Available online at www.sciencedirect.com
ScienceDirect
Catalysis Today 123 (2007) 122–132
CATALYSIS TODAY
www.elsevier.com/locate/cattod

Evidence for anchoring and partial occlusion of metallic clusters on the pore walls of MCM-41 and effect on the stability of the metallic clusters

Sangyun Lim, Chuan Wang, Yanhui Yang, Dragos Ciuparu, Lisa Pfefferle, Gary L. Haller *

Department of Chemical Engineering, Yale University, P.O. Box 208286, New Haven, CT 06520, United States

Abstract

In order to explain the high stability of the Co- and Ni-MCM-41 catalysts, the hypotheses of anchoring of small metallic clusters to cations in and partial occlusion of the metallic clusters by amorphous silica are proposed. Carbon monoxide chemisorption on model catalysts and Co-MCM-41 has given direct proof of the metal anchoring effect on the stability of metal cluster dispersion. The partial occlusion of metallic clusters, which may lead to physical confinement (inhibited migration) or chemical confinement (inhibited reaction), was monitored by CO in situ FTIR and CO methanation along with a kinetic study, which confirmed that the metallic clusters on the pore surface result in the stabilization of the catalysts against deactivation. A fine tuning of these physicochemical phenomena in the transition metal incorporated MCM-41 will make possible the design of stable catalytic systems for reactions requiring metallic active sites under severe reaction conditions.

Keywords: Co-MCM-41; Ni-MCM-41; Anchoring; Occlusion; TPR; In situ CO FTIR; CO methanation; Active site stability; CO chemisorption; TEM; Kinetic study

1. Introduction

In order to synthesize highly ordered and reproducible metal ion incorporated MCM-41 by isomorphous substitution of Si, numerous inter-relating synthesis factors have to be simultaneously considered. In the metal ion incorporated MCM-41, unlike the pure siliceous MCM-41, special care in treatment is necessary because the different physicochemical environment of metal ions in the MCM-41 results in different catalytic properties. Statistical modeling work and various experimental trial and error approaches have been carried out to improve and/or control the physical and chemical properties of the metal ion incorporated MCM-41 samples [1–10].

In the earlier work, highly dispersed size controllable sub-nanometer metallic Co clusters were produced by the radius of pore curvature effect using different pore sizes of Co-MCM-41 [9], and the Co ion location in the MCM-41 framework could be altered by the pH adjustment of the initial synthesis solution of Co-MCM-41 [8]. The sub-nanometer metallic Co clusters produced by a reduction treatment of Co-MCM-41 at 700 °C under hydrogen flow showed a high stability without formation of large particles on the pore walls, which usually results from surface migration under severe reduction conditions. The stability of these small metallic clusters on the surface was explained by suggesting an anchoring effect assumed to involve direct contact between metallic clusters and unreduced or partially reduced metal ions on the pore wall surface.

The concept of the anchoring effect was described by Yermakov [11]. Partially reduced organometallic compounds of Mo–Pt and Mo–Pd exhibited enhanced activity for ethane hydrogenolysis relative to the single metallic system, a result of increased dispersion and stability of metallic Pt and Pd anchored to the partially reduced Mo. Thereafter, a number of groups observed the interaction of metal ions and metallic clusters on the support surface in various systems [11–15], which suggested the possibility of the direct contact between these compounds. The terminology ‘‘anchoring sites’’ was first used in 1986 by two different research groups with a mono-metallic system, Ni/SiO_2 [16], and bi-metallic system, Rh–Cr [17], Pt–Fe, and Pt–Cr [18]. Bonneviot et al. [16] found a flattened shape consisting of Ni atoms in contact with Ni^+ at the metal–support interface, which exhibited a fast relaxation behavior via spin–spin or spin–lattice relaxation mechanism detected by a EPR analysis and inhibited carbon monoxide chemisorption on Ni [16]. These Ni^+ ions, as

---

* Corresponding author. Tel.: +1 203 432 4378; fax: +1 203 432 4387.
E-mail address: gary.haller@yale.edu (G.L. Haller).

0920-5861/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.03.005

well as Ni^{2+} ions, appeared to function as anchoring sites of the Ni particles. This group has reported a variety of evidence for Ni metal anchoring on Ni ions in the support surface [19–22]. At the same time, Tzou et al. [17,18] described the anchoring sites in bimetal ion exchanged zeolite catalysts such as RhCr/NaY zeolite, PtFe/NaYzeolite, and PtCr/NaY zeolite [17,18]. They found that the particle size of Rh and Pt decreased because the Cr ions or Fe ions acted as chemical anchors. This group also reported the anchoring effect with PdFe/ZSM-5 [23]. The anchoring effect in a CO impregnated catalyst was introduced by Coulter and Sault [24]; the formation of an intermediate surface cobalt silicate under specific activation conditions maximized the amount of reducible cobalt surface area available for Fischer–Tropsch reactions by maintaining a small particle size anchored to the cobalt silicate.

Although many groups have continued to report on the anchoring effect in single and bimetal impregnated or ion-exchanged systems [25–29], the stability of the metallic clusters discussed was under relatively mild conditions, usually below 500 °C, which would not be sufficient for higher temperature processes such as synthesis of single wall carbon nanotubes (SWNT). By incorporating metallic ions in the MCM-41 structure directly, the reduction stability of the metal ions dramatically improved compared to the impregnated catalyst. Transition metal oxides on the surface of a support, without formation of surface compounds, are usually reduced between 200 and 400 °C. However, by isomorphous substitution of Si by these metal ions, the reduction temperature increases to 600–900 °C without formation of a compound, but depends on the species of incorporating metal ions and the pore size of the MCM-41 as well as the initial pH of the synthesis solution [8–10]. Once metal ions are reduced, the metallic clusters migrate and aggregate, resulting in deactivation of the catalyst. By creating an anchoring site for these freshly reduced small metallic clusters, the migration and aggregation of the clusters can be curtailed or slowed, maintaining the catalytic activity. In the previous work, it was noted that, by a partial reduction of Co-MCM-41 at 700 °C for 30 min, Co metallic clusters of sub-nanometer dimensions resisted further aggregation. The anchoring effect between metallic Co clusters and Co ions was proposed to explain the stability of this catalytic system, as shown in Fig. 1. The reduction of Co ions to metallic Co in Co-MCM-41 was found to be initiated at 700 °C, as observed by X-ray absorption [9]. At this temperature, Co ions start to reduce to metallic clusters consisting of a few atoms, and unreduced (Co^{2+}) with partially reduced (Co^{1+}) Co ions are distributed in the framework and on the surface of the MCM-41 pores [30]. Some of the small metallic clusters are located on the pore surface without any confinement, and some of them are anchored to the Co ions near the pore surface as illustrated in Fig. 1(a). Under a further reduction, unconfined metallic clusters will freely migrate out of the pores producing larger particles, and the anchored clusters will retain their initial size as a result of the constraint of the anchoring sites, as depicted in Fig. 1(b). In this study, this hypothesis will be directly tested with model catalysts prepared by an incipient wet impregnation with the same amount of Co on four different supports.

