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Novel hydrodesulfurization nano-catalysts derived from Co_3O_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 Co_3O_4 nanocrystals with different morphology. Co_3O_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 Co_3O_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.

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, H_2S, 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. H_2S 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-Al_2O_3 catalyst combined with the high temperature required for effective reduction restricts commercial exploitation. Recent investigation has focused on the simultaneous removal of H_2S and COS over unsupported metal oxides in strongly reducing atmosphere by the reduction–adsorption–sulfidation process [1,16]. Moreover, it has been reported that 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/Al_2O_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 Co_3O_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 Co_3O_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 Co_3O_4 nanocrystals

All the materials were of analytical purity and were used as received without further purification. To obtain Co_3O_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 Co_3O_4 nanorods was improved on the base of ref. 23. 4.98 g of $Co(CH_3COO)_2 \cdot 4H_2O$ 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 Na_2CO_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. Co_3O_4 nanopolyhedra were prepared by a direct precipitation method, in which $Co(CH_3COO)_2 \cdot 4H_2O$ was dissolved in EG at RT, followed by adding 0.2 M Na_2CO_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% H_2, 1.1% H_2S (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 N_2 for another 2 h. The catalytic activities for COS hydrogenation were evaluated in reactant gases (0.1% COS, 10% H_2, balanced with 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 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^2 20). X-Ray Fluorescence (XRF) measurements were conducted with XRF-1800 (Shimadzu). BET surface area was estimated by 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% H_2–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 Co_3O_4 nanosized materials and their corresponding sulfided powders. From Fig. 1(A), it is clear that all the diffraction patterns of both fresh Co_3O_4 nanorods (abbreviated as "NRs") and nanopolyhedra (abbreviated as "NPs") can be indexed as the face-center cubic phase (space group $Fd3m$) 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 Co_3O_4 nanorods and nanopolyhedra are shown in Fig. 1(B), both of them can be tentatively indexed as the cubic phase of Co_9S_8 (JCPDS 65-6801).

3.2. Size and morphology

Fig. 2a shows the TEM image of the as-obtained Co_3O_4 nanorods, with a uniform diameter in 5–15 nm and a length within 200–300 nm. Fig. 2b depicts the representive HRTEM image of one Co_3O_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 Co_3O_4 nanorods prepared under semblable synthesis condition by Shen's group [23]. Fig. 2c exhibits the TEM image of uniform Co_3O_4 nanopolyhedra in the size range of 8–20 nm. The HRTEM

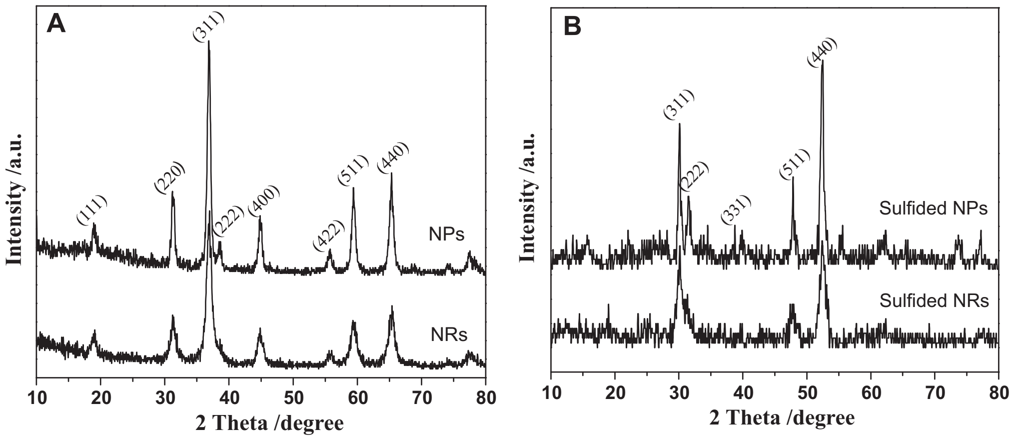


Fig. 1. XRD patterns of the as-prepared Co_3O_4 (A) and their corresponding sulfided compounds (B) with different morphology. (NRs, nanorods; NPs, nanopolyhedra).

