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COMMUNICATION

Ligand- Free Gold Nanoclusters Confined in Mesoporous Silica Nanoparticles for Styrene Epoxidation

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We present a novel approach to produce gold nanoclusters (Au NCs) in the pores of mesoporous silica nanoparticles (MSN) by sequential and controlled addition of metal ions and reducing agents. This impregnation technique was followed to confine Au NCs inside the pores of MSN without adding external ligands or stabilizing agents. TEM images show a uniform distribution of monodisperse NCs with an average size of 1.37 +/- 0.4 nm. Since the NCs are grown *in situ* in MSN pores, additional support and high temperature calcination are not required to use them as catalysts. The use of Au NCs /MSN as a catalyst for the epoxidation of styrene in the presence of tert-butyl hydroperoxide (TBHP) as a terminal oxidant, resulted in an 88% conversion of styrene in 12 h with a 74% selectivity towards styrene epoxide. Our observations suggest that the remarkable catalytic performance arises from the small size of Au NCs and the strong interaction between the gold and the MSN. This catalytic conversion is environmentally friendly as it is solvent free. We believe our synthetic approach can be extended to other metal NCs offering a wide range of applications.

Metal nanoclusters (NCs) are relatively a new class of nanomaterials consisting of only tens of core atoms and display well defined atomic and electronic structures. They are employed in several potential applications such as imaging, sensing, catalysis and for solar energy harvesting.¹⁻⁶ NCs with core size < 2 nm display superior catalytic performance compared to plasmonic nanoparticles (NPs) and bulk metals due to quantum confinement.⁷⁻¹¹ Unlike plasmonic NPs, NCs can be prepared with atomic precision and hence it is possible to correlate the structural properties of NCs with their catalytic properties as well as to determine the active sites for the catalytic activity. NCs are used in several catalytic reactions

including oxidation,^{12, 13} hydrogenation,^{14, 15} electrocatalysis¹⁶ and photocatalysis.^{17, 18} There are several factors affecting the catalytic properties of NCs such as the nature of capping ligands, doping with other metal atoms, morphology and nature of the support.¹ Unlike their NP counterparts even a minor change in the atomic composition and core size can alter the catalytic properties dramatically. For example, when a single Pd atom was doped with Au₂₅ NC, the catalytic activity improved significantly either due to the creation of highly active reaction sites on the surface of NC or due to the activation of Au sites via electronic structure modification.¹⁹ Therefore it is important to retain the integrity of NCs during catalysis.

For heterogeneous catalysis, NCs are often loaded on inert surfaces such as TiO₂,²⁰ SiO₂,²¹ carbon nanotube,²² etc. The presence of a support enhances the robustness, prevent sintering during catalysis and provides excellent recyclability of the NCs based catalysts. To attain maximum catalytic activity for NCs, it is important to have exposed metallic surface to interact with the reactants. Generally, a protecting ligand is used to stabilize and control the size of the metal NCs.²³ However, the presence of the organic ligand on the surface of the metal NCs may block or reduce the catalytic property in some cases.²⁴⁻²⁷ To avoid this, a ligand that allows the maximum exposed surface area for NC synthesis is used or the ligand is removed from the synthesized NC surface before the catalytic application. Several harsh techniques such as CO stripping,²⁵ thermal treatment at high temperature,^{28, 29} plasma and UV-ozone cleaning,³⁰⁻³² are employed to remove the coordinated ligands. Though such ligand-off catalysts show higher activity, ligand removal may result in the structure and the size modification of NCs and in some cases aggregation. Another possibility is to synthesize ligand free NCs *in situ* on proper supports for improved catalysis especially for reactions like styrene epoxidation, which has gained much attention as it is used as a starting material for small molecule drugs, a stabilizer for high molecular weight polymers, and it also plays a major role in the perfume and sweetening industries.^{33, 34}

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Herein, we developed a novel NC based catalyst based on ligand-free Au NCs on mesoporous silica nanoparticle (MSN) supports. The gold precursors were impregnated in the pores of MSN followed by reduction to obtain NCs. This catalyst was employed in the solvent-free oxidation of styrene using TBHP as an oxidizing agent. Interestingly, the catalyst was utilized without calcination, which was always required in previously reported catalysts.³⁵⁻³⁷