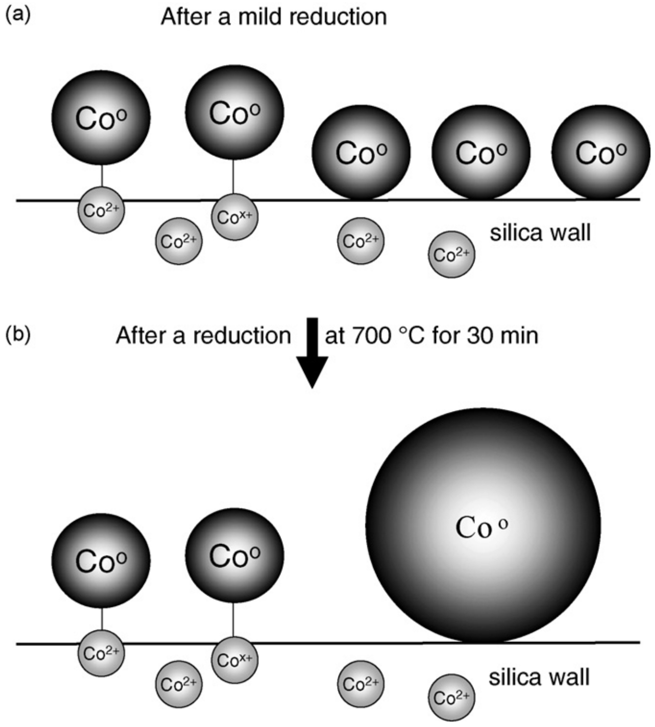

Fig. 1. Animation of the anchoring effect on the pore wall surface.

Because of the reduction resistant properties and migration from within the amorphous pore wall of Co-MCM-41, the reduced metallic clusters in this system may have different characteristics compared to that produced from impregnated samples or ion exchanged crystalline zeolites. For example, in addition to anchoring to metal ions in the support, partial occlusion of the metallic cluster surface by silica may occur. This may result in significantly different behavior of Co metals produced by a partial reduction of Co-MCM-41. The partial occlusion effect was cautiously suggested by Neto et al. [31]. They observed a reduction of the hydrogen quantity adsorbed on the Ir/Al_2O_3 catalyst and rationalized this by metal loss through erosion as well as by partial occlusion within the pores of the alumina support without proof of the occlusion effect. Therefore, in this study the partial occlusion effect will be observed by TEM, probed by CO in situ FTIR, and a CO kinetic study. As a probe reaction for the anchoring and partial occlusion effect in Co-MCM-41, as well as Ni-MCM-41, CO methanation was performed to investigate these effects on the stability of the metallic clusters in the metal incorporated MCM-41, and it will be suggested that the metal incorporated MCM-41 is a superior catalytic system compared to the impregnated catalysts of the same metal on the same support.

2. Experimental

2.1. Catalyst preparation

One weight percent of Co, Ni, and Ti were incorporated into the MCM-41 framework using 2 wt% aqueous solution of $CoSO_4{\cdot}7H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $TiCl_3$, respectively.

Isomorphous substitution of Si ions with desired metal ions was accomplished using a hydrothermal synthesis method. As a standard synthesis method of 1 wt% Co-MCM-41, 8.85 g of tetramethylammonium silicate containing 1 g of SiO_2 (19.9% in water, Sigma–Aldrich) and 50 g of de-ionized water were mixed with 2.5 g of colloidal silica, Cab-O-Sil (99.8% SiO_2, Sigma–Aldrich), for 30 min to obtain a homogeneous silica solution. As a Co source, 2 wt% cobalt sulfate heptahydrate solution was prepared, and 8.35 g of the Co solution was added to the silica solution, followed by vigorous mixing for 2 h which has been demonstrated by TPR to promote isomorphous substitution of Si ions by Co ions. In order to improve the reproducibility of the samples, an anti-foam agent (Anti-Foam A, Sigma–Aldrich), 0.2 wt% of surfactant, was added in the premixed solution. After 30 min of additional mixing, 28.79 g of 20 wt% hexadecyltrimethylammonium hydroxide (prepared by ion exchange of hexadecyltrimethyl ammonium bromide with OH group ion-exchange resin [Sigma–Aldrich] by an overnight batch mixing) was gently added as a templating material for MCM-41. As soon as the template material was added, careful pH adjustment to 11.5 was performed using a calibrated pH meter. The resulting solution was poured into a 250 ml polypropylene bottle, put in an autoclave, and maintained at 100 °C for 6 days to condense the silanol groups. After autoclaving, the sample was washed and filtered three times with de-ionized water and dried under ambient conditions over night. The dried sample was finely ground and thermally treated under flowing helium from room temperature to 540 °C for 20 h, held at the same temperature for an hour, and calcined at the same temperature for 6 h under flowing air to obtain the final Co-MCM-41 sample. One weight percent of Co or Ni impregnated MCM-41 was prepared by an incipient wet impregnation technique using the same metallic solution used for the preparation of the incorporated samples. After impregnation, the samples were dried at 150 °C overnight and calcined at 300 °C for 3 h under flowing air.

2.2. *CO chemisorption*

In order to investigate the metal anchoring effect by calculating the metallic particle size of the Co impregnated and incorporated catalysts, CO chemisorption was performed in a volumetric static adsorption system (Autosorb-1C, Quanta Chrome) at 40 °C, assuming the CO/metal stoichiometry is 1. Two hundred milligrams of each sample was loaded in a quartz flow cell and, for the impregnated samples, reduced at 400 °C for 30 min under flowing pure hydrogen (30 ml/min). After obtaining the particle size at this stage, the sample in the quartz cell was subsequently reduced at 500 °C for 30 min and 2 h, respectively, for another set of two CO chemisorptions. For the incorporated sample, 3 wt% Co-MCM-41, the reduction was performed at 700 °C with different time lengths (from 10 min to 150 min) because the reduction of Co-MCM-41 does not initiate below this temperature. After each step, oxygen back titration at 400 °C was carried out to calculate the degree of reduction under the assumption that all metallic Co is oxidized to Co_3O_4 [32].

2.3. *In situ CO FTIR*

As one of the strategies to prove the partial occlusion of the metal surface, in situ CO FTIR was performed, and the adsorption strengths between the Co impregnated and incorporated samples were compared. Twenty milligrams of each catalyst was pressed into a self-supporting disk and installed in a laboratory constructed stainless steel transmission FTIR cell. The impregnated sample was reduced by pure hydrogen at 500 °C for 30 min and purged by ultra high purity helium at the reduction temperature to remove the chemisorbed hydrogen on the metals, and the sample cell was cooled to 15 °C. Two percent of CO balanced in helium was introduced in the sample cell at this temperature and flowed for 30 min to adsorb CO on the reduced Co metal. The gas flow was switched to helium at the same temperature, and the spectrum was collected after 20 min. The adsorption strength of CO was very weak, therefore, the gas flow was kept as low as 10 ml/min to avoid a complete desorption of CO by a high helium flow. For the incorporated sample having higher reduction temperature, 700 °C and 800 °C, it was separately reduced in a quartz cell at a desired temperature and then transferred to the FTIR cell, followed by a further reduction at 500 °C for 30 min to reduce the oxidized Co by air contact while transferring the sample. The remaining procedures are the same as with the impregnated sample.

2.4. *Transmission electron microscopy (TEM)*

The TEM micrographs were recorded on a Philips Tecnai F20 TEM instrument equipped with a field emission gun and accelerating voltages of 200 kV. The point resolution and the line resolution were 0.24 nm and 0.12 nm, respectively, at a focal length of 1.7 mm. Samples were prepared by sonicating ~1 mg of the sample in 10 ml of ethanol (ACS/USP grade). A drop of this suspension was then put on a lacey carbon coated copper TEM grid and dried before the experiment.

2.5. *Temperature programmed reduction (TPR)*

The reducibility of the Co impregnated MCM-41 sample was investigated by a hydrogen temperature programmed reduction technique using the thermal conductivity detector (TCD) of a gas chromatograph (6890 plus, Agilent). Approximately 200 mg of each sample was loaded into a quartz cell. Prior to each TPR run, the sample cell was purged using ultrazero grade air at room temperature, then the temperature was increased to 500 °C at 5 °C/min, held for 1 h at the same temperature, and cooled to room temperature. This procedure produces a clean surface before running the TPR. The gas flow was switched to 5% hydrogen in argon balance, and the baseline was monitored until stable. After baseline stabilization, the sample cell was heated at 5 °C/min and held for 1 h at 900 °C to ensure complete cobalt reduction. A dry ice acetone trap was installed between the sample cell and the TCD to condense the water, produced by sample reduction.

