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Insights into the key to highly selective synthesis of oxime via ammoximation over titanosilicates

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ABSTRACT

A thorough investigation was carried out to demonstrate the key to highly selective synthesis of oxime via ammoximation over titanosilicates. The oxidation pathways of H_2O_2 between the formation of NH_2OH and deep oxidation of oxime stayed competitive, which could control product selectivity. These pathways were influenced by oxime chemical activity, NH_3 concentration, and the diffusional restriction and intrinsic catalytic activity of titanosilicates. Diffusional restriction could lower the selectivity of highly active oxime to some extent through intensifying deep oxidation. However, it was not the decisive factor in achieving high oxime selectivity, since the pathway of deep oxidation proceeded without involvement of Ti active sites. The positive role of high NH_3 concentration in promoting the pathway of generating NH_2OH was relatively limited, as the crucial step of activating H_2O_2 into Ti–OOH species was primarily determined by the intrinsic catalytic ability of titanosilicates, which was related to their Lewis acidity. It is found that titanosilicates with strong Lewis acidity of Ti active sites contribute to highly selective synthesis of oxime by promoting H_2O_2 to participate into the highly efficient formation of NH_2OH, and thus the corresponding side reaction of consecutive homogeneous oxidation of oxime with free H_2O_2 is fundamentally suppressed. By regulating the strength of Lewis acidity of titanosilicates, selectivity of oxime with various chemical activities could be improved significantly.

1. Introduction

The successful development of ketone ammoximation processes over titanosilicates has been attracting much attention, since this new simplified route is capable of serving as an environmentally benign method for synthesis of valuable oxime (e.g., ketone oxime, aldehyde oxime) using H_2O_2 as an oxidant under mild conditions [1–3]. Actually, the chemical reactions that may occur in this benign process are complicated, such as cyclohexanone ammoximation, summarized in Scheme 1. Thus, for the purpose of constructing more efficient ammoximation processes, numerous efforts have been made, which mainly focus on reaction mechanisms [4–6], reaction parameters optimization [4,6,7], preparation and post-treatment of titanosilicates [8,9], and the deactivation and regeneration of catalysts [10–13]. As a matter of fact, clean production of oxime requires a catalytic system that not only exhibits excellent catalytic activity for ammoximation but also, more importantly, can suppress the undesired reaction pathways simultaneously, as the formation of by-products can strongly affect oxime purity, even in very small quantities. Among these issues, highly selective synthesis of the desired product is the primary one in industrial catalysis research. It was reported that catalyst properties related to diffusion resistance [14], hydrophilicity/hydrophobicity [15], and Ti active species [16], as well as the additives [17], oxidant [18], and solvent [19] used for selective oxidation processes, can significantly influence the product selectivity during typical titanosilicate-catalyzed propene epoxidation and phenol or benzene hydroxylation reactions. In terms of the ammoximation of ketones or aldehydes over titanosilicates, it has been widely accepted that the typical side reaction is deep oxidation [2,20–22]. Nevertheless, the factors that determine the selectivity of various titanosilicates in specific ketone and aldehyde ammoximation reactions are not yet clear, even though considerable progress toward this has been made. Therefore, a full understanding of these factors will be favorable to developing the ammoximation process toward superior oxime selectivity and optimizing reaction conditions of ammoximation.

Previous studies of the influences on deep oxidation in ammoximation mainly concentrated on diffusion resistance, properties of titanosilicates, and NH_3 concentration. In the case of diffusion resistance, the low methyl ethyl ketone oxime (MEKO) selectivity

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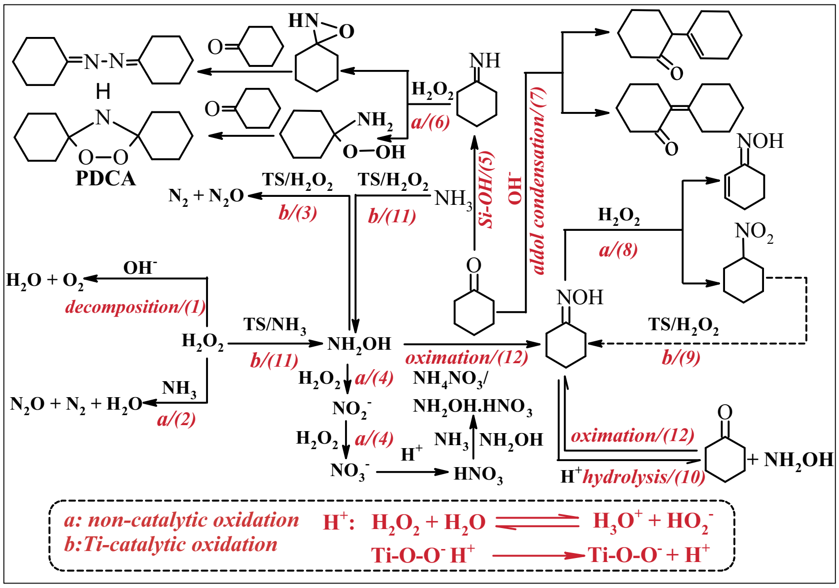
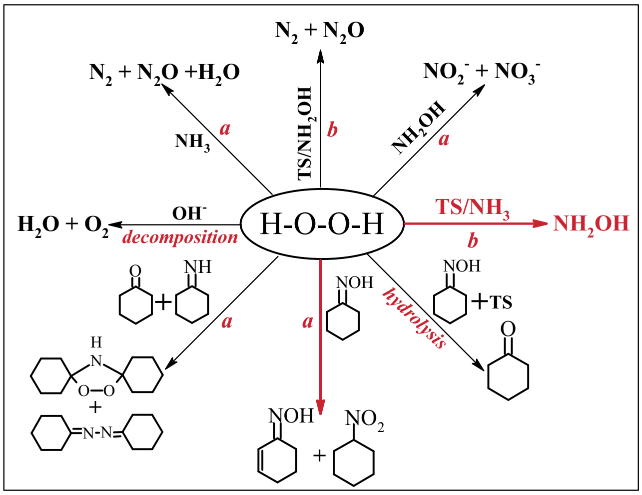


