



In situ environmental transmission electron microscopy to determine transformation pathways in supported Ni nanoparticles

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ABSTRACT

We have applied *in situ* environmental transmission electron microscopy (ETEM) to follow the dynamic phase transformations that take place in SiO₂ supported Ni nanoparticles during oxidation and reduction processes. The gas environments used for *in situ* ETEM studies were relevant to partial oxidation of methane (POM) reaction. In the presence of the CH₄ + O₂ gas mixture (in 2:1 ratio) at 400 °C, Ni transforms to NiO due to the high O-chemisorption energy. NiO void structures were formed during the oxidation because of the Kirkendall type process where diffusion of Ni cations along NiO grain boundaries is eight orders of magnitude greater than the diffusion of O anions. Reduction was performed under a CO + H₂ mixture at 400 °C (in 1:2 ratio) and also in the presence of CH₄ at 500 °C. Particle reduction processes also takes place via the diffusion of Ni cations along the NiO grain boundaries leaving NiO on the surface of the nanoparticle. NiO is the phase that is present on the surface of the nanoparticle during the intermediate stage of reduction.

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1. Introduction

Supported metal nanoparticles are of great interest as catalytic materials in the field of heterogeneous catalysis. Many heterogeneous catalysts perform gas–solid reactions under high temperature and pressure conditions. During a reaction, the catalyst may undergo several structural and chemical changes due to interactions between the material and the gases in the reactor. In order to understand the fundamental processes that take place in the catalytic materials it is important to follow the material evolution during the dynamic interaction with the gases. *In situ* environmental transmission electron microscopy (ETEM) is ideal for exploring the structures that form in the catalyst under near reactor conditions. *In situ* ETEM allows us to probe the dynamic changes in the catalyst at atomic level under reactive gas conditions and elevated temperatures providing information on morphological and chemical changes at the nanoscale. From these dynamic observations, information on intermediate phases/structure can be determined which can provide scientific information on the mechanisms of phase transformations, shape changes, etc. This kind of information on transitional forms may be difficult or impossible to obtain from *ex situ* studies of used catalysts. Moreover, *ex situ* studies may not provide a representative picture of the catalyst structure and composition in its working condition.

In situ ETEM has gained a significant importance in the field of heterogeneous catalysis in understanding the fundamental processes that takes place during the gas–solid interactions (Baker and Chludzinski, 1986; Gai, 2002). At Arizona State University, we have been using *in situ* ETEM for many years to understand the fundamental processes that take place at the nanoscale under controlled gas environments. For example, Li et al. (2005, 2006a,b, 2009), performed *in situ* studies to understand the fundamental process that takes place during the synthesis of supported mono-metallic and bi-metallic catalysts. Wang et al. (2008, 2009), performed *in situ* studies of dynamic changes that take place in the ceria-based oxides during redox process for solid oxide fuel cell application (Crozier et al., 2008).

The present work is focused in understanding the mechanisms of phase transformations in supported Ni nanoparticles under oxidizing and reducing conditions. Considerable research has been performed in the use of Ni catalyst for partial oxidation and reforming of methane (Enger et al., 2008; Tsang et al., 1995). It has been reported that during the reaction, the gas environment along the catalyst bed changes affecting the phase and morphology of the Ni nanoparticles (Chenna et al., 2011). For partial oxidation of methane at high catalytic conversions, the entrance of the catalyst bed sees mostly reacting gases (mixture of CH₄ and O₂ in 2:1 ratio) and the exit of the catalyst bed sees mostly product gases (mixture of CO and H₂ in 1:2 ratio). The gas composition along the catalyst bed changes from an oxidizing (with O₂ as the oxidation gas) to a reducing environment (with CH₄, CO and H₂ as reduction gases) changing the oxidation state of the Ni nanoparticles. *In situ* ETEM

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experiments under oxidizing and reducing gas environments that are relevant to partial oxidation of methane were performed to follow the oxidation and reduction process in supported Ni nanoparticles.

A further challenge relates to the inherent complexity that is often present in the nanostructure and composition of real working catalysts. Even under *ex situ* conditions, many “simple” heterogeneous catalysts show a variety of structures and morphologies between and within individual nanograins. Many common high surface area supports may be composed of nanocrystals possessing multiple crystal facets and complex surface defect structures. For example, in our previous work on Ni supported on TiO₂, we found that the nature of the metal–support interaction depended on whether the metal nucleated on anatase or rutile grains and on the particular crystal facet of these two different titanias (Li et al., 2005, 2006a,b). The complexity of high surface area support structures can lead to significant heterogeneity in the microstructure of supported monometallic catalyst and provide rich but complex nanostructure in bimetallic systems (Li et al., 2006a,b, 2009). For *in situ* work in which dynamic structural changes take place during reaction conditions, this structural complexity greatly complicates the interpretation of the TEM data. For this reason we have chosen to work on a simple model system consisting of Ni nanoparticles supported on SiO₂ spheres. Unlike the other oxide supports like Al₂O₃ and TiO₂, where Ni metal interact strongly with the support forming NiAl₂O₄ and NiTiO₃ respectively (Enger et al., 2008), the surface of the SiO₂ spheres is relatively homogenous and interacts only weakly with the Ni particles. Moreover, the simple geometry of this support is ideal for observing and interpreting changes in metal particle size, shape and composition during *in situ* ETEM studies.

