This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Synthesis of Co-based bimetallic nanocrystals with one-dimensional structure for selective control on syngas conversion

Rongbin Ba, a,b Yonghui Zhao, a Lijing Yu, a,b Jianjun Song, a,b Shuangshuang Huang, a,b Liangshu Zhong, a Yuhan Sun, a,b,c and Yan Zhu* a,b,c

Co-based bimetallic nanocrystals with one-dimensional (1D) branches are synthesized by heterogeneous nucleation of Co atoms onto the prenucleated seeds such Pd or Cu through a facile wet-chemical route. The peripheral branches (rod-like) of Co-Pd and Co-Cu nanocrystals spread along (001) direction and are enclosed by (101) facets. By switching the prenucleated metals to form robust Co-Pd or Co-Cu bimetallic nanocatalysts, the selectivity of CO hydrogenation could be purposely adjusted towards heavy paraffins, light olefins or oxygenates. The Anderson-Schulz-Flory chain-lengthening probabilities for products are up to 0.9 over Co-Pd nanocrystals, showing that long-chain hydrocarbons can be formed with high selectivity using the targeted design of Co-Pd nanocrystal catalysts. These Co-based bimetallic nanocrystals with 1D structure exhibit superior catalytic activities to the corresponding Co-based nanoparticles for synthesis gas conversion.

Experimental Section

Synthesis of Co-Pd nanocrystals with 1D structure

0.75 g of Co(OAc)2·4H2O and 1.065 g of stearic acid were added into 70 mL of propylene glycol to form solution A. After solution A was stirred for 30 min, appropriate amount of Pd(NO3)2·2H2O was dissolved into 40 mL of 1,2-propanediol and stirred for 10 min until it turned black (solution B). Solution B was injected into solution A...
Conversion were analyzed by Shimadzu GC-2014 with dual detectors (TCD and FID) and different columns. The chemical element analysis was determined by ICP (Optima 8000). The specific surface areas of the catalysts were calculated from \( \text{N}_2 \) adsorption isotherms using the BET and BJH methods (ASAP 2010).

**Results and Discussion**

Figure 1a displays a representative scanning electron microscopy (SEM) image of Co-Pd nanocrystals (denoted as CoPd\(_{0.005}\), where the weight percent content of Pd in CoPd\(_{0.005}\) is 0.1%). The nanocrystal is viewed as core-shell geometry, and the core is solid with 100 nm size and the shell is constructed with nanorods (20 nm diameter, 400 nm length), which are observed from transmission electron microscopy (Figure 1b). The growth direction of the nanorods is along 001, which is obtained by the lattice spacing of 0.19 nm indicating the (101) planes of hexagonal-packed Co phase (inset of Figure 1b), and the other inset of figure 1b is the fast Fourier-transform pattern also confirming that the peripheral nanorods outspread along the (001) direction. CoPd\(_{0.005}\) (0.05 wt% Pd) and CoPd\(_{0.01}\) (1 wt% Pd) nanocrystals also have 3D core-shell structure, shown in Figure 1c-d and corresponding the insets. The energy-dispersive X-ray spectroscopy (EDS) mapping analysis (Figure 1e-h) clearly points to the distribution ranges of Co (red) and Pd (green) in the CoPd\(_{0.005}\) nanocrystals, revealing a bimetallic structure. Without metal seeds at the beginning, Co nanocrystals with peripheral rod-like structure were not obtained (Figure S1). Here, the higher electronegativity of Pd caused Pd\(^{2+}\) ions to be first reduced by propylene glycol (served as the solvent and reductant) to form neutral Pd atoms. Positive Co\(^{2+}\) ions attracted the electron cloud of the Pd atoms and the Pd atoms were polarized towards Co\(^{2+}\) center. The continuous supply of electrons from propylene glycol to Pd (Pd as an acceptor, reducing agent as a donator) made electron density shift from Pd to Co until the formation of Co-Pd nucleation, and subsequently Co-Pd nucleation grew up towards Co-Pd nanocrystal. A series of experimental conditions were carried out to gain deeper insight into how the 3D core-shell structure of Co-Pd formed (see Supporting Information and corresponding Figure S1-4).

