



Short Communication

Temperature effect on the photo-epoxidation of propylene over V–Ti/MCM-41 photocatalyst

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ABSTRACT

The effect of reaction temperature on the gas-phase photocatalytic epoxidation of propylene was systematically studied over V–Ti/MCM-41 photocatalyst at different temperatures (298–393 K). Temperature significantly influences the product distribution of photo-epoxidation. Raising temperature is favorable towards the formation of propionaldehyde (PA) due to inhibition of PA transformation to propionic acid (C₂H₅COOH), the intermediate product of acetaldehyde (AA). Results indicated that the reaction temperature has a dual-action to the reaction rate: (1) improving the desorption of reaction products, which provides more active sites for reaction and (2) reducing the adsorption of propylene on the photocatalyst, which declines the reaction efficiency.

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1. Introduction

One of the most important challenges that scientists faced today is how to generate useful epoxides from photoreaction of alkenes, i.e., photo-epoxidation of propylene to propylene oxide (PO) [1,2]. Despite photocatalytic epoxidation has several advantages such as low energy consumption and the generation of eco-friendly products, their efficiency is still low, making the process far from commercialization [3]. Therefore, enhancing photo-efficiency has become an increasingly important task in chemical production as well as environmental protection.

Among a variety of metal oxides, V₂O₅ and TiO₂ with low loadings onto silica-supported photocatalysts could achieve steady-state PO formation with high selectivity (>40%) [4,5]. Recently, we have screened a series of photocatalysts such as SiO₂, TiO₂, V–Ti/MCM-41, V₂O₅/SiO₂, Au/TiO₂ and TS-1 [2]. V and Ti substituted MCM-41 material has shown the highest possibility of PO production with PO formation rate and PO selectivity achieved are 114 μmol g_{cat}⁻¹ h⁻¹ and 47%, respectively. It seems to be generally agreed that the isolated tetra-coordinated species, such as V and Ti, in the ligand-to-metal charge-transferred state is the key structure to be favorable for promoting selective photo-epoxidation. Additionally, it is interesting to observe the most efficient reaction temperature in the range of 313–333 K. However, there is still lack of information on the particular role of reaction temperature on the photocatalytic epoxidation of propylene to propylene oxide.

Generally, although reaction temperature has a significant impact on gas–solid heterogeneous reactions, it is not very sensitive on

heterogeneous photocatalysis [6]. To date, only few studies have investigated the temperature effect in gas-phase photocatalytic reactions, especially in epoxidation [7–10]. In 1979, P. Pichat et al. reported that temperature had a negative effect on the photo-epoxidation activity over the following series of UV irradiated oxides: TiO₂, ZrO₂, V₂O₅, ZnO, SnO₂, Sb₂O₄, CeO₂, WO₃, and a Sn–O–Sb mixed oxide [7]. In 2007, H.J. Zhan et al. suggested that in the epoxidation of styrene, the styrene conversion increased with temperature in the range of 343–383 K. However, the selectivity of epoxide first increased from 71.7% at 343 K to 82.3% at 353 K, then drastically dropped to approximately 61.7% at 383 K [8]. It must be emphasized that photocatalytic reactions can be conducted at the ambient temperature and do not require heating since the reaction can be activated by photons. Even though raising temperature can accelerate the surface reaction, it also reduces the adsorption of reactant on the photocatalyst surface. Hence, the effect of temperature on photo-epoxidation is relatively complicated.

To the best of our knowledge, the particular role of reaction temperature on photocatalytic epoxidation of propylene has not been systematically study yet. Therefore, the major purpose of this study is to evaluate the direct photo-epoxidation in order to elucidate the roles of reaction temperature in photocatalytic epoxidation propylene over V–Ti/MCM-41 photocatalyst under UV irradiation.

2. Experimental

2.1. Preparation and characterization of photocatalyst

The procedures for the preparation of V–Ti/MCM-41 photocatalyst were mentioned in detail in our previous work [2]. First, 21.2 g of

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sodium metasilicate monohydrate dissolved in 100 ml DI water was combined with appropriate amount of titanium oxysulfate hydrate and vanadyl sulfate hydrate (dissolved in 20 ml of 2 M H_2SO_4) to form a uniform gel. Next, 7.28 g of CTAB dissolved in 25 ml of DI water was added slowly into the mixture. After stirring for 3 h, the gel mixture was transferred into autoclave and kept in an oven at 418 K for 36 h. Then, the resulting solid was filtered, washed and dried at 383 K for 8 h. Finally, the solid was calcined at 823 K for 10 h.

