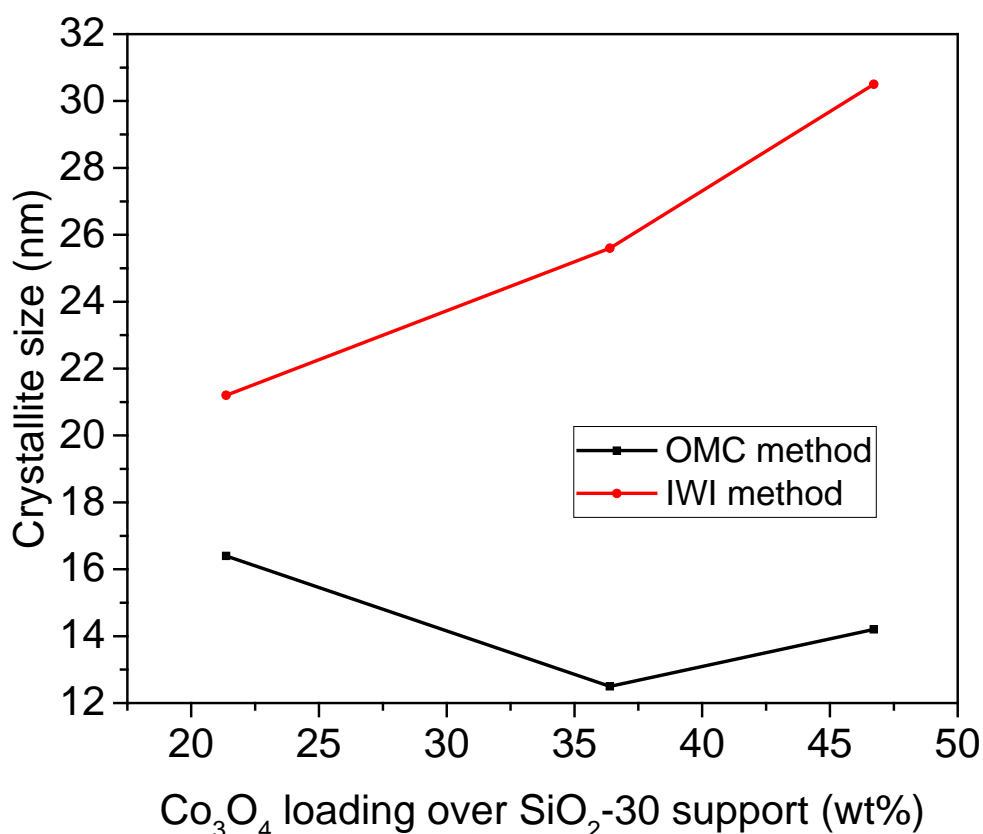


Figure 4 The changes of Co_3O_4 crystallite size with the Co loading over SiO_2 -30 support

To examine the effect of the support pore size on the crystallite size of the supported Co_3O_4 , we prepared a series of large pore support, e.g., SiO_2 -30 supported Co_3O_4 catalyst with and without urea added in the cobalt nitrate solution using impregnation. The support has a pore size of 33.5 nm, as shown in Table 1. The changes of Co_3O_4 crystallite size with the cobalt loading is shown in Figure 4. Compared with Figure 3, it can be seen that the bigger pore-sized SiO_2 supported Co catalyst has bigger Co_3O_4 crystallite than the smaller pore SiO_2 supported catalyst when no urea is added to the Co nitrate solution. When no urea was used in the catalyst preparation, Co_3O_4 crystallites size further increases with the cobalt loading rising. In the catalyst containing 46.6 wt% of Co_3O_4 , cobalt crystallite grows to 30.1 nm, which is almost the same as the support pore size. In contrast, when urea is added to the cobalt nitrate urea forming cobalt precursor solution, the resultant catalyst has Co_3O_4 crystallite size from 15.9 nm when Co_3O_4 loading 21.2 wt%, to 13.5 nm at Co_3O_4 loading of 36.0 wt.%, and further to 14.3 nm at Co_3O_4 loading of 47.1 wt.%. It is interesting to see that cobalt crystallite size remains unchanged with

the cobalt loading in the urea-added system. This again suggests that urea- $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution does depress Co_3O_4 crystallite growth during the calcination. This may be due to the urea-Co cluster of the produced gas during the preparation mentioned before.

