



# Novel hydrodesulfurization nano-catalysts derived from $\text{Co}_3\text{O}_4$ nanocrystals with different shapes

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## ABSTRACT

In this study, hydrogenation of carbonyl sulfide (COS) has been investigated over nano-catalyst derived from single-crystalline  $\text{Co}_3\text{O}_4$  nanocrystals with different morphology.  $\text{Co}_3\text{O}_4$  nanocrystals, i.e. nanorods and nanopolyhedra, are synthesized by a facile ethylene glycol route and subsequent thermal process. After *in situ* presulfidation, hydrodesulfurization (HDS) of COS is conducted on these unsupported catalysts in the temperature range of 150–300 °C. Compared with the sulfided nanopolyhedra, the catalytic activity of the sulfided nanorods is much higher especially at low temperature of 200 °C. Surface areas, crystalline phase and particle size distributions of the nanocrystals are determined by Brunauer–Emmet–Teller method, X-ray diffraction and transmission electron microscopy, respectively. It is shown that the catalytic properties of the as-prepared nanocrystals are dependent on the nature of their surface structure, and the crystal plane of  $\text{Co}_3\text{O}_4$  plays an important role in determining its degree and easiness of presulfurization and consequently HDS performance for COS. The shape-controlled synthesis of nanocrystals may be an effective means for promoting reactive activities for HDS catalysts.

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## 1. Introduction

Integrated Gasification Combined Cycle (IGCC), a potential solution to coal-related environmental problem, has caused intensive attention worldwide due to its high efficiency, low emission and multi-production, including electricity, solid oxide fuel cells and alcohol [1–3]. One of the key processes for realization of this clean coal technology is gas cleaning, i.e. removing acid gases (mainly hydrogen sulfide,  $\text{H}_2\text{S}$ , and carbonyl sulfide, COS) from the gas stream, as they are detrimental to subsequent processes either by poisoning the catalyst or/and by causing equipment damage due to corrosion.  $\text{H}_2\text{S}$  can be easily removed by metal oxides [4,5] and activated carbons [6,7], while the elimination of COS is difficult because of its low reactivity with metal oxides as well as relative neutrality. Many strategies have been developed to remove COS from coal gas, including absorption [8,9], hydrolysis [10–12] and hydrogenation [13–15], etc. Among these methods, the hydrodesulfurization (HDS) of COS has been addressed since it can take advantage of the hydrogen present in coal gas and exhibits high conversion efficiency, especially the excellent compatibility with the syntheses of alcohol and/or ether [14,15].

Up to now, various catalyst systems have been investigated for the hydrogenation reaction of COS and most of them are based on supported alumina with different active phases, such as cobalt, molybdenum, nickel oxides and their coexistence mixture [13,14]. Unfortunately, the expense of Co-Mo- $\text{Al}_2\text{O}_3$  catalyst combined with the high temperature required for effective reduction restricts commercial exploitation. Recent investigation has focused on the simultaneous removal of  $\text{H}_2\text{S}$  and COS over unsupported metal oxides in strongly reducing atmosphere by the reduction–adsorption–sulfidation process [1,16]. Moreover, it has been reported that  $\text{MoS}_2$  with various morphologies and other transition metal sulfides show much high activities for the HDS of dimethyldibenzothiophene than that of the sulfided commercial Co(Ni)Mo/ $\text{Al}_2\text{O}_3$  catalysts [17–20]. The newly significant reports that the activities of metal oxides with well-defined crystal planes for methane and carbon monoxide oxidation are enhanced remarkably by the morphology and specific facet [21–24] inspire us to explore the shape-related catalytic activity on the HDS of COS.

It has been demonstrated that the controllable synthesis of  $\text{Co}_3\text{O}_4$  nanocrystals with two different shapes, i.e. nanorods and nanopolyhedra, can be achieved through ethylene glycol routes and subsequent calcination [23]. In the present work, cobalt-based catalysts derived from  $\text{Co}_3\text{O}_4$  with different shape are selected as unsupported catalysts in the model reaction of COS hydrogenation. After presulfurization, their HDS activities are evaluated in the temperature range of 150–300 °C. Results reveal that the cat-

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alytic activity of the sulfided nanorods for the COS removal is much more reactive than that of the nanopolyhedra. This comparison has enabled the understanding of the morphology on the catalytic property of the solids.

## 2. Experimental

### 2.1. Synthesis of $\text{Co}_3\text{O}_4$ nanocrystals

All the materials were of analytical purity and were used as received without further purification. To obtain  $\text{Co}_3\text{O}_4$  of different shapes, cobalt acetate tetrahydrate (A.R. grade, Beijing Chem. Corp., China) was used as the cobalt source. The method for the synthesis of  $\text{Co}_3\text{O}_4$  nanorods was improved on the base of ref. 23. 4.98 g of  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was dissolved in 60 ml of ethylene glycol (EG) and the solution was gradually heated to 160 °C. Then 200 ml of aqueous 0.2 M  $\text{Na}_2\text{CO}_3$  solution was fed-in drop by drop for about 5 h and the slurry was further aged for 1 h under vigorous stirring and a continuous flow of nitrogen. The mixture was then allowed to cool to room temperature (RT). The final solid product was collected by filtration, and washed with deionized water to remove any possible ionic remnants, then dried at 50 °C overnight under vacuum and calcined at 450 °C for 4 h in air.  $\text{Co}_3\text{O}_4$  nanopolyhedra were prepared by a direct precipitation method, in which  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  was dissolved in EG at RT, followed by adding 0.2 M  $\text{Na}_2\text{CO}_3$  solution slowly. Then the product was obtained after filtrating, washing, drying and calcinating processes as mentioned above. All the as-prepared samples were crushed and sieved to 24–40 mesh particle size range and used as unsupported catalysts.

