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Mendeleev Commun., 2013, **23**, 337–339
Mendeleev Communications

Dependence of catalytic activity of metal-containing particles on degree of ordering rather than on size and shape. Pd and Ni-catalyzed carbon–heteroatom bond formation

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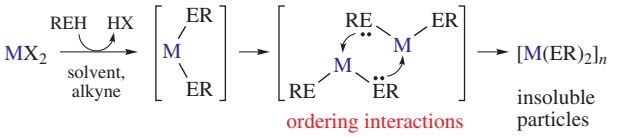
DOI: 10.1016/j.mencom.2013.11.011

High selectivity and good yields in the catalytic addition of thiols and selenols to alkynes were observed for Ni and Pd chalcogenide catalyst particles with high degree of ordering, whereas direct correlation with size and shape of the particles was not identified.

Understanding nano-scale organization of heterogeneous catalysts was the main driving force for development of new efficient catalytic processes and technologies in the recent decades. Size effect (dependence of chemical reactivity on the size of nanoparticles) and shape effect (modulation of properties of nanoparticles by their shape variations) were two primary fundamental findings studied in this field.[1–4] The ability for tuning size and shape of nanoparticles had an outstanding impact on catalysis and led to development of new generation of catalytic systems.[5–10] In addition to improved efficiency, selectivity of heterogeneous catalytic reactions was remarkably increased and in some cases it was even superior to well-established highly selective homogeneous catalytic systems.[11,12] Thus, the area of fine organic synthesis is nowadays largely influenced by heterogeneous catalysis, leaving aside traditional viewpoint of heterogeneous catalysis as industry-oriented approach only.

Here we describe our findings on the role of degree of ordering of nanoparticles as an important fundamental parameter related to catalytic activity and selectivity. We have studied catalytic properties of metal chalcogenide particles in the carbon–heteroatom bond formation exemplifying on atom-economic addition to alkynes. Metal chalcogenides represent a unique class of nanomaterials with high nano-scale diversity of morphologies and prominent potential in catalysis.[13] Addition of heteroatom groups to alkynes is a powerful green methodology that allows one to develop clean and waste-free synthetic procedures.[14,15]

In the studied system formation of catalytically active particles took place in the self-organized manner starting from easily available metal salts $Pd(OAc)_2$ and $Ni(acac)_2$. The first step involved reaction with chalcogen reagent REH (E = S, Se) and led to formation of $M(ER)_2$ species in solution followed by nucleation and growth of the particles (Scheme 1). The resulting system was heterogeneous and contained metal chalcogenide particles insoluble in most organic solvents. In our case it was important to induce self-organization process in solution to obtain unsupported particles in order to avoid possible ambiguous



