

Photo-epoxidation of cyclohexene on V-Ti-MCM41

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Abstract

Epoxides are highly reactive compounds, which can conduct numerous chemical reactions as intermediate. Epoxides are also important precursors for many fine chemicals and pharmaceuticals. Cyclohexene epoxidation is one of basic epoxidation of cyclic olefins, which has been widely investigated. The selectivity of 1,2-epoxycyclohexane is a crucial challenge. Instead of thermal driving force, photon is applied to improve the conversion and selectivity in cyclohexene epoxidation. The photo-catalytic epoxidation of cyclohexene by porous material such as MCM41 is a promising method to produce 1,2-epoxycyclohexane. Our approach is to use photo-energy as driving force to achieve high selectivity and yield to the epoxide at mild conditions. Silica-supported catalyst, V-Ti/MCM-41, was used to evaluate its performance in the photo epoxidation and achieve extra high selectivity. In-situ real-time Raman monitoring provides non-invasive insight during epoxidation of cyclohexene in the absence of solvent (dry media reaction). The progress of the reaction was monitored by the changes in intensity of the characteristic Raman bands [1]. We found that the photo-driven cyclohexene epoxidation could give higher selectivity under mild reaction condition.

Keywords: cyclohexene epoxidation, photo-catalyst, V-Ti/MCM41, in-situ Raman spectroscopy.

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1 Introduction

In recent years, there are many researchers who focus on epoxidation. However, in most cases, we face the disposal, separation, and economic problems. As other olefin epoxidation reactions, fine-chemical industry has pointed out that cyclohexene epoxidation is one of the most important reactions in industrial organic synthesis. The epoxidation of olefins such as ethylene, propylene and cyclohexene, leads to the formation of oxygenated molecules called epoxides, which are very valuable and versatile intermediates for many industrial applications.

Normally, TBHP is one of the preferred oxygen sources in industrially epoxidation process. It is a mild and stable oxidant, not very corrosive or hazardous. Most important of all, the separation process of byproduct, tert-butyl alcohol, is much easier than others[2]. After these reasons, TBHP become a popular oxidant in cyclohexene epoxidation.

Considering the separation process, high selectivity is required for the cyclohexene epoxidation. In order to increase the selectivity, MCM-41, which is a kind of mesoporous material, become a choice of catalysts to create the shape selectivity. V-Ti/MCM-41 molecular sieves were synthesized by simple hydrothermal treatment method with different metal loading ratios.

During the heterogeneous catalytic reaction, we use UV light as driving force to operate cyclohexene epoxidation and compare the results with the thermal catalytic reaction. There is 3-5 % of UV light in real solar radiation, so we could concentrate the solar radiation and guide the light into the engineering process instead of the heating, for a

more efficient use of energy. The mechanism of photo catalytic cyclohexene epoxidation has not been explored yet. We believe that the interaction between the reactant, products and active sites of catalyst is the key to understand the photo catalytic cyclohexene epoxidation.

Real-time *in-situ* Raman spectroscopy is particularly suitable to study the interaction of molecular bonding during reaction. Raman provides unique fingerprints for real-time analysis and monitoring of chemical reactions and processes [3-7]. To monitor the organic reactions, chromatography analysis is required such as gas chromatography (GC). However, these kinds of off-line analysis methods are time-consuming and may provide less information than multiparametric real-time analysis.

In this research, the epoxidation of cyclohexene using TBHP over different metal-loading ratios of V-Ti/MCM-41 catalysts was investigated using *in-situ* Raman spectroscopy and off-line gas chromatography separately. We compared the results by different measurements in this research. Also, we found out the best metal ratio for V-Ti/MCM-41. Furthermore, the effect of different driving force was studied on V-Ti/MCM-41 in cyclohexene epoxidation.

2 Experimental

Mesoporous V-Ti/MCM-41 molecular sieves were synthesized by simple hydrothermal treatment method [8-9]. The molar composition of the gel mixture was 1 SiO₂ : 0.02 metal oxides : 0.2 CTAB : 0.89 H₂SO₄ : 120 H₂O. In our research, we named each catalyst with different metal loading molar ratios, such as (V-Ti-Si), (2-0-100), (1.5-0.5-100), (1-1-100), (0.5-1.5-100), (0-2-100).

