Catalysis Today 181 (2012) 75–81

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Particle size effects in Fischer–Tropsch synthesis by cobalt

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ARTICLE INFO

Article history:
Received 11 March 2011
Received in revised form 2 June 2011
Accepted 27 June 2011
Available online 28 July 2011

Keywords:
Particle size
FT
Co/SiO_2 catalyst
Model catalyst
Oxidation

ABSTRACT

In order to study the intrinsic particle size effect of Co catalysts in Fischer–Tropsch (FT) synthesis, a series of Co/SiO_2 model catalysts with various metal coverages (0.25–6.0 ML), corresponding to sizes in the range of 1.4–10.5 nm were prepared in an ultrahigh vacuum chamber and tested at 513 K under atmospheric pressure in a batch reactor. The Co particle size distribution and the number of active sites were estimated from the TEM images. Kinetic data and post-reaction XPS spectra showed that for the small Co particles (1.4–2.5 nm), the Co surface was readily oxidized by water vapor, while for the relatively large Co particles (3.5–10.5 nm), such oxidation was not evident. The oxidation for the small Co particles leads to lower TOF and higher CH_4 selectivity, while both reactivity and selectivity were relatively constant for the relatively large Co particles. The lack of intrinsic particle size effect for the metallic Co particles in the range of 3.5–10.5 nm is consistent with structure insensitivity in FT synthesis.

1. Introduction

In history, two general approaches have evolved to produce substitutes for naturally occurring crude petroleum [1,2]. One approach is to directly convert organic materials by heating the feed at high temperatures under high pressure of hydrogen. In the second approach, the organic material is converted to syngas (a CO/H_2 mixture) and then converted to hydrocarbons by Fischer–Tropsch (FT) synthesis. This approach is known as the indirect liquefaction process. For both technological and political reasons, the direct liquefaction approach has received much more attention prior to the energy crisis of the 1970s. In the last several decades, the indirect liquefaction approach has received more attention, primarily because of the increase in environmental regulations as well as advances in FT technology [3,4].

Co and Fe are two commercially used metal catalysts for FT synthesis. Co is preferred over Fe due to its greater activity, higher chain growth probability, and lower water–gas shift activity. However Co is approximately 1000 times more expensive than Fe [5], therefore optimal design of a Co FT catalyst is essential for its utilization. This goal could be achieved by decreasing the Co particle size to increase the exposed surface area per unit mass of the Co metal. However, some investigators have reported that Co particles smaller than 10 nm show a sharp drop in activity [6–9]. The pioneering study of this particle size effect was conducted by Bartholomew's group [6] who claimed that the specific activity and molecular weight of hydrocarbon products decreased significantly with an increase of Co dispersion, consistent with a particle size effect. The catalytic performance of Co can vary with different supports, dispersions, metal loadings and preparation methods, which are indications of structure sensitivity. Interestingly, in a later work in collaboration with our group [10], Bartholomew and co-workers pointed out that FT synthesis under certain reaction condition can be structure-insensitive. The activity and selectivity appeared to be more closely related to the chemical nature of the support rather than to Co dispersion. Subsequently similar results have been reported by several other research groups [11–14]. The consensus of these studies is that there is no intrinsic particle size effect in FT synthesis. Recently Barbier [7] and Bezemer and co-workers [8] observed that the activity and selectivity are sensitive to Co particle size with particles smaller than 10 nm. More recently Borg et al. [9] emphasized the effect of particle size on selectivity, while no relationship was found between activity and Co size. Therefore, the particle size effect of Co FT catalysts with size below 10 nm is still controversial and more work is required to clarify this fundamental issue.

The metal particle size in the technical catalysts is governed by numerous parameters such as preparation method, nature of support, catalyst pretreatment and promoter effects. The interpretation of the kinetic data is complicated by heat and mass transfer within the porous supports [15,16]. These complexities make it difficult to establish a correlation between activity/selectivity and particle size. In order to circumvent these difficulties, model catalysts have recently been prepared in our group under ultrahigh vacuum (UHV) conditions and tested in an elevated-pressure cell [17,18]. Kinetic investigations have shown that our Co/SiO_2 catalyst is an ideal model for the study of FT synthesis [19].

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doi:10.1016/j.cattod.2011.06.021

Seven Co/SiO_2 model catalysts with Co particle sizes in the range of 1.4–10.5 nm were prepared to examine the possible intrinsic particle size effect in FT synthesis. Transmission electron microscopy (TEM) was used to characterize the particle size distribution and the number of active sites. The surface of the model catalysts, both before and after reaction, was analyzed by X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Apparatus

The experiments were carried out in a custom apparatus that combines an elevated-pressure cell with an UHV chamber. Both regions were capable of achieving base pressures of 2.0×10^{-10} Torr. The elevated-pressure cell (0.2 L) could be isolated from the UHV chamber with a gate valve and serve as a batch reactor for catalytic reactions. The UHV chamber was equipped with XPS, a differential ion gun and a quadrupole mass analyzer. The sample could be transferred between the reactor and UHV chamber in vacuum. The model catalysts were prepared and analyzed in the UHV chamber; the kinetic measurements were made in the batch reactor.

