Synthesis and characterization of a novel Au nanocatalyst with increased thermal stability†

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We report the synthesis of a new Au nanocatalyst with increased thermal stability. This catalyst system consisted of gold nanoparticles attached to functionalized TiO$_2$/SiO$_2$ core–shell nanocomposites, together with the encapsulation of mesoporous silica. The synthesis process mainly involved four steps, which included the synthesis of the TiO$_2$/SiO$_2$ core–shell composites, synthesis of the Au/TiO$_2$/SiO$_2$ particles, coating of Au/TiO$_2$/SiO$_2$ with silica, and etching the outer silica layer. TEM images were used to confirm the success of each of the synthesis steps, and both UV-vis adsorption spectra and the catalytic activity evaluation were employed to investigate the degree of re-exposure of Au nanoparticles after the etching treatment. In our experiments, the obtained mesoSiO$_2$/Au/TiO$_2$/SiO$_2$ catalyst showed a superior thermal stability and higher activity for CO conversion compared to the mesoSiO$_2$/Au/SiO$_2$ one. It resisted sintering during the calcination at 500 °C, whereas the unprotected one was found to sinter. Moreover, it was found that on the mesoSiO$_2$/Au/TiO$_2$/SiO$_2$ sample, the outside silica material could hinder the phase transformation of titania to some extent. Thus, small crystalline particles of TiO$_2$ anchored on the silica beads of the core–shell composites, leading to a better dispersion of small Au nanoparticles and improved catalytic capacity to resist sintering.

1. Introduction

Supported Au catalysts are known to exhibit high catalytic activity and excellent selectivity for various oxidation reactions including hydrocarbon selective oxidation, CO oxidation and propylene epoxidation.1–3 It has been reported that the size of Au particles may play a primary role in determining the reaction performances.4,5 Generally, much higher activities of the catalysts can be obtained with smaller sizes of gold particles, especially the ones at sizes of about 2 to 3 nm.6 However, during the process of reaction, these Au nanoparticles tend to coagulate and/or change shape because of their high surface energies. As a result, the loss of catalytic activity and selectivity is inevitable. In this regard, synthesis of metal nanocatalysts with high thermal stability is in great demand.

Recently, several investigations have been carried out to improve the thermal stability of metal nanocatalysts.7,8 In these studies, nanocomposite catalysts with tunable particle size and shape could be prepared by the design of the catalyst structure and the use of new synthetic nanotechnologies. For example, Joo et al.9 reported on the design and the preparation of Pt/mesoporous silica core–shell (Pt@mSiO$_2$) nanoparticles. In this system, the Pt cores were encaged within the silica shells, while the reacting molecules could directly access the Pt cores through the mesopores within the silica shells. Perhaps the main challenge for this catalyst is to make the shells sufficiently porous for the reactants and products to be able to diffuse in and out of the Pt cores.10 On the other hand, functionalization of colloidal support before the deposition of metal nanoparticles may be another method to accomplish this goal. Gude et al.11 synthesized some colloidal-supported metal nanoparticles (CSMNs) by covalently attaching palladium nanoparticles to the MPTMS- or APTES-functionalized silica colloids. It was found that the metal nanoparticles could readily attach to the surface of functionalized silica colloids because of the formation of Pd–S or Pd–N bonds. However, it is worth mentioning that this strategy is mainly suitable for the preparation of the nanocatalysts that are used for the low temperature reaction. With the increase of the reaction temperature, typically above 300 °C, the aggregation of the pristine nanoparticles is inevitable because of the decomposition of the organic capping agents, such as polymers or surfactants.9 For this reason, the size and distribution of metal nanoparticles cannot be preserved.