### 2.2. Presulfurization and catalytic activity test

The catalytic reactions were carried out at atmospheric pressure in a continuous up-flow fixed-bed quartz reactor (8 mm × 45 mm) heated in an oven. 0.1 g of catalyst was placed on a quartz sintered plate which located in the center of the reactor. Before the catalytic evaluation, the oxide catalyst was sulfided *in situ* with a gas mixture containing 4.4%  $\text{H}_2$ , 1.1%  $\text{H}_2\text{S}$  (V/V, nitrogen as balance gas, the flow rate of 25 ml/min) at 300 °C for 3 h. After sulfidation, the catalyst was cooled to room temperature and was flushed with a flow of 100 ml/min  $\text{N}_2$  for another 2 h. The catalytic activities for COS hydrogenation were evaluated in reactant gases (0.1% COS, 10%  $\text{H}_2$ , balanced with  $\text{N}_2$ , 80 ml/min) under the preset temperature. The composition of the sulfur-containing gaseous product was analyzed on-line using a GC-7890II gas chromatograph equipped with a Porapak Q column and a flame ionization detector (FPD).

### 2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max 2400 Diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418$  nm) to identify the phases and crystallinity of the catalysts. The size and morphology of the catalysts were observed under field emission scanning electron microscopy (FESEM, JSM 6700F), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM, Philips Tecnai G<sup>2</sup> 20). X-Ray Fluorescence (XRF) measurements were conducted with XRF-1800 (Shimadzu). BET surface area was estimated by  $\text{N}_2$  physisorption at 78 K in an ASAP 2000 Micromeritics instrument. The temperature-programmed reduction (TPR) of the sulfided catalyst was performed in a 12%  $\text{H}_2$ – $\text{N}_2$  mixture at a flow rate of 80 ml/min, with the heating rate of 10 °C/min from RT up to 950 °C. The effluent sulfurous gas was analyzed by GC equipped FPD detector.

## 3. Results and discussion

### 3.1. Phase identification

Fig. 1 displays the XRD patterns of the as-prepared  $\text{Co}_3\text{O}_4$  nano-sized materials and their corresponding sulfided powders. From Fig. 1(A), it is clear that all the diffraction patterns of both fresh  $\text{Co}_3\text{O}_4$  nanorods (abbreviated as “NRs”) and nanopolyhedra (abbreviated as “NPs”) can be indexed as the face-center cubic phase (space group  $Fd\bar{3}m$ ) and with a lattice constant  $a = 0.806$  nm, which are consistent with the values in the PDF card (JCPDS 42-1467). The broadening of the reflections ascribed to the polyhedra and rods distinctly indicates their nanocrystalline nature, and the sharper reflections for polyhedra implied their larger sizes and/or fewer defects as compared with the rods. The XRD patterns of two sulfided catalysts derived from  $\text{Co}_3\text{O}_4$  nanorods and nanopolyhedra are shown in Fig. 1(B), both of them can be tentatively indexed as the cubic phase of  $\text{Co}_9\text{S}_8$  (JCPDS 65-6801).

### 3.2. Size and morphology

Fig. 2a shows the TEM image of the as-obtained  $\text{Co}_3\text{O}_4$  nanorods, with a uniform diameter in 5–15 nm and a length within 200–300 nm. Fig. 2b depicts the representative HRTEM image of one  $\text{Co}_3\text{O}_4$  nanorod, which has a respective interplanar spacing of 0.286 and 0.467 nm, showing a one-dimensional growth structure with a preferred growth direction along [1 1 0] [22], similar to the case of  $\text{Co}_3\text{O}_4$  nanorods prepared under semblable synthesis condition by Shen's group [23]. Fig. 2c exhibits the TEM image of uniform  $\text{Co}_3\text{O}_4$  nanopolyhedra in the size range of 8–20 nm. The HRTEM

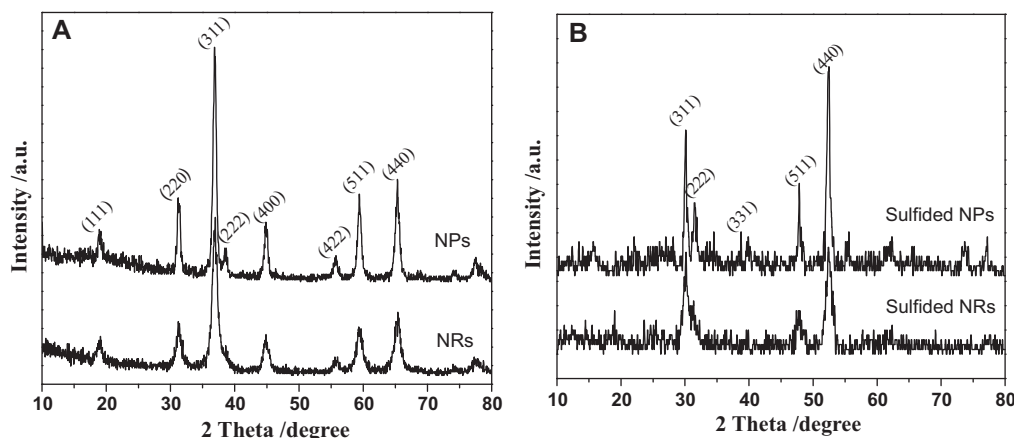


Fig. 1. XRD patterns of the as-prepared  $\text{Co}_3\text{O}_4$  (A) and their corresponding sulfided compounds (B) with different morphology. (NRs, nanorods; NPs, nanopolyhedra).

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