2.6. CO methanation

A probe reaction that is sensitive to the nature of the exposed metal domain and to dispersion and thus reflects silica occlusion and/or anchoring is useful for chemical characterization. In this study, carbon monoxide methanation was chosen and acts as a probe reaction for the anchoring and occlusion effects over a wide reaction temperature range, 150–850 °C. Catalysts prepared by two different methods, impregnation and incorporation, were reduced under flowing hydrogen at different temperatures to form metallic Co and Ni clusters as active sites for the methanation. Fifty milligrams of catalysts were loaded in a quartz, down flow reactor, and reduced at 500 °C for 30 min for the impregnated catalyst and 700 °C for the incorporated one. The reactant composition was $CO:H_2:He = 1:50:49$, and the flow rate of the reactant was 60 ml/min. In order to measure the CO adsorption strength on the catalysts, a kinetic study was carried out with different partial pressure of CO at 300 °C for Co catalyst and at 270 °C for Ni catalyst to maintain low conversion. The partial pressure of CO was varied from 0.5% to 1%, which corresponds to H_2/CO mole ratio from 8.5 to 34. The product analysis was performed by a gas chromatograph (6890+, Agilent) directly connected down stream of the reactor.

3. Results and discussion

3.1. Anchoring effect

In order to investigate the anchoring effect on the stability of the metallic clusters on MCM-41, four model catalysts were prepared by an incipient wet impregnation of the same amount of Co, 1 wt%. Four different supports were chosen for the model catalytic systems; siliceous MCM-41 for non-anchoring sites on the surface, model (a) of Fig. 2; Co-MCM-41 and Ti-MCM-41 for containing anchoring sites on the surface as Co^{2+} and Ti^{4+}, model (b) and (d) of Fig. 2, respectively; Co-MCM-41 partially reduced at 500 °C for 30 min to distribute more anchoring sites on the surface as Co^{2+} and Co^{1+} [30] model (c) of Fig. 2. After the impregnation, four different Co catalysts were dried at 150 °C over night and calcined at 300 °C for 3 h, followed by reduction treatment under flowing pure hydrogen at different temperatures and times. When the samples are reduced under mild conditions, 400 °C for 30 min, there may be no serious migration on the surface so that all four catalysts will form similarly sized metallic clusters on the surface, as shown in Fig. 2. Except in the case of Co/Si-MCM-41, some of the reduced Co clusters will be located on the surface of each support without confinement, and some will be anchored to the unreduced metallic ions. More anchoring sites, unreduced and

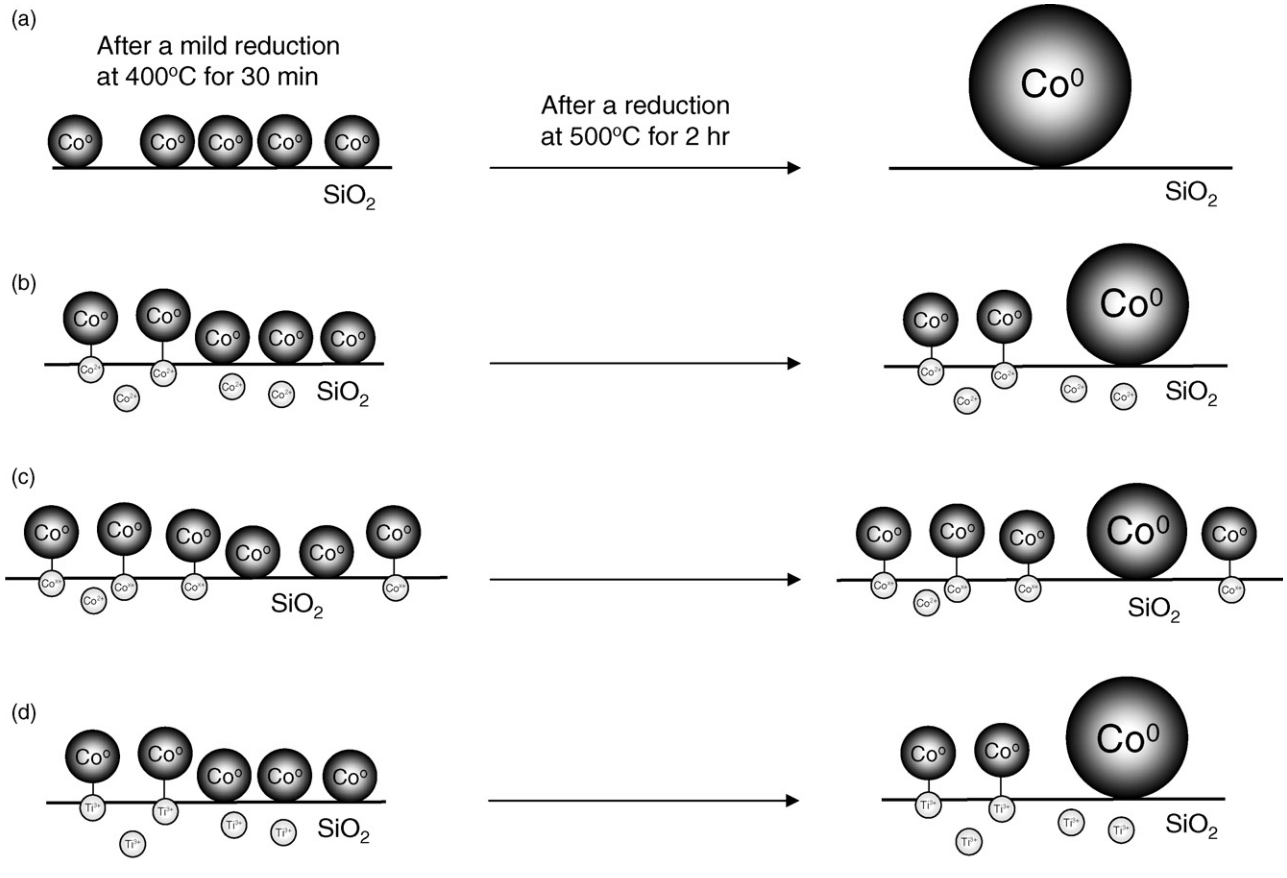

Fig. 2. Prediction of different surface state after reduction of the Co impregnated catalysts: (a) 1 wt% Co impregnated Si-MCM-41; (b) 1 wt% Co impregnated 1 wt% Co-MCM-41; (c) 1 wt% Co impregnated 1 wt% Co-MCM-41 (partially reduced at 500 °C for 30 min); (d) 1 wt% Co impregnated 1 wt% Ti-MCM-41.

Table 1
CO Chemisorption[a] results of Co impregnated catalysts[b]

Catalysts	Metal particle size (nm)[c]			Normalized ratio
	Reduced at 400 °C for 30 min	Reduced at 500 °C for 30 min	Reduced at 500 °C for 2 h	
1 wt% Co impregnated Si-MCM-41	5.9	8.2	35.9	1
1 wt% Co impregnated pre-reduced 1 wt% Co-MCM-41	5.4	5.5	10.7	3.4
1 wt% Co impregnated 1 wt% Co-MCM-41	–	–	12.0	3.0
1 wt% Co impregnated 1 wt% Ti-MCM-41	–	–	11.4	3.1

[a] CO/Co stoichiometry = 1.

[b] CO chemisorption was performed at 40 °C.