**Characterization**

X-ray diffraction (XRD) patterns of samples were recorded on a Japanese Rigaku Ultima IV powder diffractometer using Cu K\(\alpha\) radiation with the wavelength of 1.54056 Å at 40 kV and 40 mA. Rietveld refinement with MDI-Jade software was used to determine the lattice constants from the XRD diffraction analysis. The morphology and size of nanomaterials were characterized using JEOL JEM-2100 Electron Microscope (JEOL, TEM, 2011, Japan) operated at 200 kV and 54800 of Hitachi. The X-ray Photoelectron Spectroscopy (XPS) of the samples were determined on a RBD upgraded PHI-5000C ESCA System in a high-vacuum chamber with the base pressure below 1×10\(^{-8}\) Torr. Products from syngas
Reversible switch of selective control on syngas conversion can be accomplished by Cu replacing Pd as prenucleated seeds to form Co-Cu nanocrystals, since CuCo catalysts favor the insertion of non-dissociative adsorbed CO into intermediate carbon species to form oxygenates. Figure 2a-d reveal the Co-Cu nanocrystals with 1D branches including CoCu$_{0.01}$ (1 wt% Cu), CoCu$_{0.05}$ (5 wt% Cu), CoCu$_{0.1}$ (10 wt% Cu) and CoCu$_{0.2}$ (20 wt% Cu). Exact elemental analysis of Co-Cu nanocrystals (and Co-Pd) is indicated by Inductively coupling plasma (ICP) spectroscopy (Table S1). Note that the length of rod-like branches of CoCu$_{0.01}$ is up to micrometer scale. The length of peripheral branches of CoCu$_{0.05}$ is about 400 nm, which is similar to that of CoCu$_{0.1}$ but longer than that of CoCu$_{0.2}$ (200 nm). The cores of the four Co-Cu samples are similar about size of 100 nm. Interestingly, the distribution of Cu in the Co-Cu nanocrystals takes on a different look, compared to that of Pd in Co-Pd nanocrystals. The concentration of Cu in the kernel is obvious higher than that of peripheral branches, which is observed from the element maps of Cu (red) and Co (green) in CoCu$_{0.01}$ (Figure 2e-h). It also identifies the homogenous distribution of Cu and Co in 1D branches of Co-Cu nanocrystals. The control experiments with Co-Cu nanocrystals are depicted in Supporting information and corresponding results are shown in Figure S5.

Figure 1. (a) SEM image of CoPd$_{0.01}$. (b) TEM image of CoPd$_{0.01}$, and inset are HRTEM image of CoPd$_{0.01}$ and a fast Fourier transform (FFT) analysis from HRTEM. (c) SEM image of CoPd$_{0.05}$ and inset is TEM image of CoPd$_{0.05}$. (d) SEM image of CoPd$_{0.1}$ and inset is TEM image of CoPd$_{0.1}$, and inset is TEM image of CoPd$_{0.1}$. (e) Bright-field TEM image of CoPd$_{0.05}$ and (f-h) the corresponding element maps of Co (red) and Pd (green) in CoPd$_{0.05}$ nanocrystals.

The proposed formation mechanism of Co-Pd and Co-Cu nanocrystals with 1D structure was shown in Scheme 1. Firstly, the carbonyl of stearic acid and the amidogen of cetylamine showed a coordination effect with Co$^{2+}$, and this coordination effect reduced the concentration of Co$^{2+}$ in the solution which made the coordination compund as a “reservoir” to control the concentration of Co$^{2+}$ in the solution (Scheme 1a). As Pd or Cu has higher electronegativity than Co, a portion of Pd$^{2+}$ or Cu$^{2+}$ could be reduced preferentially to form Pd or Cu nuclei. The formation of Pd nuclei or Cu nuclei enhanced the reduction of Co$^{2+}$ to Co by lowering the activity energy of this reduction process, resulting in the decomposition of the coordination compound to liberate Co$^{2+}$ ions slowly (Scheme 1b). With the slow release of Co$^{2+}$ from the “reservoir” as well as the reduction of Co$^{2+}$ to Co, these Pd or Cu nuclei recondense to form the cores of multipods. Meanwhile hexadecylamine and stearic acid liberated from “reservoir” also started to absorb on these growing cores (Scheme 1c). Surfactants like hexadecylamine and stearic acid can coordinate along the c axis of the hcp structure and make the (001) facets of hcp structured domains of the core exposed to the incoming cobalt atoms (Scheme 1d). The hexadecylamine and stearic acid continued to coordinate to the (101) crystal face of the hcp structure, where the grow occurred preferentially along (001) directions. Eventually, the dissolving, diffusion and deposition of Co in the reaction system evolved in to 1D nanostructure with the help of surfactants and prenucleated seeds (Scheme 1e).

Scheme 1. The proposed formation mechanism of Co-Pd and Co-Cu nanocrystals with 1D structure.