2.2. Model catalyst preparation

A tantalum foil (10 mm × 10 mm) was mounted on a transferable probe and used as the substrate for the model catalysts. The sample could be heated to 1500 K resistively or to 2400 K by electron beam bombardment. The sample temperature was monitored with a W–5% Re/W–26% Re (C-type) thermocouple spot-welded to the backside of the foil. The sample was cleaned by Ar^+-sputtering, oxidation (1200 K, 5.0×10^{-8} Torr O_2) and electron beam bombardment (2100 K, in vacuum). This procedure was repeated for several cycles until no impurities were detected by XPS analysis.

The Co/SiO_2 model catalysts were prepared by vapor-deposition from silicon and cobalt sources. The silicon source used for SiO_2 deposition was a high-purity Si wafer (1 mm × 1 mm × 8 mm) wrapped with a W wire. The SiO_2 was deposited by evaporating Si onto the Ta foil in a background of 1.0×10^{-5} Torr O_2, followed by an anneal at 700 K [20,21]. The thickness of the SiO_2 support (10 nm) was determined by XPS using the published electron escape depth for SiO_2 [22]. Co was deposited onto the SiO_2 support from a Co doser which was made of a high-purity Co wire (99.99%) wrapped in a W filament. The Co dosing rate was calibrated using the break-point in a plot of the overlayer XPS intensity versus deposition time [23]. In this work, the Co coverage is reported with respect to the atomic density of the Mo(1 0 0) single crystal surface (Mo(1 0 0) = 1.01×10^{15} atoms/cm^2). One Co atom per Mo(1 0 0) surface atom corresponded to 1.0 monolayer (ML) Co. The deposited Co/SiO_2 model catalysts were annealed at 700 K for 10 min in vacuum before FT synthesis. Such prepared model catalysts avoid the use of cobalt salts as the precursor and exhibit 100% of reducibility, as confirmed by XPS spectra.

2.3. Catalytic testing

The Co/SiO_2 model catalysts were tested at 513 K under atmospheric pressure for FT synthesis. The reactant gases (H_2:CO:N_2 in a volume ratio of 6:3:1) were premixed in an aluminum cylinder and passed through a liquid nitrogen cooled molecular sieve trap prior to use. The sample was resistively heated to the reaction temperature and held for 4.5 h to reach steady-state. The products were analyzed by a HP 5890 gas chromatograph equipped with a HP-PLOT Al_2O_3 capillary column and a flame ionization detector. Activity and selectivity values were defined in terms of carbon balance from the detected hydrocarbons. Blank experiments were performed with SiO_2 on the Ta foil and no activity was observed under our reaction condition.

2.4. Catalyst characterization

Co particle size and the number of active sites were determined by TEM on a JEOL 2010 microscope operating at 200 kV. The sample for TEM study was prepared by depositing the Co/SiO_2 model catalyst directly onto a carbon-coated Mo grid. The Mo grid, coated with a thin carbon film (~20 nm), was spot-welded to a Ta foil which was then mounted on the transferable probe. After preparation of the Co/SiO_2 model catalyst, the sample was passivated with 0.5 vol% O_2 and removed from the vacuum chamber for TEM characterization. The Co metal particle size was corrected for the contraction of CoO to Co as described previously [24]. The average Co particle size (diameter) was determined using >200 particles from different imaged areas.

The surface of the model catalysts before and after catalytic testing was investigated by XPS. XPS spectra were acquired using a Mg Kα X-ray source and a precision PHI hemispherical analyzer with a pass energy of 58.70 eV. All binding energies are referenced to the Si 2p peak in SiO_2 at 103.4 eV with an experimental error of ±0.05 eV.

3. Results and discussion

3.1. TEM study

In order to investigate the Co particle size effect in FT synthesis, seven Co/SiO_2 model catalysts were prepared with different particle sizes by varying the Co coverage (0.25–6.0 ML). Shown in Fig. 1 are the representative TEM images and the corresponding metallic cobalt particle size distributions, corrected for oxidation, of 1.0, 2.0, 4.0 ML Co/SiO_2 model catalysts. According to these images it is evident that the Co particles are well dispersed on the SiO_2 support. The Co particle size distributions are narrow with standard deviations within 20% of the average size. Moreover, the average Co particle size increased with the Co coverage. The unique features for these model catalysts, including high dispersion, 100% reduction, and tunable particle size, make them prime candidates for studies of particle size effects on catalytic activity.

Recently our laboratory has characterized a series of model metal catalysts, with metal nanoparticles supported on a planar oxide support, and demonstrated that microscopy techniques can be used to estimate the number of surface metal atoms [25,26]. This approach provides a method for calculating the number of active sites from the particle size. In this work, we estimate the active sites based on the following assumptions: (i) one Co surface atom corresponds to one active site; (ii) the Co particles form a hemispherical cap on the SiO_2 support [25]; and (iii) the surface atom density for Co particles is 1.46×10^{15} atoms/cm^2 [27]. The results of this calculation are summarized in Fig. 2a. Also presented in Fig. 2b are the average particle size and the standard deviation for the Co/SiO_2 model catalysts with various Co coverages.