[c] O_2 titration was performed at 400 °C after CO chemisorption to calculate the degree of reduction of Co for the normalization of the chemisorption results; the metal particle size is based on CO chemisorption normalized for the amount of reduced metal measured by O_2 titration. Particle size (d) = $100Lf/(\text{ASA} \times Z)$, where L is mass of metal; Z the density of metal; ASA the surface area of metal (ASA = $N_m S A_m/166$, where N_m is number of adsorbed gas molecules; S the adsorption stoichiometry; A_m the cross-sectional area occupied by each active surface atom), f is the particle shape correction factor (6 for spherical particles).

partially reduced metal ions, can be formed in the near surface by a partial reduction treatment of Co-MCM-41 at 500 °C for 30 min, Fig. 2(c), because no metallic Co clusters were formed at this reduction condition [9]. Further reduction at higher temperature for a longer time will cause a significant migration of metallic clusters on the surface, and the mobility of the clusters will vary according to the surface situation such as number of anchoring sites, surface roughness, and perhaps the degree of wall curvature. Siliceous MCM-41 is expected to form the biggest Co metallic particles on the surface because there was no surface confinement to slow the mobility of the metallic clusters. The average Co particle size on the other catalytic systems are expected to be smaller than Co/Si-MCM-41 due to the constrained mobility of the Co clusters by the anchoring effect, probably resulting in the smallest Co cluster size in the partially reduced Co-MCM-41 because of the greater anchoring bonding of metallic clusters on this surface than is the case for non-partially reduced catalysts. Here we assume that the cation of lowest charge and chemically the most similar to the metal, i.e., Co^{1+}, will make the strongest bonds.

In order to prove this assumption, CO chemisorption was performed at 40 °C with these model catalysts, and the results are shown in Table 1. After a mild reduction at 400 °C for 30 min under flowing hydrogen, there is no significant difference in the metallic Co cluster sizes of Si-MCM-41 and the partially reduced Co-MCM-41, one of the catalytic systems with anchoring sites, resulting from the reduction of Co oxides on the surface without migration at this mild condition. However, these two catalytic systems start to show a difference in the particle size after further reduction at 500 °C for 30 min, 8.2 nm for Co/Si-MCM-41 and 5.5 nm for Co/partially reduced Co-MCM-41. A substantial difference in the particle size between non-anchored and anchored systems is observed after reduction for 2 h at 500 °C. The values normalized by the largest particle size produced on Co/Si-MCM-41 show that the particle size of anchored systems are approximately 3–3.5 times smaller than non-anchored system and, as expected, partial reduction of Co-MCM-41 creates more anchoring sites on the surface, resulting in the smallest Co particle size among these systems. Thus, by using model catalysts, we obtained circumstantial evidence for the anchoring effect hypothesized in the previous report [9]. Given the tentative confirmation, the next step of our work is to show that Co-MCM-41 actually exhibits the anchoring effect.

Different amounts of Co in the MCM-41 framework exhibited different reduction stability; as the amount of Co increases, the temperature of the maximum reduction rate shifts to lower temperature [33]. MCM-41 with 1 wt% of Co starts to show reduction behavior at 700 °C, presumably the Co ions located in the near surface of the pore wall are reduced first, and reduction is only partial at this temperature maintaining anchoring sites, and resulting in sub-nanometer metallic Co clusters without further aggregation [8,9]. Thus, a higher loading of Co-MCM-41, 3 wt%, having lower reduction stability than 1 wt% Co-MCM-41 was chosen to investigate the behavior of the Co metallic clusters at 700 °C. The higher reduction temperature could be used with 1 wt% Co-MCM-41, however, the anchoring effect will not exist in this system because all of the Co ions will eventually be reduced at temperatures higher than 700 °C. Not surprisingly, the reduction appears to be autocatalytic, i.e., the initial reduction and formation of Co metal catalyzes the increase in rate of reduction by hydrogen dissociation and spillover. Fig. 3 illustrates the results of CO chemisorption at 40 °C on 3 wt%

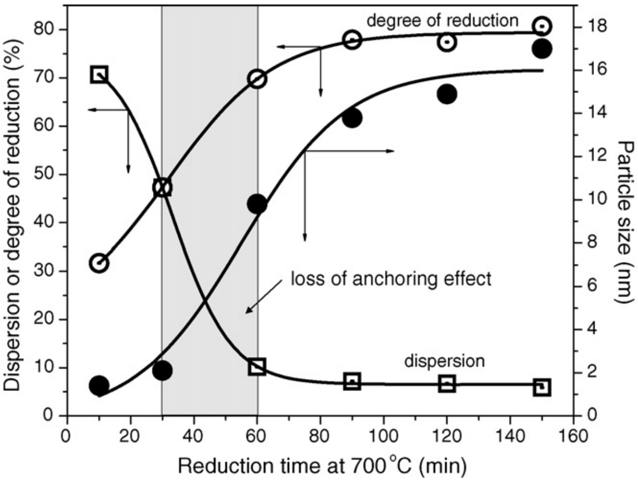

Fig. 3. CO chemisorption result of 3 wt% Co-MCM-41.

Co-MCM-41. After 30 min of reduction at 700 °C, the dispersion of the metallic Co clusters obtained by O_2 titration at 400 °C decreases dramatically from 50% to 10%, and a sudden increase of the particle size is observed at the same time. The growth of the Co particles slows after 60 min of reduction, and the dispersion does not change significantly. In the reduction time between 30 min and 60 min, small metallic Co clusters produced at the early stage of reduction at 700 °C start to migrate rapidly likely because the remaining anchoring sites are reduced at this reduction temperature. The migration rate of the particles decreases with reduction time after 60 min due to the particle size effect. This result clearly shows the existence of the anchoring effect in the Co-MCM-41 catalytic system, resulting in the high stability of the metallic Co clusters as predicted in our earlier reports [8,9]. The size of the Co particles obtained by CO chemisorption in Fig. 3 needs to be addressed. The particle size is much larger than expected; the metallic cluster size after reduction at 700 °C for 30 min was sub-nanometer based on an EXAFS spectroscopy experiment [8,9]. The earlier EXAFS particle size was not corrected for degree of reduction (and is thus and under estimate of particle size), but correction would not bring it into agreement with the chemisorption estimate of particle size. At this point, it can be only speculated that the size of metallic Co particles in this system may be over estimated by CO chemisorption, and this is probably related to the surface state of reduced Co-MCM-41 as compared with the Co impregnated sample. This speculation will be supported by experiment in the following section.

3.2. Partial occlusion effect

Fig. 4 illustrates one of the CO methanation results, which was carried out as a probe reaction of the metal anchoring effect, on the impregnated and incorporated Co catalysts. The Co impregnated catalyst reduced at 500 °C for 30 min under flowing hydrogen shows a superior CO conversion compared to Co-MCM-41 reduced at different temperatures. Even after Co-MCM-41 was reduced at 900 °C for 30 min, all of Co ions in the framework will be reduced at this condition [8], the catalytic activity did not exceed the impregnated catalyst. Two predictable differences in the reduced Co metallic clusters on the surface of the impregnated and incorporated catalysts can be suggested. After a reduction treatment of the impregnated catalyst, all of the reduced metallic Co clusters will be distributed on the support surface with complete exposure, Fig. 4(a). In the incorporated sample, however, some of the reduced metallic Co clusters will be completely exposed on the surface as in the impregnated catalyst, and some of the Co atoms are still buried in the amorphous silica or partially occluded by silica because of the slow reduction rate of Co ions in the MCM-41 framework and amorphous silica surrounding Co ions, as shown in Fig. 4(b). When CO is introduced in these catalytic systems, the completely exposed metallic Co clusters will strongly adsorb CO and create an adsorption species participating in the reaction. On the other hand, the partially occluded Co clusters will not be able to create strongly adsorbed species because of the perturbation by surface silica, resulting in the low catalytic activity.