Comparing with the above-mentioned strategies, surface encapsulation of metal nanoparticles with mesoporous...
materials, typically silica, may be an effective way to increase the catalyst stability.\textsuperscript{12,13} As reported, the existence of mesoporous silica can not only keep the metal nanoparticles stable, but also promote efficient mass transfer to encapsulated metal nanoparticles.\textsuperscript{14} For this purpose, Zaera and his coworkers proposed an interesting strategy named “encapsulation and etching” when they synthesized the mesoSiO\textsubscript{2}/Pt/SiO\textsubscript{2}-bead catalysts.\textsuperscript{12,15} In this procedure, the nanoparticles were firstly fixed via their encapsulation with a freshly deposited silica layer; then the mesoporous shell structure could be produced by etching this new silica layer with base solution. Nevertheless, the metal oxide (SiO\textsubscript{2}) is one of the inert materials for CO oxidation, which is intrinsically less active with respect to reducible transition metals, such as TiO\textsubscript{2} and Fe\textsubscript{3}O\textsubscript{4}.\textsuperscript{16} In the process of CO oxidation, TiO\textsubscript{2} may provide reactive oxygen, which then participates in the oxidation reaction, resulting in a significantly enhanced activity for CO oxidation. In this contribution, we demonstrated a catalytic system for preventing Au nanoparticles from sintering, which was supported on the TiO\textsubscript{2}/SiO\textsubscript{2} nanocomposites, then coated with another layer of amorphous silica, finally etching the outer silica to convert the dense SiO\textsubscript{2} shell into porous ones. The detailed structure and synthetic procedure are depicted in Fig. 1. The obtained catalysts showed a superior thermal stability, as the encapsulated gold nanoparticles resisted sintering up to 500 °C in air. Furthermore, in this catalytic system, due to the protection of the outside silica material, the crystallization of TiO\textsubscript{2} is suppressed, resulting in a thin layer and small crystalline particles. Therefore, Au nanoparticles can have a strong interaction with the TiO\textsubscript{2} support by more connection points, which is favorable for the dispersion of metal nanoparticles.

2. **Experimental**

2.1 **Synthesis of SiO\textsubscript{2} particles**

The silica colloids were synthesized by using Stöber’s method.\textsuperscript{17} Tetraethyl orthosilicate (TEOS, 1.92 mL), deionized water (8.6 mL) and concentrated ammonia solution (28 wt%, 1.24 mL) were mixed with ethanol (46 mL). The mixture was allowed to react for 6 h at room temperature. The resulting product was separated and collected by centrifugation, followed by washing with deionized water and ethanol for 3 times, respectively.

2.2 **Synthesis of TiO\textsubscript{2}/SiO\textsubscript{2} core–shell composites**

The TiO\textsubscript{2}/SiO\textsubscript{2} composites were synthesized by following the strategy described in our previous work.\textsuperscript{18} The previous SiO\textsubscript{2} suspension (30 mL) was dispersed in a mixture of hydroxypropyl cellulose (HPC, 0.2 g), ethanol (40 mL), and deionized water (0.2 mL) under sonication. Then, a stock solution containing 2 mL of tetrabutyl titanate (TBOT) and 10 mL of ethanol was injected into the mixture for at least 10 min. After stirring at 85 °C under refluxing conditions for an additional 100 min, the SiO\textsubscript{2}/TiO\textsubscript{2} colloids were collected by centrifugal separation, washed with ethanol and dispersed in deionized water (40 mL). In order to obtain a thicker TiO\textsubscript{2} layer, the above coating process was repeated.

2.3 **Synthesis of Au/TiO\textsubscript{2}/SiO\textsubscript{2**}

The above TiO\textsubscript{2}/SiO\textsubscript{2} particles were transferred into a mixture of isopropanol (50 mL) and 3-aminopropyl-trioxysilane (APTES, 500 μL) and heated up to 80 °C for 12 hours to functionalize the titania surface with amino groups. The NH\textsubscript{2}–TiO\textsubscript{2}/SiO\textsubscript{2} colloids were washed with isopropanol and dispersed back into de-ionized water (5 mL). In a separate reaction, Au nanoparticles were synthesized using the Turkevich method.\textsuperscript{19} Typically, 5 mL of a H\textsubscript{2}AuCl\textsubscript{4} solution (9.5 mg mL\textsuperscript{-1}) was mixed with 100 mL distilled water and heated to boiling. A sodium citrate solution (10 mL, 20 mg mL\textsuperscript{-1}) was injected into the boiling solution quickly. After stirring for a further 1 h and adding the above NH\textsubscript{2}–TiO\textsubscript{2}/SiO\textsubscript{2} colloids to the Au sols under sonication for 10 min, the Au/TiO\textsubscript{2}/SiO\textsubscript{2} colloids were centrifuged and dispersed in deionized water (50 mL).

2.4 **Coating of Au/TiO\textsubscript{2}/SiO\textsubscript{2} with silica**

The previous Au/TiO\textsubscript{2}/SiO\textsubscript{2} solution was mixed with a PVP solution (25 mL, M\textsubscript{w} ≈ 50 000 g mol\textsuperscript{-1}) with a concentration of 0.02 g mL\textsuperscript{-1} under sonication. The mixture was subjected to sonication for 15 min, then centrifuged to remove the unbound polymer and then dispersed in a mixture of ethanol (46 mL), water (8.6 mL), aqueous ammonia (1.24 mL) and TEOS (1.92 mL) for the growth of a silica shell wrapping the Au nanoparticles. Finally, the SiO\textsubscript{2}/Au/TiO\textsubscript{2}/SiO\textsubscript{2} colloids were washed with water and ethanol, and then dispersed in deionized water (20 mL).