The whole synthesis procedure is shown in **Figure 1**. In a typical synthesis procedure, 21.2 g of sodium metasilicate monohydrate dissolved in 100 ml DI water was combined with the appropriate amount of metal precursors like titanium oxysulfate hydrate and/or vanadyl sulfate hydrate (dissolved in 20 ml of 2 M H₂SO₄) for the titanium and vanadium sources, respectively. The resulting mixture was stirred vigorously for 30 minutes. Then, 2 M H₂SO₄ was added to the above mixture to adjust the pH to 10.5 with

constant stirring to form a uniform gel. After stirring, the solution containing 7.28 g of CTAB dissolved in 25 ml of DI water was added slowly into the above mixture and the combined mixture was stirred for three additional hours. The surfactant, cetyltrimethylammonium bromide (CTAB), was used as the structure-directing template. The resulting gel mixture was transferred into a Teflon coated autoclave and kept in an oven at 145°C for 36 hours. After cooling to the room temperature, the resulting solid was recovered by filtration, washed with DI water and dried in an oven at 80°C for 8 hours at least. Finally the organic template was removed by calcination at 550°C for 10 hours.

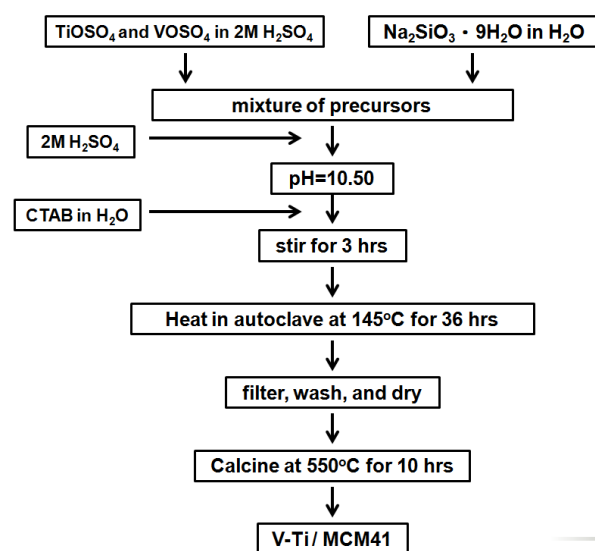


Figure 1: the synthesis procedure of V-Ti/MCM41.

The catalysts were analyzed by BET surface area and BJH pore size distribution. The phase and microstructure of MCM-41 were measured by X-ray diffraction (XRD). Furthermore, Raman spectroscopy was used to reveal the reaction intermediates of epoxidation.

Two kinds of analysis method were applied on cyclohexene epoxidation, one was off-line gas chromatograph (GC), and the other one was *in-situ* Raman spectroscopy. With different kinds of analysis methods, we try to compare the experimental results of cyclohexene conversion and the selectivity and yield 1,2-epoxycyclohexane. Also, we modified our reaction system in order to fit the analysis instruments.

In the lab of CSIC at Madrid Spain, the liquid-phase cyclohexene epoxidation experiments were performed in a three-neck reactor in a temperature-controlled oil bath. At beginning, 50mmol of tert-butyl hydroperoxide and 5 mol % of catalysts were mixed with the solution. Then, the reaction mixture was magnetically stirred and heated until the desired temperature. The reaction was started by adding 25 mmol of cyclohexene in the reactor. The reaction was held for 6 hours. During the reaction, the immersed Raman probe was immersing under the liquid level of solution to get the real-time Raman spectra.

Raman spectra were obtained with a single monochromator Perkin-Elmer Raman Station 400F system equipped with a thermoelectrically cooled CCD detector (-73°C) and Edge filter. The samples were excited with near-infrared 785 nm line. The spectral resolution was 3 cm^{-1} , and the spectrum acquisition was 6 accumulations of 10 seconds for each sample in every 10 minutes. The concentration of cyclohexene and 1,2-epoxycyclohexane were calculated by the evaluation Spectrum QUANT+ V4.51 software. At 20 different compositions of cyclohexene and 1,2-epoxycyclohexane were used in the calibration curves. The correlation coefficient R^2 of those calibration curves are more than 99% and the average errors of analysis are less than 2%.

