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Increased Selectivity for Allylic Oxidation of Cyclohexene Using TiO₂

Modified V₂O₅/MoO₃ Catalysts

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1. Introduction

The addition of oxygen to hydrocarbons is one of the simplest methods to manufacture value-added chemicals. Oxidation of hydrocarbons to epoxides, alcohols, aldehydes, and acids is a large category of catalytic organic reactions. For example, the oxidation of cyclic olefin, such as cyclohexene $(C_6H_{10}, (1))$, produces several oxygenated derivatives of great industrial interests, as shown in Scheme 1.[1] As a model compound, cyclohexene (1) is particularly interesting as it has two active groups in the molecule, namely the C-H bond at the allylic site and the C=C bond. In the epoxidation pathway, the C=C bond is oxidized leading to formation of cyclohexane oxide (2) and a subsequent hydration product cyclohexane-1,2-diol (3). In the allylic oxidation pathway, the C-H bond is attacked, resulting in formation of α, β unsaturated alcohol and ketone, namely 2cyclohexene-1-ol (4) and 2-cyclohexene-1-one (5). Both pathways are industrially important. The epoxidation pathway could eventually lead to the formation of adipic acid $((CH_2)_4(COOH)_2)$, a chemical intermediate with high market demand. [2, 3] The α , β unsaturated alcohol and ketone generated via allylic oxidation pathway are important intermediates in the fragrance industry and industrial organic synthesis.[4] Besides the industrial significance, understandings of the selective oxidation of cyclohexene could potentially help to design next generation catalysts for direct oxidation of hydrocarbons with two or more active groups.



Scheme 1. Catalytic oxidation of cyclohexene

MoO₃-based catalysts have been regarded as active catalysis for selective oxidation of hydrocarbons.[5, 6] Particularly, Mo^{6+}/Mo^{5+} pairs are considered catalytic centers where Mo^{6+} oxo-peroxo species catalyzes the oxidation reaction and is simultaneously reduced to $Mo^{5+}.[5, 7]$ The Mo^{5+} can be subsequently oxidized back to Mo^{6+} oxo-peroxo species by oxygen sources such as O₂ and H₂O₂,[8] The replenishing process can potentially benefit from the presence of vanadium oxides. When heated, the surface vanadium oxides can be re-dispersed to isolated VO₄ active sites.[9] These site isolated VO₄ species is known to help to replenish the oxygen vacancies. The synergistic effects between MoO₃ and V₂O₅ enable highly active catalysts for selective oxidation reactions.[10, 11]

Titanium silicalite-1 (TS-1) is commercially used to catalyze propylene to propylene oxide.[12] The presence of site-isolated Ti sites is believed important to improve the propylene epoxidation selectivity. Similarly, studies show that the presence of Ti sites favors the direct epoxidation pathway for selective oxidation of cyclohexene.[13] However, the selectivity could be affected by composition of materials and operation conditions. For example, high local concentration of H_2O_2 near Ti sites could lead to allylic oxidation pathway.[14] In other studies, Ti-grafted mesoporous silica catalysts favored allylic oxidation pathway. This study will focus at the effect of Ti in promoting V_2O_5 -MoO₃/SiO₂ for selective oxidation of cyclohexene.

Atomic layer deposition (ALD) is a thin film deposition technique.[15] Taking advantages of surface self-limiting reactions, it enables conformal coatings of nanoparticles and thin films on high surface area supports with atomic precision. This feature makes it a promising tool to precisely synthesize advanced heterogeneous catalysts with well-controlled structure.[16, 17] In this work, we used TiO₂ ALD to modify the surface the SiO₂ support. The presence of TiO₂ significantly suppressed the formation of cyclohexene oxide, leading to its selectivity decreased from 21% to 1.7%. This results in an increase in the selectivity to unsaturated alcohol and ketone from 67% to 79% at similar cyclohexene conversion.

