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Ammoximation of cyclohexanone to cyclohexanone oxime using ammonium chloride as nitrogen source

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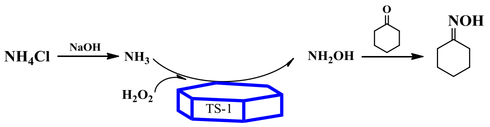
HIGHLIGHTS

- Novel approach to acquire cyclohexanone oxime using ammonium chloride as nitrogen source.
- Nearly 100% of cyclohexanone was converted to cyclohexanone oxime.
- The reaction mechanism was proposed by combining experiments with density functional theory calculations.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel process was designed for synthesis of cyclohexanone oxime using ammonium chloride as nitrogen source. Various reaction parameters were optimized such as the amount of ammonium chloride, catalyst and H_2O_2, reaction temperature, reaction time. Under the suitable reaction conditions, nearly 100% of conversion of cyclohexanone and 100% selectivity of cyclohexanone oxime were obtained at ambient condition. The reaction mechanism was proposed by combining experiments with density functional theory calculations.

1. Introduction

Cyclohexanone oxime is an important intermediate in chemical industry, particularly as a key precursor of ε-caprolactam for nylon production (Chen et al., 2014; L. Li et al., 2015, Z. Li et al., 2015; Wu et al., 2014). Usually cyclohexanone oxime is produced from the condensation of cyclohexanone with hydroxylamine salts, using hydroxylamine as nitrogen source. The conventional technology of oxime production is multi-step, environmentally unfavorable and produces ammonium sulfate as by-product, which causes disposal problem (Anilkumar and Hoelderich, 2015; Xu et al., 2014). In the 1980s, the discovery of titanium silicalite-1 (TS-1) opened up many good catalytic processes (Lin et al., 2014; Liu et al., 2012, 2014; Saxena et al., 2007; Yip et al., 2009), including the route of preparation of cyclohexanone oxime via ammoximation of cyclohexanone with ammonia as nitrogen source (**Reaction (1)**).

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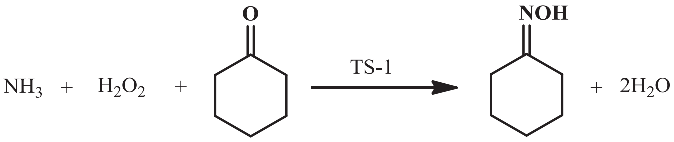
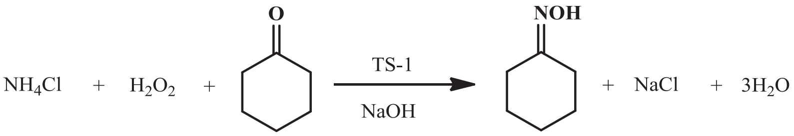


(Reaction (1))

Additionally, ammonium chloride was a by-product in the production of sodium carbonate with Alkaline Hou Shi system in China. Ammonium chloride was mainly used as a nitrogen fertilizer in agriculture and also applied in the fields of food, medicine, hydrometallurgy and battery, etc. However there is still much left to do. Hence, there is a growing incentive for the development of a new environmental friendly utilization of ammonium chloride. More recently, Sooknoi and Chitranuwatkul (2005) studied a series of weak acids ammonium salts, such as acetate, citrate and carbonate, can be used as nitrogen sources for the ammoximation in acetic acid solvent. However, the ammonium salts of strong acid like ammonium chloride can hardly be used as reagent in the reaction. The reason may be that the K_a of the conjugated acid of ammonium salts is high. Considering these, a flash idea came into our mind. If alkali was added to the cyclohexanone ammoximation (**Reaction (1)**), could a new reaction be proceeded with ammonium chloride as nitrogen source as shown in **Reaction (2)**?



(Reaction (2))

The objective of this study was to investigate the possibility of synthesizing cyclohexanone oxime efficiently using ammonium chloride as nitrogen source. Various reaction conditions including catalyst amount, reaction temperature and reaction time were investigated for optimization of the reaction. Moreover, the possible reaction pathways were also verified via experiments and density functional theory calculations.

2. Materials and methods

2.1. Materials and reagents

Titanium silicalite-1 (TS-1), TS-2, Ti-MWW and Ti-MOR were obtained commercially and tested as catalyst. All other chemicals (AR grade) were commercially available and used without further purification.

2.2. The reaction process

The catalytic ammoximation was carried out in a 100 mL three-necked flask equipped with a stirrer and a condenser. Many studies suggested the ammoximation over TS-1 proceeds very well in pure water (Thangaraj et al., 1991; Wu et al., 2002; Xu et al., 2015). Therefore, no organic solvent (tert-butanol) was used as reaction media in this study. At each experiment, an amount of TS-1 catalyst, ammonium chloride, sodium hydroxide aqueous solution and 62 mmol of cyclohexanone were charged into the flask. The mixture was heated to reaction temperature. Then hydrogen peroxide solution (30 wt%) was added dropwise (6.4 mL/h) to avoid H_2O_2 decomposition. Then the reaction was performed for several hours, the solid TS-1 catalyst was filtered, collected, regenerated by drying at 80 °C for 12 h and calcinations at 500 °C for 4 h. The filtrate was extracted three times with toluene.

The obtained organic phase contained cyclohexanone, cyclohexanone oxime and toluene, which was identified by comparison of their retention time with those of authentic samples, and by a Thermo Trace DSQ gas chromatography mass spectrometry. The concentrations of organic components were analyzed by an Agilent 7890B gas chromatography. Cyclohexanone conversion (X_{Cyo}) and cyclohexanone oxime selectivity ($S_{\text{Cyo-O}}$) were calculated by the following Eqs. (1) and (2) (Liu et al., 2012; Yang et al., 2014).

$$X_{\text{Cyo}} = \left[1 - \frac{6 \cdot \frac{W_{\text{Cyo}}}{M_{\text{Cyo}}}}{\sum \left(n_i \frac{W_i}{M_i} \right)} \right] \cdot 100\% \tag{1}$$

$$S_{\text{Cyo-O}} = \frac{6 \cdot \frac{W_{\text{Cyo-O}}}{M_{\text{Cyo-O}}}}{\sum_{i \neq \text{Cyo}} \left(n_i \frac{W_i}{M_i} \right)} \cdot 100\% \tag{2}$$

where

W_{Cyo} is the weight percentage of cyclohexanone in the products.
M_{Cyo} is the molar mass of cyclohexanone.
$W_{\text{Cyo-O}}$ is the weight percentage of cyclohexanone oxime in the products.
$M_{\text{Cyo-O}}$ is the molar mass of cyclohexanone oxime.
n_i is the number of carbon atoms in each molecule of i component.
W_i is the weight percentage of i component in the products.
M_i is the molar mass of i component.

2.3. Characterization methods

The compositions of catalysts were analyzed by PerkinElmer Optima 7300 V inductive coupling plasma (ICP-AES) spectrometer. The BET data was obtained with a Micromeritics ASAP 2020 analyzer. The samples were heated under vacuum at 200 °C for 4 h prior to the nitrogen adsorption-desorption experiments. The melting point was measured with a WRS-1B Digital Melting Point Apparatus. The chemical composition of mixture samples were determined by a Thermo Electron Corporation CHNS-O Analyzer. Infrared spectra of the samples were recorded with a Nicolet Nexus 470 FT-IR spectrometer using the potassium bromide pellet technique.