2.5 **Etching of the outer silica layer**

PVP K14-16 (1 g) was dissolved in a SiO\textsubscript{2}/Au/TiO\textsubscript{2}/SiO\textsubscript{2} solution (20 mL) by mechanical stirring. Refluxed at 100 °C for 3 hours, the solution was cooled down to room temperature naturally. A NaOH solution (5 mL, 0.16 g mL\textsuperscript{-1}) was injected into the system to start the etching. After stirring for desired time periods, the solution was centrifuged and washed with water.
several times. The particles were finally dried in a vacuum oven at 70 °C and prepared for catalysis.

The synthesis process of the mesoSiO$_2$/Au/SiO$_2$ catalyst is similar to that of the mesoSiO$_2$/Au/TiO$_2$/SiO$_2$ one, except for the absence of the deposition of a TiO$_2$ layer.

2.6 Characterization

A Tecnai T12 Transmission Electron Microscope (TEM) was used to characterize the morphology of the prepared samples in each step. Samples dispersed in ethanol at an appropriate concentration were cast onto a carbon-coated copper grid, followed by evaporation under vacuum at room temperature. Nitrogen adsorption–desorption measurements were carried out using a Micromeritics ASAP 2020 instrument to determine the BET surface area, single point total pore volume and BJH pore size distribution. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance Diffractometer (Germany) with CuK$_\alpha$ radiation ($\lambda = 1.5406$ Å). Fourier transform infrared (FT-IR) spectra were measured using a Nicolet Magna-IR 750 spectrophotometer. UV-vis absorption spectra analysis was performed using a Shimadzu UV 3600 spectrometer.

2.7 Catalytic test: CO oxidation

The catalytic activity was measured in a fixed-bed stainless-steel tubular reactor using 50 mg catalyst powder diluted with 100 mg crushed quartz. Prior to the test, the catalyst was activated by three oxidation–reduction cycles at 300 °C and cooled down to room temperature. The reaction temperature was controlled with a thermocouple placed in the catalyst bed and the reaction gas contains 1% CO balanced with air at a total flow rate of 65 mL min$^{-1}$. After 25 min of reaction, the effluent gases were analyzed by GC-14C gas chromatography on-line, equipped with a thermal conductivity detector (TCD) and a 23% SP-1700 on an 80/100 Chromosorb PAW column. Nitrogen (98% purity) was used as the carrier gas. The activity of the catalyst was evaluated by CO conversion.

3. Results and discussion

3.1 Structure and morphology of the mSiO$_2$/Au/TiO$_2$/SiO$_2$ catalyst

The work aims to intentionally synthesize a multifunctional system in which Au nanoparticles are encapsulated by mesoporous silica shells. The synthesis starts with the preparation of monodisperse TiO$_2$/SiO$_2$ core–shell particles, which were prepared through the sol–gel reaction of TBOT with HPC as the surfactant. The size of the core–shell particles is ~200 nm estimating from the TEM image (Fig. 2a), with ~10 nm thickness of TiO$_2$ shells. What is more, the thickness of the titania layer can be conveniently controlled by carrying out multiple coating processes (Fig. S1†). Raising the number of TiO$_2$ coating steps increases the thickness to ~30 nm and 77 nm, respectively. Taking into account that the structure of TiO$_2$/SiO$_2$ nanocomposites is relatively uniform, just one coating step of TiO$_2$ has been carried out in the following work.