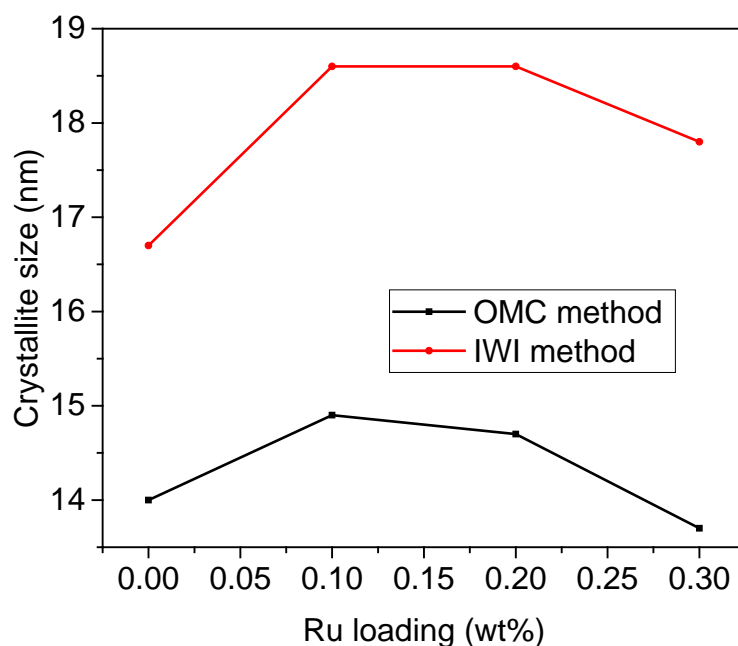


Figure 5 Changes of the Co_3O_4 crystallite size with the Ru loading over SiO_2 -10 support

Noble metal is often added to Fischer-Tropsch synthesis catalyst to improve the catalyst performance, which is often assigned to the enhancement of the Co reduction catalysed by Ru.[26, 27] However, little is known about the effect of Ru addition on the catalyst preparation. Here we have added various Ru nitrosyle nitrate solution into cobalt nitrate solution with or without urea and impregnated the solution with SiO_2 -10, and then drying and calcination, the changes of the Co_3O_4 crystallite size with the Ru loading is shown in Figure 5. In the catalyst prepared without urea, the overall Co_3O_4 crystallite size of the catalyst has bigger crystallite size than the catalyst prepared with urea, suggesting that urea has a bigger impact in determining the crystallite size of the cobalt oxide, as we mentioned before, it may form complex with the cobalt. However, in the catalyst without Ru, the one prepared without urea has Co_3O_4 size of 19.0 nm, but decreases to 18.6 nm when adding 0.08 wt.% Ru in the Co solution. The cobalt oxide

crystallite size is almost unchanged when Ru increases to 0.2 wt%, but become slightly smaller to 17.8 nm when Ru content increased to 0.3 wt%.

When urea is present in the solution of $\text{Co}(\text{NO}_3)_2$ and Ru nitrate solution for impregnation step, the resultant catalysts generally have smaller Co_3O_4 crystallite size than the one without urea addition, which is in agreement with the catalyst series prepared without any Ru addition. The addition of 0.1 wt. % only slightly decreases the Co_3O_4 crystallite size from 15.0nm to 14.9nm, and when Ru content increase to 0.2 wt. % in the catalyst, Co_3O_4 crystallite size decrease to 14.7 nm, and further drops to 13.8 nm when Ru loading is increased to about 0.3 wt. %.

The above results clearly show that in the small pore SiO_2 -10 supported Co_3O_4 catalyst system, adding Ru solution in $\text{Co}(\text{NO}_3)_2$ solution does have an effect on cobalt oxide crystallite size, although its effect is not as significant as that with the addition of urea. In both the series of catalysts, Ru tends to help to decrease Co_3O_4 crystallite size; higher loading of Ru has more significant effect.

For comparison, the SiO_2 supports with bigger pore size e.g., SiO_2 -30 has been used for the preparation of Co catalyst with Co loading of 36.0 wt. %. The effect of Ru addition on the catalyst with and without urea is shown in Figure 6. It is seen that with urea addition, the resultant catalyst has Co_3O_4 crystallite size pore more or less the same between the big pore and small pore SiO_2 supported, it is from 14-15 nm without Ru addition, but with urea. When 0.1 wt. % Ru is added the catalyst, Co_3O_4 over SiO_2 -30 is almost unchanged at about 13.9 nm, but decreases to 13.1 nm when Ru content increase to 0.2 wt. %. However, it is interesting to see that increasing Ru content to 0.3 wt% in the SiO_2 -30 supported catalyst lead to Co_3O_4 crystallite size rise to 15.0 nm.