2. Experimental

2.1. Catalyst Preparation

Silicycle S10040M SiO₂ with a surface area of ~ 100 m²/g was used as the catalyst support. TiO₂ ALD was performed by a viscous flow benchtop reactor (Gemstar-6, Arradiance) as described previously.[18] One ALD cycle of TiO₂ was deposited at temperatures of 200 °C using alternating exposure to titanium isopropoxide (TTIP, Sigma-Aldrich, 99.999%) and

deionized water. In this work, the resulting TiO_2 modified SiO_2 is represented as $1cTiO_2/SiO_2$. The growth rate of TiO_2 ALD is ~0.3 Å/cycle which corresponds to an estimated ~4 wt% loading of TiO_2 on SiO_2 .[19]

Deposition of V_2O_5 -MoO₃ composite oxide nanomaterials were carried out by hydrothermal deposition on SiO₂ and 1cTiO₂/SiO₂ as supports, respectively. 1.7421 g (1.410 mmol) (NH₄)₆Mo₇O₂₄·4H₂O (Sigma-Aldrich, 99.98%) and 0.1027 g (0.878 mmol) NH₄VO₃ (Sigma-Aldrich, 99.996%) were added to 50 mL of deionized water and the suspension was dissolved under stirring. After dissolved, stirring was continued for additional 15 minutes. Afterward, all 50 mL of the aqueous solution was added into 3 g of either the 1cTiO₂/SiO₂ or SiO₂, and mixed again for 15 minutes in order to make the support is very well covered with aqueous solution. As a result, the as-prepared catalysts contain 1 wt% V₂O₅ and 24 wt% MoO₃. Finally, the suspension was put in furnace at 100 °C for 19.5 hours, and the solid powder was immediately calcined at 600 °C for 3 hours. The as-prepared sample was sealed in a capped glass vail in the dark for further analysis or use.

2.2. Catalyst Characterization

Transmission electron microscope (TEM) images and energy dispersive x-ray spectroscopy (EDX) were obtained with a JEM-200CX microscope operated at 100 kV. The specimens for TEM were prepared by ultrasonically suspending the sample in acetone and depositing a drop of the suspension onto a grid. X-ray photoelectron spectroscopy (XPS) was performed in a PHI 5000 VersaProbe spectrometer equipped with an Al K α X-ray source in ultrahigh vacuum (UHV) (<10–10 Torr). Binding energies (±0.2 eV) were referenced to the C1s peak at 284.6 eV as graphite. X-ray diffraction (XRD) patterns were recorded on a Rigaku

MiniFlex 600 powder X-ray diffractometer equipped with a rotating anode using Cu K_{α} radiation (40KV, 15 mA). The Fourier transform infrared (FT-IR) spectra of the samples were recorded on a ThennoNicolet NEXUS870 FT-IR instrument (KBr discs) in the 4000–400 cm⁻¹ region.

2.3 Catalyst Activity Test

The liquid phase catalytic oxidation of cyclohexene was carried out in a magnetically stirred round-bottom flask (25 mL) connected to a reflux condenser. 5 mmol of cyclohexene, 10 mL of acetonitrile, 0.5 mmol of o-dichlorobenzene (o-DCB) as internal standard, and 10 mg of catalyst were placed into the glass flask. The reaction was initiated by adding 30 wt% H₂O₂ solution with vigorous stirring. The quantitative analysis of reactants and products was performed on a Shimadzu GC2014 gas chromatograph equipped with a WondaCAP-5 capillary column (5% Diphenyl 95% Dimethylpolysiloxane 30m×0.32mm×0.25µm) with a flameionization detector. A Shimadzu GCMS-QP2010 was used to identify substrates and their oxidation products resulting from catalysis. Cyclohexane oxide, cyclohexane-1,2-diol, 2cyclohexene-1-ol and 2-cyclohexene-1-one are identified as major oxidation products. Other byproducts include adipaldehyde, 2,3-epoxycyclohexanol and 2,3-epoxycyclohexanone. Pristine SiO₂, TiO₂/SiO₂, and titanium silicalite (TS-1) were tested under reaction conditions as control experiments. The cyclohexene conversion was negligible. In the reusability measurements, the spent catalysts were recycled using high-speed centrifugation, washed by diethyl ether, and dried at 60 °C overnight.

3. Results and Discussion

3.1. Catalyst Characterization

Figure 1 shows the HR-TEM images of V_2O_5 -MoO₃@SiO₂ and V_2O_5 -MoO₃@(TiO/SiO₂) catalysts, respectively. For V_2O_5 -MoO₃@SiO₂ catalyst, spherical shape MoO₃ nanoparticles of ~13.2 nm in diameter are supported by SiO₂ gel. Due to the higher Z-number, MoO₃ appears to be darker spheres. The HR-TEM images show clear crystalline structure of MoO₃ with a plain distance of 3.35 Å, consistent with the (021) facet of MoO₃. Interestingly, for V_2O_5 -MoO₃@(TiO/SiO₂) catalysts, the MoO₃ appears in the shape of nanorod with a length of ~20.8 nm and width of ~6.4 nm. The surface of the nanorod also shows a fringe of ~3.35 Å, similar to what was observed to MoO₃ in the V_2O_5 -MoO₃@SiO₂ catalysts. EDX measurements were carried out on both catalysts to qualitatively determine the purity of the samples (please see Figure S1 in the Supplemental Information (SI)). While there were V, Mo, Ti and Si in V_2O_5 -MoO₃@(TiO/SiO₂) catalysts, only V, Mo and Si were detected in V_2O_5 -MoO₃@SiO₂ catalysts.



