The role of CO_2 in dehydrogenation of ethylbenzene over pure α-Fe_2O_3 catalysts with different facets

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ABSTRACT

The replacement of superheated steam with CO_2 for ethylbenzene (EB) dehydrogenation to produce styrene (ST) is of great importance from both scientific and practical perspectives, while it is still a big challenge to design and synthesize catalysts for dehydrogenation in the presence of CO_2. Research into shape-controlled nanocrystals has proved that well-defined facets are of great importance for understanding the catalytic phenomena due to their definite surface structure. In the present work, α-Fe_2O_3 nanocrystals enclosed by various crystal facets provide us the clue to understand the role of CO_2 in dehydrogenation. O(III) (the triply coordinated surface oxygen atom) is found to play an important role in activating CO_2 under reaction conditions, which is supported by both experimental and theoretical results. These results have deepened knowledge about the role of CO_2 in dehydrogenation over pure α-Fe_2O_3 catalysts, which is significant in designing relative catalysts rationally.

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1. Introduction

Heterogeneous catalysis is of great importance, and one of its ultimate goals is to ascertain active sites and then design and synthesize high-efficiency catalysts [1,2]. Shape-controlled metal oxides in heterogeneous catalysis serve as model catalysts to bridge the gap between activities and structures, because shape variation always results in different crystal facets whose definite atomic arrangements are crucial for the relationship between structure and activity [3]. As is known, styrene (ST) is one of the most important raw materials that are commercially produced by the dehydrogenation of ethylbenzene (EB) in the presence of superheated steam [4–9]. During this process, a large amount of energy is lost in the gas–liquid separator, and the equilibrium efficiency is quite low even at high temperatures, for example, 69.7% at 983 K [7]. The replacement of superheated steam with CO_2 is believed to be energy-saving and theoretically favorable, but commercial Fe–Cr–K catalysts do not work effectively in the new system. Because dehydrogenation is a structure-sensitive reaction and the active sites with or without potassium promoted might be

identical [10–12], study of the dehydrogenation performance of shape-controlled hematite (α-Fe_2O_3), the main component of the commercial dehydrogenation catalysts, could not only help us systematically understand dehydrogenation reaction at the molecular level, but also guide the rational design of catalysts with higher activity [13,14].

Controlled synthesis of α-Fe_2O_3 nanocrystals with different crystal facets has been extensively investigated [15–19]. However, the various existing synthetic systems are unsuited to exploring facet-dependent properties, as there still exists controversy about the role of the remaining capping agents used to maintain the specific shapes of catalysts when interpreting the catalytic properties [20]. For example, detailed study of the influence of iron on catalytic activity has revealed that using ferric chloride as an iron source led to low activities due to the presence of chloride ions in the crystal [21]. Sugimoto et al. have proved that the adsorption ability of sulfate ions on α-Fe_2O_3 of different morphologies is different [22]. Meanwhile, it has also been confirmed that residual sulfate on the surface could promote catalytic activity [22–24]. Although α-Fe_2O_3 with different facets has been synthesized, most of them could not be utilized directly because the existence of impurity ions will interfere with the effect of facets and introduce uncertainty and complexity into the reaction system. Therefore, it

is necessary to synthesize samples by introducing the same capping agents, which can be removed thoroughly.

In the present work, we synthesized three kinds of uniform α-Fe_2O_3 nanocrystals, octadecahedral α-Fe_2O_3 nanocrystals (OcFe) with (113) and (104) facet exposure, rhombohedral ones (RhFe) with (104) facet exposure, and pseudo-cubic ones (PCFe) with (102) facet exposure. They were prepared in the presence of organic amines, which can be removed thoroughly. In addition, the crystal size and surface area of the three samples are controlled to be similar, which provides an ideal model for investigating the facet-dependent catalytic reactivity of α-Fe_2O_3.

2. Experimental

2.1. Preparation and characterization

Both OcFe and PCFe were synthesized by a new strategy, while RhFe was obtained on the basis of previous literature and with some modifications [16]. Methods for the preparation of different morphologies are as follows.

OcFe: In a typical synthesis, 45 mM $Fe(NO_3)_3$ was first dissolved in 8 M formamide. Distilled water was added to the solution until the volume was 120 ml. After ultrasonic treatment for 10 min, the mixture was transferred into Teflon-lined autoclaves of 150 ml and maintained at 220 °C for 24 h.

RhFe: 0.1 M $Fe(NO_3)_3$, 0.5 M urea, and 1 M formamide were dissolved in 120 ml distilled water. After ultrasonic treatment for 10 min, the mixture was transferred into Teflon-lined autoclaves of 150 ml and maintained at 160 °C for 24 h.

PCFe: 0.05 M $Fe(NO_3)_3$ and 0.12 M ammonium acetate were dissolved in 60 ml ethanol, and 3 ml distilled water was added to the solution. After ultrasonic treatment for 10 min, the mixture was transferred into Teflon-lined autoclaves of 150 ml and maintained at 180 °C for 24 h.