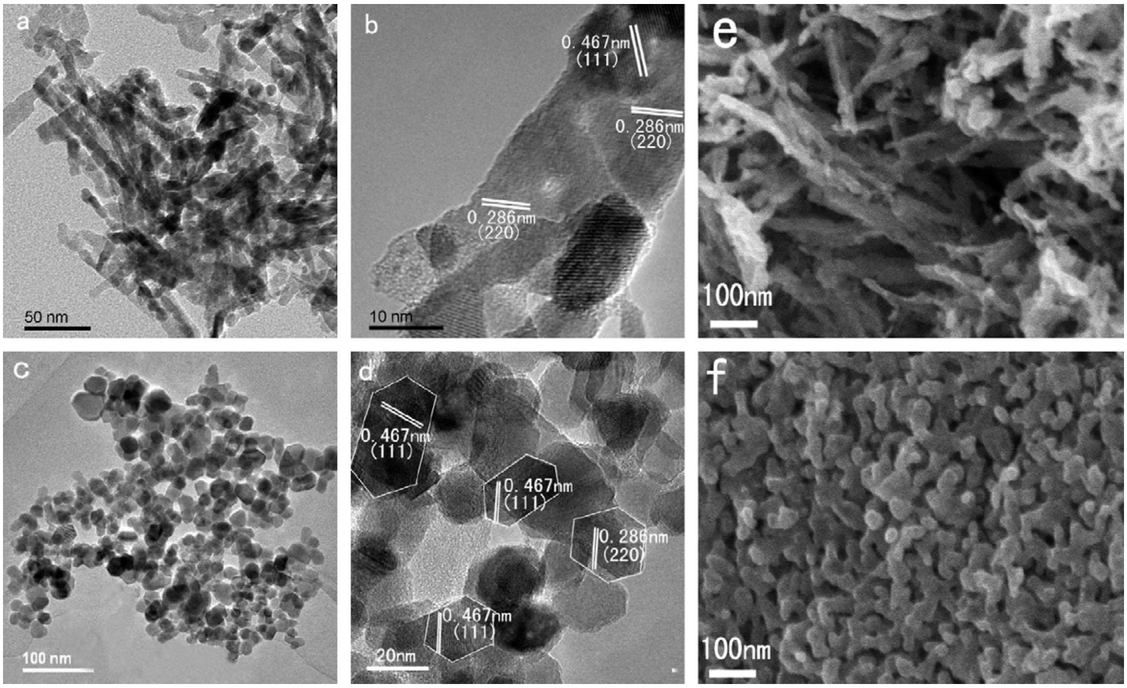


Fig. 2. Electron microscopic images of the as-made nanocrystals. (a, b) TEM and HRTEM images of Co_3O_4 nanorods, (c, d) TEM and HRTEM images of Co_3O_4 nanopolyhedra, (e, f) FESEM images of sulfided nanorods and nanopolyhedra.

image in Fig. 2d shows the clear (1 1 1) and (2 2 0) lattice fringes with the interplanar spacing of 0.467 and 0.286 nm, respectively, revealing that the Co_3O_4 nanopolyhedra are dominated by a truncated octahedral shape enclosed by the {1 1 1} and {1 0 0} facets [22,25]. For the purpose of comparison, the morphologies of two sulfided catalysts after hydrogenation reaction are also observed by FESEM (Fig. 2e and f). It can be seen that there is no significant changes between the shape of fresh Co_3O_4 particles and the sulfided catalysts.

3.3. Catalytic activity

3.3.1. Influence of presulfidation

Prior to the hydrogenation of COS, the cobalt oxides were presulfided with hydrogen sulfur at different temperatures: 250, 300, 350 and 400 °C. The breakthrough curves for H_2S over Co_3O_4 nanorods and nanopolyhedra are presented in Fig. 3a and b. It can be seen that the curves for both oxides exhibit similar shape, however, a significant difference between them is evident. As seen, at the same sulfidation temperature, for example 250 °C, the penetration time of H_2S (defined as the sulfur species in the off-gas can be detected by GC) for the nanorods (Fig. 3a, 42 min) is much longer than that for the nanopolyhedra (Fig. 3b, 18 min). This phenomenon indicates that the Co_3O_4 nanorods have a higher reactivity and capacity towards H_2S than the nanopolyhedra [6,7], which may probably lead to a better catalytic performance for the HDS of COS. When the sulfidation temperature is increased, the similar variation is displayed over two cobalt oxides. It is found that the penetration time of H_2S is shortened when the temperature exceeds 300 °C, such as from 120 min at 300 °C decreasing to about 70 min at 350 °C for the nanorods (while for the nanopolyhedra, from 60 min at 300 °C to 45 min at 350 °C), suggesting that high temperature is not suitable for sulfidation process. This is due to that the sulfidation of metal oxide is an exothermal reactions, which could give occasion to the local increasing of sulfidation temperature and eventually results in metal oxide partly reduced to metal or the agglomeration of metal nanoparticles by hydrogenation (above 316 °C) [13,26], therefore detrimental to the sulfidation.