2. Materials and methods

Amorphous SiO₂ spheres prepared by Stober et al.'s (1968) method were used as a support for Ni metal. The simple geometry of these SiO₂ spheres is ideal for TEM studies because they facilitate the interpretation of the image making it easier to follow the materials evolution under reacting gas conditions (Datye and Long, 1988). SiO₂ was loaded with the desired amount of Ni by impregnating SiO₂ spheres with nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O) solution using incipient wetness impregnation techniques according to the procedure outlined by Banerjee and Crozier (2012). After impregnation, the sample was dried at 120 °C followed by reduction in 5% H₂/Ar atmosphere at 400 °C for 3 h.

In situ transmission electron microscopy was performed in an FEI Tecnai F20 field emission environmental transmission electron microscope (ETEM) operating at 200 kV with a point resolution of 0.24 nm and an information limit of 0.13 nm. The *in situ* reaction cell was based on the design developed by (Boyes and Gai, 1997). This instrument is equipped with a differential pumping system to restrict the gas flow into the gun area while maintaining gas pressures near the sample region (Sharma et al., 2003). The gas reaction cell or environmental cell (essentially a flow microreactor) of this instrument allows us to perform atomic level observations of gas–solid interactions at pressures up to a few Torr and temperatures up to 800 °C. The instrument is also equipped with a Gatan Imaging Filter permitting electron energy-loss spectroscopy (EELS) to be performed. *In situ* electron microscope images and diffraction patterns were recorded with a Gatan CCD camera using DigitalMicrograph 3.1TM software. All the gases are 99.999% pure and were admitted into the microscope *via* the mixing tank. For different gas mixtures, gases were premixed in the mixing tank in the desired ratio. We combine the gases by injecting appropriate pressures into a mixing tank assuming Dalton's law (molar ratios = ratio of

partial pressures). Dalton's law applies only to ideal gases whereas we are dealing with real gases composed of interacting gas molecules (Atkins and de Paula, 2002). However, in our case the pressures are equal to or less than one atmosphere where the compressibilities are close to unity giving errors in molar ratios of less than a few percent.

Gas pressures of 0.1–2.6 Torr were used during *in situ* studies. Electron energy-loss spectra of gases were acquired to measure the gas composition inside the cell during the *in situ* studies. Energy-loss spectra were recorded with a typical energy resolution of about 1.2 eV and an acquisition time of 4 s. Inner-shell spectra were recorded with convergence and collection semi-angles of 2.3 and 1.9 mrad, respectively. Detail procedures of EELS of gases can be found in Crozier and Chenna (2011). The Ni/SiO₂ samples were gently crushed between glass microscope slides, loaded onto platinum grids and placed onto a Gatan Inconel heating holder. The error in determining local sample temperature is ± 25 °C. Electron beam damage effects were minimized by using low-dose image conditions and blanking the beam during the temperature ramp. Furthermore, to check that electron beam effects were not important, the irradiated areas were compared with the non-irradiated areas to make sure that phase and phase transformations were identical between the two areas.

3. Results and discussions

3.1. Ni metal oxidation

Fig. 1(a) shows the *in situ* ETEM image of Ni/SiO₂ in presence of 0.8 Torr of H₂ at 400 °C along with the diffraction pattern confirming that the nanoparticles are nickel metal. Nickel metal particles are de-wetting the SiO₂ surface. Fig. 1(b), shows the *in situ* ETEM image in the presence of 0.8 Torr of CH₄ and O₂ mixture in 2:1 ratio at 400 °C (this gas ratio is relevant to reacting gas mixture for the partial oxidation of methane reaction). The Ni nanoparticles transform to structures showing void-like morphologies that wet the SiO₂ surface. The distinct contrast in the nanoparticles indicates the presence of voids. Electron diffraction shows that the void-like particles are FCC NiO. Similar void structures were observed in NiO nanoparticles by Nakamura et al. (2008a,b), during the oxidation of Ni metal nanoparticles.

To investigate the initial void formation we processed a series of image frames recorded during heating in a mixture of methane and oxygen. We know from prior work that the voids begin to form at around 300 °C (Chenna et al., 2011). Fig. 2(a)–(e) shows a sequence of images capturing the growth of a void during the transformation of Ni metal to NiO in the presence of CH₄ and O₂ mixture. The catalyst was initially reduced in H₂ at 400 °C for 2 h. The sample was cooled to 200 °C and the H₂ was removed from the cell. One Torr of (2CH₄ + O₂) was introduced and the temperature in the cell was ramped up to 300 °C over a period of 10 min. At 300 °C, image recording was started. This kind of information is not easy to obtain during *in situ* studies because of the thermal drift associated with the holder when the reacting gases are introduced into the environmental cell. In this case, the interface between the particle and the silica surface is approximately parallel to the electron beam. The sequential images in Fig. 2 were obtained from a series of images recorded at 15 frames per second during the reaction. Drift in the image is corrected by using a spatial drift package (SDSD) (Schaffer et al., 2004). To reduce noise, 20 individual frames were averaged to get each single image. The larger particle in the first frame shows a core–shell type structure with a lighter shell and darker core indicating that the outside of the particle has already started to oxidize. In the upper right side of the interface between the particles and the silica, there is a bright line which looks similar to a Fresnel fringe.