The second step is associated with the preparation of metallic Au NPs with uniform dispersion. Afterwards, these nanoparticles deposit on the surface of TiO$_2$/SiO$_2$ nanocomposites. To improve the attachment of the metal nanoparticles onto the colloids, the TiO$_2$/SiO$_2$ particles were first modified with functional groups (APTES). As shown in Fig. 2b, the gold nanoparticles readily attach to the TiO$_2$/SiO$_2$ particle surface since in this case these functionalized colloids have amine groups available for the Au NPs to bind. Obviously, the covalent attachment of the gold nanoparticles occurs by the formation of the Au–N bond. Also, from this figure, it can be seen that the dispersion of Au NPs is relatively uniform and the average size is 5.6 nm. However, a different phenomenon can be found as for the core–shell particles without functionalization of APTES. In this case, fewer Au NPs adhere to the particles’ surface (Fig. S2†), demonstrating that modification of the particles’ surface is favorable for the deposition of Au NPs. To further probe the surface modification of the TiO$_2$/SiO$_2$ nanoparticles before and after the functional treatment, the samples were characterized by the FTIR technique. As exhibited in Fig. S3† after the surface modification, the material shows some absorption bands at 2976 cm$^{-1}$ and 2929 cm$^{-1}$, corresponding to the vibrations of −N–H and −CH$_2$, respectively. Obviously, this finding reveals that the surface of the particles has been successfully modified with the functional groups.

Afterwards, coating with a silica layer onto the surface of the as-synthesized Au/TiO$_2$/SiO$_2$ particles is done via a modified Stöber’s method. Moreover, it is found that the thickness of the silica can be readily tuned from 20 nm to 100 nm by changing the amount of TEOS used. Fig. 2c and 3a show the images of the particles after deposition of a silica layer, with ~30 nm thickness of the silica shell. Apparently, the
encapsulated particles show a monodisperse multi-core–shell structure and negligible changes in the size of Au NPs are seen after silica coating.

In this work, the etching procedure is carried out with the "surface-protected etching" strategy, as described by Lee et al. 12 As a consequence, the Au NPs become available to the chemical reactants and the freshly formed porous silica may act as a physical barrier preventing the aggregation of the Au NPs. It is known that during the process of etching, the existence of PVP may play an important role to re-expose the gold nanoparticles without losing the anchoring properties that prevent nanoparticle sintering. 14 Furthermore, the polymer of PVP as a stabilizer may protect the outside silica from etching through the formation of strong hydrogen bonds between the carbonyl groups and the silanol groups. 21,22 From Fig. 2d, the freshly deposited silica layer has become much rougher and less homogeneous, which implies the formation of porous structure. Besides, the etching time has an obvious influence on the structure and morphology of the catalysts. As presented in Fig. 3b, when the etching time is 45 min, it is interesting to note that the gold nanoparticles become exposed and they are still embedded inside the silica layer. In this case, the average sizes of Au nanoparticles are almost unchanged. Nevertheless, this outside silica layer becomes much thinner and incomplete after the over-etching treatment (90 min, Fig. 3c). Possibly, with prolonging the etching time, more amounts of NaOH solution may diffuse through the silica surface and continuously etch the unprotected silica; thus dissolution of the outside silica layer is inevitable. Meanwhile, it is worthy to mention that this over-etching treatment has little influence on the interior silica beads of the TiO2/SiO2 particles. Clearly, this behavior may be interpreted in terms of the protection effect of the titania layer. In this situation, the inert nature of titania may prohibit and/or decrease the amount of etchant that diffuses through the outer titania layer. As a consequence, dissolution of the interior silica beads can be avoided.

The representative N2 adsorption/desorption isotherms together with the corresponding pore size distribution of the samples are displayed in Fig. 4. As can be observed, the sample after 45 min of etching has a mesoporous structure. The BET surface area and the total pore volume for this sample are 82.0 m2 g−1 and 0.12 cm3 g−1, respectively. The Barrett-Joyner-Halenda (BJH) pore size distribution (PSD, inset of Fig. 4) obtained from the isotherm exhibits a bimodal distribution with one centered in the mesoporous range (3.5 nm) and the other around 30 nm. By contrast, the BET surface area and the total pore volume decrease to 36.4 m2 g−1 and 0.07 cm3 g−1 after etching treatment for 90 min (Fig. S4†). In the meantime, the PSD is appreciably shifted to larger pore diameter in the absence of the distribution center in the low mesoporous range. Possibly, the increase of pore size may be attributed to the calculations that have included the residual solid core and re-exposed Au nanoparticles. 14 With respect to the decrease of the total pore volume, this may be related to the removal of the outside silica layer. As mentioned before, the etching process directly transforms the dense silica coatings into porous shells. Therefore, the decrease of the pore volume is inevitable in the absence of the outside silica.

