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Impact of the Cu_2O microcrystal planes on active phase formation in the Rochow reaction and an experimental and theoretical understanding of the reaction mechanism

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ABSTRACT

In heterogeneous catalysis, on one hand, people always want to know about reaction details, such as what the most active phase is, how it is formed, and what is the reaction mechanism. On the other hand, it is still very challenging to probe these reaction details, particularly at high reaction temperatures and pressures. Here, we report the microcrystal plane-controlled catalytic performance on well-defined Cu_2O cube, octahedron, and rhombic-dodecahedron catalysts in the Rochow reaction. It was found that the Cu_2O cube exposing {1 0 0} crystal planes gave the highest dimethyldichlorosilane selectivity and yield, while the Cu_2O rhombic-dodecahedron exposing {1 1 0} crystal planes showed the lowest selectivity and yield. Our experimental observation, as well as density functional theory calculations, demonstrated that the enhanced selectivity and yield stemmed from the stronger dissociative adsorption of methyl chloride on the Cu_2O{1 0 0} plane, which greatly promoted the transformation of Cu_2O into Cu_3Si active phases under the reaction conditions. This work reveals a new strategy for controlling the surface structure of catalysts in order to enhance their catalytic performance.

1. Introduction

In recent years, it has been found that some catalysts possessing certain exposed crystal planes with specific atomic arrangements exhibit enhanced catalytic performance in a wide variety of catalytic reactions, including gas phase oxidation [1,2], CO_2 reduction [3,4], organic catalysis [5–10], electrocatalysis [11], and photocatalysis [12,13]. For example, mixed 26-facet and 18-facet Cu_2O nanopolyhedra with dominant {1 1 0} facets displayed higher activity in the photocatalytic decomposition of methyl orange than Cu_2O nanooctahedra with dominant {1 1 1} surfaces and cubes with {1 0 0} surfaces [14]. Li et al. observed that Co_3O_4 nanocrystals with different morphologies exhibited crystal-plane-dependent catalytic activity in methane combustion, with the activity following the order {1 1 2} > {0 1 1} ≫ {0 0 1} [15]. In the catalytic hydrogenation of benzene, Somorjai et al. discovered that Pt cubic nanoparticles with mainly exposed {1 0 0} surfaces were more active than Pt cuboctahedral nanoparticles with exposed mixed {1 0 0} and {1 1 1} surfaces [16]. Furthermore, Huang et al. synthesized a series of Cu_2O nanocrystals with different structures and found that rhombic dodecahedra exposing only the {1 1 0} facets exhibited greatly enhanced photocatalytic activity toward photodegradation of methyl orange in comparison with cubes exposing the {1 0 0} faces and octahedra exposing the {1 1 1} faces [17]. These studies highlight the importance of crystal plane control in the preparation of highly efficient catalysts. In most of the studied cases, the catalysts accelerate the rate-determining step by lowering reaction activation energy, and the catalysts themselves do not undergo much change in structure—e.g., the single-crystal catalysts studied under high vacuum conditions [18–22]. It seems that there are still very few reports on how to tune catalyst structures at the microscopic level to enhance their catalytic performance, and particularly to promote the active phase or key

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intermediate formation where the catalysts themselves undergo great structural changes or even damage.

Since the discovery of the Rochow reaction (Scheme S1, Supporting Information) in the 1940 s [23], its methylchlorosilane (Me_nSiCl_{4-n}, n = 1–3) products, in particular dimethyldichlorosilane (Me_2SiCl_2, M2), have been important monomers for the industrial production of silicon-based materials such as silicone resins, elastomers, and oils. In the past several decades, great efforts have been dedicated to the development of efficient catalyst systems to improve M2 selectivity and yield [24–27], and it is generally recognized that Cu-based catalysts are effective for the Rochow reaction; furthermore, their catalytic performance depends on their morphology. In contrast to most other catalyst systems, in the Rochow reaction, Cu-based oxide catalysts go through large structural changes under reaction conditions, e.g., in situ reduction of Cu oxide to generate active Cu atoms. However, these active Cu atoms are difficult to capture. In addition, so far, the catalytic mechanism for this complicated heterogeneous catalytic reaction is still not fully understood. The reported major reaction mechanisms include the free radical mechanism [23], the catalytic adsorption mechanism [28], and the silylene addition mechanism [29]. Among these, the most popular is the catalytic adsorption mechanism based on the fact that the copper–silicon alloy acts as the catalytic active phase. However, a molecular-level understanding of this adsorption mechanism's details still remains ambiguous; thus the exploration for high-performance Cu-based catalysts is still mainly based on a trial–error–trial approach. Traditionally, nanocrystal systems with size less than 100 nm are intrinsically inappropriate for mechanistic studies due to the lack of high controllability in their morphology and structure. In this regard, sub-micrometer-scale crystals (microcrystals) that expose specific faces are more suitable model catalysts for fundamental studies of such complex heterogeneous reactions.

In principle, the copper–silicon alloy active phase formed in the Rochow reaction can be utilized as an indirect replacement for active Cu atoms derived from Cu oxide catalysts for tracking the progress of the reaction. Here, we report the formation of a microcrystal plane-controlled active phase and its impact on the catalytic performance in the Rochow reaction by using well-defined Cu_2O microcrystals (cubes, octahedra, and dodecahedra) with size range 500–800 nm as model catalysts. Furthermore, we reveal the detailed reaction mechanisms at the molecular level through combined experimental and theoretical studies.