Figure 1. TEM (up, left) and HRTEM (down, left) images of V2O5-MoO3@SiO2. TEM (up,

right) and HRTEM (down, right) images of V2O5-MoO3@(1cTiO2/SiO2).

The purity of the sample was further confirmed using XPS survey scans (please see Figure S2 in the SI). The elements observed in each sample were consistent with the EDX results. Figure 2 and Table 1 compared the Mo 3d spectra obtained from the as-prepared and spent samples. Mo $3d_{5/2}$ and $3d_{3/2}$ spin-orbit splitting of doublets were observed in Mo 3d XPS spectra. The difference in binding energy between the doublets is 3.1 eV which matches well with the literature values for Mo oxides. [20] In the as-prepared catalysts, only one component appears at binding energies of Mo 3d_{5/2} peak at 232.9 eV and commonly assigned to Mo⁶⁺ species in octahedral coordination. The used V_2O_5 -MoO₃@SiO₂ catalysts have three components which can be ascribed to Mo^{5+} species (232.3 eV), Mo^{6+} species in an octahedral coordination (233.0 eV), and Mo^{6+} species in tetrahedral coordination (233.6 eV). With the additional of TiO₂, the used V_2O_5 -MoO₃@(TiO/SiO₂) catalysts only have two components which are Mo⁵⁺ species (232.3) eV) and Mo⁶⁺ species in the octahedral coordination (233.0 eV). During the allylic oxidation reaction, both catalysts were partially reduced from Mo⁶⁺ to Mo⁵⁺. The Mo⁵⁺ components accounts for 68.3% and 71.3% of the molybdenum species in the used V₂O₅-MoO₃@SiO₂ and V_2O_5 -MoO₃@(TiO/SiO₂), respectively. The presence of Mo^{6+/}Mo⁵⁺ pairs is consistent with the literature where the pairs are considered as catalytic centers.

V $2p_{3/2}$ and $2p_{1/2}$ spin-orbit splitting of doublets were observed with a difference in binding energy of 7.6 eV (please see Figure S3 in SI). The as-prepared catalysts have two components of vanadium, i.e., V⁵⁺ (518.0 eV) and V⁴⁺ (517.0 eV).[21] The V⁵⁺ : V⁴⁺ ratio is about 1 : 1 in the as-prepared catalysts. Due to the low loading of vanadium and possible

leaching during the allylic oxidation reaction, the signal-to-noise of vanadium XPS spectra is not sufficient to provide meaningful discussion, and therefore is not presented.

	VMo@SiO ₂	VMo@(TiO ₂ /SiO ₂)	VMo@SiO ₂ used	VMo@(TiO ₂ /SiO ₂) used	
	BE (eV)	BE (eV)	BE (eV)	BE (eV)	
Mo 3d _{5/2}	232.9	232.9	232.3 233.0 233.6	232.4 233.1	Mo ⁵⁺ Octahedral Mo ⁶⁺ Tetrahedral Mo ⁶⁺
V 2p _{3/2}	518.0 517.0	518.0 517.0	2	-	$\begin{matrix} V^{5+} \\ V^{4+} \end{matrix}$

Table 1. The binding energies of Mo $3d_{5/2}$ and V $2p_{3/2}$ excitation.



Figure 2. Mo 3d XPS spectra of the fresh and used catalysts.

XRD was used to probe the structure of the as-prepared catalysts. The as-prepared catalysts contain α -MoO₃ structure, as shown in Figure 3a, which matches well with the XPS data fittings. Figure 3b shows several features determined using FT-IR spectroscopy. Two

features can be ascribed to the presence of SiO₂, including the Si-O-Si stretch vibration mode (1103 cm⁻¹) and Si-O-Si rocking mode (471 cm⁻¹). [22] The feature at 868 cm⁻¹ is likely the symmetric stretching mode of Mo-O-Mo and the Si-O-Si bending mode. The feature at 819 cm⁻¹ is attributed to the stretching mode of vibration of asymmetric bridging oxygen in Mo-O-Mo. [23] The feature at 990 cm⁻¹ is assigned to the Mo=O characteristic stretching vibration of α -MoO₃.[24] The loading of vanadium and titanium were probably too low to be detected by IR spectroscopy.