The XRD studies show that as-synthesized Co-Pd nanocrystals are typically indexed as the (100), (002), (101), (102) and (110) diffractions, matching well with Co nanocrystals (Figure 3a). Diffraction peaks from CoCu$_{0.05}$ nanocrystals are similar to Co nanocrystals, but CoCu$_{0.1}$ and CoCu$_{0.2}$ made a difference show that (111) and (200) peaks (red triangle) located at 2θ = 43.5°and 50.6° correspond to cubic Cu phase (JCPDS No.04-0836). The surface areas of the Co-Pd and Co-Cu nanocrystals were determined from N$_2$ sorption measurements shown in Figure 3b. The surface areas, shown in Table S2, of Co-based nanocrystals with 1D branches are small. The electronic properties of Co, Co-Pd and Co-Cu
nanocrystals were studied by XPS, as presented in Figure 3c and Figure S6. The occurrence of satellite structure leads to the deconvolution of Co 2P_{1/2} and 2P_{3/2} excitations. The presence of Co\(^{2+}\), Co\(^{3+}\), and Co\(^{3+}\) in Co 2p spectra of all samples, while Co\(^{2+}\) dominates the surface of samples, demonstrating the existence of CoO. Co 2P\(_{1/2}\) electron binding energy of CoPd\(_{0.01}\) is 1.0 eV higher than the value characteristic of CoCu\(_{0.01}\) and the shift in binding energy reflects the fact that the effect of Pd on electronic properties of Co is bigger than that of Cu, suggesting that Co-Pd nanocrystals give rise to unusual catalysis. Cu 2p spectra could be found in Co-Cu nanocrystals, as shown in Figure 3d. Noted that the peak at 933.9 eV is assigned to Cu\(^{2+}\) and the peak at 933.2 eV is assigned to Cu\(^{3+}\), which indicates Cu\(^{3+}\) state dominates the surface of Co-Cu nanocrystals.

Figure 3. (a) XRD patterns of Co, CoPd\(_{0.001}\), CoPd\(_{0.01}\), CoCu\(_{0.01}\), CoCu\(_{0.1}\), CoCu\(_{0.2}\) nanocrystals. (b) Nitrogen absorption isotherms of Co, CoPd\(_{0.001}\), CoPd\(_{0.01}\), CoCu\(_{0.01}\), CoCu\(_{0.1}\), CoCu\(_{0.2}\) nanocrystals. (c) Co 2p electron region of XPS profiles of Co, CoPd\(_{0.001}\), and CoCu\(_{0.01}\) nanocrystals. (d) Cu 2p electron region of XPS profiles of CoCu\(_{0.01}\), CoCu\(_{0.1}\), and CoCu\(_{0.2}\) nanocrystals.

Bimetallic Co-Pd and Co-Cu nanocrystals with 1D structure were evaluated to catalyze syngas conversion (Table S3-7). Co-Pd nanocrystals exhibited higher CO conversion and gave rise to lower CH\(_4\) selectivity than Co-Cu nanocrystals (Figure 4a and Figure S7a). With temperature, the catalytic activity of these catalysts increased and especially CoPd\(_{0.001}\) nanocrystals gave rise to 71.2 % CO conversion at 260 °C. Among the Co-Cu nanocrystals, CoCu\(_{0.1}\) showed the highest CO conversion, compared to CoCu\(_{0.05}\) and CoCu\(_{0.2}\). Figure S7b-c indeed confirmed that Co-Pd nanocrystals gave much high selectivity towards hydrocarbons, while Co-Cu nanocrystals made a little high selectivity for alcohols. For all of these Co-based nanocrystals studied here, CO\(_2\) selectivity is quite low over a range of temperatures (Figure S7d). Moreover, CO conversion over Co-Pd nanocrystals was higher than Co nanocrystals (the morphology of Co is shown in Figure S1a-b), revealing that appropriate Pd into Co nanocrystals can enhance hydrogenation activity of Co catalysts (Table S8). An intriguing observation is the high selective towards long-chain products over Co-Pd nanocrystals. From Anderson-Schulz-Flory (ASF) plots based on distribution of products over different catalysts (Figure S8), Co-Cu nanocrystals favor the formation of light products (C\(_1\)-C\(_8\) hydrocarbons and C\(_2\)-C\(_4\) alcohols), and Co-Pd nanocrystals favor the carbon chain growth to obtain heavy hydrocarbons (C\(_n\), n>7). ASF chain-lengthening probabilities for products are up to 0.91 over CoPd\(_{0.001}\).