M = Pd, Ni
E = S, Se
X = OAc, acac

Scheme 1

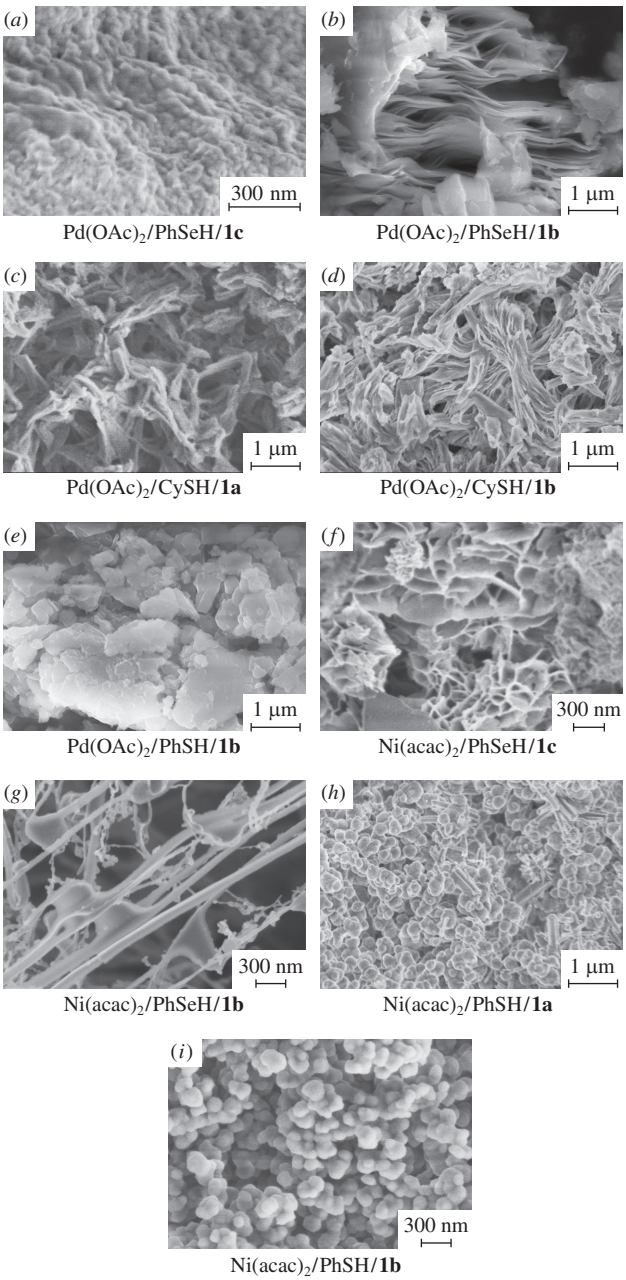


Figure 1 Selected FE-SEM images of the isolated metal chalcogenide particles (the reagents are indicated below image in each case).

Table 1 Characteristic sizes and morphology of nanoparticles and catalytic activity in the studied addition reaction at 100 °C, 1h for **1a** and 100 °C, 7 h for **1b** (*l* is the length, *d* is the diameter, *h* is the thickness).

M	REH	Alkyne	Morphology	Degree of ordering	Yield (%)	Selectivity **2**:**3**
Pd	PhSeH	**1b**	Layers (size of 4–6 μm, *h* = 30–50 nm)	High	40	98:2
		1c	Spheres (*d* = 10–30 nm)	High	89	95:5
	PhSH	**1a**	Non-ordered	Low	10	85:15
		1b	Non-ordered	Low	6	22:78
	CySH	**1a**	Rods (*l* = 2–3 μm, *d* = 0.1–0.2 μm)	High	47	91:9
		1b	Rods (*l* = 1–3 μm, *d* = 0.1–0.6 μm)	Medium	69	24:76
Ni	PhSeH	**1b**	Fibres (*d* = 0.05–0.15 μm)	Medium	63	66:34
		1c	Flakes (*h* = 20–50 nm)	Medium	81	81:19
	PhSH	**1a**	Spheres (*d* = 0.2–0.4 μm), needles (*l* = 1–2 μm, *d* = 0.05–0.2 μm)	High	48	100:0
		1b	Spheres (*d* = 0.1–0.3 μm)	Medium	57	30:70
	CySH	**1a**	—	—	25	76:24
		1b	—	—	10	36:64

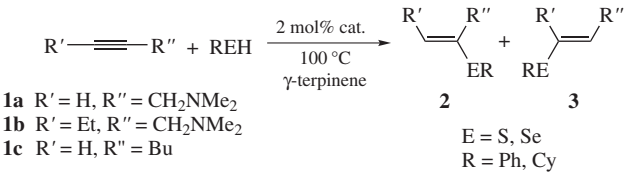
influence of support. Morphology of the synthesized nanoparticles was highly sensitive to the nature of metal and chalcogen reagent, as well as to the nature of the second reagent (alkyne) presented in the reaction mixture during self-organization process.

Amazingly, a broad variations of morphology of the particles were observed for the metal chalcogenide material composed of the similar $M(ER)_2$ structural unit. The changes in the metal (Pd or Ni) and in the reagents (REH and alkyne) led to a variety of structural forms – spheres, flakes, layers, rods and fibres (Figure 1). Undoubtedly, metal chalcogenides represent a unique material with outstanding ability of morphology tuning and generation of particles of various size and shape.