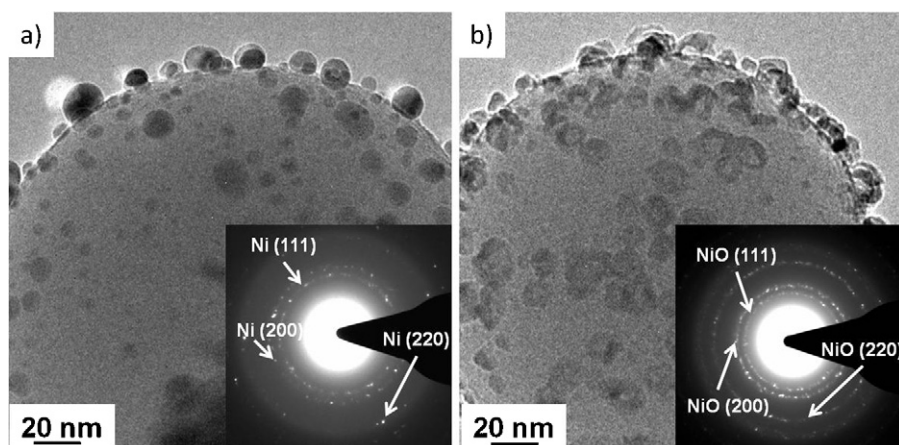


Fig. 1. *In situ* ETEM image and electron diffraction of Ni/SiO₂ in presence of (a) 0.8 Torr of H₂ at 400 °C and (b) 0.8 Torr of CH₄ and O₂ (in 2:1 ratio) at 400 °C.

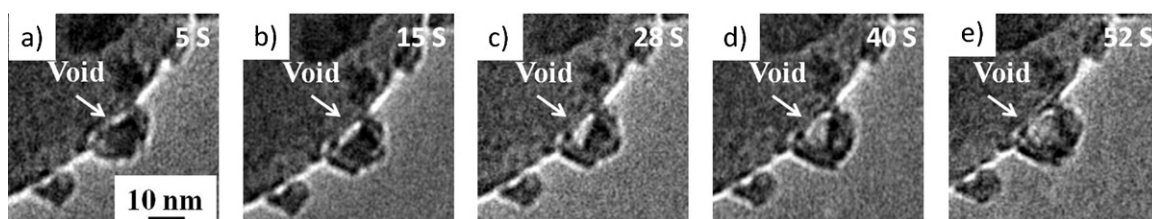


Fig. 2. Sequential images of void formation in NiO in presence of CH₄ and O₂ (in 2:1 ratio).

However this extends along the interface by the second frame and continues to grow into the void in subsequent frames. Moreover, the dark metallic core of the particle appears to be consumed as the void grows. From the sequential images it is clear that the void nucleates at the interface of the Ni/SiO₂ and grows away from the interface until the Ni oxidation is complete. Fig. 3 shows a high resolution *in situ* ETEM image of a void structured NiO particle at 400 °C in the presence of CH₄ and O₂ mixture 60 min into the reaction. The high-resolution image shows that the particle contains multiple grains and grain boundaries; the nanoparticle also contains restricted long-range ordering due to the presence of line and planar defects.

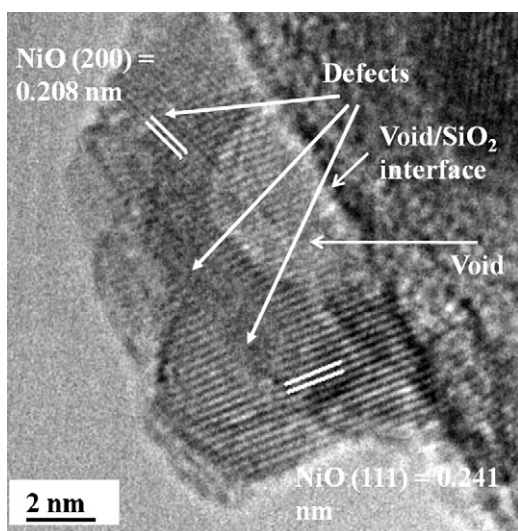


Fig. 3. *In situ* high resolution TEM image of void structured NiO/SiO₂ in presence of 0.8 Torr of CH₄ and O₂ in 2:1 ratio at 400 °C.