Powder X-ray diffractometer (XRD, Xray-M03XHF, Ultima IV) was used to verify the crystalline structure of the photocatalyst. All peaks identified by XRD were checked and assigned to known crystalline phases. The light absorption of photocatalyst was fully characterized by ultraviolet–visible light (UV–vis) spectroscopy (Varian Cary-100). The adsorption/desorption isotherm and pore size distribution of catalysts were characterized by nitrogen adsorption (ASAP2010 Micromeritics) at 77 K. Before analysis, the catalyst was degassed at 100 °C for 12 h to remove adsorbed vapors or gases.

2.2. Photocatalytic epoxidation of propylene

The experimental system, which was conducted continuously in the reactant gas mixture of $C_3H_6:O_2:N_2 = 1:1:18$ (GHSV = 6000 h^{-1}) under atmospheric pressure, can be found in our previous study [2]. First, 20 mg of photocatalyst was evenly spread in a photo-reactor (0.55 cm^3) equipped with a quartz window on the top for transmission of light. Then, light from Mercury-Arc-lamp ($0.2\text{ mW}\cdot\text{cm}^{-2}$, 320–500 nm) was guided by an optical fiber and irradiated on the photocatalyst. A hot plate was used to control the reaction temperature in this study.

The stream was analyzed online periodically using a gas chromatograph (Young Lin, YL6100 GC) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Carbon dioxide (CO_2) and oxygenated products (propylene oxide (PO), propionaldehyde (PA), acetone (AC), acetaldehyde (AA) and ethanol (ROH)) were separated periodically using a Porapak-N packed column and analyzed by FID (except CO_2 via TCD), while the lighter gases (O_2 and N_2) were separated by a molecular sieve-5A capillary column and analyzed by TCD. The propylene conversion and the selectivity of products in the reaction were calculated directly by Eqs. (1) and (2) as defined below.

$$C_3H_6 \text{ conv. rate} = \sum \text{rate of all products converted to } C_3 \quad (1)$$

$$\text{Product selectivity} = \left(\frac{\text{product converted to } C_3}{\text{all products converted to } C_3} \right) \times 100\%. \quad (2)$$

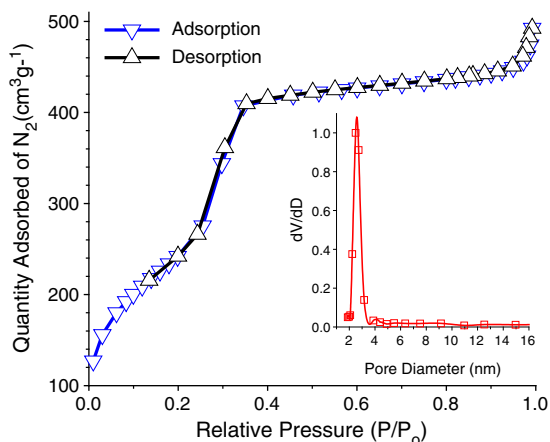


Fig. 1. The nitrogen adsorption/desorption isotherms of the photocatalyst and its pore size distribution curve (inset).

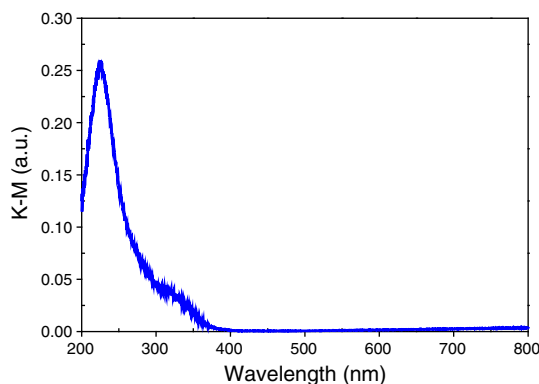


Fig. 2. UV–vis absorption spectrum of the photocatalyst.

3. Results and discussion

3.1. Characteristics of photocatalyst

The nitrogen adsorption/desorption isotherms and a clear single and narrow pore size distribution of V–Ti/MCM-41 are depicted in Fig. 1. The BET surface area of V–Ti/MCM-41 is approximately $790\text{ m}^2\cdot\text{g}^{-1}$ while BJH average pore diameter is around 2.9 nm which was estimated by the BJH method from the desorption branches. It suggests that the photocatalyst obtained has a very uniform pore structure.

Fig. 2 shows the UV–vis spectrum of the photocatalyst. A strong band centered at about 220 nm is generally attributed to the transition of ligand-to-metal charge transfer involving tetra-coordinated both of titanium species (Ti^{+4} state) and vanadium species (V^{+5} state) in the framework of MCM-41 photocatalyst. A weaker band at around 340 nm is also attributed to the charge transfer on tetra-coordinated V-oxide species [11].