In order to prove this hypothesis, a kinetic study of CO was performed with different catalytic systems to investigate the adsorption strength under reaction conditions using the methanation probe reaction. The change of the reaction rate, resulting from different CO partial pressure, was monitored. Fig. 5 depicts the CO kinetic study results performed on the Co and Ni impregnated and incorporated catalysts. The Co and Ni impregnated catalysts reduced at 500 °C for 30 min show a

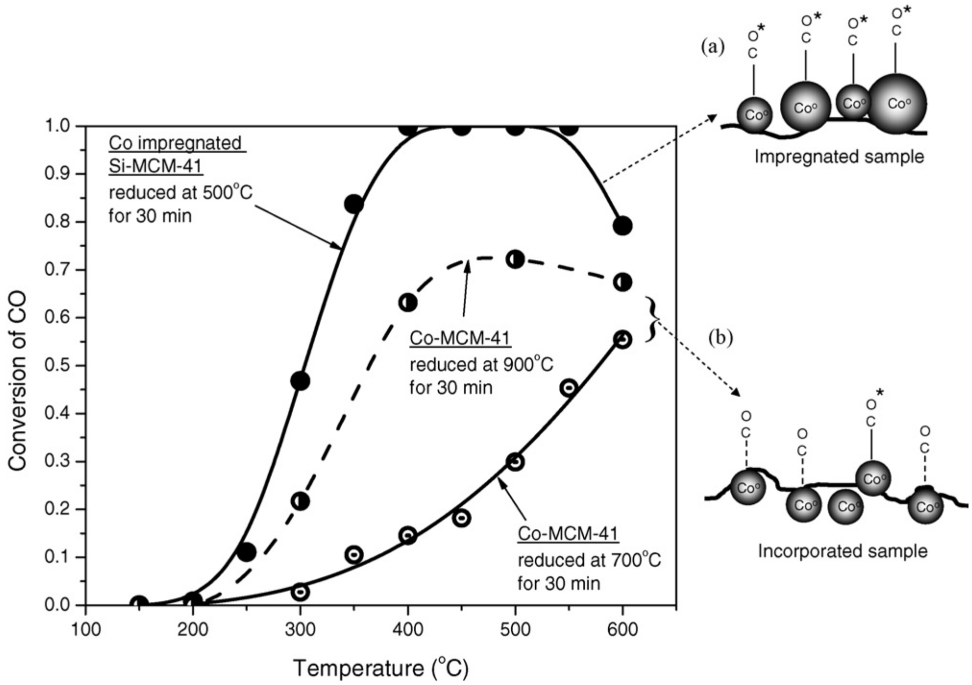

Fig. 4. Different CO methanation activity between the impregnated and incorporated Co catalysts. The asterisk marks chemisorbed CO not perturbed by silica occlusion.

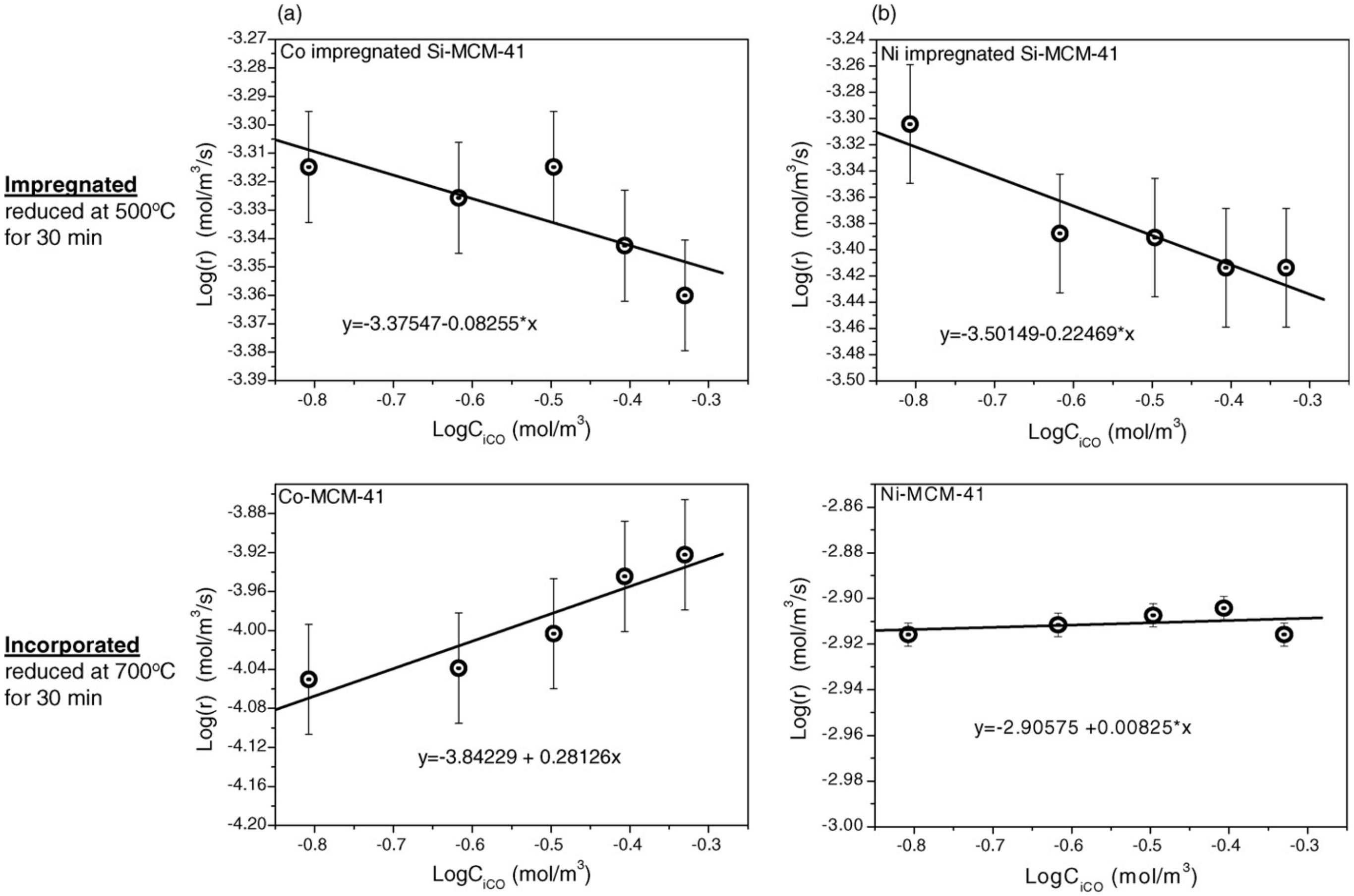

Fig. 5. CO methanation kinetic study results on the (a) Co and (b) Ni impregnated and incorporated catalysts.

negative slope indicating a strong adsorption of CO on the metallic clusters with modest self-inhibition; however, the incorporated catalysts reduced at 700 °C for 30 min exhibit a positive slope suggesting weak adsorption strength between CO and active sites. This result supports the hypothesis of a different surface situation between the impregnated and incorporated catalysts. The slope of Ni-MCM-41 approaches zero, indicating stronger adsorption strength than Co-MCM-41, which results from the faster reduction rate [10] suggesting Ni-MCM-41 is a superior catalyst relative to Co-MCM-41 in CO methanation as is well known in the impregnated catalysts.