We were initially somewhat surprised to see the formation of NiO, since the gas composition was rich in reducing gas (CH₄). Bulk thermodynamic calculations were performed using Factsage (Bale et al., 2002) and the calculations suggest that Ni should exist in metallic form at 400 °C in the presence of 2:1 CH₄:O₂ mixture. However our *in situ* and *ex situ* experiments repeatedly show that Ni transforms to NiO at 400 °C if the CH₄–O₂ ratio is 0.5. To check the gas composition in the environmental cell, we have performed electron energy-loss spectroscopy of gases in the environmental cell (Crozier and Chenna, 2011). Fig. 4 is a background subtracted energy-loss spectrum from a mixture of CH₄ and O₂ in 2:1 pressure ratio during the *in situ* studies, showing C K-edge and O K-edge from CH₄ and O₂, respectively. The background was extrapolated beyond the edge, the K-edges integrated over a 100 eV range and the signal ratio converted to elemental ratios using Hartree Slater cross sections. The result from quantification gave an average value for the O/C ratio of 1.14 ± 0.01 . These values lie within about 15% of the nominal value of 1.0 that we would expect based on ratios of the two gases in the mixing tank. This confirms that the Ni–NiO

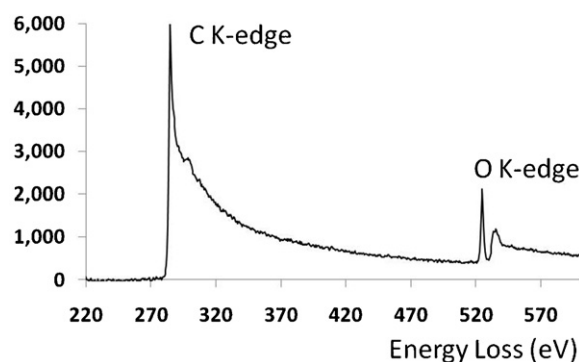


Fig. 4. Background subtracted energy-loss spectrum from a mixture of 2.6 Torr CH₄ and O₂ in 2:1 ratio showing C and O K-edges.

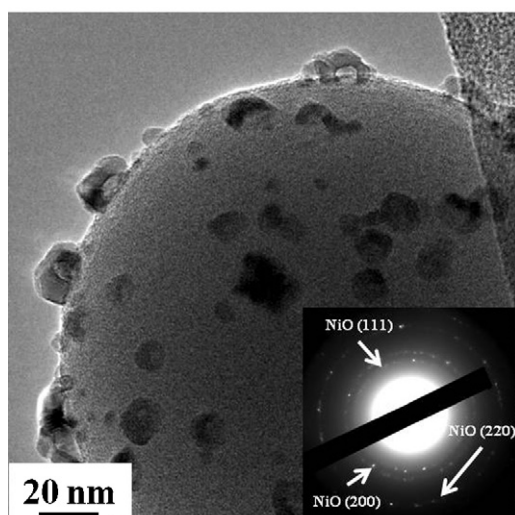


Fig. 5. *Ex situ* TEM image and electron diffraction pattern of Ni/SiO₂ after ramping in CH₄ and O₂ followed by rapid cooling to room temperature in He.

transformation takes place even though the gas composition is rich in CH₄.

As a further check on the validity of the *in situ* observations, Ni/SiO₂ was heated to 400 °C in an *ex situ* quartz tube reactor in the presence of CH₄ and O₂ in 2:1 ratio atmosphere pressure, with He as the carrier gas. To follow similar procedures to those of the *in situ* ETEM, the sample was reduced in H₂ gas at 400 °C and cooled down to 200 °C followed by ramping in CH₄ and O₂ in 2:1 ratio to 400 °C and held there for 60 min. The sample was rapidly cooled to room temperature in flowing He and immediately loaded into the TEM for characterization. Fig. 5, shows the typical *ex situ* TEM image confirming the formation of void-structured nanoparticles and the diffraction pattern also confirms the void-structures are of NiO. This comparison between *in situ* and *ex situ* observations is an important validation of the ETEM approached for studying the phase transformations taking in the Ni/SiO₂ system.

The presence of CH₄ may not influence the phase transformation in the presence of O₂, because the chemisorption energy of O₂ on Ni is greater than the chemisorption energy of CH₄ (chemisorption energies for the Ni (1 1 1) surface are 481 kJ mol⁻¹ for the O-atom, and 192.28 kJ mol⁻¹ for CH₃⁻ adsorption) (Siegbahn and Wahlgren, 1992; Siegbahn and Panas, 1990). Though the gas mixture consists of twice as much CH₄ as O₂ the coverage on the Ni particle is dominated mostly by O species because of the higher chemisorption

energy. The presence of higher oxygen coverage on the Ni particle thermodynamically favors the formation of NiO (Gaskell, 2003).