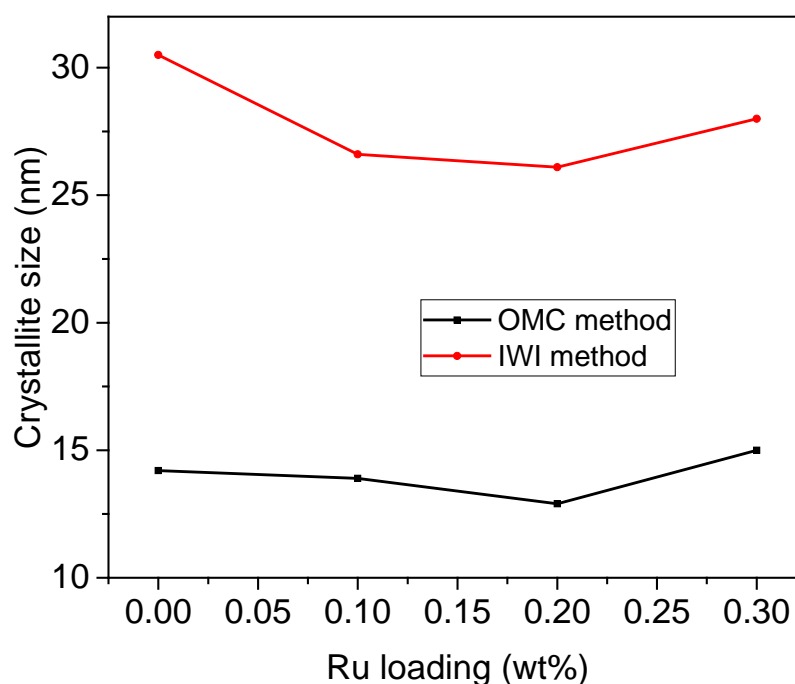


Figure 6 Changes of the Co_3O_4 crystallite size with the Ru loading over SiO_2 -30 support

In contrast, the catalyst prepared without urea has bigger Co_3O_4 crystallite size, when no Ru is added. It is 30.5 nm, much bigger than over SiO_2 -10 support. When 0.1 wt% Ru is added in the catalyst, there is a big decline in the Co_3O_4 crystallite size, staying at about 16.3 nm, and almost unchanged even when Ru content increases to 0.2 wt%. Again more or less the same trend is seen as in the urea containing catalyst system, Co_3O_4 crystallite size increases to 28 nm when Ru content increases to 0.3 wt %. This suggests that over the bigger pore SiO_2 -30 support, the effect of Ru can make Co_3O_4 have higher dispersion when its amount is low. A higher amount of Ru addition leads to the Co_3O_4 re-crystallize and forms bigger crystallite particles.

TEM results of the Co_3O_4 catalyst prepared with and without urea

To differentiate the effect of urea on the cobalt oxide, we have prepared bulk Co_3O_4 from the decomposition of cobalt nitrate and a cobalt nitrate-urea solution. The TEM images with various multitudes of the bulk Co_3O_4 obtained directly from $\text{Co}(\text{NO}_3)_2$ decomposition are shown in Figure 7. It is seen that the Co_3O_4 crystallite shows long lump shape, which is about 10-20 nm thick, but 30-100 nm long, the crystallite aggregates to various clusters, as there is not support used in the preparation. Both the small aggregates and single particles are crystalline

phases, most of them show some indication of porosity. Electron dispersive X-ray spectrum analysis (EDX) studies with a 3 nm probe of many points over the sample gave a Co to O ratio of approximately 55 to 45%. The elemental mapping results of the bulk cobalt oxide are shown in the bottom of Figure 7. It is shown that the cobalt distribution are more or less the same as oxygen distribution, cobalt element shows long lumps shape, which is more or less in agreement with the TEM results, as the cobalt oxide derived from cobalt nitrate without adding urea appears to be long lump.

