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Short communication

Solvent effect on the allylic oxidation of cyclohexene catalyzed by nitrogen doped carbon nanotubes

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ABSTRACT

A wide spectrum of, up to 22, organic solvents, including aprotic/protic aliphatics/aromatics, was studied to achieve a comprehensive understanding to the solvent effect on the cyclohexene oxidation. It was found that the catalytic activity was significantly influenced by the viscosity, polarity and basicity of solvents in this reaction. Among these solvents, the polar aprotic aliphatic solvents displayed higher catalytic reactivities than other types of solvents. A volcano curve was found describing the dependence of activity on solvent basicity because of the suitable stability of intermediates. Among the solvents investigated, acetonitrile afforded the highest activity and selectivity of 2-cyclohexen-1-one, because of a good compromise between strong polarity and moderate basicity.

1. Introduction

The selective oxidation of hydrocarbons towards oxygenated derivatives is a significant chemical value-chain, through which the relatively cheap molecules can be converted into value-added products [1–3]. Numerous studies have demonstrated that solvents display a dramatic influence on the catalytic activity and products distributions, especially for the oxidation of alkenes [2,4–7]. The solvent properties, such as polarity, dielectric constant and basicity, influenced the activity of the epoxidation of styrene, 1-hexene and cyclohexene over titanosilicate catalysts [6,8]. In addition, a synergistic effect between the solvent property and the hydrophilicity–hydrophobicity of the zeolite also affected the catalytic activity, as observed in the case of 1-hexene oxidation towards the production of alcohol and 2-cyclohexen-1-one [9]. Fan et al. investigated the solvent effects on the activity, epoxide selectivity, and H_2O_2 efficiency in the liquid-phase epoxidation of 1-hexene and cyclohexene over three types of zeolites (TS-1, Ti-Beta, and Ti-MWW) [6].

The literature results indicate that solvents may interplay with the active sites on catalyst surfaces, thereby modify the reaction pathway and the distribution of products in the alkene oxidation reactions [6,10]. However, the manner of solvent affecting the reaction might be changed as the catalyst is upgraded. Nanocarbons have attracted great attentions from the research and industrial communities in the past two decades as metal-free catalysts, due to their unique chemical and physical properties [11–13]. Recently, nanocarbons, especially nitrogen doped carbon nanotubes (NCNTs), displayed excellent performance in the allylic oxidation of cyclohexene, affording a high selectivity of 2-cyclohexene-1-none [14]. The remarkable activity can be explained by the stabilization of peroxyl and cycloxyl radicals and the charge transfer between NCNTs and radicals, which is facilitated by delocalized electrons in graphene layers [14–16]. The significant solvent effect in the selective oxidation of hydrocarbons catalyzed by carbons has been observed. For instance, Yang et al. found that the unique catalytic efficiency of the hydroxylation of benzene catalyzed by graphene in immiscible water as solvent, because the products can be rapidly transferred to solvent to avoid the over-oxidation [5]. Our very recently work also revealed that solvents could greatly influence the activity of α-pinene oxidation over CNTs [17]. Despite these achievements, a comprehensive understanding to the solvent effect on the alkene oxidation is so far unavailable, because the library of solvents was usually too small to uncover the general tendency of solvent effect. Moreover, the synergy between solvents and carbon catalysts has not been revealed.

In this work, we have studied the effect of solvents on the allylic oxidation of cyclohexene catalyzed by NCNTs. To achieve an in-depth understanding, 22 organic solvents were investigated, which are categorized into four types, namely protic/aprotic aliphatics/aromatics,

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according to their properties and structures. By correlating the catalytic performance with the solvent properties, i.e. viscosity, polarity and scale of basicity, the solvent effect could be rationalized.

2. Experimental

2.1. Preparation of catalysts

The NCNTs were produced according to our previous works [14,18]. In brief, the NCNTs were synthesized by a CVD method using aniline as carbon and nitrogen sources. The growth of NCNTs was carried out at 800 °C in NH_3 at 500 $Ncm^3\ min^{-1}$. The metal impurities were removed by concentrated HCl for 4 h before catalytic tests.

2.2. Cyclohexene oxidation

The cyclohexene oxidation reaction was carried out as same as the previous work [14]. 22 solvents were used in this work and their physical/chemical properties are summarized in Table S1. Typically, 10 mL cyclohexene, 20 mL solvent, 2 mL o-dichlorobenzene (o-DCB) as internal standard and 50 mg catalyst were charged into the autoclave. Before reaction, the reactor was flushed with N_2. Then, the reactor was heated to 80 °C, and subsequently pure O_2 was fed into the reactor (1 MPa, 4 h). The products were analyzed by gas chromatography.