The photo-catalytic cyclohexene epoxidation were operated in the same condition as thermal reaction, except the UV light irradiation and lower operating temperature (60°C). While we operate the photo-reaction, the UV light was irradiated from EXFO S1500 equipped with 200W mercury-arc lamp and guided by an optical fiber which can insert into the three-necked reactor. The light intensity was measured by Goldilux Radiometer/Photometer with UV-A probe. The light intensity we used in this research is $0.5\text{mW}/\text{cm}^2$ in UVA region. We collected the experimental results by GC analysis with different metal loading ratio catalysts.

3 Results and Discussion

3.1 Characteristics of Catalysts

Table 1 lists the surface area and average pore diameter of

V-Ti/MCM41. We can see that all of the BET surface area is around $850\text{ m}^2/\text{g}$, BJH average pore diameter are near 2.9 nm. From the results, we know that no matter the surface area or the pore size of the support of our catalyst were, the structure of MCM41 were very uniform in our preparation. Our catalysts were successfully synthesized with the same pore size distribution as shown in **Figure 2**. The pore of catalyst can provide the shape selectivity for olefin epoxidation.

Table 1: the Surface Area and Average Pore Diameter of V-Ti/MCM41.

Catalyst	BET Surface Area (m^2/g)	BJH Average Pore Diameter (nm)
V-Ti / MCM41 (2-0-100)	856	2.96
V-Ti / MCM41 (1.5-0.5-100)	815	3.04
V-Ti / MCM41 (1-1-100)	891	2.89
V-Ti / MCM41 (0.5-1.5-100)	841	2.89
V-Ti / MCM41 (0-2-100)	850	2.87

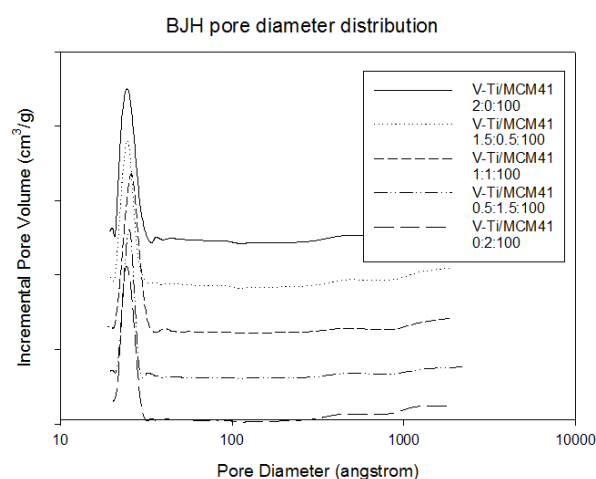


Figure 2: the Pore Size Distribution Curves of V-Ti/MCM41.

One of the characteristics of MCM41 is the hexagonal structure by XRD pattern. From the XRD patterns in **Figure 3**, the hexagonal structure of MCM41 was revealed by the small diffraction angle, 2θ , near 2.5 and 5 degrees. Most of the metal oxides might hide inside the hole, so we could not observe the peaks of bulk V_2O_5 and TiO_2 .

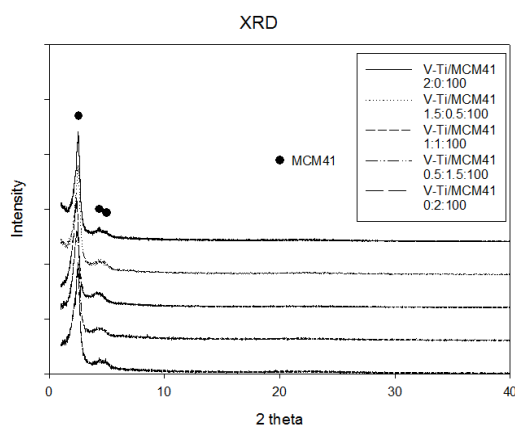


Figure 3: XRD Patterns of V-Ti/MCM41

Raman scattering indicates that there are no vibrations of V_2O_5 crystallites and of TiO_2 anatase or rutile phases on the surface of MCM-41, as shown in **Figure 4**. From Raman analysis, we could assume that all of those metal oxides are molecularly dispersed in internal/external surface of MCM-41.