Spent catalysts were studied by TEM to observe the Co dispersion after reaction. A typical TEM image is shown in Fig. 3a and the corresponding metallic cobalt particle size distribution for the 2.0 ML Co/SiO_2 spent catalyst is displayed in Fig. 3b. By comparing Fig. 3 with Fig. 1b, the TEM image for 2.0 ML Co/SiO_2 catalyst before reaction, it is apparent that no significant sintering occurs during FT synthesis. Similar results have also been reported previously [8,28].

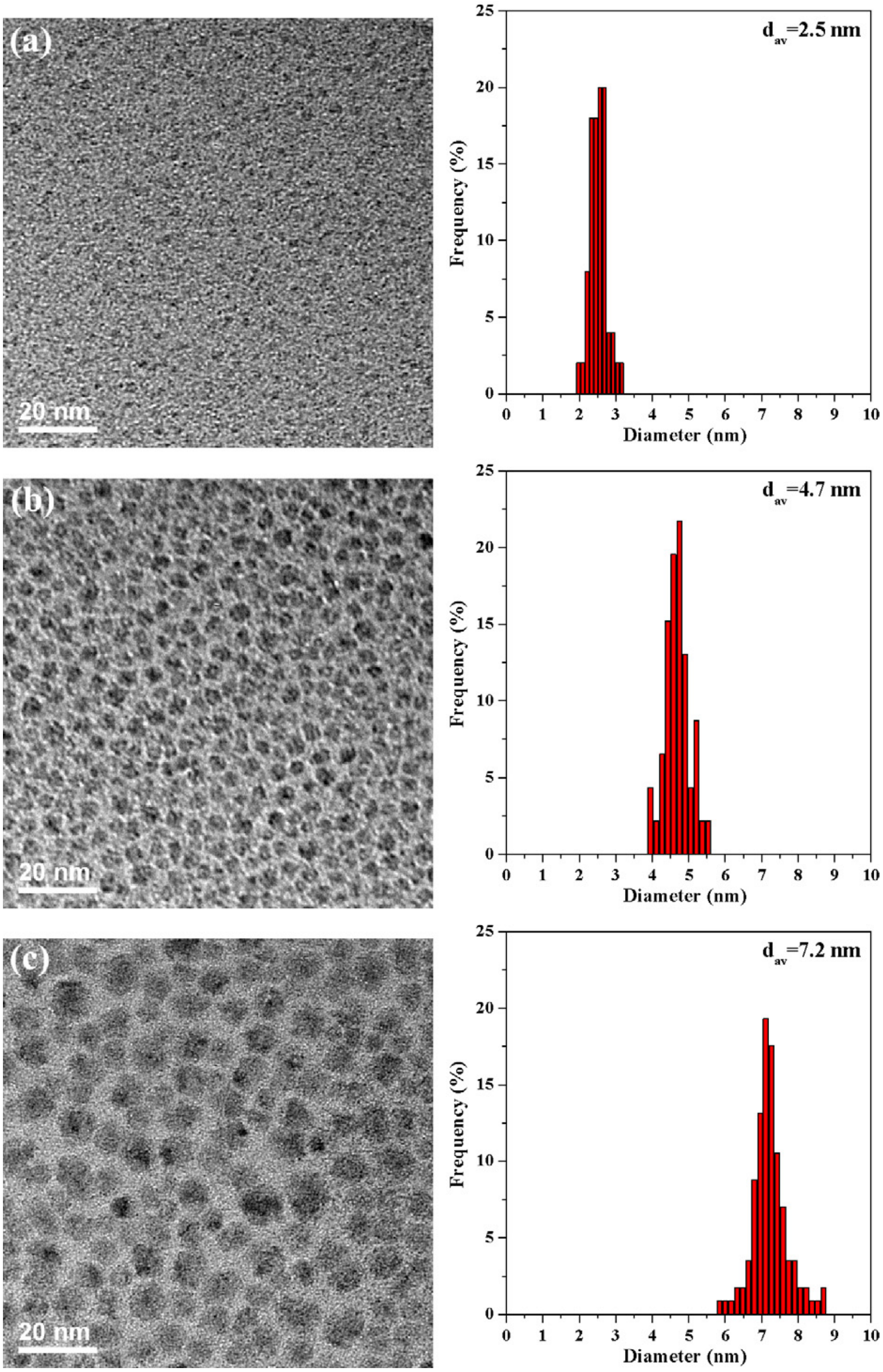

Fig. 1. Representative TEM images and the corresponding particle size distribution histograms for the Co/SiO$_2$ model catalyst with different metal coverage: (a) 1.0 ML; (b) 2.0 ML; (c) 4.0 ML. The metallic Co particle size in the histogram has been corrected for oxidation.