Powder low-angle X-ray diffraction (XRD) pattern of V–Ti/MCM-41 photocatalyst is shown in Fig. 3 which clearly indicates the characteristic low-angle peaks of mesoporous materials, featuring pattern with narrow (1 0 0) peaks. There are no peaks corresponding to metal oxides observed in this study, suggesting that metal ions are atomically dispersed in the framework of mesoporous MCM-41. Additionally, (1 1 0) and (2 0 0) reflection peaks essentially merge into one broad peak, indicating that the mesostructure is changed by metal incorporated. Karthik et al., who synthesized Si, Cu and Al incorporated MCM-41 materials, also observed this phenomenon [12]. They suggested that it might also be due to the partial loss of long-range crystallographic order and the formation of metal oxide species by calcination at 823 K.

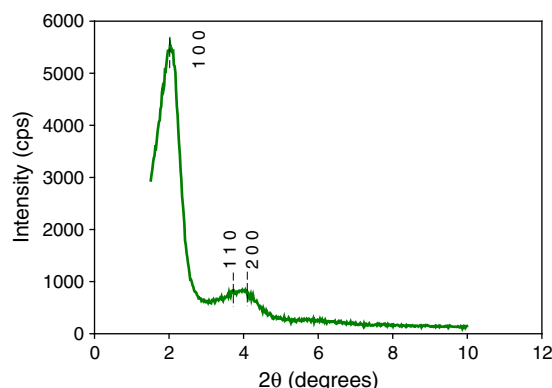


Fig. 3. Low angle X-ray diffraction pattern of the photocatalyst.

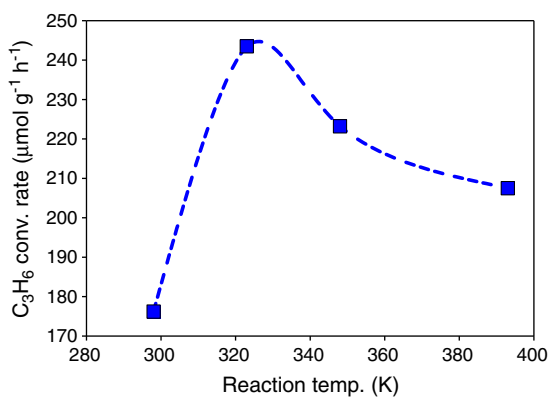


Fig. 4. The effect of reaction temperature on photocatalytic epoxidation rate. The C₃H₆ conversion rate was obtained on stream after 4 h, calculated by Eq. (1).

3.2. Effect of reaction temperature on photo-epoxidation

From the epoxidation result, no activity was observed either in the absence of photocatalyst with UV illuminated or with the photocatalyst in the absence of UV irradiation, meaning that the epoxidation over V-Ti/MCM-41 photocatalyst is mainly photocatalytic epoxidation. It also suggests that temperature can affect the photo-epoxidation reaction by altering the adsorption of propylene and the desorption of the reaction products on the photocatalyst. Adsorption is an exothermic process; therefore, increase of temperature tends to inhibit the process. Alternatively, high temperature is beneficial to desorption process since it is an endothermic process. In order to elucidate the effect of reaction temperature, experiments were carried out at 298, 323, 348 and 393 K.

Fig. 4 shows that there is no monotonic relationship in the epoxidation rate and the reaction temperature. Generally, the photo-reaction does not require heat due to the photonic activation. Kim and Lee mentioned that the true activation energy E_t is nil in photo-reaction; as a result, the activation energy is the apparent activation energy E_a which is very small [13]. Hence, the rate on desorption of the final product should become the limiting step and E_a tends to the heat of adsorption of the product in the medium temperature range. In other words, raising temperature improves the desorption of the photocatalytic reaction products, which enhances the reaction efficiency by releasing more active sites for reaction. The result in Fig. 4 confirms the reaction efficiency increases in the range of 300–330 K which passes or overlaps the boiling points of main products (Table S.2) and consists of above explanation. In contrast, raising temperature might cause the difficulty of propylene

adsorption on a photocatalyst, which declines the reaction efficiency. To the end, the reaction temperature has a dual-action to the reaction rate in this study.

Additionally to PO, other products such as PA, AC, AA and ROH were detected and their selectivity was calculated. The selectivity of products on stream as shown in Fig. 5 is very stable and it shows very similar and stable time-dependent behavior for the photocatalytic epoxidation. Moreover, it is noted that temperature has a significant effect on product distribution. For instance, epoxidation selectivity slowly increases with the rising of temperature. However, at temperature higher than 323 K, a slightly loss of selectivity towards PO is observed, which is due to the competition of multiple reactions towards different products.