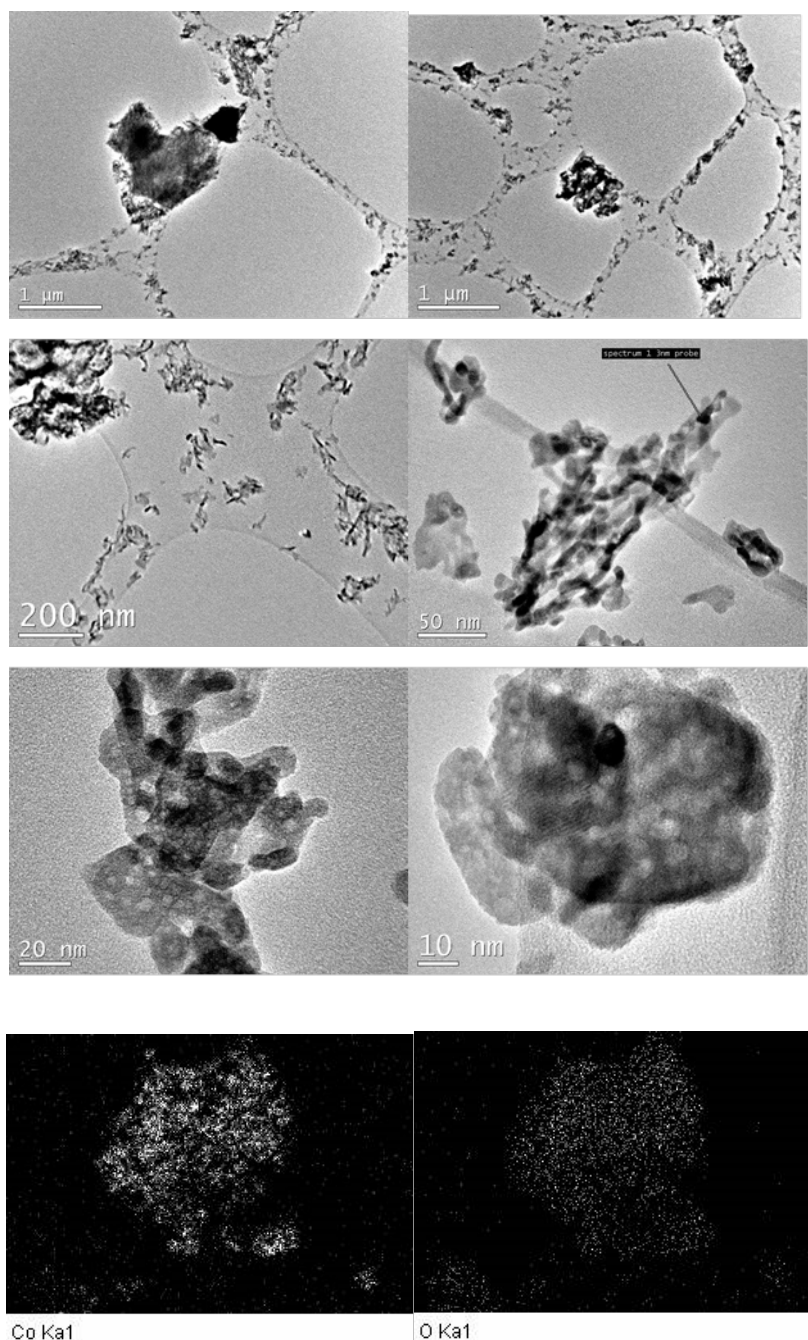


Figure 7 The TEM and elemental mapping images of the cobalt oxide derived from the decomposition of bulk $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

The cobalt oxide sample prepared from the decomposition of cobalt nitrate and urea solution has been prepared under the same conditions as that for the silica supported catalysts, and the TEM images with various magnitudes were shown in Figure 8. It is clearly seen in the picture of $1\mu\text{m}$ barred and $0.5\mu\text{m}$ barred that most particles were small aggregates (diameter 5-50nm), but some micrometer sized aggregates could also be seen. Compared with Figure 7 of the sample derived from the cobalt nitrate only, the Co_3O_4 sample derived from the system with urea has more isolated iso-metric particles. In contrast the longer lumped sample, these aggregates appear more iso-metric, and generally more single particles could be seen. Combined these results, we can conclude that the reason of the smaller crystallite size of the Co_3O_4 derived from the urea containing cobalt nitrate catalyst system is due to the urea effect, not the support pore size effect. This result is in agreement with the previous XRD results of the Co_3O_4 over SiO_2 with various sizes. It is interesting to see that the Co_3O_4 exists mostly as small aggregates and single particles with crystalline structure. However, they have shown no clear evidence of porosity, which means there are no pore formed between the crystallite, as they are more isolated by the presence of urea, which restricts the growth of the cobalt oxide particle links. We also measured several points of the catalyst using EDX with a 3 nm probe, the average composition of the cobalt Co to O ratio is the same as that of the oxide obtained without urea, its atomic ratio is approximately 55 to 45%. This also suggests that the presence of urea did not reduce cobalt oxide during the calcination, as it is believed that urea decomposition can release ammonia, a reducing agent. Also the elemental mapping results of the prepared cobalt oxide particles are given in the bottom of Fig. 8. Only cobalt and oxygen elements were detected and the distribution of the two elements is in consistent shape and spotted, suggesting that they are indeed bonded, as only cobalt oxide is the decomposed product from the preparation. Compared to the elemental mapping results in Fig 7, the cobalt spots in Fig 8 is smaller and more