3.2. Catalytic performance

Activity and selectivity were measured with CO conversion lower than 0.1%. The reaction rates, expressed as CO molecules converted per second, were much lower for the small Co particles (0.25, 0.5, 1.0 ML) than those for the relatively large Co particles (1.5, 2.0, 4.0. 6.0 ML). Shown in Fig. 4 are the reaction rates for 1.0 and 2.0 ML Co/SiO$_2$ model catalysts as a function of reaction time. Deactivation is apparent for the 2.0 ML Co/SiO$_2$ catalyst whereas no activity change with reaction time is detected for the 1.0 ML sample. Deactivation for the FT catalysts during the initial reaction period has been reported in the literature and attributed to sintering, oxidation, and/or carbonaceous deposition [29]. The TEM results for spent catalysts in Fig. 3 rule out sintering as the cause of deactivation. XPS data in the following section will demonstrate that oxidation does not occur during FT synthesis for the relatively large Co particles. On the other hand, C 1s XPS spectra (data not shown) show a distinct feature at 284.6 eV after reaction, indicative of carbonaceous deposition. The deposited carbon species arise mainly from the hydrocarbon products adsorbed on the metal surface. For the relatively large Co particles, the reaction rates are much higher, therefore more hydrocarbon products will deposit on the metal catalyst surface, and thus lead to deactivation. Similar results relating carbonaceous deposition with deactivation has been reported

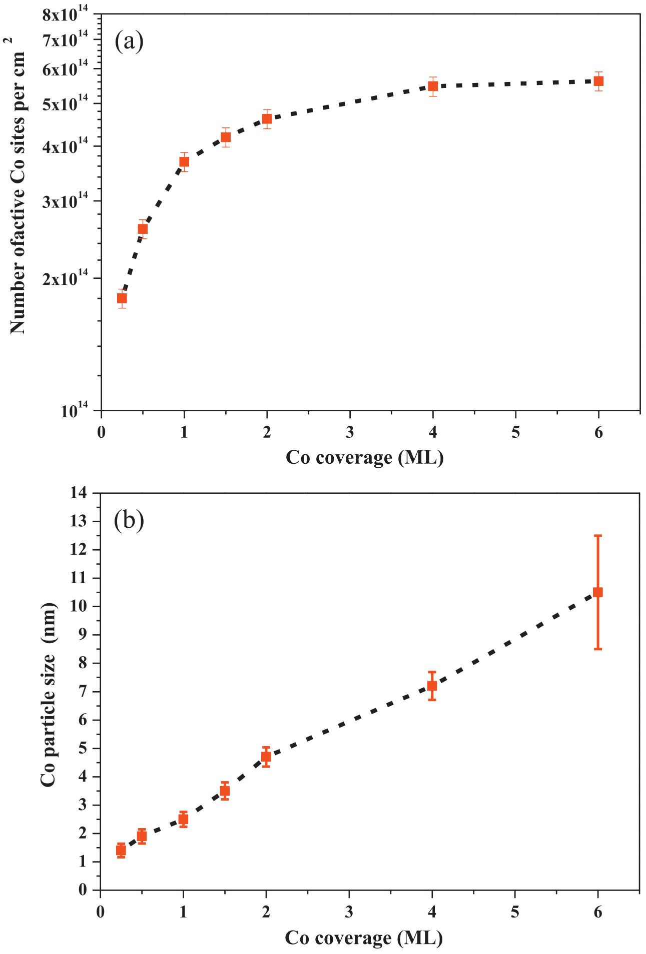

Fig. 2. Number of the active Co sites (a) and the average particle size (b) as a function of metal coverage estimated from TEM data.

previously [19]. In the following sections, activity and selectivity will be reported only for the steady state condition, i.e., after 3 h of reaction.

Turnover frequencies (TOF, number of CO molecules converted per active site per second) were calculated using the number of active sites estimated by TEM (Fig. 2a). As plotted in Fig. 5, an apparent particle size effect is observed. For catalysts with small Co particle sizes (1.4, 1.9 2.5 nm), the TOF is ~$6.0 \times 10^{-3}\ s^{-1}$. A much higher TOF, ~$5.0 \times 10^{-2}\ s^{-1}$, is obtained for the samples with relatively large Co particle size (3.5, 4.7, 7.2, 10.5 nm). The TOF values for both small and large particle sizes are constant. The TOF's for the relatively large particles are in agreement with the corresponding technical catalysts [30,31]. The methane selectivity also displayed two distinct regions (Fig. 6). CH_4 selectivity for the small Co particles (~90 mol%) is much higher than that for the relatively large Co particles (~72 mol%).