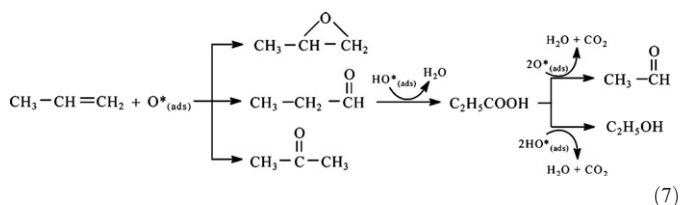
Generally, when photocatalyst is irradiated with UV-light, a series of reactions occurs to generate the active species: oxygen radicals



With the humidity in the gas stream, the water molecules could trap holes (h^+) to form hydroxyl radicals $\text{OH}^*(\text{ads})$



Following is the competing reaction pathways of photo-epoxidation of propylene via atomic oxyradicals $\text{O}^*(\text{ads})$ and hydroxyl radicals $\text{OH}^*(\text{ads})$.



In the previous study, we have mentioned that the surface atomic oxyradicals $\text{O}^*(\text{ads})$ can react with propylene to yield three isomerization products via the angle of H-atom abstraction from the propylene attacked by $\text{O}^*(\text{ads})$ [2]. Hence, temperature should not play important roles for the change of the selectivity of products. Interestingly, however, high temperature inhibits the water molecules migrate to the photocatalyst surface where the hydroxyl radicals $\text{OH}^*(\text{ads})$ intermediates can be generated. Therefore, it will inhibit PA transform to propionic acid ($\text{C}_2\text{H}_5\text{COOH}$) –

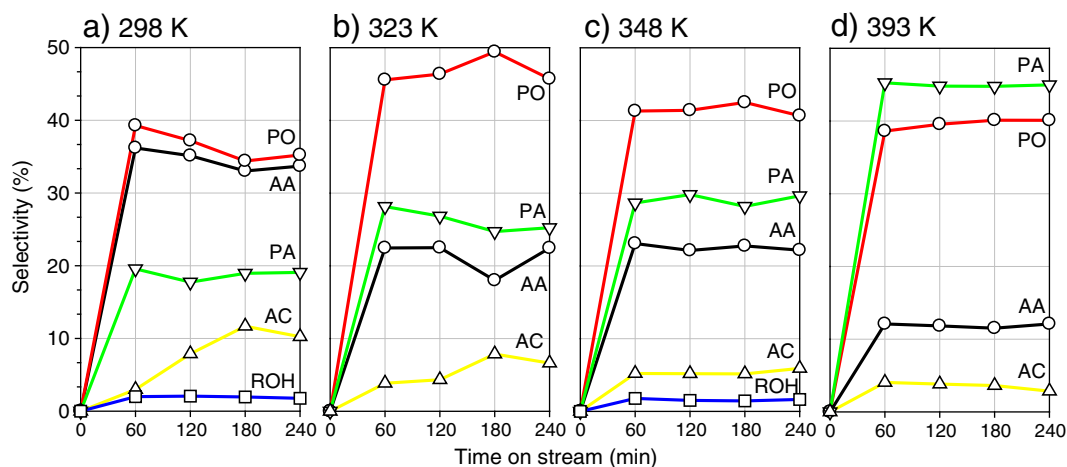


Fig. 5. The selectivity of epoxide products on stream calculated by Eq. (1) for different temperature conditions: (a) 298 K; (b) 323 K; (c) 348 K and (d) 393 K.

the intermediate product of AA, the resulting is PA increases and AA decreases with the temperature.

Additionally, in the photocatalytic epoxidation, it is very difficult to distinguish the photo and thermal effects on the reaction because the heating may enhance not only the desorption of products but also the partial and/or total oxidation of intermediates. Even at room temperature, the thermal effect may not be negligible; therefore, reaction temperature just above the boiling point of those products was selected in order to reduce the thermal effect to reaction. It confirms that products in this reaction are partially adsorbed and the desorption of these products requires heating. However, increase the reaction temperature also changes the partial oxidation; as a result, products distribution will be re-arranged. The results in this study show that high temperature is favorable towards the formation of propionaldehyde, one of the most reactive aldehydes. Yoshida et al. reported a re-arrangement of selectivity over vanadium oxide supported on silica. They also found that temperature was favorable towards the formation of aldehydes [14].

4. Conclusion

The effect of temperature on the photocatalytic epoxidation of propylene over V-Ti/MCM-41 was investigated by carrying out the reaction at 298, 323, 348 and 393 K. The photo-epoxidation can be conducted at room temperature without any heating. However, we found that the most efficient temperature is 323 K in this study. Results indicated that the reaction temperature has a dual-action to the reaction rate of photo-epoxidation over V-Ti/MCM-41 photocatalyst. Additionally, raising the reaction temperature also changes the partial oxidation, as a result, product distribution will be re-arranged towards the formation of propionaldehyde.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2012.12.024>.

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