Fig. 6(a) and (b) shows *in situ* ETEM images of Ni/SiO₂ and NiO/SiO₂ from the same area in presence of H₂ and 2CH₄ + O₂ at 400 °C, respectively. Superposition of Fig. 6(a) and (b) shows that the void size is almost equivalent to the initial Ni particle size (Fig. 6(c)). This suggests a Kirkendall type processes (Smigellkas and Kirkendall, 1947) where Ni cations diffuse faster than the O-anions through the NiO. After the initial oxidation of the Ni surface there are two possible mechanisms by which complete particle oxidation can take place, either by the diffusion of O-anions through NiO to oxidize subsurface Ni or by the diffusion of Ni-cations through the NiO shell to react with dissociated oxygen on the surface. The dominant mechanism depends on the rate of diffusion of Ni or O in NiO. The diffusion process can take place either *via* bulk diffusion or along easy diffusion paths like grain boundaries or other extended defects. Fig. 3 shows that the NiO particles are composed of more than one grain and that many grains appear to show a high concentration of defects and restricted long-range order. These defects may act as easy diffusion paths during the oxidation process. The diffusion coefficient of Ni-cations and O-anions along the NiO grain boundaries at 400 °C are 10⁻¹³ cm²/s and 10⁻²¹ cm²/s, respectively (Atkinson and Taylor, 1978; Atkinson et al., 1986; Peraldi et al., 2002). Thus, it can be seen that the diffusion coefficient of Ni in NiO along the grain boundaries is eight orders of magnitude greater than that for O.

These TEM observations together with consideration of diffusion coefficients confirm that Ni diffusion is the dominant mechanism for oxidation of Ni nanoparticles and Kirkendall void formation. Fig. 7, shows a schematic representation of the mechanism of void formation in NiO. During the initial oxidation, multiple NiO grains form on the surface of the Ni nanoparticle and grow forming grain boundaries and other defects. As oxidation proceeds, Ni from the particle interior diffuses along the defects in the NiO shell to the surface leaving a vacancy inside the metallic core. These vacancies agglomerate together at the interface forming a void. It is energetically favorable to form a single large void rather than multiple vacancies inside the nanoparticle. When there are no grain boundaries, the oxidation process depends on the bulk diffusion of Ni or O species. The bulk diffusion coefficients of Ni at 400 °C are about 10⁻²⁵ cm²/s and 10⁻²³ cm²/s in Ni and NiO, respectively and the bulk diffusion coefficients for O at 400 °C are about 10⁻¹⁹ cm²/s and above 10⁻³⁰ cm²/s in Ni and NiO, respectively (Atkinson et al., 1986). Diffusion of Ni in NiO is orders of magnitude greater than that of the diffusion of O in NiO; again Ni is the main diffusing species during the oxidation process which forms void-structured NiO nanoparticles. Void structures were observed in Ni nanoparticles of size greater than 4 nm. No void structures were seen in metal

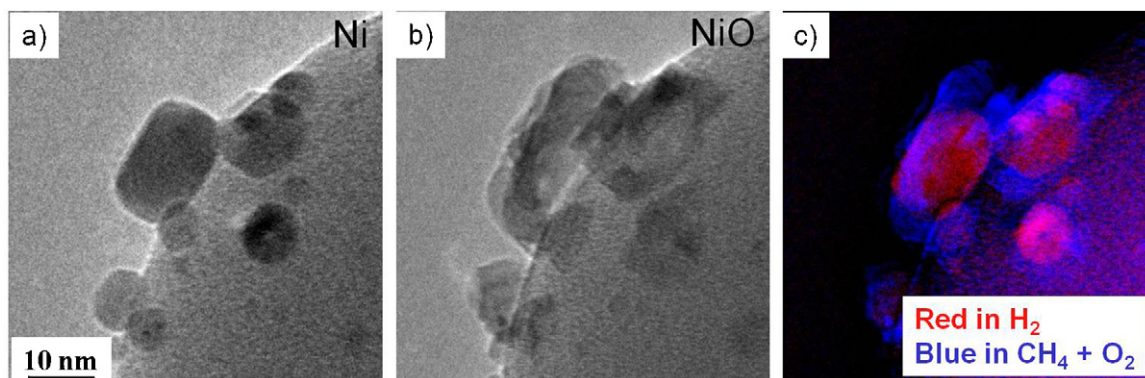


Fig. 6. *In situ* ETEM images of Ni/SiO₂ (a) in presence of 0.8 Torr of H₂ at 400 °C (b) from the same region in presence of 0.8 Torr of mixture of CH₄ and O₂ in 2:1 ratio at 400 °C (c) superposition of colorized images shown in panels (a) and (b).

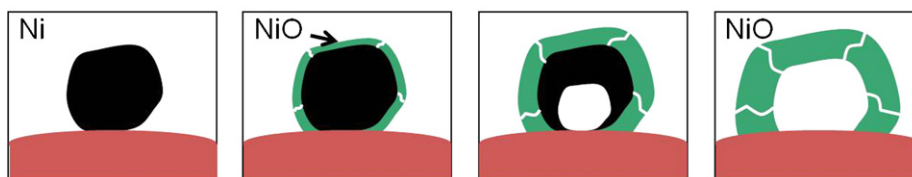


Fig. 7. Schematic representation of mechanism of void formation in NiO by Kirkendall process during Ni oxidation.

nanoparticles that were less than 4 nm. For these particles, the diffusion distances are very short and it becomes kinetically possible for the oxide particles to achieve their thermodynamic equilibrium shape of a solid particle.