The apparent particle size effect in this study is at variance with that claimed by other investigators. Barbier et al. [7] observed that the TOF gradually increased with the Co particle size in the range of 4.4–9.2 nm; however, their TOF values were much lower than previously reported. Bezemer and co-workers [8] reported that the TOF and CH_4 selectivity were constant for catalysts with Co particle size larger than 6.0 nm, while both the selectivity and the activity changed continuously for catalysts with smaller particles. When the Co particle size was reduced from 6.0 to 2.6 nm, the TOF decreased from 1.2×10^{-2} to $1.3 \times 10^{-3}\ s^{-1}$ and the CH_4 selectivity increased from 40 to 53 wt%. In the following work [32], the group carried out steady-state isotopic transient kinetic measurements and concluded that the lower TOF for Co particles <6 nm was caused by both blocking of edge/corner sites as well as a lower intrinsic activity at the small terraces. The higher CH_4 selectivity for the small Co particles was attributed to their higher hydrogen coverages.

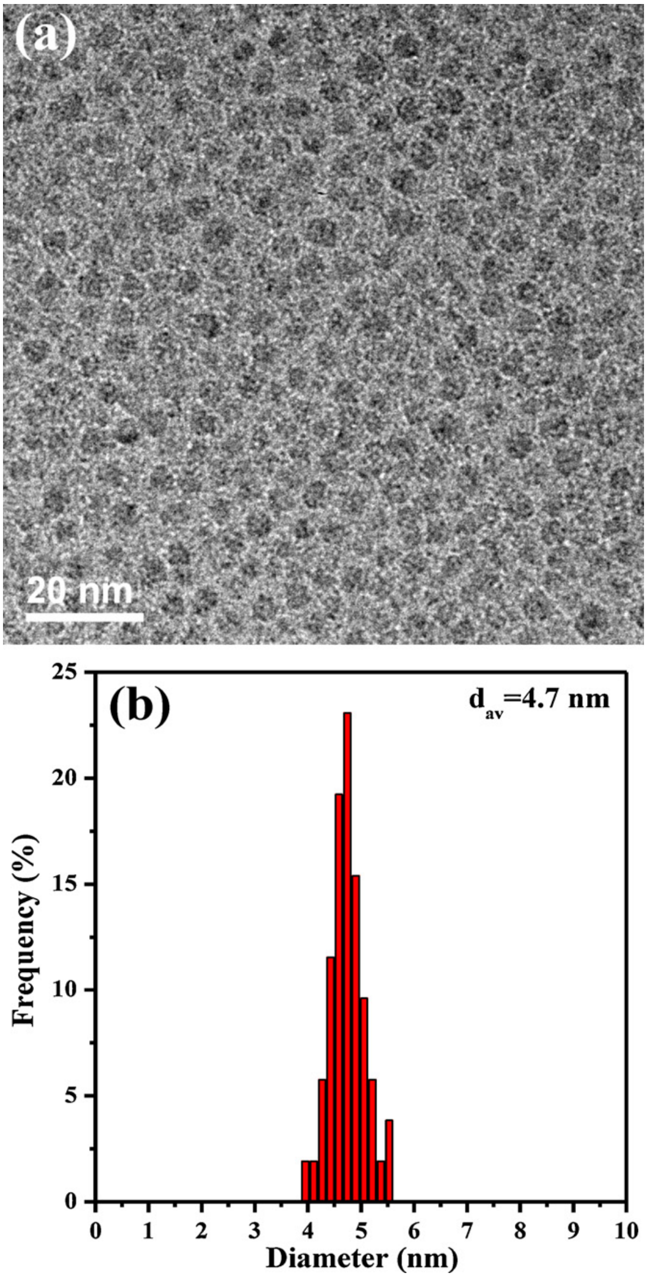

Fig. 3. Typical TEM image (a) and the corresponding particle size distribution histogram (b) of 2.0 ML Co/SiO_2 spent catalyst.

3.3. XPS characterization

To reveal the origin of the apparent particle size effect in the current work, the Co/SiO_2 model catalysts were analyzed by XPS both before and after reaction. Fig. 7 compares the XPS spectra of the fresh catalyst with that of the spent catalyst for 1.0 ML and 2.0 ML Co/SiO_2 sample, respectively. For the small Co particles (Fig. 7a), characteristic metallic Co 2p peaks were observed at 778.2 and 793.2 eV before reaction. After reaction, these two peaks decayed dramatically and another four features developed. The two features

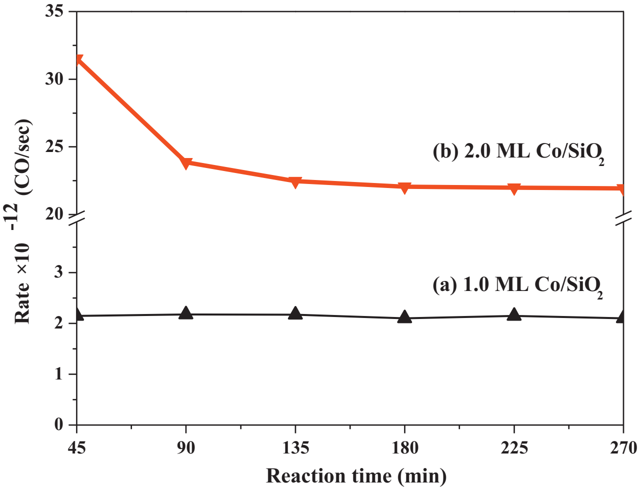

Fig. 4. Reaction rates as a function of reaction time for 1.0 (a) and 2.0 ML (b) Co/SiO_2 model catalysts. Reaction condition: 513 K; 760 Torr; H_2:CO:N_2 = 6:3:1 (volume ratio).