The HDS catalytic activities of the above sulfided catalysts are determined at 200 °C, and the results are shown in Fig. 4. It is clear

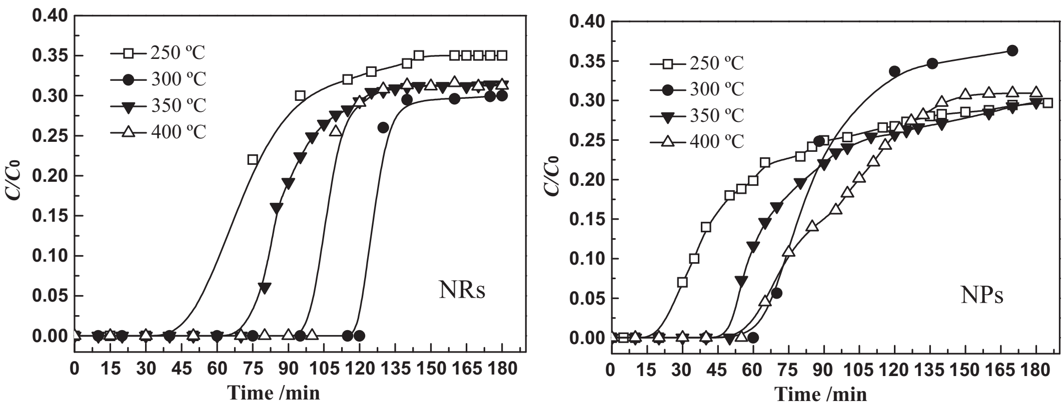


Fig. 3. Breakthrough curves for H_2S at different temperature over Co_3O_4 nanorods and nanopolyhedra.

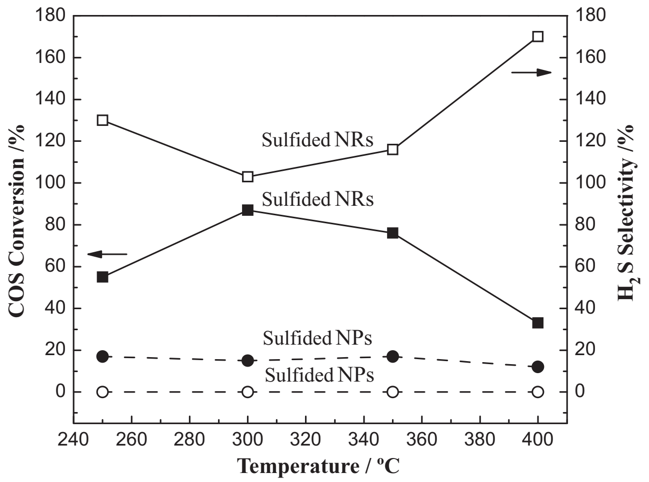


Fig. 4. Effects of presulfidation temperature on COS conversion (solid mark) and H_2S selectivity (hollow mark) over sulfided Co_3O_4 nanorods (line) and nanopolyhedra (dot). (Reaction conditions: 200 °C, COS 0.1%, H_2 10%, balanced with N_2, GHSV = 8000 h^{-1}).

that in the range of sulfidation temperature, both the COS conversion and the H_2S selectivity for the nanorods are greatly superior to that for the nanopolyhedra, in accordance with the above penetration time at different temperature. Undoubtedly, the sulfidation temperature at 300 °C for the nanorods is optimal with the longest penetration time (120 min) and the highest COS conversion (90%). Whereas for the nanopolyhedra under the same conditions, the COS conversions are always kept below 20% accompanied by the negligible H_2S formation, which reflects that the performance of catalyst might depend strongly on their morphologies [21,22]. Compared to the previous reports, i.e. HDS temperature for COS is usually in the range of 300–400 °C on Co(Ni)-Mo based catalysts [13,14,27], the fact that the as-prepared catalyst with nanorod morphology exhibiting such high HDS activity at low temperature (200 °C) encourages us to investigate it deeply.