Thermodynamic considerations can explain why the void nucleates at the interface between the metal particle and the silica. The surface energy of silica is about 0.605 J/m^2 (Regalbuto et al., 1987) whereas that of metal is approximately 2.2 J/m^2 (Li et al., 2006a,b). For a void of volume V , it is easy to show that the total surface energy is approximately 10% lower for void formation at the silica interface *versus* at the center of the Ni particle. Moreover, from our earlier work it is known that Ni metal interacts very weakly with silica so the interfacial energy will be high (Chenna et al., 2011). Thus the Ni would prefer to de-wet the silica so this provides an additional driving force for void formation at the interface.

3.2. NiO reduction

In situ reduction was performed under different gas environments in order to understand the NiO reduction process. Initial reduction experiments were performed in a mixture of CO and H_2 (in 1:2 ratio) which is relevant to the product gas ratio that forms during the partial oxidation of methane. Fig. 8, shows a selected area electron diffraction pattern recorded during the intermediate stage of reduction of NiO–Ni in presence of 0.1 Torr of CO and H_2 in 1:2 ratio at 400°C . The d-spacings of Ni (1 1 1) and NiO (2 0 0) are 0.203 nm and 0.208 nm, respectively, and are difficult to resolve in the diffraction pattern from nanoparticles. However, formation of Ni metal during reduction may be recognized from the appearance of Ni (2 0 0) reflections with d-spacing of 0.176 nm. Fig. 9, shows an *in situ* high resolution ETEM image along with the Fast Fourier Transforms (FFT) of Ni/SiO₂ during the initial stage of reduction in the presence of 0.1 Torr of CO and H_2 at 400°C . Lattice spacing on the surface of the nanoparticle matches the NiO (2 0 0) spacing of 0.21 nm. The FFT from the core region near to the SiO₂ interface shows two fundamental reflections from the lattice spacings of approximately 0.21 and 0.20 nm. These reflections are in good

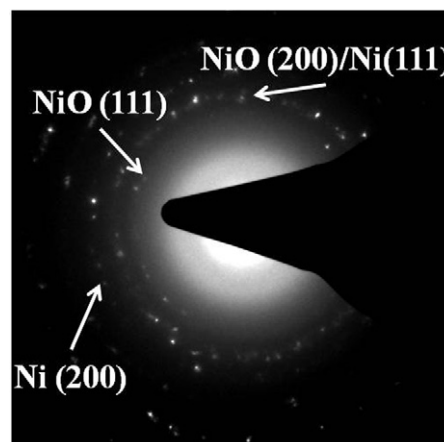


Fig. 8. Electron diffraction pattern of Ni/SiO₂ during the reduction in presence of CO and H_2 (in 1:2 ratio) at 400°C .

agreement with the NiO (2 0 0) and Ni (1 1 1) spacings of 0.208 nm and 0.203 nm respectively, suggesting the formation of a Ni–NiO core–shell structure. It is also possible that we are looking at two particles that are adjacent to each other and aligned along the electron beam directions. In this case, the smaller particle is mostly reduced to Ni metal.

In situ reduction was also performed in the presence of a CH_4 atmosphere which is one of the reducing gases in the reactor during the partial oxidation of methane. CH_4 is not as strong a reducing gas as H_2 and CO and the reduction processes are slower allowing us to follow the NiO–Ni transformation process more carefully. (Moreover the presence of Ni on the surface can be detected by the formation of graphene layers which will be formed by the decomposition of CH_4 on the metallic Ni surface.) During the earlier stage of reduction, some regions in the NiO particles may contain Ni nanodomains. The initial stage of the reduction process was difficult to capture at atomic resolution due to specimen drift during the gas switching. After oxidation of the Ni is complete at 400°C , the

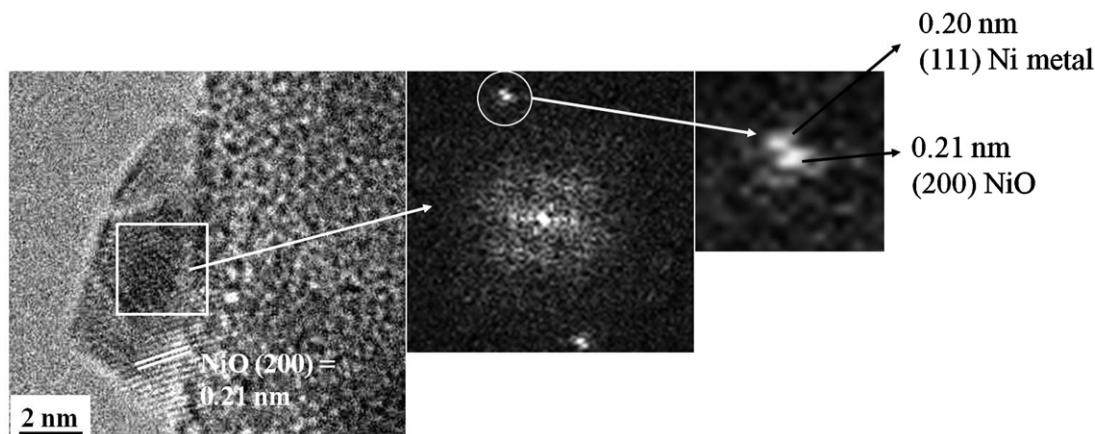


Fig. 9. *In situ* high resolution ETEM image along with the FFT's of Ni/SiO₂ during the reduction in presence of 0.1 Torr of CO and H_2 (in 1:2 ratio) at 400°C .