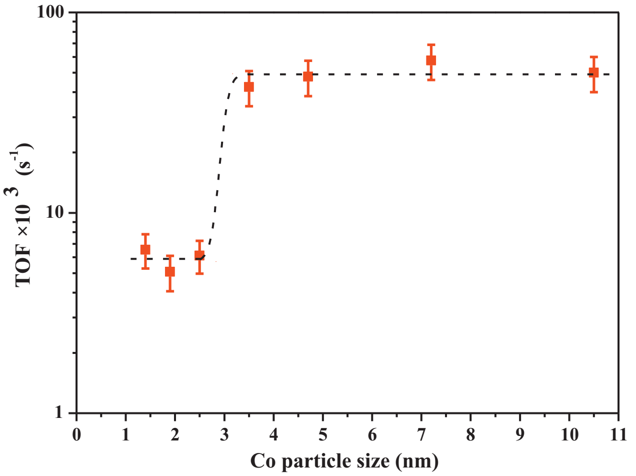

Fig. 5. TOF values as a function of Co particle size for the Co/SiO_2 model catalysts (513 K, 760 Torr, H_2:CO:N_2 = 6:3:1 (volume ratio)).

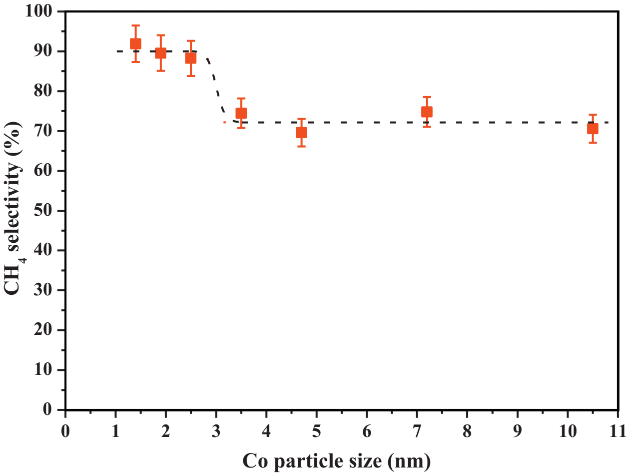

Fig. 6. CH_4 selectivity as a function of Co particle size for the Co/SiO_2 model catalysts (513 K, 760 Torr, H_2:CO:N_2 = 6:3:1 (volume ratio)).

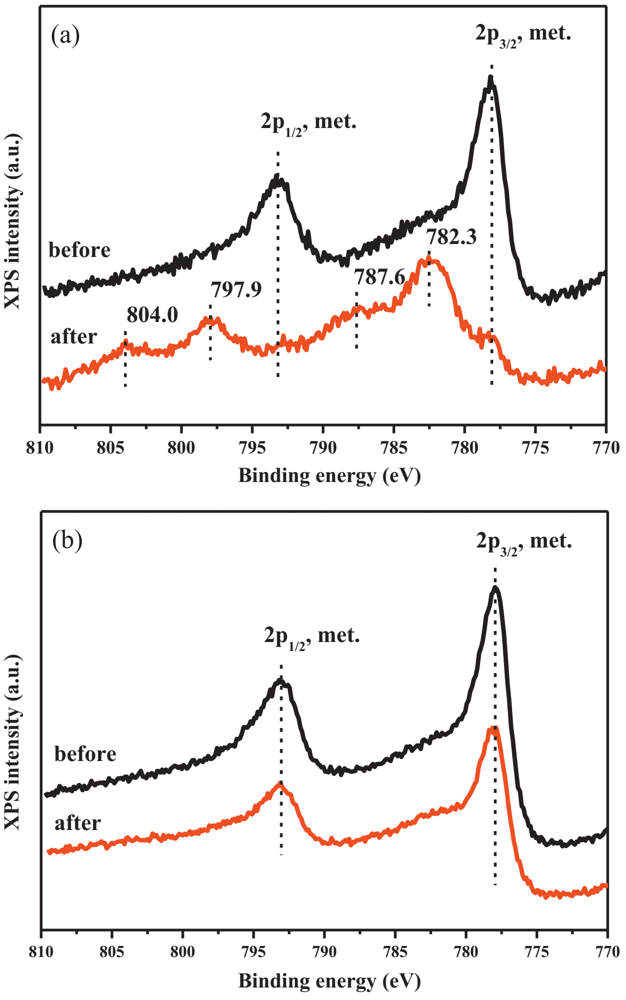

Fig. 7. Co 2p XPS spectra of the fresh and spent sample for 1.0 ML (a) and 2.0 ML (b) Co/SiO_2 model catalyst.

at 782.3 and 797.9 eV correspond to 2p peaks for Co^{2+} species, while the other two features at 804.0 and 787.6 eV are the shake-up satellite peaks for the Co^{2+} species [33]. The distinct difference between the fresh and spent catalyst clearly showed that significant oxidation occurred during FT synthesis on the small Co particles. As a matter of fact, the oxidation of the small Co particles took place readily, even after 10 min under reaction conditions. On the other hand, no evident change with respect to the chemical state of Co was detected for the relatively large Co particles (Fig. 7b).