3. Results and discussion

3.1. Effect of viscosity

The viscosity of solvent plays significant roles in the liquid-phase reactions through altering the mass transfer, resulting in the different activity [19]. In this work, the solvent viscosity varies across a wide range. The effect of viscosity on the cyclohexene conversion is partially presented in Fig. 1. Within the scope of solvent investigated, there is not universal tendency showing a common effect of viscosity on activity. Fig. 1 shows a serious decrease of conversion with increasing viscosity in the case of protic —OH containing solvents, probably due to the negative effect of viscosity on mass transfer in liquid phase. However, the dependence of conversion on the viscosity of —C═O group containing solvent is quite weak. Similar situation can be observed for other solvents, such as the aprotic aliphatic/aromatics solvents, displaying the opposite tendency in the cyclohexene oxidation between those two kinds of solvents (not shown). These inconsistent even opposite responses suggest that the viscosity has minor influence on the cyclohexene oxidation, but is not the essential factor under current conditions. Therefore, we focus on the effects of specific physical/chemical property of solvents, for instance polarity and basicity, on the cyclohexene oxidation.

3.2. Effect of polarity

Polarity of solvent has a significant influence on the reactivity in the cyclohexene oxidation, since it plays a significant role on stabilizing the transition state (intermediate radical species) and the proton transfer [20–22]. In this work, the effect of polarity of protic/aprotic aliphatics/aromatics solvents was investigated, respectively. The dependences of cyclohexene conversion on polarity are plotted in Fig. 2. For the four types of solvents, the conversion increased along with the polarity, indicating that solvents with higher polarity are favorable for the catalytic efficiency. Clear pseudo-linear relationships between polarity and conversion were observed for aprotic and protic aliphatics. It may be attributed to the enhanced solubility of polar oxides produced in polar solvents. The solvents with strong polarity probably enhanced the desorption of polar oxide products to avoid blocking the active sites on NCNTs [4–5,17]. Some exceptional results are observed, e.g. acetone, chloroform and acetonitrile, with large deviations from other aprotic aliphatics. Acetone is probably unstable under the current reaction conditions, because it may be decomposed to acetic acid as a protic solution suppressing the reactivity. The higher activities in chloroform and acetonitrile may be attributed to their lower viscosities (see Table S1). Nevertheless, the dependence of conversion on polarity demonstrates that polarity may be a good indicator to a rational selection of reaction solvents, which may lead to a huge difference of reactivity from 20% to 60% conversion under the same conditions.

Within the aromatic solvents investigated, there is not clear tendency describing the dependence of cyclohexene conversion on polarity. In general, aromatics exhibits lower conversions than the aliphatic solvents. This is probably because the conjugated competitive adsorption of solvent and cyclohexene upon NCNTs, since aromatics molecules may strongly interact with sp2 carbon systems [14,23]. For example, toluene can strongly adsorb on and block active sites [17]. It could be argued that aromatic solvents might be reactive on the benzyl position. However, our previous work demonstrated that the oxidation of ethyl benzene or aromatic solvents needs more severe conditions, such as high temperatures (>145 °C) and pressures (>1.5 MPa), without additives or co-reactants [24]. Hence, in this study, the lower reactivity in aromatics could be mainly attributed to the competitive adsorption between substrate and toluene upon active sites of NCNTs.

It can be clearly observed that the aprotic solvents displayed higher reactivity than the protic ones in this study. This behavior could be

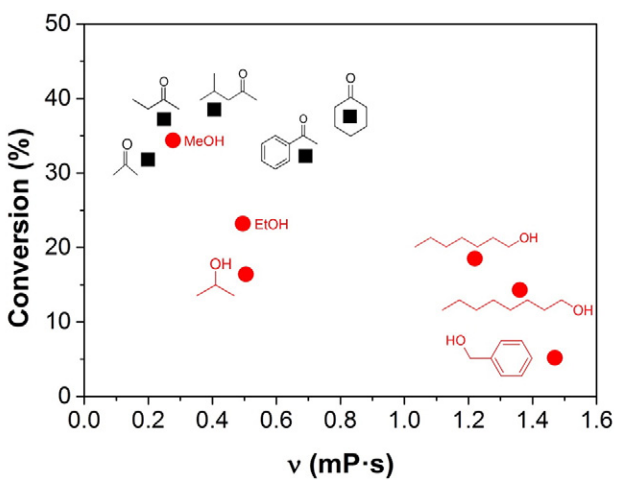

Fig. 1. Effect of solvent viscosity on the conversion of cyclohexene.

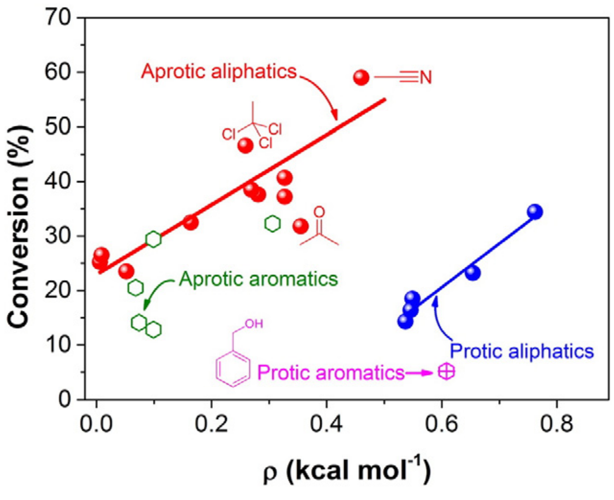

Fig. 2. Effect of solvent polarity on the conversion of cyclohexene.