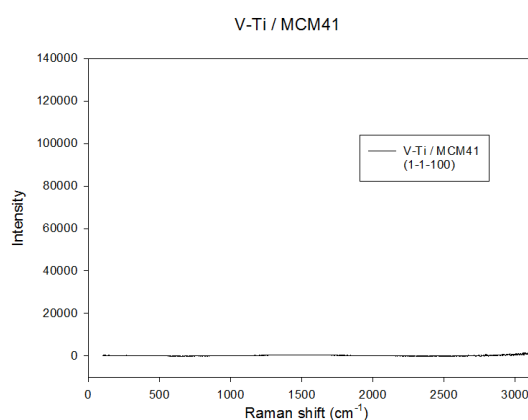


Figure 4: the Raman spectra of V-Ti/MCM41 (1-1-100)

3.2 Photo catalytic cyclohexene epoxidation of

V-Ti/MCM41

In the in-situ Raman monitoring system, we recorded spectra every 10-minute and draw a series of spectra to show the trend of reactants and products. At reaction temperature 80°C , the thermal driving force is high enough to activate the epoxidation of cyclohexene. Real-time Raman spectra in **Figure 5** clearly distinguishes the reactant (cyclohexene), the product (1,2-epoxycyclohexane) and the oxidant, tert-butyl hydroperoxide (TBHP). A chemometric analysis of spectra allows calculating selectivity and conversion values vs. run-time. As shown in **Figure 5**, the reactant, cyclohexene, was consumed, while the product, 1,2-epoxycyclohexane, was gradually increased during 6-hour thermal reaction. The oxidant was in excess, so its intensity hardly changed.

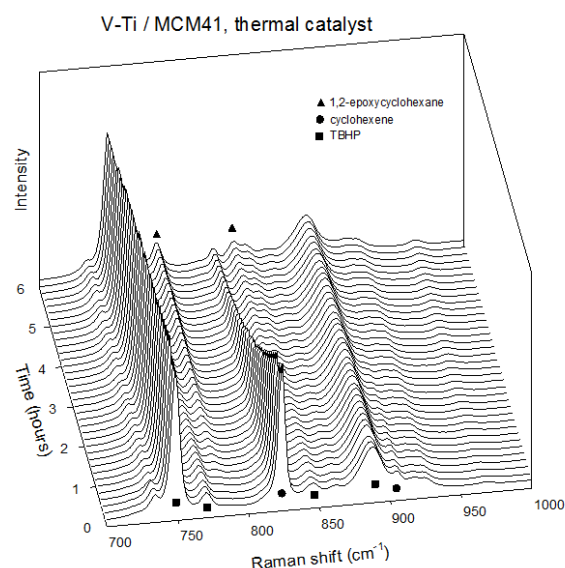


Figure 5: in-situ, real-time Raman spectra of cyclohexene epoxidation with thermal-reaction at 80°C .

GC analyses deliver the quantitative amounts of certain compounds by calibration curves, and calculate the cyclohexene conversion and the selectivity of 1,2-epoxycyclohexane. The results of thermal-catalytic cyclohexene epoxidation at 80°C for 6 hours on V-Ti/MCM41 (1-1-100) are listed in **Table 2**. The conversion of cyclohexene is higher than 50%, the selectivity of 1,2-epoxycyclohexane is more than 10%.

Table 2: Experiment Results of GC Analysis by

Thermal-Catalytic Epoxidation at 80°C

Conversion of Cyclohexene	58.35%
Selectivity of 1,2-epoxycyclohexane	10.87%

The GC analysis results of photo-catalytic cyclohexene epoxidation over different metal loading ratios are summarized in **Table 3**. We could see that the photo-catalyst V-Ti/MCM41 (1-1-100) has highest selectivity of 1,2-epoxycyclohexane, 23%, in photo-catalytic cyclohexene epoxidation at 60°C in the 6-hour photo epoxidation.