Au NCs were successfully synthesized in the pores of MSN NPs via wet chemical reduction of impregnated gold precursors. For this, amination of MSN NPs was carried out before introducing Au precursor to facilitate electrostatic interaction between the MSN NPs and the added gold precursor ions. This may eliminate the possibility of formation of NCs in solution outside the silica NPs as well as the aggregation of the formed particles. Furthermore, to control the amination process with (3-aminopropyl)triethoxysilane (APTES), the amount of hydroxyl group on the surface of silica was estimated by titration with methyl lithium (MeLi) (quantitative evolution of methane) and found to be 0.4 ± 0.2 mmol of Si-OH per 1 g of MSN. After the amination process, MSN-NH₂ was characterized by elemental analysis (CHN) and solid-state NMR. The elemental analysis of MSN-NH₂, indicated the presence of 2.0 wt. % of N (~ 1.4 mmol of N grafted on 1 g of MSN). The atomic ratio of N/OH was calculated to be 3.5, which mean that each unit of APTES is reacting with 3 units of hydroxyl group on silica. The C analysis was found to be 10 wt.% (~ 8.5 mmol of C). The ratio of C/N was calculated to be 5 (expected 3 C for N). The excess of carbon content due to the presence of solvent (toluene) adsorbed on the support, which was not completely removed after the washing process. Furthermore, MSN-NH₂ was analyzed by multinuclear solid-state NMR to provide detailed information of the molecular structure of the grafted ($\equiv\text{Si-CH}_2\text{-CH}_2\text{-CH}_2\text{-NH}_2$) fragment. The ¹H NMR spectrum exhibited a significant signal at 2.8, 1.3 and 0.36 ppm arising from protons of Si-CH₂-CH₂-CH₂-NH₂, respectively. The sharp peak at 1.3 ppm is assigned to the protons of NH₂. The ¹³C NMR spectrum shows intense peak at 11.6, 23.0 and 44.5 ppm assigned to Si-CH₂-CH₂-CH₂-NH₂ fragment.³⁸ Furthermore, extra three peaks appeared at 23 ppm and 129 ppm corresponding to excess amount of toluene, which was not removed completely during the drying process (Figure S1). TEM images of MSN before and after amination are shown in Figure S3 confirming no change in the size and morphology of MSN NPs after amination. The size of the MSN NPs is in the

range of 100-150 nm. In the absence of amination, aggregated gold nanoparticles were formed on the surface of MSN as shown in Figure S4. After the amination, zeta potential of MSN changed from zero mV to 23.9 mV as shown in Figure S5. The formation of Au NCs was initiated by the addition of Au precursor to aminated MSN NPs followed by reduction with NaBH₄. The dispersion colour changed from light yellow to dark brown after reduction suggesting the formation of NCs. TEM images presented in Figure 1a showed that MSN retained spherical morphology after NC growth. Highly uniform Au NCs with an average size distribution of 1.37 ± 0.4 nm are embedded throughout MSN NPs as shown in Figure 1b. The larger AuNCs of near 2 nm size with less population are grown outside the pores of MSN, thus had no constraints on their growth. 2D projection image of MSN (Figure 1c) confirm the presence of AuNCs inside MSN pores up to a depth of 30 nm. The absence of particle aggregation and formation of NPs or NCs outside the MSN NPs proved that NCs can be successfully synthesized inside MSN NPs via our method. There was no aggregation of formed gold nanoclusters as confirmed by High-angle annular dark-field scanning TEM (HAADF-STEM) in Figure 1d. The elemental composition of AuNCs/MSN-NH₂ was determined via EDX spectroscopy as well elemental mapping (Figure 1).

Diffuse reflectance UV-vis spectra of AuNCs/MSN-NH₂ was measured in the range of 300-800 nm and is shown as Figure S6. The absence of the plasmonic peak characteristic of Au nanoparticles (NPs), around 550, confirms that no NPs are formed.