Oriented growth of the $M(ER)_2$ species resulted in formation of ordered particles with particular specific shape, while regular growth gave material without specific shape (amorphous). The dominance of only specific type of morphology constituted to high degree of ordering, while the absence of specific shape constituted to low degree of ordering. The presence of both ordered and non-ordered structures composed the material with medium degree of ordering. Although a quantitative estimation of degree of ordering is, in principle, possible, in the present communication we use only three levels of qualitative gradations (high–medium–low degree of ordering) to highlight the main effect. Representative morphologies were tentatively assigned to high [(*a*)–(*c*),(*h*)], medium [(*d*),(*f*),(*g*),(*i*)] and low [(*e*)] degrees of ordering (see Figure 1). Prevalence of a single particular structural type and uniformity of morphology (size and shape) are the key factors to assess degree of ordering.

The synthesized particles of metal chalcogenide were used as catalysts under *in situ* conditions in the corresponding addition reactions (Scheme 2).† Selectivity and yields of the reactions were monitored by ^{1}H NMR spectroscopy.‡ Morphology of catalyst particles was examined by field emission scanning electron microscopy (FE-SEM) and composition was confirmed using energy-dispersive X-ray spectroscopy (EDX-SEM).

We have carried out a set of 30 experiments with reaction monitoring and catalyst characterization under different reaction conditions (room temperature, 5 h; 100 °C, 1 h; 100 °C, 7 h). Among the studied reactions a combination of good yields and



Scheme 2

selectivities was observed only in catalytic systems with high degree of catalyst ordering. Lower performance of the catalytic reaction was observed for the catalyst particles with medium degree of ordering. Selected representative results on the yields, selectivity and particles morphology are summarized in Table 1. Note, that characteristic size of catalyst particles changed drastically from micrometer to nanometer scales.

Pd-catalyzed addition of PhSeH to both alkynes proceeded with excellent selectivity and moderate to good yields. Under studied reaction conditions catalytic addition of PhSH showed poor performance and was accompanied with low degree of ordering of the catalyst particles. High selectivity in the Pd-catalyzed addition of CySH was found in the reaction mediated by ordered particles. In the Ni-catalyzed transformation excellent selectivity was observed for addition of PhSH to **1a**, where formation of ordered particles was detected. Addition of CySH to the alkynes mediated by Ni species occurred under homogeneous conditions (without precipitate formation) and showed poor reaction outcome.

In both cases, for the Ni and Pd catalysts no direct correlation between particles size/shape and catalytic activity was found. The size of metal particles changed in a large range with varying scale on different dimensions (Figure 1). The shape of the particles showed diverse variations and possess many structural motifs. However, the performance of the studied catalytic reaction correlated with degree of ordering of the isolated particles.

To summarize, we have observed a qualitative relationship between degree of ordering of catalyst particles and catalytic properties. Better performance in the catalytic reaction was revealed for more ordered materials, while no direct correlation of catalytic activity with size and shape was possible to identify. The results suggest that degree of ordering of nanostructured materials is an important fundamental parameter. We can propose that the presence of ordering interactions between principal metal-containing units on the particle preparation step (see Scheme 1) leads to formation of uniform catalyst active sites in the final material. In the absence of ordering interactions, size and shape variations alone are not sufficient to produce an efficient catalyst. It should be noted that the present communication describes only a preliminary qualitative correlation, further detailed studies are required to clarify the role of ordering effect.

† The metal salt $Pd(OAc)_2$ or $Ni(acac)_2$ (0.02 mmol) was placed in a tube equipped with magnetic stirrer, then alkyne (1 mmol), γ-terpinene (1 mmol) and REH (1.1 mmol) were added. The reaction vessel was flushed by argon and sealed with a screw cap. The mixture was stirred at 100 °C for 1–7 h. Liquid phase was analyzed by ^{1}H NMR and solid phase was separated and studied by FE-SEM. γ-Terpinene was used as radical trap to avoid side-reactions.

‡ We did not perform special optimizations to increase selectivity and yields of the addition reaction as described in the literature.[14,15] Instead, the aim of this work was to carry out comparative study of metal chalcogenide particles with varying morphologies and different selectivities/yields.

This work was supported by the Russian Foundation for Basic Research (project no. 13-03-01210) and the Ministry of Education and Science of the Russian Federation (project nos. 8441 and 8431). The authors are grateful to A. S. Kashin for assistance with microscopy and to Dr. N. V. Orlov for helpful discussions.

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Received: 21st October 2013; Com. 13/4230