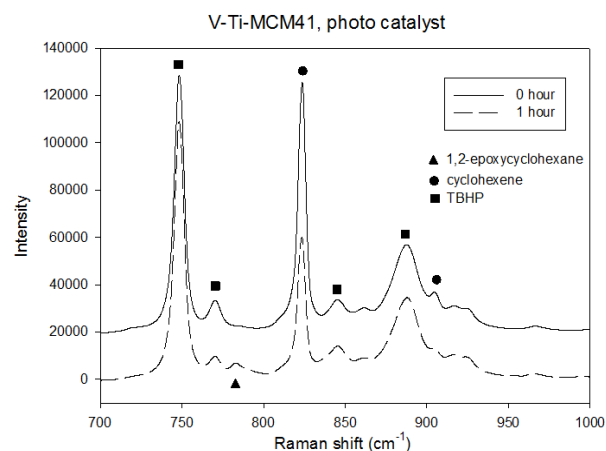
Table 3: Experiment Results of Photo Cyclohexene

Epoxidation at 60°C for 6 hours

Catalyst	Conversion of Cyclohexene	Selectivity of 1,2-epoxycyclohexane
V-Ti / MCM41 (2-0-100)	36.83%	3.98%
V-Ti / MCM41 (1.5-0.5-100)	43.49%	4.06%
V-Ti / MCM41 (1-1-100)	34.54%	23.15%
V-Ti / MCM41 (0.5-1.5-100)	38.29%	5.10%
V-Ti / MCM41 (0-2-100)	46.71%	3.38%

If the temperature is not high enough to activate the reaction, we can use UV light as driving force in addition of thermal activation. For cyclohexene epoxidation, V-Ti/MCM41 can switch its function from thermocatalyst to photocatalyst. By one-hour UV irradiation with 0.5 mW/cm² light intensity, we observed trace amounts of 1,2-epoxycyclohexane, which was our target product as shown in **Figure 6**. The Raman band located at 780 cm⁻¹ is

the most intense peak of 1,2-epoxycyclohexane.

**Figure 6:** the Raman spectra of cyclohexene epoxidation with photoreaction after 1 hour.

We can use GC analysis to analyze the experimental results with V-Ti/MCM41 (1-1-100) at different temperatures. **Table 4** lists the results of thermal and photo epoxidation reactions. The selectivity of 1,2-epoxycyclohexane is higher than thermal reaction with UV light source as driving force of epoxidation at 60° C. However, the selectivity of 1,2-epoxycyclohexane of photo-epoxidation at 25° C is not as high as that at 60° C. One of the reasons of such phenomenon might be the temperature effect to desorption of epoxide. Room temperature may not be high enough to enable epoxide desorption from the surface of catalyst, which would be the major reason of the low selectivity of epoxide.

Table 4: Thermal and Photo Cyclohexene Epoxidation with V-Ti/MCM41(1-1-100) for 6 hours

Temperature	Conversion of Cyclohexene	Selectivity of 1,2-epoxycyclohexane
80°C thermal reaction	58.35%	10.87%
60°C photo reaction	34.54%	23.15%
25°C photo reaction	19.72%	2.09%

4 Conclusion

In-situ real-time Raman analysis can reveal the evolution of concentration of organic compounds during a reaction. We can monitor the photo-catalytic reaction by in-situ Raman spectroscopy without the interference of UV light. Unfortunately, we have not find any interaction between organic compounds and the active sites on catalyst.

V-Ti/MCM41 (1-1-100) was the best catalyst for photo-catalytic cyclohexene epoxidation, which had highest selectivity while operating reaction at 60° C, 0.5 mW/cm² of UVA for 6 hours. Comparing the results with different driving forces and operating temperatures, we found that operating epoxidation with UV-light irradiation at 60°C gave higher 1,2-epoxycyclohexane selectivity.

In the future, we will explore the catalysts that have high selectivity of epoxide in thermal olefin epoxidation and photo-catalytic activity. Thus we can operate the cyclohexene epoxidation with lower temperature under light irradiation in order to increase product selectivity, and to save thermal energy by sunlight.

Acknowledgments

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