2. Experimental

2.1. Chemicals and materials

All the chemicals were purchased from Sinopharm Chemical Reagent Co., China, and used as received without further purification. These chemicals include copper chloride dehydrate ($CuCl_2{\cdot}2H_2O$, analytical reagent (AR), ≥99.0 wt%), copper sulfate pentahydrate ($CuSO_4{\cdot}5H_2O$, AR, ≥99.0 wt%), polyvinylpyrrolidone (PVP, chemical pure (CP), MW = 30,000), oleic acid (OA, AR), sodium hydroxide (NaOH, AR, ≥96.0 wt%), ascorbic acid (Vc, AR, ≥99.7 wt%), and glucose (AR) and Cu_2O powders (AR, 97.5 wt%). Silicon powders (99.5 wt%, 20–50 mesh; the content of impurities is shown in Table S1) were provided by Jiangsu Hongda New Material Co., China.

2.2. Synthesis of Cu_2O microcrystals

2.2.1. Cubic Cu_2O

Cubic Cu_2O microcrystals were synthesized following reported procedures with some modifications [30]. Typically, 0.171 g of $CuCl_2{\cdot}2H_2O$ was dissolved in 100 mL of deionized (DI) water, followed by the dropwise addition of 10 mL of NaOH solution (2 M, 1 drop/s). After continuous stirring for 0.5 h, 10 mL of Vc aqueous solution (0.6 M) was added dropwise. The mixture was then aged for 3 h before being centrifuged at 6000 rpm for 5 min. All of these experiments were carried out in a water bath at 60 °C. The obtained precipitates were washed several times with excessive DI water and ethanol and then dried under vacuum at 50 °C for 10 h. The as-synthesized cubic Cu_2O microcrystals are denoted as C-Cu_2O.

2.2.2. Octahedral Cu_2O

Octahedral Cu_2O microcrystals were synthesized following reported procedures with some modifications [30]. Typically, 0.171 g of $CuCl_2{\cdot}2H_2O$ and 9.9 g of PVP were simultaneously dissolved in 100 mL of DI water. Subsequently, 10 mL of NaOH aqueous solution (2 M) was added dropwise (1 drop/s) with continuous stirring for 0.5 h, followed by the addition of 10 mL of Vc aqueous solution (0.6 M). The precipitates were aged, washed, and dried following the same procedures as those for cubic Cu_2O. The as-synthesized octahedral Cu_2O microcrystals are denoted as O-Cu_2O-PVP.

2.2.3. Dodecahedral Cu_2O

Dodecahedral Cu_2O microcrystals were synthesized according to a published procedure with some modifications [31]. Typically, 0.25 g of $CuSO_4{\cdot}5H_2O$ was dissolved in 40 mL of DI water to form a clear solution. Then 4 mL of OA and 20 mL of ethanol were added successively with vigorous stirring; the solution was heated to 100 °C and kept for 0.5 h. Subsequently, 10 mL of NaOH solution (8 mM) was added dropwise (1 drop/s) and kept for 10 min until the solution became homogeneous. Finally, a solution of glucose in DI water (3.42 g; 30 mL) was dropped in and the mixture was continuously stirred for another 60 min. The resulting precipitate was collected by centrifugation and decanting, then washed with DI water and ethanol several times, and finally dried under vacuum at 50 °C for 10 h. The as-synthesized dodecahedral Cu_2O microcrystals are denoted as D-Cu_2O-OA.

The surfactants PVP and OA were removed via a redox process. Typically, 0.1 g of as-synthesized O-Cu_2O-PVP and D-Cu_2O-OA microcrystals were loaded into a quartz U-tube and purged in N_2 flow (10 mL min^{-1}) at room temperature for 30 min to remove oxygen. Then the stream was switched to a gas mixture of C_3H_6, O_2, and Ar (volume ratio C_3H_6:O_2:Ar = 2:1:22, flow rate 10 mL min^{-1}) and the sample was heated to defined temperatures (220 °C for O-Cu_2O-PVP; 205 °C for D-Cu_2O-OA) at a rate of 2 °C min^{-1}. After the controlled oxidation treatment was carried out for 30 min, the sample was cooled to room temperature under a stream of N_2 (flow rate 10 mL min^{-1}). The thus obtained Cu_2O octahedra and dodecahedra are denoted as O-Cu_2O and D-Cu_2O, respectively.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytica X'Pert PRO MPD using Cu Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA from 10.0° to 90.0°. The microscopic features of the samples were observed by field-emission scanning electron microscopy (FESEM; JEM-6700F, JEOL, Japan) with liquid-nitrogen-cooled energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM; JEM-2100, JEOL, Tokyo, Japan) under a working voltage of 200 kV. Infrared spectra (IR) were measured on a Nicolet 8700 Fourier transform infrared spectrometer in transmission mode with spectral resolution 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was conducted on a Model VG ESCALAB 250 spectrometer (Thermo Electron, U.K.) using nonmonochromatized Al Kα X-ray radiation ($h\nu$ = 1486.6 eV). The sample charging effects were compensated for by all binding energies (BE) being