The adsorption strength of CO on the active sites was also checked by an in situ FTIR technique. Diluted CO, 2% in He, was introduced to the stainless steel in situ cell containing a free standing Co catalyst disk for 30 min at 15 °C. After adsorption of CO, the sample cell was purged with a low flow of He, 10 ml/min, to prevent desorption of weakly adsorbed CO, and the spectrum was collected after 20 min of He purging. As illustrated in Fig. 6, the spectrum shows three major peaks at $\nu = 2052\ \mathrm{cm}^{-1}$, $2117\ \mathrm{cm}^{-1}$, and $2171\ \mathrm{cm}^{-1}$, which are assigned to a single bonded CO on Co^0, a single bonded CO on Co^{x+}, and a single bonded CO on Co^{2+}, respectively [34,35]. It does not show any bridged bonded CO on Co^0 around $\nu = 1950\ \mathrm{cm}^{-1}$. The impregnated Co catalyst shows the strongest single bond of CO–Co^0, based on kinetic inhibition, see Fig. 5. However, the incorporated catalyst shows a small peak at the same position, indicating a smaller amount of CO adsorbed on the metallic Co clusters resulting from the weaker adsorption strength of CO on the incorporated sample relative to the impregnated catalyst because of the partial occlusion effect. The peak intensity of the incorporated sample increases as the reduction temperature was increased to 800 °C, which

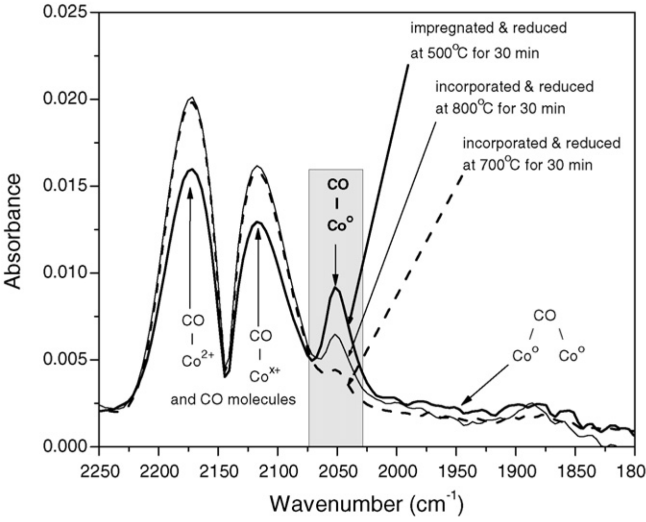

Fig. 6. In situ FTIR spectra of CO chemisorbed Co catalysts synthesized in different methods.

suggests that more metallic Co clusters can be exposed on the surface by a reduction treatment at higher temperature. Note that both after 700 °C and 800 °C, the Co-MCM-41 (incorporated catalysts) shows strong CO adsorption on Co cations.

As a complementary experiment to the kinetic study and in situ FTIR of CO, TEM analysis was performed with Co-MCM-41 reduced at 900 °C for 1 h. Monitoring sub-nanometer metallic Co clusters in the partially reduced Co-MCM-41 (reduced at 700 °C for 30 min under flowing H_2) by TEM has not been successful, therefore, a completely reduced Co-MCM-41 after TPR was selected as a sample to be monitored. Although the sample was completely reduced and formed many large Co particles, several different environments of the particles on the surface may be easily observed, as shown in Fig. 7. Some of the large particles are completely covered by amorphous silica as shown in Fig. 7(a) on which there will be no adsorption of CO; some of them are partially occluded as shown in Fig. 7(b) on which a weak adsorption of CO will be created; and some of them are completely exposed on the surface as shown in Fig. 7(c) on which a surface adsorbed CO species will contribute to the CO methanation. From these results, the occlusion of Co in reduced Co-MCM-41 was clearly demonstrated, which affects the CO methanation negatively in a short time reaction. This result can also explain the over estimated metallic Co cluster size in the Co-MCM-41 system, measured by CO chemisorption and discussed earlier. The complete and/or partial occlusion of metallic Co clusters will not allow the strong chemisorption of CO on the surface, which will cause no adsorption and/or easy desorption by gas purging or vacuum treatment in the process of CO chemisorption, resulting in the under estimation of total CO adsorption volume. The Co cluster size was obtained by the normalization of the CO adsorption volume with total Co loading in Co-MCM-41. Therefore, the under estimation of CO adsorption volume resulted in the over estimation of the Co particle size.

3.3. Probe reaction (CO methanation)

Catalytic activity can be a powerful catalyst characterization tool. Here, CO methanation was performed as a probe reaction to provide complementary evidence for anchoring and occlusion on the Co- and Ni-MCM-41 catalysts. Fig. 8 shows a temperature programmed CO methanation results on the impregnated and incorporated Co catalysts. The incorporated catalyst, Fig. 8(a), shows gradual improvement of the CO conversion as the reduction temperature increases from 700 °C

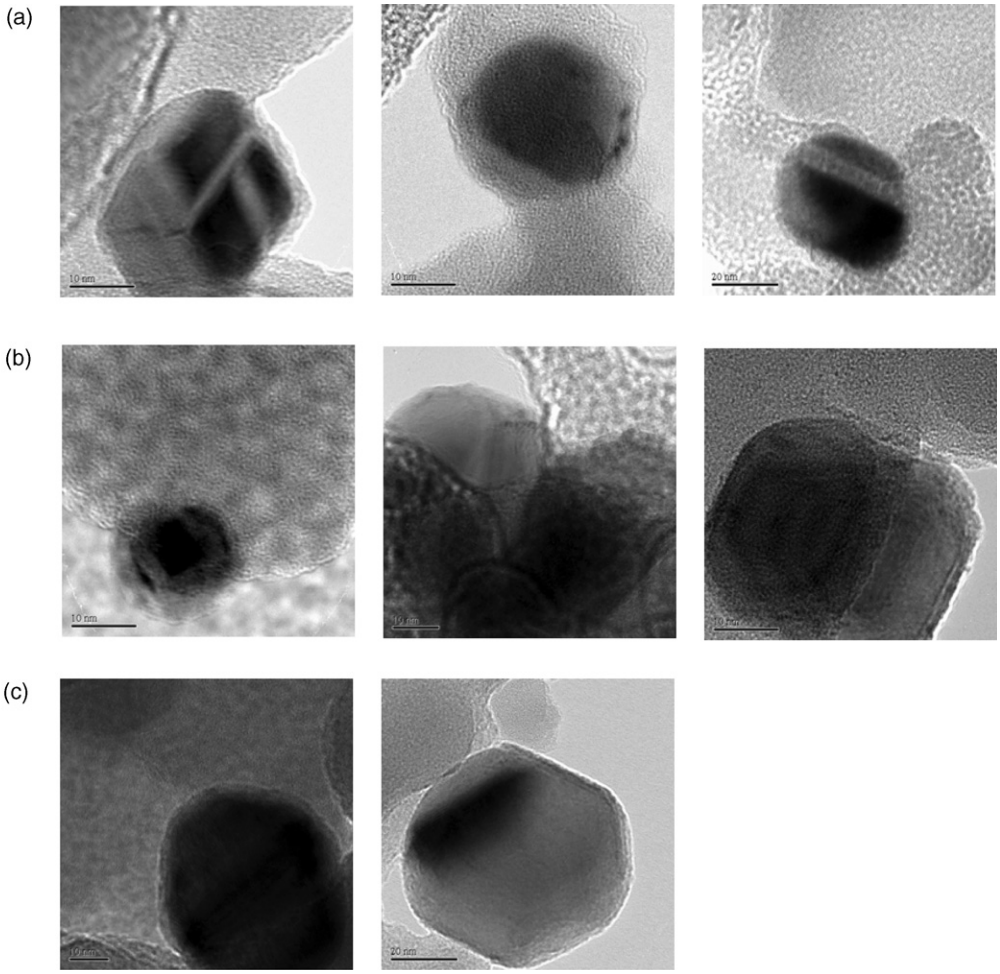

Fig. 7. TEM images of Co-MCM-41 after complete reduction at 900 °C for 1 h: (a) complete coverage; (b) partial coverage; (c) complete exposure.

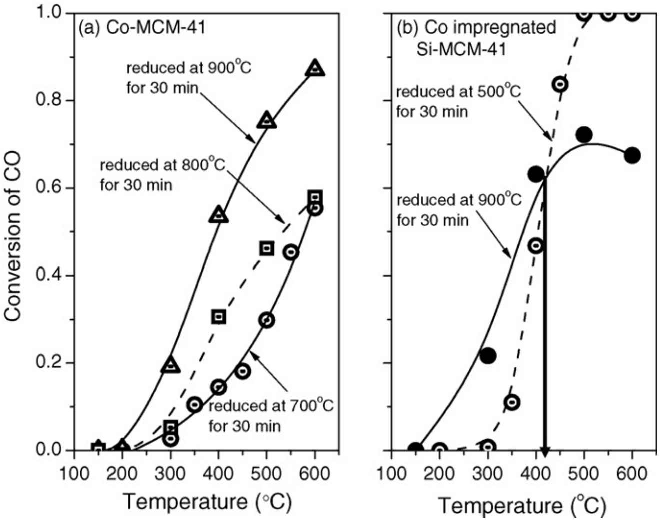

Fig. 8. CO methanation results of Co impregnated and incorporated catalysts.