populated, which again suggest that the addition of urea to the cobalt nitrate during the preparation give more dispersed cobalt oxide particles even without support being used.

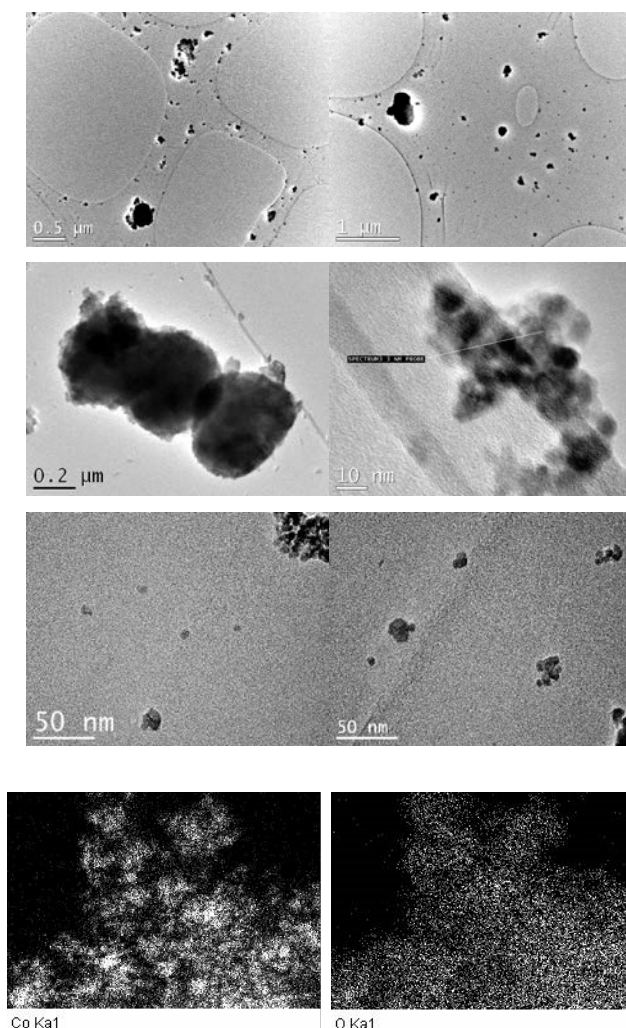


Figure 8 The TEM images of the cobalt oxide derived from the decomposition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + 2\text{Urea}$ mixture calcined at 350°C

It is widely known that the catalyst activity largely depends on the dispersion of the active components [26, 28-32]. Poor dispersion of the metal active components not only increases the cost of the catalyst due to the high loading, but also gives lower activity of the catalyst due to the aggregation, sometime even worse, the stability is affected. However an ultra-high dispersion of the active components may easily lead to strong interaction between the metal and support, forming inert phase. Moreover, ultra-small metal particles may give lower selectivity, which is detrimental to the catalyst performance, and they are easy to sinter, which often leads to catalyst deactivation. Here by adding proper amount of urea, which may form cobalt-urea complex, can generate a proper range of Co_3O_4 crystallite size, which then give the

right cobalt metal cluster, thus leads to high activity and selectivity in Fischer Tropsch reaction. Of course this method has been applied to HDS catalyst preparation [33, 34], and showed more uniform molybdenum oxide dispersion, thus giving a better HDS catalyst performance, as published in Sergio's paper.[34]

Fischer Tropsch synthesis activity and selectivity comparison of $\text{Co}_3\text{O}_4/\text{SiO}_2\text{-10}$ catalysts prepared with and without urea.