To identify the properties of the Au nanoparticles before and after SiO2 deposition and etching treatment, some samples were probed by UV-vis spectra. As shown in Fig. 5, over the Au/TiO2/SiO2 sample, an absorption band at about
529 nm arises from the excitation of surface plasmon mode of the Au NPs (Fig. 5a). Apparently, this phenomenon indicates the presence of Au NPs on the surface of TiO2/SiO2 core–shell particles. For comparison, when the Au/TiO2/SiO2 nanoparticles are coated with a silica shell, the thick shell would mask the optical property of Au NPs. As a result, this adsorption becomes too weak to see (Fig. 5b). However, on converting the dense silica shell to a porous one, the characteristic absorption band of Au NPs returns (Fig. 5c), demonstrating that the Au NPs become exposed again after the etching process to some extent.

The effect of the presence of a mesoporous silica layer on the thermal stability of catalysts has been tested in this paper. Fig. 6 displays TEM images of the different catalysts with or without the outside silica after they have been treated in air at 500 °C. As can be seen, in the case of the mSiO2/Au/TiO2/SiO2 sample, the size of Au NPs is about 6.4 nm. Compared with the as-prepared Au/TiO2/SiO2 sample (Fig. 2b), little changes in the size of Au NPs are observed, suggesting that the Au NPs are effectively prevented from sintering up to 500 °C after the protection of a mesoporous silica layer. However, sintering of Au NPs starts to occur as for the unprotected one (Fig. 6b).

Over this sample, the formation of large Au agglomerates is found and the average size of Au NPs increases to about 16 nm. As commented before, in our experiments the outer mesoporous silica encapsulates and isolates the catalytically active nanoparticles. That is to say, in the catalyst system, the Au nanoparticles are sandwiched between the TiO2/SiO2 solid core and the outside porous silica shell. Such a configuration allows the catalyst particles to remain stable against sintering with the increase of the thermal treatment temperature, which may have a positive impact on the catalytic performances.

Furthermore, during the above mentioned process, the alteration of crystal shape should also be considered. As shown in Fig. 7, significant differences can be observed for the Au/TiO2/SiO2 sample before and after calcination. The calcinated sample exhibits characteristic peaks at 2θ = 38°, 44° and 65° due to the reflection (of X-rays) from the (111), (200) and (220) crystal planes, respectively, of the Au nanoparticles.23 Obviously, this finding reveals that over this sample, relatively larger size Au nanoparticles have formed after the thermal treatment, which is identical to the above analysis of TEM experiments. Compared with this, for the mSiO2/Au/TiO2/SiO2 particles (Fig. 7c), only a broad and blurred peak at 38° appears and the diffraction peaks for Au (200) and Au (220) are not visible. A similar phenomenon is also found before the calcination (Fig. 7d), which indicates again that the existence of the outside silica layer can increase the catalyst’s capacity to effectively resist sintering. In the meantime, it is well-known that the phase transformations of titania from amorphous to anatase will take place with the increase of calcination temperature (typically to 500 °C). As a result, the calcined sample may exhibit some characteristic peaks of the corresponding anatase titania phase.24 However, as shown in Fig. 7c, only a broad peak between 20° and 35° emerges as for the mSiO2/Au/
The mSiO2/Au/SiO2 particles in the absence of titania (Fig. 8a), confirm this point with great certainty. It can be seen that on silica shell. Meanwhile, in the case of the TiO2/SiO2 core-shell particles, the restriction of the phase transformation of titania may promote the formation of small grain size TiO2, which results in a well-dispersed TiO2 crystal on the SiO2 surface. In this way, strong interactions between the TiO2 layer and Au NPs may exist through their “strong metal–support interaction”, which is favorable for the dispersion of metal nanoparticles. The TEM images of the different samples confirm this point with great certainty. It can be seen that on the mSiO2/Au/SiO2 particles in the absence of titania (Fig. 8a), the Au nanoparticles are not well distributed and some agglomerated particles appear when the calcination temperature increases to 500 °C. Comparatively, the existence of titania in the SiO2/Au/TiO2/SiO2 catalyst system (Fig. 8b) results in the relatively homogeneously distributed metal nanoparticles under the same thermal treatment.