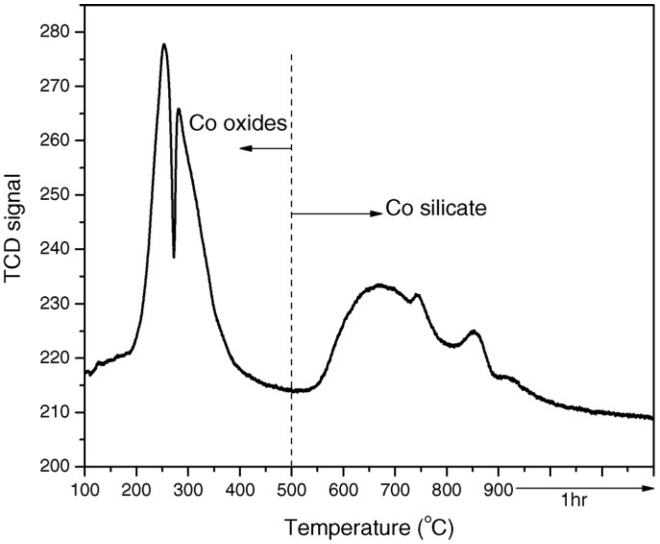

Fig. 9. Hydrogen temperature programmed reduction (TPR) result of Co impregnated catalyst.

to 900 °C without degradation of the activity. As previously reported, all of the Co ions will be completely reduced at 900 °C, and presumably large metallic particles are formed by rapid migration on the surface, resulting in the deactivation of catalyst [8]. However, Co-MCM-41 reduced at 900 °C shows the highest activity without any deactivation, which suggests that there is another factor making metallic clusters stable other than the anchoring effect (because all Co has been reduced leaving no ions as anchors). Partial occlusion of small metallic clusters by amorphous silica, as observed earlier, can constrain the migration of clusters on the surface, resulting in a stabilization of catalytic activity. On the other hand, the impregnated Co catalysts show different patterns of CO methanation, Fig. 8(b), depending on the reduction temperature. The impregnated Co catalysts reduced at 500 °C for 30 min and 900 °C for 30 min show opposite CO methanation results under and over 400 °C. In order to explain this phenomenon, hydrogen TPR was carried out for the Co impregnated catalyst, and the result is depicted in Fig. 9. Two major species are detected on the surface of the Co impregnated catalyst; cobalt oxide, Co_3O_4 and CoO, under 500 °C and cobalt silicate like material over 500 °C [36]. Therefore, if the catalyst is reduced at 500 °C for 30 min, only approximately half of the Co can be reduced to metallic clusters, resulting in the lower CO methanation activity compared to the sample reduced at 900 °C for 30 min in which all Co species are completely reduced. There will not be a serious migration at the moderate temperature, 400 °C. However, significant migration of the reduced metallic clusters on the surface will start as the reaction temperature increases beyond 400 °C, resulting in lower activity of the sample reduced at 900 °C. When the Co impregnated sample is reduced at 500 °C, a significant amount

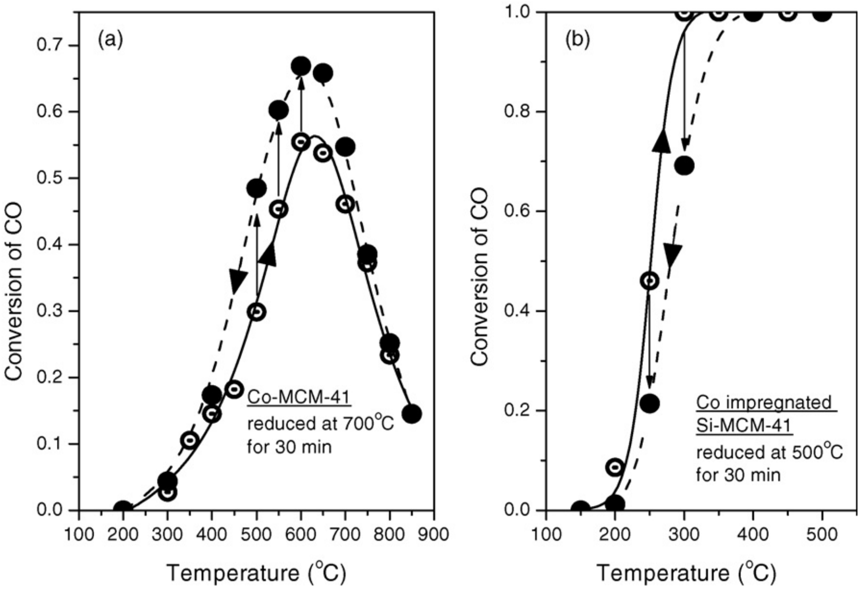

Fig. 10. Comparison of the catalyst stability between the Co impregnated and incorporated catalysts by reverse CO methanation.

of irreducible cobalt silicate like material exists on the surface, as proved by running TPR. This material can act as anchoring sites for the metallic clusters to a certain extent [24], therefore, the higher catalytic activity was observed in this sample compared to the one reduced at 900 °C.

The anchoring strength between unreduced or partially reduced Co ions in Co-MCM-41 and the cobalt silicate like materials in the impregnated sample was tested by a reversible temperature programmed CO methanation. The reaction temperature was increased from 150 °C to 500 °C for the impregnated catalyst and to 850 °C for the incorporated sample. Fig. 10(a) shows the case of the incorporated sample and Fig. 10(b) of the impregnated sample. The CO conversion of the impregnated catalyst increases as the reaction temperature approaches to 500 °C, and the catalytic activity decreases more than 20% when the temperature is reduced under the same reaction conditions. This indicates that there is a deactivation at this moderate reaction condition, 500 °C, resulting from the migration of metallic clusters by losing anchoring sites and/or carbon deposition. The measured carbon deposition amount was under 0.05 wt%, therefore, it can be suggested that the loss of anchoring sites is dominant in the deactivation process. When the same experiment was carried out with the incorporated sample over the extended temperature range, as shown in Fig. 10(a), the increase in activity of 10–15% is noted when the reaction temperature decreased after reaching 900 °C. This strongly suggests that the anchoring strength of Co ions on the pore surface of Co-MCM-41 is stronger than that of the cobalt silicate like material on the impregnated catalyst. Additionally, the stability of this catalyst is somewhat related to the partial occlusion of the metallic clusters when the reaction temperature reached 900 °C, deduced from a result discussed above. The decrease of CO conversion after 600 °C in the incorporated sample may be due to the weak adsorption of CO on the surface and the fast desorption rate at high temperature; CO temperature programmed desorption (TPD) may provide some insight on this behavior.

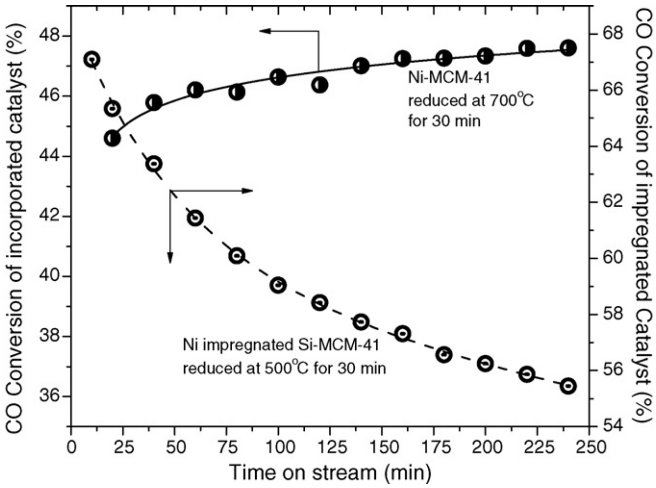

Fig. 11. CO methanation result of the Ni impregnated and incorporated catalysts.