Scheme 1. Reaction network of cyclohexanone ammoximation over titanosilicates.

obtained over TS-1 with medium pores was considered to derive from the catalytic oxidation of linear oxime to 2-nitrobutane over Ti active sites located inside the zeolite channel [2], whereas previous reports demonstrated that, in cyclohexanone ammoximation, nitrocyclohexane could be produced from the homogeneous oxidation of oxime without the participation of Ti active sites [20,21]. Additionally, although TS-1 showed better selectivity for cyclohexanone oxime than for linear oximes such as MEKO, which was due to the fact that large cyclic molecules were unable to enter the pore for further oxidation, it was proved that the pores owned by TS-1 zeolite were also able to absorb cyclohexanone molecules in the liquid phase, which indicates that cyclic oximes would be generated inside the TS-1 channels and be oxidized successively on Ti active sites as well [23]. Thus, it seems that the influence of diffusional restriction by the catalyst on deep oxidation remains inconclusive. Among catalyst properties, the hydrophilicity/hydro phobicity, the porosity, and the nature of Ti active sites were presumed to affect the product selectivity. Ti-MWW was reported to exhibit much higher MEKO selectivity than TS-1 because it was inactive to oxime oxidation [2], and Ti-MOR exhibited superior selectivity of acetaldehyde oxime (AAO) to other titanosilicates, due to its porosity and good hydrophobicity [3]. However, no further studies were performed to correlate these properties with the ammoximation mechanism to elucidate the inner reasons. Furthermore, many studies supported the conclusion that oxime selectivity could be noticeably improved by adopting an excess of NH_3 and deep oxidation reactions would be intensified by lowering the NH_3 concentration [2–4,20], but this positive role of excessive NH_3 is limited and depends on the type of titanosilicates. For instance, the linear oxime selectivity gained by TS-1 (around 95%) still fails to reach the level obtained by Ti-MWW (>99.5%) even if the mole ratio of NH_3/ketone is as high as 4 [2].

Thus, a comprehensive understanding of the reaction network will contribute to elucidating the key factors in product selectivity in ammoximation catalyzed by titanosilicates. Scheme 1 shows the overall reaction behavior of cyclohexanone ammoximation following the hydroxylamine mechanism, which has been fully confirmed [6,7]. This network consists of three parts: (a) the inorganic side reactions involving the unproductive decomposition of H_2O_2 as well as the consecutive oxidation of NH_2OH and NH_3 to form nitrogen derivatives [14,24–26] (steps 1–4), which would decrease ketone conversion but not affect product selectivity; (b) the organic side reactions containing aldol condensation of ketone [20], the formation of imine and its consecutive oxidation [4,21], together with the hydrolysis and deep oxidation of oxime [2,6,20,22] (steps 5–10), which reasonably have a great influence on product selectivity; (c) the main reactions, consisting of the catalytic formation of NH_2OH as a result of oxidation of NH_3 and H_2O_2 on Ti sites and the noncatalytic oximation of ketone with NH_2OH to oxime [6,7] (steps 11 and 12), which are able to influence both the ammoximation activity and selectivity. It is surprising to find that the oxidant H_2O_2 is involved in most reaction steps, so the corresponding reaction network adopting H_2O_2 as reactive center is summarized in Scheme 2. Apparently, it indicates that product selectivity depends greatly on the reaction pathways of free H_2O_2 in ammoximation, especially on the competition of oxime and NH_3 in oxidation, which form the typical by-product of nitrocyclohexane and ammoximation intermediates of NH_2OH, respectively. Although the hydrolysis pathway of oxime caused by H_2O_2 or others decreases its yield, it will not influence the product selectivity directly. This implies that to gain oxime selectivity as high as possible, it is necessary to control the oxidation pathways



Scheme 2. Multiple oxidation pathways of H_2O_2 in cyclohexanone ammoximation over titanosilicates.