X-ray photoelectron spectrum (XPS) survey spectrum showed the presence of the elements Au, N, C, O and Si (see Figure S7). The atomic percentage of the observed elements are exhibited in the inset of Figure S7. The binding energies of gold 4f_{7/2} and 4f_{5/2} shown in Figure S8 were determined via high resolution to be 83.4 and 87.0 eV which is slightly lower than the thiolated NCs, which was matching the literature data.³⁹ This is expected as the NCs are ligand free (exclude the grafting of amine). From the full range XPS spectrum, sodium and oxygen appear at higher binding energies 1072 eV (Na 1s) and 532 eV (O 1s) as shown in Figure S7 (SI). The remaining peaks at 400 eV, 285 eV and 103 eV correspond to N 1s, C 1s, Si 2p, respectively.



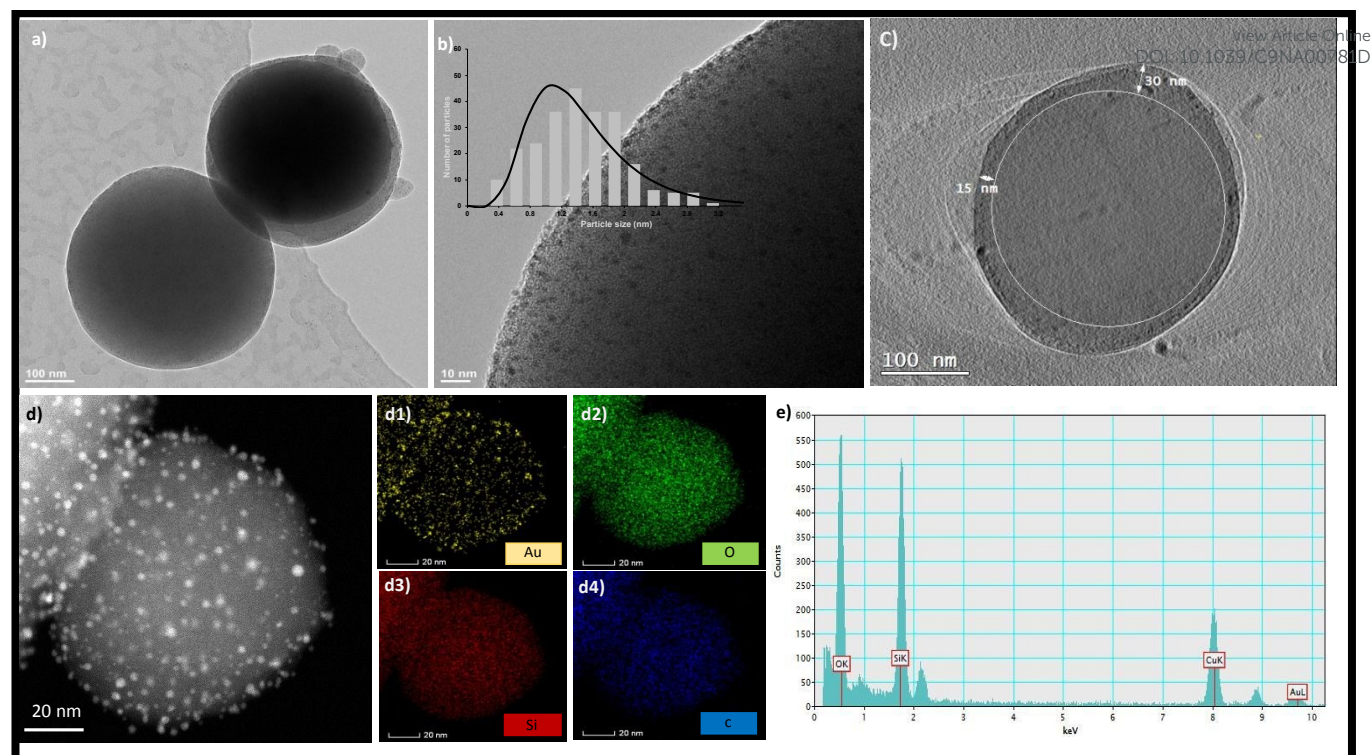


Figure 1. a-b) Bright-field TEM, c) volume-slice electron tomography image. d) HAADF-STEM image, and STEM EDX mappings of AuNCs/MSN-NH₂: Au, O, Si, and O are shown in (d1-d4), respectively. E) EDX spectrum of AuNCs/MSN-NH₂.