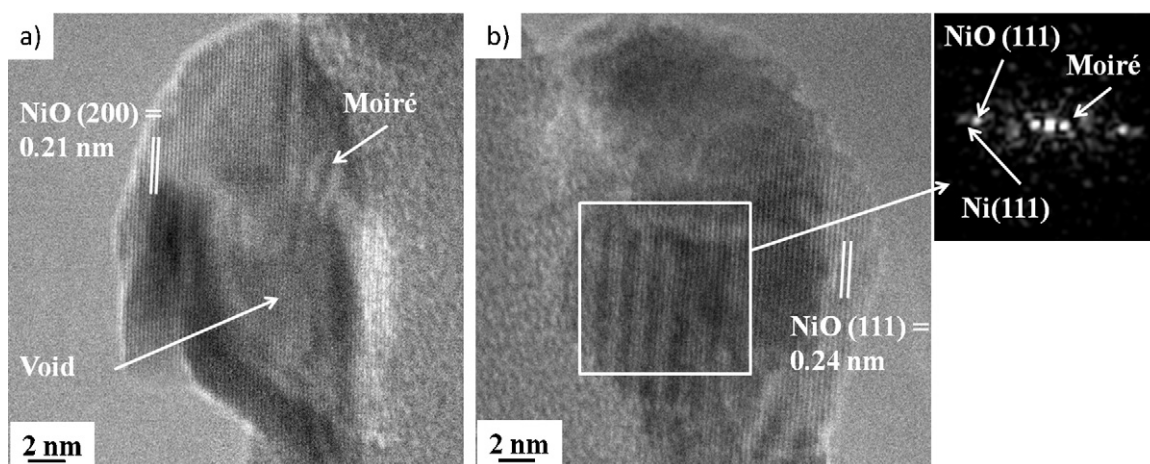


Fig. 10. *In situ* high resolution ETEM image NiO particles during the reduction in presence of 0.3 Torr of CH_4 at 500°C (a) during the initial stage of reduction (b) intermediate stage of reduction and accompany Fourier transform from the Moiré pattern.

sample was cooled to 200°C and the CH_4 and O_2 gas pumped out. CH_4 was reintroduced and the temperature was ramped to 500°C . It typically takes about 30 min for the drift to stabilize sufficiently to allow high-resolution images to be recorded. Even at this stage of reduction, significant Ni metal has already migrated and nucleated in the interior of the NiO particles as evidenced by the Moiré patterns at the particle center. Fig. 10(a) shows an *in situ* high resolution ETEM image of a NiO particle in the presence of 0.3 Torr of CH_4 at 500°C and 30 min into the reduction process. The accumulation of Ni at the center makes the contrast from the void less pronounced because of the increase in projected mass thickness as Ni diffuses into the particle. Imaging the partially filled void required a significant under focus as shown in Fig. 10(a). The Moiré pattern present in Fig. 10(a) comes from a small area and the crystal is not well defined but this phenomenon appears in many of the NiO particles.

Moiré patterns appear in HREM images due to the superposition of lattice fringes from the oxide and the metal (Williams and Carter, 1996). However, Moiré patterns can also occur due to superposition of two overlapping NiO crystals. Thus a careful analysis is necessary to decompose the Moiré into two fundamental reflections to ensure correct interpretation. Fig. 10(b) shows the NiO reduction in the presence of CH_4 during the later part of the reduction processes (after 150 min) when the Moiré pattern is more extensively developed and well defined. The image shows a Moiré in the core region suggesting overlapping crystals. The lattice spacing on the surface of the nanoparticle is 0.24 nm corresponding to NiO (1 1 1). FFT from the Moiré region shows two fundamental reflections of 0.24 nm

and 0.20 nm corresponding to NiO (1 1 1) and Ni (1 1 1) spacings with a Moiré reflection of spacing 1.3 nm formed between the two fundamental reflections. These observations suggest a core-shell structured nanoparticle with a Ni core and NiO shell.

After the initial reduction of the NiO surface, there are two possible ways for the complete particle reduction to take place, as shown in Fig. 11. Mechanism I proceeds by the diffusion of O anions to the surface through the Ni metal (Fig. 11(a)). Mechanism II proceeds by the diffusion of Ni cations into the subsurface through the NiO (Fig. 11(b)). If O anions are the main diffusing species, after the initial reduction, O anions diffuse onto the surface through the Ni shell leaving O-vacancies and the reduction process continues until completion leaving a Ni metal shell with a void at the center. If Ni cations are the diffusing species, after the initial reduction, Ni diffuses into the subsurface region exposing fresh NiO on the surface giving a core shell structure which upon complete reduction gives a solid Ni metal particle.