In addition, it is noted that the H_2S selectivity over the nanorods surpasses 100%, especially at high temperature, which might be derived from the sulfur losing from the sulfided catalyst, on account of the insufficient sulfur species in gaseous phase and the sulfur disequilibrium between the sulfided catalyst and gas phase [26]. However, this phenomenon emerges just at initial reaction stage, it would be disappeared when the reaction system stabilizes. Furthermore, we notice that the extent of sulfur losing is obviously related to the presulfidation temperature (Fig. 4), i.e. the sulfidation degree. For instance, 300 °C is the optimal presulfidation temperature for the nanorods (Fig. 3). Thus, the lengthening of the penetration time means the deep degree of sulfidation for the catalyst, and could bring the catalyst on the excellent reactive performance.

3.3.2. *Catalytic hydrogenation of COS*

The HDS activity of COS for sulfided Co_3O_4 nanocrystals was performed at specific reaction conditions after being presulfided at 300 °C for 3 h. Fig. 5(A) shows the effect of reaction temperature on the catalytic properties of different-shape nanocrystals. It is clear that the nanorods are more active than the nanopolyhedra within the temperature range employed. The start-up reaction takes place at about 150 °C in the case of nanorods, while for nanopolyhedra the temperature above 190 °C. With increasing reaction temperature from 150 to 280 °C, the conversions of COS over two catalysts are all along increased, but the activity gap between them become widening, the nanorods display a surprisingly wonderful performance at low temperature zone (<300 °C). The 50% conversion of COS on the nanorods can be attained at temperature of 170 °C (labeled as "T_{50}"), while for the nanopolyhedra T_{50} is high up to 230 °C. In addition, on the nanorod catalyst, when temperature reaches to 200 °C the COS conversion is promptly enhanced to about 100% and COS can be completely converted into H_2S at 250 °C (labeled as "T_{100}"). Whereas over the nanopolyhedra, only 10% and 70% of COS conversion can be achieved at 200 °C and 250 °C, respectively. Until the temperature is elevated above 280 °C, the HDS activity of sulfided nanopolyhedra can reach 100%. These differences between two catalysts with distinct shapes might originate from their unique nanocrystal structures and would be discussed as follows.

Moreover, the HDS stability of two kinds of catalysts was tested at both 180 °C and 200 °C. The results of performing the long-run tests are shown in Fig. 5(B). As can be seen, the catalysts show almost no deactivation during 8 h on stream and the performance of the COS hydrodesulfurization over sulfided nanorods is still much higher than that over sulfided nanopolyhedra, the 90% conversion of COS has been kept on the nanorods at 200 °C. As much as we know, the excellent performance of sulfided Co_3O_4 nanorods for the HDS of carbonyl sulfide has not been reported in the literatures.

3.3.3. *Analysis of enhanced catalytic activity of Co_3O_4 nanorods*

In order to understand the differences in the catalytic performance, the details on the active phase and the surface feature of two kinds of catalysts have to be investigated. Information about the components and the BET specific surface areas of the as-made samples are obtained from the detection of XRF spectrum and the nitrogen adsorption isotherms, respectively. The XRF analysis shows that the relative contents of cobalt and sulfur species, which is calculated as CoO and SO_3 respectively, are obviously distinct for two types of sulfided Co_3O_4 nanocrystals. After the same presulfu-

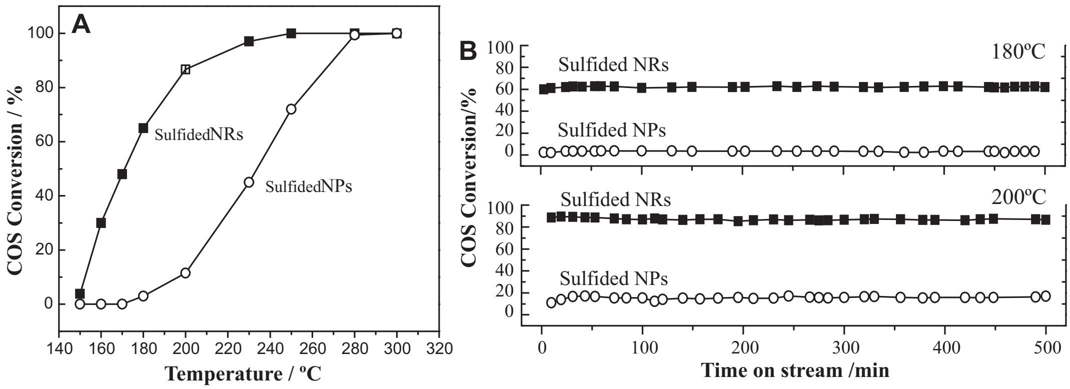
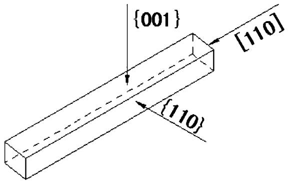
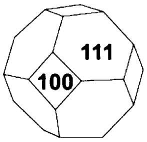