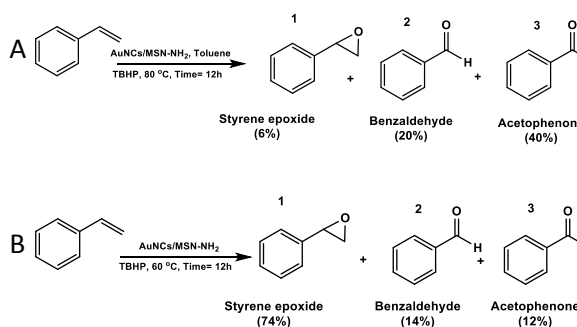
The powder X-ray diffraction data (Figure S9) confirm the presence of AuNCs in MSN-NH₂. Several distinct 2 theta peaks were observed for AuNCs, which show face-centered cubic at 39°, 44°, 65° and 79° corresponding to (111) and (200), (220) and (311) lattice planes, respectively. The low-angle XRD pattern of MSN before and after the formation of Au NCs shows an intense peak at 2Theta= 1.3°, confirming the ordered mesoporous structure of silica (Figure S10) and was in accordance with the literature.⁴⁰ The BET surface area of AuNCs/MSN-NH₂ was 361 m²/g, which is two times less than the surface area of aminated MSN NPs (721 m²/g) (SI). This further confirms the loading of NCs in the pores of MSN NPs. The amount of gold loading was defined via ICP-OES analysis, to be 10 wt% for high loading and 1 wt% for low loading of gold.

Catalytic activity of gold clusters

The selective epoxidation of styrene was investigated to evaluate the catalytic performance of AuNCs/MSN-NH₂ as shown in (Scheme 1) in the presence of TBHP as oxidant due to its high performance for alkene epoxidation reactions.⁴¹

Furthermore, the investigation of the reaction parameters, such as the temperature and the presence of a solvent, has been

studied. During the reaction, various products have been obtained including styrene epoxide (1), benzaldehyde (2), acetophenone (3), and 1-phenylethane-1,2-diol (4) (Scheme 1 A and B), which are valuable and extensively used in industry.⁴²



Scheme 1. Evidence of solvent effect in the selective styrene epoxidation by using AuNCs/MSN-NH₂ as catalyst using toluene solvent (A) and without solvent (B).

The preliminary results of using AuNCs/MSN-NH₂ as a catalyst for the epoxidation reaction of styrene are shown in Table 1. Using gold clusters Au NCs/MSN-NH₂ as a catalyst in toluene, a moderate conversion of styrene was obtained (c.a. 72%) after 12 h at 60 °C.



Table 1. The catalytic performance of Au NCs/MSN-NH₂ catalysts for styrene epoxidation with TBHP and in the presence of Toluene as solvent.

Catalysts	Temperature (°C)	Time (h)	Conversion (%)	Selectivity for (1)	Selectivity for (2)	Selectivity for (3)	Selectivity for (4)
AuNCs/MSN-NH ₂	60	6	63	24	8	27	41
		12	72	18.5	8	26	47
AuNCs/MSN-NH ₂	80	6	70	20	6	32	42
		12	94	6	20	40	34
		24	100	21.5	4	44	30.5

However, within a similar duration, the catalyst shows an enhanced activity when the reaction temperature was raised to 80 °C. The conversion of styrene reaches up to 95 % after 12 h of the reaction. In both cases, the acetophenone (**3**) and 1-phenylethane-1,2-diol (**4**) were formed as major products,

while styrene epoxide was the minor product (Table 1). The low selectivity of styrene epoxide (**1**) was attributed to the presence of the solvent, which obstructs the transformation of the electrons from and to gold nanocluster, as it has been observed in previous studies.⁴³⁻⁴⁵

Table 2. The catalytic performance of AuNCs/MSN-NH₂ and pristine MSN-NH₂ catalysts for styrene epoxidation with TBHP (Solvent-Free) at 60 °C.

