Journal of Molecular Catalysis A: Chemical 344 (2011) 53–61

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

Role of CO_2 in ethylbenzene dehydrogenation over Fe_2O_3(0 0 0 1) from first principles

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ARTICLE INFO

Article history:
Received 12 February 2011
Received in revised form 28 April 2011
Accepted 1 May 2011
Available online 7 May 2011

Keywords:
DFT
Ethylbenzene dehydrogenation
CO_2
Fe_2O_3(0 0 0 1)

ABSTRACT

First-principles calculations based on density functional theory have been performed to elucidate the reaction mechanism for ethylbenzene dehydrogenation and the role of CO_2 in H removal. On the basis of the experimental information and theoretical prediction, three model surfaces with Fe-, ferryl- and O-termination are constructed to represent the active Fe_2O_3(0 0 0 1) surface. The calculated results indicate that on all of the three surfaces the C–H activation in the methylene group followed by the dehydrogenation of the methyl group is kinetically more favorable. The energy barriers for ethylbenzene dehydrogenation are lowest on the O-terminated surface, but the generated styrene is adsorbed too strongly to be released. As CO_2 decomposition and the formation of HCOO are hindered by the relatively high activation energies, CO_2 cannot serve as the oxidant to recover the O- and ferryl-terminated surfaces to keep the redox cycle. At the steady state of the reaction the coupling mechanism dominates on the Fe-terminated surface, with the synergistic effect between ethylbenzene dehydrogenation and the reverse water–gas shift reaction. Since the energy barrier for the formation of COOH is comparable to that for H_2 formation, both the one-step and two-step pathways are predicted to contribute to the coupling mechanism, although the former is more probable.

1. Introduction

The dehydrogenation of ethylbenzene to produce styrene is an important industrial process, which is carried out over iron oxide-based catalyst at temperatures around 870 K in the presence of steam. As this commercial process consumes a large amount of energy, CO_2 is recently used instead as the co-feed gas, which is believed to be energy-saving and environmentally friendly. Furthermore, through the coupling of ethylbenzene dehydrogenation with the reverse water–gas shift reaction, the ethylbenzene conversion can be significantly improved, arising from the simultaneous hydrogen elimination [1–4].

Two mechanisms, namely the coupling mechanism and the redox cycle mechanism, are traditionally proposed for ethylbenzene dehydrogenation in the presence of CO_2, as illustrated in Fig. 1. In the coupling mechanism, the generated H atoms through the dehydrogenation of ethylbenzene react with CO_2 to produce OH, COOH or HCOO which further combines with H to form H_2O. Alternatively, the detached H atoms first combine to produce H_2, and then H_2 is dissociated to yield H atoms for the subsequent reverse water–gas shift reaction. These two pathways are generally called one-step and two-step pathways [5,6].

In the redox cycle mechanism, the H atoms in ethylbenzene are abstracted by lattice O atoms to form H_2O, leading to the reduction of catalyst surfaces. Then CO_2 is decomposed to compensate for surface O to keep the catalyst activity and achieve the reaction cycle.

Some experimental efforts have been devoted to interpreting the mechanism for this coupling system. Badstube et al. [7] investigated the dehydrogenation of ethylbenzene over iron oxide catalyst supported on activated carbon in the presence of CO_2. Apart from styrene, benzene, and toluene, CO and H_2O were captured with the constant molar ratio of 0.8 during the process. Comparing the experimental data to the postulated mechanisms, they believed that both the reverse water–gas shift reaction and the redox cycle mechanism make contributions to ethylbenzene dehydrogenation. Likewise, Chang et al. [8] examined the beneficial effect of CO_2 on the dehydrogenation of ethylbenzene to styrene over zeolite-supported iron oxide catalyst. Styrene, H_2O, CO, and a small amount of H_2 were produced. As shown in Fig. 1, the coupling mechanism succeeds in accounting for the formation of H_2 while the detected CO and H_2O may be yielded either through the decomposition of CO_2 followed by H abstraction from ethylbenzene by surface O or via the reverse water–gas shift reaction. Hence, they proposed that both the coupling and redox cycle mechanisms are probable.

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doi:10.1016/j.molcata.2011.05.002

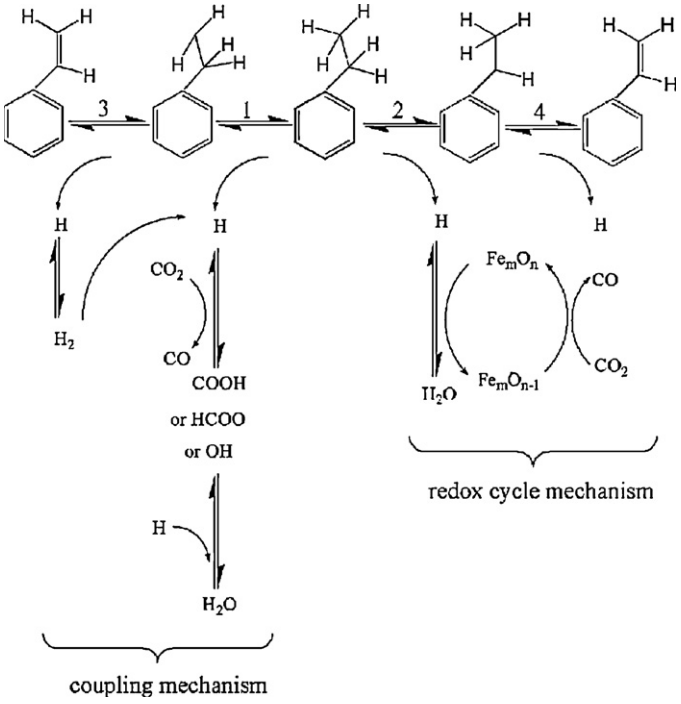

Fig. 1. Two reaction mechanisms for ethylbenzene dehydrogenation in the presence of CO_2.