The difference between the impregnated and incorporated catalysts can be noted more clearly in the Ni catalyst system, as illustrated in Fig. 11. The catalyst pretreatment condition was the same as used for the Co catalyst; reduction at 500 °C for 30 min for the impregnated catalyst and 700 °C for 30 min for the incorporated catalyst. Carbon monoxide methanation was performed at 400 °C to monitor more significant differences between the impregnated and incorporated catalysts. This reaction temperature is higher than the optimum CO methanation temperature of Ni impregnated catalyst; CO conversion reaches 100% at 300 °C without significant deactivation. However, we chose 400 °C to intentionally create the migration of Ni clusters on the surface of the impregnated catalyst, resulting in deactivation. The incorporated catalyst will be stable at this temperature by anchoring and occlusion effect as observed earlier in Co-MCM-41. As expected, two different catalysts show completely different activity patterns. The impregnated catalyst shows a gradual decrease of the CO methanation activity with increased reaction time, and the incorporated sample shows an opposite trend, increasing with reaction time. The difference in the catalytic behavior between these two catalytic systems becomes larger as the reaction time increases further, which indicates that the Ni ion incorporated MCM-41 catalyst is more stable than the impregnated catalyst as a result of anchoring and occlusion effect as demonstrated for Co-MCM-41.

From these results, it can be suggested that the Co and Ni ions directly incorporated into MCM-41 catalysts are a superior system compared to the impregnated catalysts as far as the stability is concerned. The catalytic stability is an important factor for a reaction requiring a long lifetime and high reaction temperature under harsh conditions.

4. Conclusions

Anchoring of small metallic clusters and partial occlusion effect on the stability of Co- and Ni-MCM-41 catalysts were directly proved by model catalysts and an actual catalyst system using various characterization techniques as well as a probe reaction. By a direct contact between sub-nanometer metallic clusters and unreduced or partially reduced metal ions on the surface of the pores, the stability of the reduced metallic clusters was significantly improved, resulting in maintaining catalytic activity without deactivation. Because of the slow reduction and amorphous silica pore wall, the reduced metallic clusters formed from CO incorporated Co-MCM-41 were partially occluded by silica, which also stabilized the clusters by preventing the unconfined migration on the surface. From CO methanation as a probe reaction, Co and Ni incorporated catalysts were superior catalytic systems compared to the impregnated catalysts based on stability of activity.

Acknowledgement

We are grateful to the DOE, Office of Basic Energy Science, for the financial support under grant numbers DE-FG02-01ER15183 and DE-FG02-05ER15732.

References

[1] S. Lim, G.L. Haller, Stud. Surf. Sci. Catal. 130 (2000) 3053.
[2] S. Lim, G.L. Haller, J. Phys. Chem. B 106 (2002) 8437.
[3] S. Lim, D. Ciuparu, C. Pak, F. Dobek, Y. Chen, D. Harding, L. Pfefferle, G.L. Haller, J. Phys. Chem. B 107 (2003) 11048.
[4] S. Lim, D. Ciuparu, Y. Chen, L. Pfefferle, G.L. Haller, J. Phys. Chem. B 108 (2004) 20095.
[5] Y. Yang, S. Lim, C. Wang, G. Du, G.L. Haller, Micropor. Mesopor. Mater. 74 (2004) 133.
[6] Y. Yang, S. Lim, C. Wang, D. Harding, G.L. Haller, Micropor. Mesopor. Mater. 67 (2004) 245.
[7] P. Amama, S. Lim, D. Ciuparu, L. Pfefferle, G.L. Haller, Micropor. Mesopor. Mater. 81 (2005) 191.
[8] S. Lim, Y. Yang, D. Ciuparu, C. Wang, Y. Chen, L. Pfefferle, G.L. Haller, Top. Catal. 34 (2005) 31.
[9] S. Lim, D. Ciuparu, Y. Chen, Y. Yang, L. Pfefferle, G.L. Haller, J. Phys. Chem. B 109 (2005) 2285.
[10] Y. Yang, S. Lim, G. Du, Y. Chen, D. Ciuparu, G.L. Haller, J. Phys. Chem. B 109 (2005) 13237.
[11] Y.I. Yermakov, Catal. Rev. Sci. Eng. 13 (1976) 77.
[12] Y.I. Yermakov, B.N. Kuznetsov, Y.A. Ryndin, J. Catal. 42 (1976) 73.
[13] R.G. Bowman, R.L. Burwell Jr., J. Catal. 63 (1980) 463.
[14] T. Huizinga, R. Prins, J. Phys. Chem. 87 (1983) 173.
[15] M. Ichikawa, T. Fukushima, T. Yokoyama, N. Kosugi, H. Kuroda, J. Phys. Chem. 90 (1986) 1222.
[16] L. Bonneviot, M. Che, D. Olivier, G.A. Martin, E. Freund, J. Phys. Chem. 90 (1986) 2112.
[17] M.S. Tzou, B.K. Teo, W.M.H. Sachtler, Langmuir 2 (1986) 773.
[18] H.J. Jiang, M.S. Tzou, W.M.H. Sachtler, Appl. Catal. 39 (1988) 255.
[19] M. Che, C.O. Bennett, Adv. Catal. 36 (1989) 55.
[20] Z.X. Cheng, C. Louis, M. Che, Z. Phys. D: At. Mol. Clusters 20 (1991) 445.
[21] C. Louis, Z.X. Cheng, M. Che, J. Phys. Chem. 97 (1993) 5703.
[22] J.C. Yang, Y.G. Shul, C. Louis, M. Che, Catal. Today 44 (1998) 315.
[23] B. Wen, J.F. Jia, W.M.H. Sachtler, J. Phys. Chem. B 106 (2002) 7520.
[24] K.E. Coulter, A.G. Sault, J. Catal. 154 (1995) 56.
[25] G. Meitzner, G.H. Via, F.W. Lytle, S.C. Fung, J.H. Sinfelt, J. Phys. Chem. 92 (1988) 2925.
[26] J.T. Wrobleski, M. Boudart, Catal. Today 15 (1992) 349.
[27] D. Guillemot, M. PolissetThfoin, J. Fraissard, D. Bonnin, J. Phys. Chem. B 101 (1997) 8243.
[28] C.A. Lin, J.C.S. Wu, J.W. Pan, C. Yeh, J. Catal. 210 (2002) 39.
[29] G. Riahi, D. Guillemot, M. Polisset-Thfoin, A.A. Khodadadi, J. Fraissard, Catal. Today 72 (2002) 115.
[30] D. Ciuparu, P. Haider, M.F. Garcia, Y. Chen, S. Lim, G.L. Haller, L. Pfefferle, J. Phys. Chem. B 109 (2005) 16332.
[31] T.G.S. Neto, A.J.G. Cobo, G.M. Cruz, Appl. Catal. A: Gen. 250 (2003) 331.
[32] R.C. Reuel, C.H. Bartholomew, J. Catal. 85 (1984) 63.
[33] Y. Chen, D. Ciuparu, S. Lim, G.L. Haller, L. Pfefferle, Carbon 44 (2006) 67.
[34] H.K. Lin, C.B. Wang, H.C. Chiu, S.H. Chien, Catal. Lett. 86 (2003) 63.
[35] E.L. Rodrigues, J.M.C. Bueno, Appl. Catal. A: Gen. 232 (2002) 147.
[36] E. van-Steen, G.S. Sewell, R.A. Makhothe, C. Micklethwaite, H. Manstein, M. de Lange, C.T. O'Connor, J. Catal. 162 (1996) 220.