For further realizing selective control on syngas conversion towards heavy paraffins, light olefins or alcohols via incorporating appropriate second metal on Co catalyst, in detail, we contrasted the catalysis of Co, CoPd\(_{0.001}\) and CoCu\(_{0.1}\) nanocrystals in different product range including C\(_1\), C\(_2\)-C\(_4\), C\(_5\)-C\(_12\), C\(_{13}\)-C\(_{20}\) and C\(_n\)>20 (Figure 4b). In C\(_1\) composition (CH\(_4\) and CH\(_3\)OH), CoPd\(_{0.001}\) nanocrystals could achieve less undesirable CH\(_4\)/CH\(_3\)OH in comparison with Co and CoCu\(_{0.1}\). For C\(_2\)-C\(_4\) products (gases), CoCu\(_{0.1}\) nanocrystals exhibited higher selectivity for light products including olefin, oxygenate and paraffin among these three catalysts. Although Co nanocrystals can give more gasoline (C\(_5\)-C\(_8\)), CoPd\(_{0.001}\) nanocrystals can obtain more diesel (C\(_{13}\)-C\(_{20}\)). For C\(_n\)>20 product range (waxes), CoPd\(_{0.001}\) nanocrystals gave rise to more wax products. Additionally, in C\(_2\)-C\(_4\) composition range, the ratio value of olefin to paraffin on CoCu\(_{0.1}\) (0.66) is much higher than the values on Co (0.36) and CoPd\(_{0.001}\) (0.22), which infers that CoCu\(_{0.1}\) nanocrystals can act as catalyst for more light olefins.
Figure 5. CO adsorption energies on the top sites of Co (101), Cu/Co (101) and Pd/Co (101) surfaces versus the d-band center. Here, a 8 layers with p(2×3) Co (101) supercell slab models was utilized and one surface Co on the step was substituted by a Pd or Cu atom. Adsorption and reaction were performed on one side of the exposed surface with substituted Pd or Cu atom. Each slab was separated by 13 Å of vacuum normal to the surface.

It is well known that oxygenates selectivity is controlled by the capabilities of catalysts to perform hydrogenation/dissociation/coupling of intermediate carbon species CH₂ and C-C chain formation by CO/CHO insertion into CH₂. To improve the selectivity of oxygenates, we need tune the relative activity of CO/CHO insertion into CH₂, that is, there must be a certain amount of CO kept on the surface for further insertion reaction without dissociation. To provide a mechanistic understanding of selective control on syngas conversion over the experimentally observed Co-Pd and Co-Cu (101) surfaces, the corresponding CO adsorption energies versus the d-band center on the Cu/Co (101) and Pd/Co (101) surfaces were investigated by density functional theory calculation. Figure 5 reveals that the adsorption energy of CO at the top site on Pd/Co (101) surface (-1.21 eV) was 0.36 eV more exothermic than that on the Cu/Co (101) surface (-0.85 eV), indicating that CO diffusion on the Cu/Co (101) surface is easier than Pd/Co (101) surface. The calculated d-band center for the surface Cu and Pd atom on the two surface are -3.26 eV and -2.89 eV, respectively, as shown in Figure 5. The farther location of the d-band center (ε_d) relative to the Fermi level results in the weaker adsorption energy obtained in case of CO adsorption on the Cu/Co (101) surface, due to the closer d-band center to the Fermi level, the stronger the adsorption energy. These energy data reveal the high mobility of CO on the Cu/Co (101) surface, therefore, it becomes possible to spot metal like Cu on the Co (101) surface to improve oxygenates formation.

In contrast, conventional CoPd (0.1 wt% Pd) and CoCu (10 wt% Cu) nanoparticles were prepared using coprecipitation methods, and the morphology and surface areas of these nanoparticles were displayed in Figure 59. It is found, as shown in Figure 6a-b, that CoPd0.001 and CoCu0.1 nanocrystals with 1D structure are more effective than conventional CoPd (0.1 wt% Pd) and CoCu (10 wt% Cu) nanoparticles for the catalytic hydrogenation of CO, respectively. Figure S10a-b show that CoPd0.001 and CoCu0.1 exhibited enhanced catalytic activity per unit surface area for CO hydrogenation, as compared to conventional nanoparticles. An interesting feature emerges by comparing product selectivity of Co-based bimetallic nanocrystals with conventional nanoparticles. CoPd0.001 nanocrystals can achieve more heavy hydrocarbons (C₄H₈), (C₅H₁₀) than CoPd (0.1 wt% Pd) nanoparticles (Figure 6c), and ASF chain-lengthening probability for products over CoPd0.001 nanocrystals (α=0.91) is higher than that over CoPd (0.1 wt% Pd) nanoparticles (α=0.62) (Figure S10c). However, CoCu0.1 nanocrystals and CoCu (10 wt% Cu) nanoparticles were found to be similar catalytic selectivity for syngas conversion (Figure 6d). The different phenomena suggest that the catalytic selectivity of Co-based bimetallic catalysts is ascribed not only to the structure effect but also to the synergistic action of metals. It is also reflected by XPS studies, that is, Co 2p binding energy of CoCu0.1 is similar with that of CoCu (10 wt% Cu) nanoparticles, whereas Co 2p electron binding energy of CoPd0.001 is 1.2 eV higher than the value characteristic of CoPd (0.1 wt% Pd) nanoparticles (Figure 7). It reflects that the effect of Pd on electronic properties of Co is related to the structure of CoPd, therefore the structure of CoPd catalysts determines their catalytic performance. The phenomena are inspiring and further study is in progress.