Catalysts	Time (h)	Conversion (%)	Selectivity for (1)	Selectivity for (2)	Selectivity for (3)
AuNCs/MSN-NH ₂	3	55	73	18	9
	6	83	78	15	8
	12	88	74	14	12
Pristine MSN-NH ₂	3	6	75	4	21
	6	11	76	5	19
	12	17	74	7	19

As reported in the literature, the nature of the solvent plays a main role in the catalytic activity of the catalysts such as conversion and selectivity towards the oxidation reaction of alkenes.^{43, 46, 47} Moreover, in order to optimize the reaction conditions, the oxidation of styrene was investigated with TBHP in the absence of solvent at 60 °C (Table 2). Interestingly, a significant influence in the selectivity for styrene epoxide has been observed. The conversion of styrene has reached 88 % after 12h, with a very high selectivity for styrene epoxide (c.a.74%). It is worth noting that at the same conditions, the pristine MSN-NH₂ shows a very low conversion of styrene (less than 17 %).

A kinetic study was performed at the optimized conditions (solvent-free) at different temperatures (60 °C and 80 °C) (Figure S17) for 6h. In addition, a blank test was performed at 60 °C in the presence of pristine MSN-NH₂. The obtained results show that the catalytic activity of AuNCs/MSN-NH₂ at 80 °C was higher compared to 60 °C at the beginning of the reaction; without any appearance of the induction period. The initial activity of AuNCs/MSN-NH₂ at 80 °C is 10.9 mmol/g[Au].h, whereas the activity was 6.4 mmol/g[Au] h at 60 °C. However, the pristine MSN-NH₂ shows a very low initial activity with an induction period of 60 min (curve red). As to the selectivity for styrene epoxide (**1**), a constant selectivity (75 ± 5 %) has been

obtained during the reaction under either temperature 80 °C or 60 °C (Figure S17).

Under optimized reaction conditions (60 °C, over 12 h, solvent-free), we attempted to study the recyclability of Au NCs/MSN-NH₂ during the epoxidation reaction of styrene. After the first run of the catalyst, the reaction mixture was allowed to cool to room temperature, and the catalyst was separated by centrifugation, washed twice with ethanol and allowed to dry at room temperature. The recycled gold catalyst was then used without any regeneration under the same reaction conditions. The conversion of styrene dropped from 88% to 80% after 5 cycles (Figure 2). The selectivity of styrene epoxide (**1**) was consistent (~75%) during the 5 cycles. Furthermore, the weight percent of gold leaching after 5 runs was examined by ICP-OES to be 3.6 wt% out of 10 wt %.



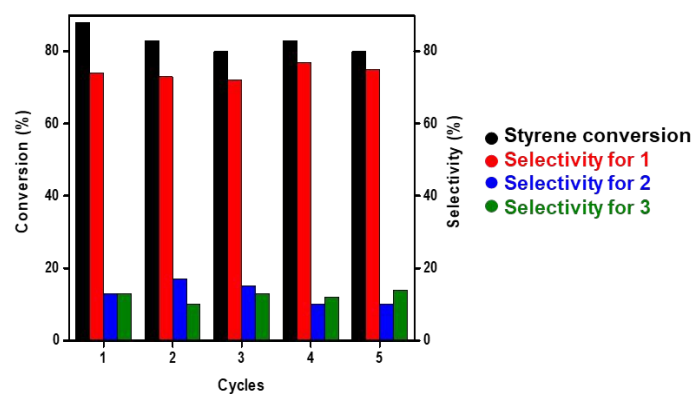
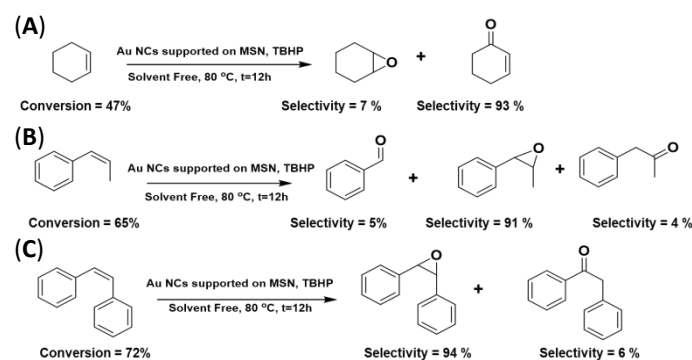


Figure 2. Recycling graph of styrene epoxidation at 60 °C using AuNCs/MSN-NH₂ catalyst.