Several researchers claimed enhanced activity over the surface cobalt oxide compared to the metallic cobalt [34,35]. In order to clarify this issue, an oxidized Co/SiO_2 model catalyst was prepared by annealing a 2.0 ML Co/SiO_2 at 700 K in 5.0×10^{-8} Torr O_2 for 20 min. As shown in Fig. 8a, the XPS spectrum for the oxidized 2.0 ML Co/SiO_2 sample was similar as that for the spent 1.0 ML Co/SiO_2 catalyst. Fig. 8b depicts the reaction rates versus reaction time for 1.0 ML and 2.0 ML Co/SiO_2 catalyst as well as the oxidized 2.0 ML Co/SiO_2 sample. It is clear that the oxidized cobalt surface exhibited a much lower activity than the metallic cobalt. The activity for the oxidized 2.0 ML/SiO_2 catalyst was in the same order of the 1.0 ML Co/SiO_2 catalyst, which further confirmed that the low TOF for the small Co particles was caused by the oxidation of cobalt during reaction.

In Co-catalyzed FT synthesis, the lower water gas shift activity leads to high water accumulation. The partial pressure of water during reaction depends on the feedstock, conversion, and reac-

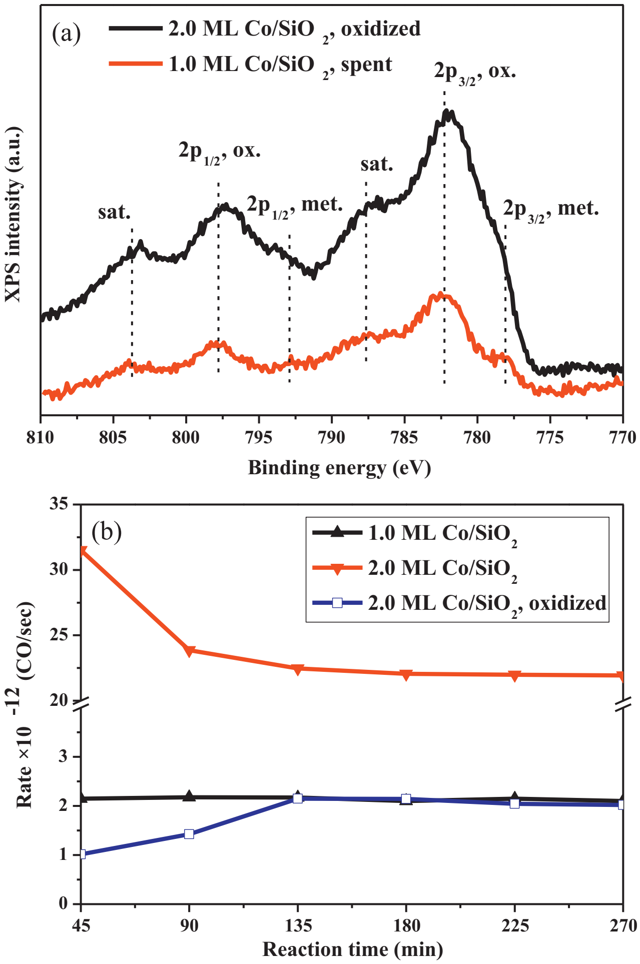

Fig. 8. (a) Co 2p XPS spectra for the oxidized 2.0 ML Co/SiO_2 sample and the spent 1.0 ML Co/SiO_2 catalyst; (b) the reaction rates versus reaction time for 1.0 ML and 2.0 ML Co/SiO_2 catalyst as well as the oxidized 2.0 ML Co/SiO_2 sample.

tor system. Although bulk oxidation of metallic cobalt by water during FT synthesis is not thermodynamically favored, the surface oxidation of cobalt particles has been documented by both thermodynamic analysis and experimental results [36–38]. Lahtinen and co-workers proposed that the Co particles may be oxidized by oxygen produced by CO dissociation [39]. In order to exclude this possibility, a 1.0 ML Co/SiO_2 model catalyst was exposed to 228 Torr CO at 513 K for 4.5 h. Fig. 9 demonstrates that the small Co particles are not oxidized under the same CO partial pressure as in the kinetic testing. The reduced Co intensity may be due to carbon deposition onto the cobalt surface by CO disproportionation reaction. Therefore we conclude that the small Co particles were oxidized by the water under our reaction condition.