3.2 Catalytic performance

Considering that the Au-supported TiO2 catalyst has been extensively studied for photo-catalysis and CO oxidation, in this work we have preliminarily tested the catalytic activity of the prepared catalysts using CO oxidation as a probe reaction. The catalytic activity of the different catalysts is shown in Fig. 9. It can be seen that the mSiO2/Au/TiO2/SiO2 catalyst after 45 min of etching exhibits significantly enhanced catalytic activity with a high CO conversion of 76.2% even at 10 °C. Moreover, the value of activity increases linearly with increasing reaction temperature. Note that 100% CO conversion is reached at about 50 °C, revealing good activity of the Au nanocatalyst with the encapsulation of mesoporous silica. For comparison, the mSiO2/Au/SiO2 catalyst exhibits relatively lower activity. At the temperature of 10 °C, the catalytic activity is about 74.3%. Over this sample, the temperature increases to about 60 °C when 100% CO has been converted, suggesting that the loss of activity occurs in the absence of a titania layer. With respect to the SiO2/Au/TiO2/SiO2 sample without the etching treatment, the lowest values of activity are observed. It is worth noting that the activity can reach 100% when the reaction temperature increases to 110 °C.

It is apparent that the mSiO2/Au/TiO2/SiO2 catalyst shows a significantly improved catalytic activity. As discussed before, the enhanced catalytic performance might be ascribed to the following reasons. First, the encapsulation of gold nanoparticles with a silica layer is quite effective in preserving the size and distribution of the Au nanoparticles. As mentioned before, in our experiments, the investigated catalysts will be activated by oxidation–reduction cycles at 300 °C for several times before the test. Therefore, the catalytic capacity to resist sintering may have an important influence on the reaction performance. In other words, the aggregation of the nanoparticles in the process of pretreatment may lead to the loss of catalytic activity. From the TEM images (Fig. 6), over the mSiO2/Au/TiO2/SiO2 catalyst, the silica barrier surrounds each Au NP, which is beneficial to isolate the contiguous Au nanoparticles and prevent them from coming together even when the calcination temperature increases to 500 °C. Thus, it can be deduced that the Au NPs are effectively prevented from sintering after the pretreatment in the reaction stage. Second, in terms of this catalyst system, the etching treatment has little influence on the silica beads of TiO2/SiO2 core–shell particles because of the inert nature of titania, which is advantageous to tune the metal and porous characters of the catalyst. As can be observed in Fig. 4 and 5, the mesoporous structure of the outside silica layer has formed and the Au NPs have become exposed again after the etching treatment. In this way, the newly formed porous silica allows the catalyst nanoparticles to become accessible to the reacting species. Thus, the diffusion of reactants through the outside pores may be enhanced, which is believed to be responsible for the increased catalytic efficiency. Contrary to this, as for the SiO2/Au/TiO2/SiO2 sample without the etching treatment, the nanocatalysts
cannot become available to the chemical reactants, which results in the lowest catalytic activity. Thirdly, the protection effect originating from the outside silica material restricts the phase transformation of titania during the process of calcination. In this situation, small crystalline particles of TiO₂ may anchor to the silica beads of TiO₂/SiO₂ core–shell particles. Combining the XRD patterns (Fig. 7) with the TEM images (Fig. 8), it is reasonable that the limitation of phase transformation is beneficial to improve the dispersion of Au NPs because of the strong metal–support interaction. Therefore, higher catalytic activity can be obtained than that for the mSiO₂/Au/TiO₂/SiO₂ catalyst. The excellent thermal stability of the catalyst makes us believe that this sample may be tested in high temperature reaction, such as the gas phase oxidation of ethanol. At present, work is still in progress in our laboratory to investigate the reaction performances.

4. Conclusions

A new strategy has been developed to synthesize the mesoSiO₂/Au/TiO₂/SiO₂ catalyst and several possible reasons for the improved thermal stability have been discussed. According to the characterization results, TiO₂/SiO₂ nanocomposites with uniform structure are obtained. After the functionalization with APTES, attachment of Au nanoparticles onto the surface of TiO₂/SiO₂ composites occurs by the formation of the Au–N bond. Furthermore, encapsulation of Au nanoparticles with mesoporous silica can be achieved after the coating with a new silica layer and the etching treatment. It is found that the existence of a titania layer in the catalyst system is beneficial to protect the silica beads of TiO₂/SiO₂ core–shell particles and the Au NPs become exposed again during the process of etching. Meanwhile, the outside silica material can hinder the phase transformation of titania to some extent. In this case, small grain size TiO₂ may anchor on the SiO₂, which is favorable for the dispersion and increased thermal stability of Au NPs because of the strong metal–support interaction. In our experiments, the prepared mesoSiO₂/Au/TiO₂/SiO₂ catalyst displays the desired behavior in terms of the improved thermal stability and enhanced catalyst activity for CO oxidation. As revealed by TEM images, the size of Au nanoparticles shows virtually no changes after calcination at 500 °C and 100% CO can be converted when the temperature increases to about 50 °C under the experimental conditions.

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