From our *in situ* observations under different reducing conditions, we never observed the formation of metal shells and we always observed NiO on the surface during the intermediate reduction stage. This indicates that Ni is the primary diffusing species during NiO reduction. This is again consistent with the literature which shows that the diffusion coefficient of Ni cations through the NiO grain boundaries is about $10^{-12} \text{ cm}^2/\text{s}$ at 500°C and is much greater than the diffusion of O through the Ni metal, about $10^{-16} \text{ cm}^2/\text{s}$ at 500°C (Peraldi et al., 2002; Lloyd and Martin, 1972). After reduction is complete we see graphite formation over all of the Ni particles. Fig. 12, shows the *in situ* ETEM image in

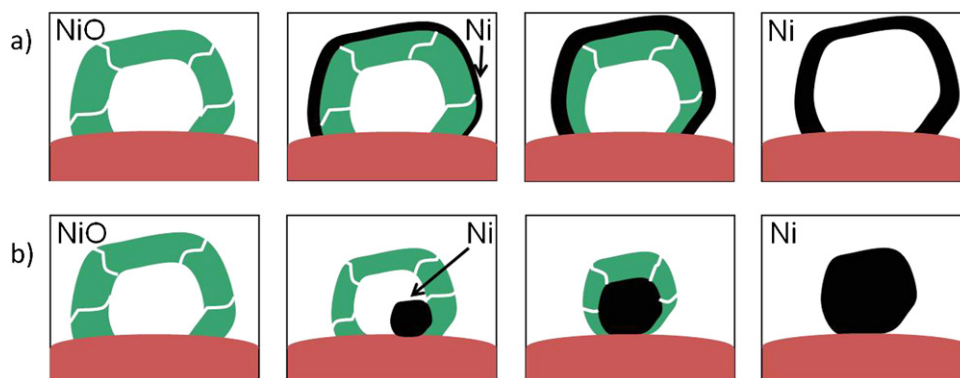


Fig. 11. Schematic representation of NiO–Ni transformation under two different mechanisms (a) mechanism I: O is the dominant diffusing species (b) mechanism II: Ni is the dominant diffusing species.

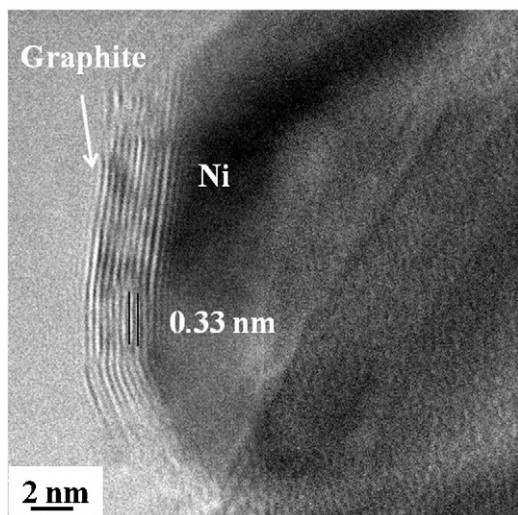


Fig. 12. *In situ* high resolution ETEM image of Ni/SiO₂ showing graphite formation of Ni after the complete reduction of NiO in presence of 0.3 Torr of CH₄ at 500 °C.

presence of 0.3 Torr of CH₄ after the reduction of NiO showing graphite overlayer formation on the Ni surface by the dissociation of CH₄ according the reaction $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$ (Tsang et al., 1995). Thus for experiments performed in pure CH₄, a clear indicator of metallic Ni on the surface is the formation of graphite which is easily observed in the HREM image. All the above mentioned observations collectively show that, during the intermediate stage of reduction, NiO remains on the surface of the nanoparticle and the reduction process takes place *via* the diffusion of Ni cations along the grain boundaries in NiO shell (Reduction Mechanism II).

4. Conclusions

In situ environmental TEM is a powerful technique to follow the dynamic phase transformations and allows us to determine the reaction pathways in metal nanoparticles *via* direct observation of intermediate phase/structures. We employed *in situ* ETEM to follow the mechanisms of phase transformation during the oxidation and reduction process on supported Ni nanoparticles. The gas environments used in this study are relevant to the catalyst activation processing taking place during partial oxidation of methane. The morphology of the nanoparticles after oxidation and reduction processes provide information on the diffusion rates of O and Ni during the phase transformation. Both oxidation and reduction takes place *via* the preferential migration of Ni cations along the NiO grain boundaries. In the presence of a CH₄ and O₂ mixture (in 2:1 ratio) at 400 °C, Ni transforms to a NiO void structures due to the faster diffusion of Ni-cations along NiO grain boundaries, void nucleates at the interface and grows away from the interface. During subsequent NiO reduction in the presence of CO + 2H₂ and in presence of CH₄, NiO is the phase that is present on the surface of the nanoparticle during the intermediate stage of reduction. During reduction in CH₄, the formation of graphite layers on the nanoparticle is a convenient way to detect the presence of metallic Ni on the surface of the nanoparticle. Nickel metal species are on the surface only at the end of the reduction process.

Acknowledgements

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