3.4. General discussion

The combination of kinetic data and XPS characterization in the present work demonstrates very clearly that (i) for the relatively large Co particles (3.5–10.5 nm), no evident oxidation of cobalt was observed. The TOF and CH_4 selectivity were relatively constant, which indicated no intrinsic particle size effect for FT synthesis; (ii) the small Co particles (1.4–2.5 nm) could be easily oxidized during FT synthesis, which leads to a lower TOF and higher CH_4 selectivity; (iii) the oxidation of the small Co particles was caused by the water vapor formed during reaction, not by oxygen produced by CO dissociation.

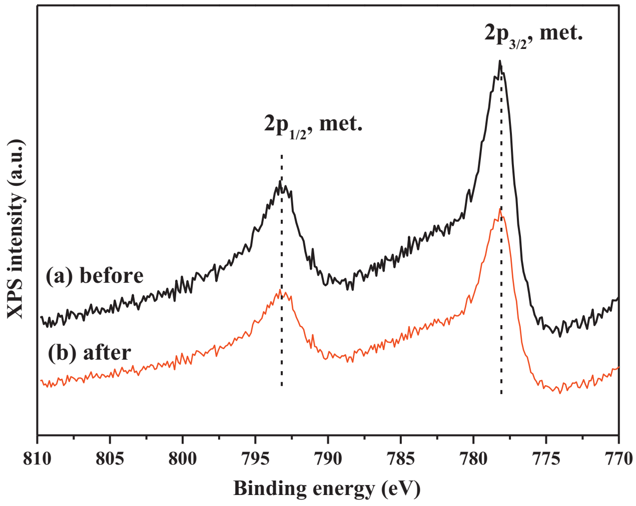

Fig. 9. Co 2p XPS spectra for 1.0 ML Co/SiO_2 model catalyst before (a) and after (b) being exposed to 228 Torr CO at 513 K for 4.5 h.

The literature concerning the intrinsic Co particle size effect in FT synthesis with the size smaller than 10 nm was scattered. The divergence may be caused by the difficulty in preparing well dispersed Co nanoparticles with high reducibility as well as the complexity of FT synthesis on technical catalysts. The obtained kinetic data from technical catalyst are flawed due to issues such as artifacts, metal–support interaction, incomplete reduction of the metal, and heat and mass transport [40]. For these reasons, model catalysts are particularly advantageous because they simplify the preparation process and offer a better control towards chemical nature of the support and dispersion of the metal particles. The coupling of an elevated pressure cell for the kinetic testing with a UHV chamber for the surface science study allows a clear picture of the intrinsic particle size effect to be developed.

In a previous collaboration work between Bartholomew's and our group, we have investigated the role of surface structure and dispersion in FT synthesis by comparing the steady-state activity and selectivity of submonolayer Co deposited on W(1 1 0) and W(1 0 0) with those of carbonyl-derived Co/Al_2O_3 catalysts of varying dispersion and extent of reduction [10]. The two Co/W surfaces have different geometries but exhibit similar activity. The activity matches that of the highly active, highly reduced Co/Al_2O_3 catalysts. All of these data suggested that FT synthesis is structure-insensitive. The structure-insensitive nature of FT synthesis on Co was also confirmed by the surface study on Co single crystals with different exposed crystal planes [41,42]. TOF on zigzag grooved Co(1 1 $\bar{2}$ 0) surface and closed-packed Co(0 0 0 1) surface differ within a factor of two while the apparent activation energies for methane and ethane formation are approximately equal to each other on both single crystal surfaces. The SiO_2 supported Co model catalyst in the present work is closer to "reality" and makes the study of the particle size effect possible. No intrinsic particle size effect for the metallic Co particles corroborates that FT synthesis is not sensitive to the dispersion or surface structure.

4. Conclusion

Seven Co/SiO_2 model catalysts with various metal coverages (0.25–6.0 ML), corresponding to different Co particle size (1.4–10.5 nm), were prepared and tested to investigate the intrinsic particle size effect in FT synthesis. TEM images were employed to estimate the particle size distribution and the number of active sites for each model catalyst. Kinetic data and XPS spectra demonstrated that no intrinsic particle size effect was observed for the metallic

Co particles in the range of 3.5–10.5 nm. For the smaller Co particles (1.4–2.5 nm), the metallic Co was easily oxidized by the water vapor, which lead to lower TOF and higher CH_4 selectivity.

The results in the present work are in good agreement with our previous surface study with submonolayer coverage Co deposited on single crystal substrates; both of which demonstrate that FT synthesis is independent of dispersion and not intrinsically structure-sensitive. The clear picture developed by model catalyst research versus the scattered data from technical catalyst studies highlights the significant importance of exploring the particle size effect or structure sensitivity on the well-defined surface.

Acknowledgements

We acknowledge with pleasure the financial support of this work by the Department of Energy (DE-SC0001058) through the Louisiana State University Energy Frontier Research Center, and the Robert A. Welch Foundation (Grant No. A-0030). Z.W. thanks the Chinese Scholarship Council for support as a Visiting Scholar.

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