Fig. 5. (A) Temperature dependence of COS conversion for the hydrogenation of COS over two catalysts. (B) COS conversion as a function of time on stream for two catalysts. (Solid block, sulfided Co_3O_4 nanorods; hollow spheres, sulfided Co_3O_4 nanopolyhedra. Reaction conditions: COS 0.1%, H_2 10%, balanced with N_2, and GHSV = 8000 h^{-1}).

Table 1
Exposed crystal planes, BET specific area, and catalytic activity of different Co_3O_4 nanocrystals for COS hydrogenation.

Sample	Co_3O_4 nanorods	Co_3O_4 nanopolyhedra
Structural models		
Exposed crystal planes	(1 1 0)+(0 0 1)	(1 1 1)+(1 0 0)
S_{BET}/(m^2 g^{-1})	94.2	50.4
T_{50}/°C^a	170	230
T_{100}/°C^b	250	280

[a,b] Corresponding to 50% and 100% conversion of COS over sulfided Co_3O_4 nanocrystals, respectively.

rization (300 °C for 3 h), there are more sulfur species retained in the nanorods (SO_3 46.1%) than in the nanopolyhedra (SO_3 36.8%). These results reflect the fact that the nanorods are more easier to be sulfided than the nanopolyhedra, it is just consistent with the above-mentioned breakthrough curves over two catalysts (see Fig. 3). Obviously, the high presulfidation degree is helpful for the formation of more active sites for the HDS reaction, and giving rise to excellent performance of the sulfided nanorods.

The model crystal structures, the exposed crystal planes, the BET specific surface areas, the temperature of T_{50} and T_{100}, are summarized in Table 1. It is evident that, compared with the nanopolyhedra, the hydrogenation over the nanorods starts-up fast and exhibits a much higher catalytic activity for COS at low temperature: either T_{50} or T_{100} on the nanorods is far more less than that of the nanopolyhedra. In general, high-surface-area nanocatalytic materials exhibiting numerous crystal faces, edges, and corners, which are conventionally considered active sites for the adsorption of reactants [21,28], should generate better catalytic performance. In the present work of Co_3O_4 nanocrystals, the BET surface area of the rods is about twice that of the polyhedra (94.2 and 50.4 m^2 g^{-1}, respectively), it is reasonable to believe that there should be more active sites for presulfurization, therefore the deeply sulfided nanorods are more active and demonstrate a stable property for the HDS of COS. These results for two different shape nanocrystals also lead us to believe that specific crystal planes may be another determining factor that proves to be useful [21,29].

From the crystallographic point of view, Co_3O_4 holds a spinel structure containing Co^{3+} in an octahedral coordination and Co^{2+} in a tetrahedral coordination. The {0 0 1} and {1 1 1} planes contain only Co^{2+} cations, while Co^{3+} cations are present solely on the {1 1 0} plane [22,23,30]. Further considering that the nanorods are enclosed by four (1 1 0) and two (0 0 1) planes, and nanopolyhedra are enclosed by eight (1 1 1) and six (1 0 0) planes [21–23] (shown in Table 1), a correlation can be drawn between the catalytic performance and the crystal planes. It is probably suggested that the exposure of (1 1 0) surface might cause the nanorods a stronger reactive property than the nanopolyhedra, and facilitates the formation of more sulfur species on the rods during presulfurization stage, thus enhances their subsequent HDS activity for COS, which has been consistent with our experimental results (see Fig. 3 and Fig. 5).