For all samples, the precipitate was separated by centrifuging, washed with distilled water and absolute ethanol alternately to remove possible impurities on the surfaces of samples, and then dried at 80 °C. Before further characterization and evaluation, the product was calcined at 550 °C for 3 h to thoroughly remove organic remains. Last, the obtained catalysts were crushed and sieved into granules of 40–80 mesh for the reaction.

The composition of the as-prepared samples was determined by powder X-ray diffraction (XRD) patterns recorded on a D8 Advance Bruker AXS diffractometer, using CuKα radiation (λ = 1.5406 nm) at 40 kV, 40 mA, employing a scanning rate of $0.01°s^{-1}$ in the 2θ ranging from 10° to 90°. The morphology and structure of the as-prepared samples were observed using a scanning electron microscope (SEM, JSM-7001F) and a transmission electron microscope (TEM, JEM-2100F and JEOL-2010). Energy-dispersive X-ray spectroscopic (EDX) analysis was performed on a scanning electron microscope (JSM-7001F) to measure the composition at the surfaces of catalysts. The specific surface areas of the samples were measured by Brunauer–Emmett–Teller (BET) nitrogen adsorption using a TriStar 3020 physisorption analyzer. CO_2 temperature-programmed desorption (CO_2 TPD) was performed on the homemade apparatus. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies were performed on a TENSOR 27 spectrometer and X-ray photoelectron spectroscopy analysis (XPS) was carried out using an AXIS ULTRA DLD spectrometer.

2.2. Catalytic tests

Catalytic reactions were performed in a stainless steel tube (i.d. 8 mm) at 823 K under atmospheric pressure. A 500 mg sample of catalyst was used per run in the presence of CO_2, while the amount

of catalyst was decreased to 200 mg when the reaction was conducted in the presence of Ar because the severe carbon deposition in direct dehydrogenation may block the reactor. Before each test, the catalyst was first activated under Ar flow for 2 h at 823 K before EB was introduced by a Double Piston Micro Injection pump, and then Ar flow was switched into CO_2. The molar ratio of CO_2 to EB was fixed at 10 and the weight hourly space velocity (WHSV) was controlled at $3.48\ h^{-1}$. The products were analyzed by gas chromatography on a GC-950, and aromatic compounds were analyzed by a FID detector using a capillary column of PEG-6000. In all cases, ST is the major product, accompanied by small amounts of benzene and toluene as byproducts. The catalytic performance was evaluated in terms of the conversion of EB and the selectivity for ST according to the following equations, where EB_{in} was obtained by conducting the reaction without catalysts:

$$EB \text{ conversion } (\%) = \frac{EB_{in} - EB_{out}}{EB_{in}} \times 100, \tag{1}$$

$$ST \text{ selectivity } (\%) = \frac{\text{mol of desired product}}{\text{mol of reacted ethybenzene}} \times 100. \tag{2}$$

2.3. Reverse water-gas shift reaction

The reverse water-gas shift (RWGS) reaction was carried out in self-built equipment. A sample of 80 mg of catalyst was first heated to 873 K under Ar for 1 h; then a mixture of CO_2 and H_2 (CO_2 = 30 ml/min, H_2 = 3 ml/min) was introduced. The products were observed by an online quadrupole mass spectrometer (Omnistar GSD 30103) which was directly connected to the outlet of the reactor. The mass spectrometer scanned the ions of parent peaks of the four compounds, m/z = 2, 18, 28, and 44 within 10 s, and repeated scans were collected with a personal computer.

2.4. CO_2 TPD and DRIFTS

CO_2 TPD was performed on self-built equipment to determine the basicity of catalysts. Prior to the introduction of CO_2, 50 mg of catalyst was preheated under Ar of 18 ml/min at 823 K for 1 h. When the temperature was decreased to 323 K, pure CO_2 of 36 ml/min was introduced for 30 min. Then Ar purging was performed for 1 h and CO_2 desorption was performed from 323 to 1073 K. Before each DRIFTS experiment, the samples were first treated under Ar (9 ml/min) at 673 K for 30 min, and then cooled to operation temperature (473, 573, or 673 K). Unless stated otherwise, infrared spectra were recorded against a background of the sample at the corresponding temperature under Ar. The absorbance spectra were recorded with co-addition of 64 scans with a resolution of $4\ cm^{-1}$. A quantity of 100 ml of CO_2 was then injected at a constant speed and the spectra were recorded.

3. Results and discussion

3.1. Morphology and structure

Fig. 1a shows the XRD patterns of all the samples obtained under different conditions. All the diffraction peaks can be indexed as the hexagonal phase of ferric oxides (JCPDS No. 33-0664). No other impurities such as Fe_3O_4, $Fe(OH)_3$, and FeOOH are detected, revealing the high purity and crystallinity of the products.

Octadecahedra: OcFe, with twelve (113) facets and six (104) facets exposure, has been obtained in different systems [25]. In this study, we synthesized OcFe under the influence of formamide. To avoid chloride ions that are stubborn but toxic for dehydrogenation, iron nitrate is chosen as iron source. SEM (Fig. 1b) and TEM