However, some groups suggested that only one of the two mechanisms is dominant in this process. Sun et al. [9] have examined the dehydrogenation of ethylbenzene over a series of Fe and V supported catalysts in the presence of CO_2 by means of temperature-programmed desorption. The experimental data indicated that the ethylbenzene conversion is associated with the conversion of CO_2, and that there exists a synergistic effect between ethylbenzene dehydrogenation and the reverse water–gas shift reaction. In addition, CO_2 was considered to be activated through either basic or redox sites, and both the one-step and the two-step pathways were proposed. In contrast, Sugino et al. [2] investigated ethylbenzene dehydrogenation over activated carbon-supported iron oxide catalyst by X-ray diffraction analysis. They found the amounts of CO and H_2O produced during the reaction agree well with the amount of styrene, indicating a redox cycle as follows: (1) lattice O atoms abstract H from ethylbenzene to give styrene; (2) CO_2 oxidizes O defects in the iron oxide phase.

Thus, while many attempts have been made to elucidate the mechanism for ethylbenzene dehydrogenation in the presence of CO_2, the way how CO_2 is activated and the role of CO_2 activation in H removal are still under debate.

On the other hand, the active centers for ethylbenzene dehydrogenation and CO_2 activation remain elusive as well. Iron oxide catalyst has been extensively applied in the dehydrogenation of ethylbenzene, which shows an excellent performance [5–7,10–15]. Zhu et al. [16] has investigated the dehydrogenation of ethylbenzene over potassium-promoted iron oxide-based catalyst with high time resolution using on-line mass spectroscopy, and claimed that the fully oxidized iron phases containing only Fe^{3+} ions are responsible for the high catalytic activity. However, Kuhrs et al. [17] suggested that while Fe_3O_4 is inactive towards this reaction, an induction period is necessary before Fe_2O_3 becomes active. Similarly, Weiss et al. [18–20] investigated ethylbenzene dehydrogenation over single-crystalline iron oxide model catalyst films grown epitaxially onto Pt(1 1 1) substrates. It was found that atomic surface defects act as the active centers, whereas Fe_3O_4(1 1 1) is always inactive.

In this contribution, first-principles calculations based on density functional theory (DFT) are performed to explore ethylbenzene dehydrogenation in the presence of CO_2 on the Fe-, ferryl- and O-terminated Fe_2O_3(0 0 0 1) surfaces. Firstly, on the basis of the experimental information, three models are constructed for the three surfaces. Secondly, the adsorption energies of the reaction intermediates and the activation energies for the elementary steps involved are calculated to elucidate the dominant active surface and reaction pathway. Finally, we conclude by discussing the implication of our results for understanding the reaction mechanism for ethylbenzene dehydrogenation and the key role of CO_2 in H removal.

2. Computational details

The first-principles calculations have been performed by the VASP code [21–23]. The generalized gradient approximation functional proposed by Perdew et al. was used [24]. The interactions between valence electrons and ion cores are represented by Blöchl's all-electron-like projector augmented wave method (PAW) [25], which regards the d7s1 states as the valence configuration for Fe, s2p4 for O and s2p2 for C. A plane wave energy cutoff of 400 eV was used in the present calculations. Geometries were relaxed using the conjugate gradient algorithm [26] until the forces on all the unconstrained atoms are less than 0.03 eV/Å. There is a magnetic element (Fe) involved in the system, and therefore spin-polarized effect has been considered. The calculations performed by Bergermayer [27] showed that surface magnetism plays a key role in the quantitative description of total energy.

α-Fe_2O_3 has a hexagonal close-packed structure of slightly distorted O, with 2/3 of the interstitial octahedral sites being occupied by Fe ions [28]. It is very stable and often the end form of the transformation of other iron oxides. DFT calculations have been previously carried out to explore the geometry of α-Fe_2O_3 [29,30], and through the surface energy calculations it was found that the (0 0 0 1) surface is most stable [19].

Starting from bulk α-Fe_2O_3, several terminations are possible to derive the (0 0 0 1) surfaces. The previous theoretical work indicated that at low O chemical potential (i.e., low O_2 partial pressure or high temperature), the Fe-terminated surface shown in Fig. 2(a) is found to be the most stable surface, whereas at high O chemical potential the (0 0 0 1) surface of hematite is completely covered with O atoms [the O-terminated surface shown in Fig. 2(b)] [27,31–33].

Experimentally, the (0 0 0 1) surface has been characterized in detail under ultra high vacuum, indicating that both the Fe- and O-termination can be observed with a somewhat complex mixture of surface phases existing under different temperatures and O_2 partial pressures [34,35]. On the other hand, Chambers et al. [36] investigated the termination of the epitaxial α-Fe_2O_3(0 0 0 1) prepared by oxygen–plasma-assisted molecular beam, and claimed that despite the highly oxidizing conditions the Fe-terminated surface is most stable.

Besides, a ferryl (Fe=O) termination which can be regarded as one special type of defects was proposed [37–39], as represented schematically in Fig. 2(c). Ferryl species are predicted to be active in the selective oxidation and dehydrogenation reactions, and coexist with the domains of Fe-termination at certain O_2 pressures. Bergermayer et al. [27] claimed that the Fe-terminated surface has the ability to accept and release O under the thermodynamic conditions applied in the catalytic oxidation of ethylbenzene, and the shuttling between the Fe-termination (Fe–O3–Fe) and the ferryl-termination (O–Fe–O3–Fe) may play a key role in the reaction mechanism.

As a result, these three surfaces are singled out to investigate the dehydrogenation of ethylbenzene in the presence of CO_2. A