Temperature-programmed reduction (TPR) by H_2 has been used extensively in the literatures to characterize the surface and bulk oxygen reducibility of metal oxides. Thus, TPR detection of the sulfided catalyst with different shape was conducted by illustrating the production of H_2S, in order to evaluate quantitatively the sulfur species along with the reduction process. Fig. 6 describes the profiles of H_2S production over two catalysts in the temperature range of 25 °C to about 950 °C. The TPR traces of all sulfides contain both a small peak at relative low temperature and broader features at higher temperatures, which are probably produced by hydrogenation of the sulfides existed in surface and bulk, respectively. It is clear that either the low-temperature reduction peak or the high-temperature one for the nanorods is stronger than that for the nanopolyhedra, indicating a greater amount of sulfur or deep presulfurization over the nanorods, in keeping with the above results of breakthrough curves and XRF analyses of the catalysts. The area of low-temperature reduction peak is much bigger for the nanorods than the nanopolyhedra, indicating more surface sulfur on sulfided nanorods.

Furthermore, we can see from the low-temperature peak, the peak for the nanorods is 272 °C, whereas for the nanopolyhedra is up to 371 °C. It is generally accepted that the low-temperature reduction process is a reduction of the surface sulfur species, which can be used for assessing the strength of Co–sulfur bond [19]. Nørskov et al. also demonstrated that the differences in reaction rate for the various transition metal sulfide are dominated by the differences in the number of vacancies at the sulfide surface [30]. Thus, the catalytic HDS activity is shown to follow the trend in the metal–sulfur (M–S) bond strengths, the relatively unstable property of M–S bond implies they may be inclined to produce more sulfur vacancies and exhibits high catalytic activity [19,31,32]. As can be seen, the distinct gap of reduction temperature between two catalysts indicates that Co–S bond strengths in the sulfided nanorods may be weaker than that in the sulfided nanopolyhedra. Consequently, in the reducing environment of HDS reaction, there would be more sulfur vacancies (active sites) produced on the surface of the nanorods catalyst than the nanopolyhedra, ensuring the

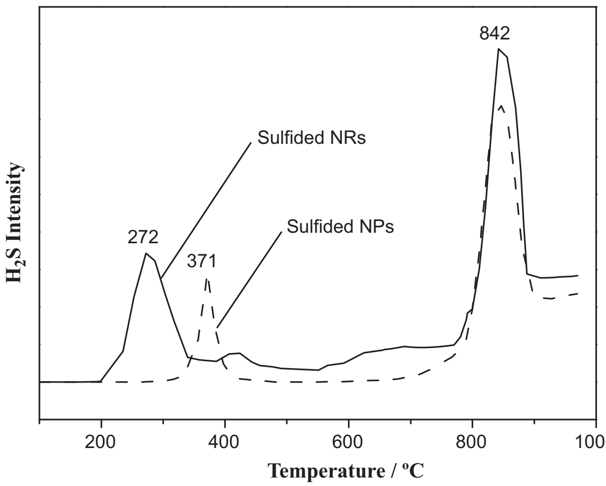


Fig. 6. H_2S production during H_2-TPR of the sulfided catalysts. (Solid line, sulfided Co_3O_4 nanorods; dotted line, sulfided Co_3O_4 nanopolyhedra. Reaction conditions: 12% H_2, balanced with N_2, 80 ml/min, temperature rate 10 °C/min).

perfect catalytic activity of the nanorods for COS reduction. Such vacancies have recently been observed on model catalysts by use of scanning tunneling microscopy (STM) [33]. The present results indicate that the shape effect of Co_3O_4 nanocrystals plays an important role in the HDS of carbonyl sulfide. Further investigation needs to be carried out in order to gain a better understanding of the COS conversion mechanism over these nanocrystal catalysts.

4. Conclusion

In summary, we demonstrate that the hydrogenation of carbonyl sulfide can be successfully conducted over novel nanocatalysts derived from Co_3O_4 nanorods and nanopolyhedra. Cobalt-based nanorods exhibit high activity in presulfurization process and the resultant sulfide is superior to nanopolyhedra in the HDS of carbonyl sulfide. The significant enhancement in sulfidation activity of the nanorod-shape catalyst is originally attributed to more reactivity of Co_3O_4 nanorods, which bring on deeper sulfidation and more active sulfur species to the sulfided catalyst than the nanopolyhedra. The present results suggest that hydrodesulfurization catalysts may be designed from the controlled synthesis of transition metal oxides with different sizes and morphologies. It can be concluded that the selective fabrication of transition metal sulfides from these oxides with uniform and different reactive crystal planes at nanoscale may be worthwhile to pursue.

Acknowledgements

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