Scheme 2. Epoxidation of various substrates (cyclohexene, 1-Phenylpropene and Cis-stilbene) using AuNCs/MSN-NH₂ catalyst (solvent free).

The catalytic activity of AuNCs/MSN-NH₂ catalyst was further tested with various olefins; the reaction was carried out under the above-mentioned conditions. As clarified in Scheme 2(A), the conversion of cyclohexene is 47% after 12 h at 80 °C, when the C=C is oxidized two products are formed. Cyclohexene epoxide (~7% selectivity) and cyclohexen-1-one (~93% selectivity). The dominance of cyclohexen-1-one over cyclohexene oxide was comparable to the best reported results of the cyclohexene epoxidation in the presence of Au/C.^{43, 48} Interestingly, only Titanium Silicate (TS-1) gives 100% selectivity for cyclohexene epoxide.⁴⁹ This low selectivity for cyclohexene oxide may be restricted to non-aromatic alkenes with this catalyst. The double bond in cyclohexene interacts differently with AuNCs surface in comparison with aromatic alkene. The disappearance of other side products was attributed to the absence of solvent. On the other hand, a moderate conversion of phenylpropene was achieved (~65%), and the selectivity for phenylpropene oxide was very high 91% (Scheme 2(B)). In addition, it was found that stilbene oxide was produced with a high selectivity of 95% at a conversion 72% of cis-stilbene (Scheme 2 (C)). It is worth to note that previous work have reported high efficiency and selectivity for olefin epoxidation in the absence of any solvent.⁵⁰ The high conversion of Cis-stilbene and 1-Phenylpropene compared to cyclohexene is attributed to the stability and the position of the double bond. The internal

alkene double bonds are more stable and less accessible by the catalyst compared to the external double bonds. Therefore, the external π -electrons in Cis-stilbene and 1-Phenylpropene favour the chemisorption of the aromatic rings to the gold surface and thus the approach of the double bond to the surface. In cyclohexene however, such approach is not favoured.

In conclusion, ligand-free Au NCs confined in MSN-NH₂ NPs were synthesized successfully by using the chemical impregnation technique. Mesoporous silica with 2-3 nm pore size was used to control the size of Au NCs. The average size of Au NCs was estimated from HR-TEM to be 1.37 +/- 0.4 nm. The synthesized catalyst was characterized by NMR, zeta potential, BET, ICP-OES, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) techniques. The catalytic activity of this material was systematically investigated via solvent-free oxidation reaction of styrene. Interestingly, AuNCs/MSN-NH₂ can achieve an 88% conversion of styrene with a 74% selectivity towards styrene oxide. Our heterogeneous catalyst is sufficiently stable and can be successfully recovered and reused for five runs. Furthermore, the oxidation of cyclohexene, 1-Phenylpropene and Cis-stilbene to the corresponding epoxide were detected with high selectivity. This is a "green" approach to petrochemical epoxidation where the use of organic solvents and high temperatures are not required. We believe that this strategy could be applied to a wide range of noble metals which drastically increases the possibility of selective catalytic reactions.

Author Contributions

B.S. and W.M. contributed equally. The manuscript was written through contributions of all authors.

Conflicts of interest

The authors declare no conflict of interest.

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Notes and references

- J. Fang, B. Zhang, Q. Yao, Y. Yang, J. Xie and N. Yan, *Coord. Chem. Rev.*, 2016, **322**, 1-29.
- G. Li, H. Qian and R. Jin, *Nanoscale*, 2012, **4**, 6714-6717.
- H. Chong, P. Li, J. Xiang, F. Fu, D. Zhang, X. Ran and M. Zhu, *Nanoscale*, 2013, **5**, 7622-7628.
- A. Shivhare, S. J. Ambrose, H. Zhang, R. W. Purves and R. W. Scott, *Chem. Commun.*, 2013, **49**, 276-278.
- H. Yamamoto, H. Yano, H. Kouchi, Y. Obora, R. Arakawa and H. Kawasaki, *Nanoscale*, 2012, **4**, 4148-4154.