![Figure 7(a) Co 2p electron region of XPS spectra of CoPd0.001 nanocrystals and CoPd (0.1 wt% Pd) nanoparticles. (b) Co 2p electron region of XPS spectra of CoCu0.1 nanocrystals and CoCu (10 wt% Cu) nanoparticles.](image)

The 3D core-shell geometry of Co-based bimetallic nanocrystals appears to be robust during the catalytic processes.
The structure of Co-Cu nanocrystals has changed very little after catalytic reaction, though the core of Co-Pd became larger and the length of peripheral branches was shorter (Figure 8a-b and Figure S11a,f,g). Distribution of Pd and Co is still homogenous in spent Co-Pd nanocrystals (Figure S11b-e). The space distribution of elements of spent Co-Cu nanocrystals showed a similar vision to that of fresh ones, indicated by the element mapping (Figure 8c-f), where the concentration of Cu in the kernel is obvious higher than that on the periphery. The surface areas and lattice structure of these Co-based catalysts after catalytic tests were unchanged (Figure S12). However, XPS studies indicated that the surface composition of Co-Cu nanocrystals after catalytic reactions seems to reorganize, although the mobility of Co and Cu or Pd was not found by element mapping. The content of Cu on the surface of spent catalysts was lower than that of fresh ones (Table S1). The phenomenon might be ascribed to the segregation of Co and Cu, as well as the mobility of Co under syngas exposure, which is agreement with results of literature.26 From Figure 9, the Co 2p spectra of spent CoPd₀.001 and CoCu₀.₁ catalysts contain Co²⁺, Co³⁺ and Co⁴⁺, however, the relative intensities of Co⁵⁺ is higher than those of fresh ones. Corresponding Cu 2p spectra of spent CoCu₀.₁ are unchanged compared with those of fresh one (Figure S13). These results manifest the compositional reorganization of surface phases, and still call for a more in-situ spectroscopic investigation.

Conclusions

In summary, robust Co-Pd and Co-Cu nanocrystals with 1D structure have been fabricated through a heterogeneous nucleation of Co atoms onto the prenucleated Pd or Cu seeds. By switching the prenucleated metal to form Co-Pd or Co-Cu nanocrystals, selectivity control on syngas conversion could be purposely adjusted towards light olefins, heavy paraffins or alcohols. Appropriate Pd incorporation into Co nanocrystals favors the carbon chain growth to obtain more long-chain hydrocarbons and appropriate Co introduction into Co nanocrystals improves the selectivity of light olefins and oxygenates. Co-based bimetallic nanocrystals with 1D structure are more effective than the corresponding Co-based nanoparticles for CO hydrogenation. Selective control on catalytic reactions by switching second metal nucleated on one metal should aid in the design of bimetal nanocatalysts for specific reaction and the correlation their structure with properties.

Acknowledgements

We are grateful for financial support by National Natural Science Foundation of China (21273151, 21403277), Shanghai Pujiang Program (13PJ1407700), Shell Global Solutions International B. V. and Hundred Talent Program of CAS.

Notes and references


Figure 8. SEM images of (a) CoPd₀.001 and (b) CoCu₀.₁ nanocrystals after catalytic tests. (c) Bright-field TEM image of CoCu₀.₁ and (d-f) the corresponding element maps of Co (green) and Cu (red) in CoCu₀.₁ nanocrystals after catalytic test (220 °C, 6 MP, 24 hr).

Figure 9. (a) Co 2p region of XPS profiles of fresh and spent CoPd₀.001. (b) Co 2p electron region of XPS profiles of fresh and spent CoCu₀.₁.
19. N. D. Subramanian, G. Balaji, C. S. S. R. Kumar and J. J. Spivey, 