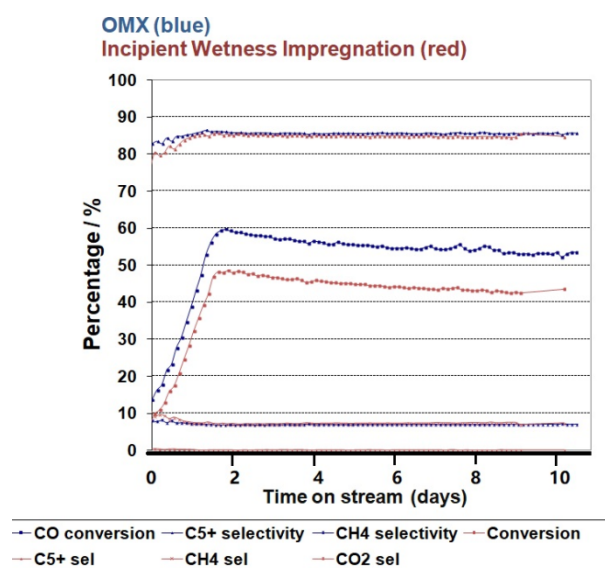


Fig.9. CO conversion and product selectivity for syngas conversion over $\text{Co}/\text{SiO}_2\text{-10}$ catalyst prepared with urea (OMX) and without urea (incipient wetness). Test conditions: pressure: 2.0 MPa, $\text{H}_2/\text{CO}=2:1$, Temperature: 200°C, GHSV: 6000 h^{-1} , fixed bed reactor, catalyst to SiC volume ratio: 1:1.

The $\text{SiO}_2\text{-10}$ supported Co catalysts prepared with urea (named Organic Matrix method, OMX) and without urea (incipient wetness method) have been tested for Fischer Tropsch synthesis and the results are presented in Fig. 9. The CO conversion for the $\text{Co}/\text{SiO}_2\text{-10}$ catalyst prepared without urea showed an initial CO conversion about 48.5% and tends to stabilize at 42% in 8-day time on stream, while the C_5^+ selectivity is about 85.0% on day 2 and remain almost constant during the whole test period. Selectivity to methane is about 7.3%, which tends to decrease slightly with the time on stream. CO_2 yield is less than 0.5%, which is relatively very low, the good performance of the $\text{Co}/\text{SiO}_2\text{-10}$ catalyst prepared using incipient wetness method may be due to the high loading of Co_3O_4 . Over the catalyst prepared using urea namely the OMX

method, it is seen that the initial CO conversion reached 60.0%, nearly 12% higher than the catalyst prepared without urea addition. However, the C_5^+ selectivity of the two catalysts are almost equivalent, at about 85.5%, but the selectivity to methane is lower. This suggests that the catalyst prepared using OMX method has higher activity, e.g., more active sites are available for the CO conversion, this is because the addition of urea increases the dispersion of Co, as shown by the XRD and TEM results. However, the urea addition does not change the catalyst selectivity very much.

Conclusion

Silica supported cobalt catalysts have been prepared using the organic matrix combustion method give smaller Co_3O_4 crystallite size, which remains unchanged with the cobalt loading increase; in contrast, the Co_3O_4 crystallite size in the SiO_2 supported catalyst prepared using a conventional method, e.g., incipient wet impregnation (IWI) method without urea addition increases with the cobalt loading, this change is more significant for supports with larger pore size.

For both silica supported cobalt catalysts prepared using OMC or IWI method, Ru addition has a little effect on Co_3O_4 crystallite size. The Ru addition has more significant effect on the catalyst prepared without urea addition in the cobalt nitrate solution. Lower amount of Ru addition over smaller pore support increase the Co_3O_4 crystallite size, and higher Ru addition seems to have less effect. Over large pore support, addition of lower amount of Ru decreases Co_3O_4 size, which is more obvious over the catalyst prepared using IWI. Higher Ru loading (above 0.3 wt%) tends to have less effect on cobalt oxide crystallite size. .

The Co_3O_4 crystallite tends to aggregate and grows longer when no urea is used in the preparation. However, when urea is used, the crystallite shapes are often iso-metrical. The Co/ SiO_2 -10 catalysts prepared with urea addition showed higher CO conversion than the catalyst without urea in Fischer Tropsch synthesis, however, both catalysts showed equivalent

selectivities to C_5^+ and CO_2 . This may be due to the higher dispersion of the cobalt crystallites in the catalyst prepared with urea addition.

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