6. S. Antonello, M. Hesari, F. Polo and F. Maran, *Nanoscale*, 2012, **4**, 5333-5342.
7. S. Yamazoe, K. Koyasu and T. Tsukuda, *Acc. Chem. Res.*, 2014, **47**, 816-824.
8. S. Das, A. Goswami, M. Hesari, J. F. Al-Sharab, E. Mikmeková, F. Maran and T. Asefa, *Small*, 2014, **10**, 1473-1478.
9. M. Valden, X. Lai and D. W. Goodman, *science*, 1998, **281**, 1647-1650.
10. M. Turner, V. B. Golovko, O. P. Vaughan, P. Abdulkin, A. Berenguer-Murcia, M. S. Tikhov, B. F. Johnson and R. M. Lambert, *Nature*, 2008, **454**, 981-983.
11. Y. Lu and W. Chen, in *Functional Nanometer-Sized Clusters of Transition Metals*, 2014, pp. 261-290.
12. Z. Wu, D.-e. Jiang, A. K. Mann, D. R. Mullins, Z.-A. Qiao, L. F. Allard, C. Zeng, R. Jin and S. H. Overbury, *J. Am. Chem. Soc.*, 2014, **136**, 6111-6122.
13. Z. Wu, G. Hu, D.-e. Jiang, D. R. Mullins, Q.-F. Zhang, L. F. Allard Jr, L.-S. Wang and S. H. Overbury, *Nano Lett.*, 2016, **16**, 6560-6567.
14. T. Abdollahi and D. Farmanzadeh, *Comptes Rendus Chimie*, 2018, **21**, 484-493.
15. S. Fehn, M. Zaheer, C. E. Denner, M. Friedrich and R. Kempe, *New J. Chem.*, 2016, **40**, 9252-9256.
16. S. Zhao, R. Jin, H. Abroshan, C. Zeng, H. Zhang, S. D. House, E. Gottlieb, H. J. Kim, J. C. Yang and R. Jin, *J. Am. Chem. Soc.*, 2017, **139**, 1077-1080.
17. H. Chen, C. Liu, M. Wang, C. Zhang, N. Luo, Y. Wang, H. Abroshan, G. Li and F. Wang, *ACS Catalysis*, 2017, **7**, 3632-3638.
18. B. Samai, S. Chall, S. S. Mati and S. C. Bhattacharya, *Eur. J. Inorg. Chem.*, 2018, **2018**, 3224-3231.
19. S. Xie, H. Tsunoyama, W. Kurashige, Y. Negishi and T. Tsukuda, *ACS Catalysis*, 2012, **2**, 1519-1523.
20. H. Tada, K. Teranishi, Y.-i. Inubushi and S. Ito, *Langmuir*, 2000, **16**, 3304-3309.
21. X. Huang, S. A. Shahzad, Y. Li, Y. Zhang, L. Sang, H. Zhou, H. Jiang, K. K.-W. Lo and C. Yu, *Anal. Chim. Acta*, 2017, **988**, 74-80.
22. H. J. Hwang, O.-K. Kwon and J. W. Kang, *Solid State Commun.*, 2004, **129**, 687-690.
23. Z. Lei, X.-K. Wan, S.-F. Yuan, J.-Q. Wang and Q.-M. Wang, *Dalton Transactions*, 2017, **46**, 3427-3434.
24. Y. Lu, Y. Wang and W. Chen, *J. Power Sources*, 2011, **196**, 3033-3038.
25. Y. Lu, Y. Jiang, H. Wu and W. Chen, *The Journal of Physical Chemistry C*, 2013, **117**, 2926-2938.
26. K. M. Yeo, S. Choi, R. M. Anisur, J. Kim and I. S. Lee, *Angew. Chem.*, 2011, **123**, 771-774.
27. H. Al-Johani, E. Abou-Hamad, A. Jedidi, C. M. Widdifield, J. Viger-Gravel, S. S. Sangaru, D. Gajan, D. H. Anjum, S. Ould-Chikh and M. N. Hedhili, *Nature chemistry*, 2017, **9**, 890.
28. Y. Liu, H. Tsunoyama, T. Akita and T. Tsukuda, *Chem. Commun.*, 2010, **46**, 550-552.
29. J. Fang, J. Li, B. Zhang, X. Yuan, H. Asakura, T. Tanaka, K. Teramura, J. Xie and N. Yan, *Nanoscale*, 2015, **7**, 6325-6333.
30. Y. Lu and W. Chen, *Chem. Commun.*, 2011, **47**, 2541-2543.
31. W. Chen, J. Kim, S. Sun and S. Chen, *PCCP*, 2006, **8**, 2779-2786.
32. W. Chen, J. Kim, S. Sun and S. Chen, *Langmuir*, 2007, **23**, 11303-11310.
33. S. Enomoto, M. Inoue, O. Ohura, T. Kamiyama and H. Nitoh, *Journal*, 1991. DOI: 10.1039/C9NA00781D
34. U. Caudillo-Flores, M. J. Muñoz-Batista, A. B. Hungria, M. L. Haro, M. Fernández-García and A. Kubacka, *Applied Catalysis B: Environmental*, 2019, **245**, 49-61.
35. J. Liu, T. Chen, P. Jian and L. Wang, *J. Colloid Interface Sci.*, 2019, **553**, 606-612.
36. J. Liu, R. Meng, J. Li, P. Jian, L. Wang and R. Jian, *Applied Catalysis B: Environmental*, 2019, **254**, 214-222.
37. B. Sarkar, R. K. Singha, R. Tiwari, S. Ghosh, S. S. Acharyya, C. Pendem, L. S. Konathala and R. Bal, *RSC Advances*, 2014, **4**, 5453-5456.
38. C.-H. Chiang, N.-I. Liu and J. L. Koenig, *J. Colloid Interface Sci.*, 1982, **86**, 26-34.
39. B. Liu, H. Yao, W. Song, L. Jin, I. M. Mosa, J. F. Rusling, S. L. Suib and J. He, *J. Am. Chem. Soc.*, 2016, **138**, 4718-4721.
40. Q. Lu, Z. Wang, P. Wang and J. Li, *Nanoscale research letters*, 2010, **5**, 761.
41. P. Lignier, F. Morfin, S. Mangematin, L. Massin, J.-L. Rousset and V. Caps, *Chem. Commun.*, 2007, 186-188.
42. Y. Zhu, H. Qian, M. Zhu and R. Jin, *Adv. Mater.*, 2010, **22**, 1915-1920.
43. M. D. Hughes, Y.-J. Xu, P. Jenkins, P. McMorn, P. Landon, D. I. Enache, A. F. Carley, G. A. Attard, G. J. Hutchings and F. King, *Nature*, 2005, **437**, 1132.
44. M. Brust, C. J. Kiely, D. Bethell and D. J. Schiffrin, *J. Am. Chem. Soc.*, 1998, **120**, 12367-12368.
45. J. Zhao and R. Jin, *Nano Today*, 2018, **18**, 86-102.
46. S. Bawaked, N. F. Dummer, N. Dimitratos, D. Bethell, Q. He, C. J. Kiely and G. J. Hutchings, *Green Chemistry*, 2009, **11**, 1037-1044.
47. M. Zare, Z. Moradi-Shoeili, P. Esmailpour, S. Akbayrak and S. Özkaz, *Microporous Mesoporous Mater.*, 2017, **251**, 173-180.
48. F. Kerdi, V. Caps and A. Tuel, *Microporous Mesoporous Mater.*, 2011, **140**, 89-96.
49. J. Bu, S.-H. Yun and H.-K. Rhee, *Korean J. Chem. Eng.*, 2000, **17**, 76-80.
50. S. S. M. Kalajahi, M. Hajimohammadi and N. Safari, *Reaction Kinetics, Mechanisms and Catalysis*, 2014, **113**, 629-640.
51. J. McMurry, *Fundamentals of organic chemistry*, Brooks/Cole, Belmont, Calif., 2011.