Figure 3. (a) XRD patterns and (b) FT-IR spectrums of the catalysts. *Red line*: V_2O_5 -MoO₃@(1cTiO₂/SiO₂). *Black line*: V_2O_5 -MoO₃@SiO₂.

3.2. Catalyst Performance Evaluation

Reaction conditions such as the choice of solvent, reaction temperature, amount of catalysts in use, hydrogen peroxide to cyclohexene ration were optimized by carrying a series of controlled experiments. Table S1 shows the results obtained by testing nine different solvents. including acetone (CH₃COCH₃), methanol (CH₃OH), ethanol (CH₃CH₂OH), acetonitrile (CH₃CN), dichloromethane (CH₂Cb), chloroform (CHCl₃), tetrahydrofuran ((CH₂)₄O, THF), benzonitrile (C_6H_5CN), and water (H_2O). The non-polar solvent chloroform favored the formation of cyclohexene oxide. The polar protic solvents (methanol, ethanol, and water) resulted in high selectivity to α , β unsaturated alcohol or ketone and the selectivity to cyclohexene oxide decreased with increasing solvent dielectric constant (DC). However, neither non-polar nor polar protic solvents were ideal solvents for selective oxidation of cyclohexene as they suffered from lower cyclohexene conversion (1% - 2%). Polar aprotic solvents in general offered higher cyclohexene conversion as compared to non-polar and polar protic solvents. However, the reaction pathway seemed independent of dielectric constant of the polar aprotic solvents. While dichloromethane (DC = 9.1) and benzonitrile (DC = 26.0) favored the formation of cyclohexene oxide, other polar aprotic solvents (DC = 7.5 - 37.5) resulted in the formation of α , β unsaturated alcohol or ketone. In terms of reaction activity, highest conversion (11%) was achieved when acetonitrile was used as the solvent. Therefore, acetonitrile was chosen as the solvent for the rest of the study due to its 94% combined selectivity towards α , β unsaturated alcohol and ketone and a relative high conversion.

The proper reaction temperature was determined by evaluating the catalysts in temperature range from 35 °C to 75 °C with 10 °C interval (please see Figure S4). The conversion increases with increasing reaction temperature. After 10 h, the conversion of the reaction at 75 °C almost reaches 100% while the conversion at 35 °C is only 24%. In terms of

selectivity, high temperature favors epoxidation pathway forming epoxy and diol and low temperature favors allylic oxidation pathway forming α , β unsaturated alcohol and ketone. With increasing reaction temperature, the combined selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-1-one gradually decreased from 83% at 35 °C to 23% at 75 °C. Particularly, at 75 °C the selectivity to cyclohexane-1,2-diol increases significantly to 58% with minimal cyclohexane oxide. It implies that high temperature favors epoxidation pathway and significantly improves the reaction rate of the subsequent hydration to form cyclohexane-1,2-diol. As a result, a reaction temperature of 55 °C was chosen to carry out future catalyst evaluations due to its relatively high conversion and combined selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-1-one.

The proper amount of catalyst used in the reaction was evaluated 55 °C, as shown in Figure S5. The conversion of cyclohexene is negligible when no catalyst is added. The conversion increases with increasing the amount of catalyst from 0 mg to 20 mg. However, the conversion decreases when the amount of catalyst further increases. The conversion decrease is probably because the catalyst starts to effectively accelerate the disproportionation of H₂O₂ into O₂ and H₂O. In addition, the selectivity to cyclohexane-1,2-diol increases from 10% to 34% when the amount of catalyst increases from 5 mg to 40 mg. As a consequence, 10 mg - 20 mg catalysts were determined to be the proper quantity of catalysts to be used in the reaction.

The effect of H_2O_2 was studied by varying the H_2O_2 /cyclohexene ratio from 0.5, 1, 1.5 to 2.0 (please see Figure S6). Under H_2O_2 poor condition (H_2O_2 : cyclohexene = 0.5 : 1), the combined selectivity to 2-cyclohexene-1-ol and 2-cyclohexene-1-one are 91% without any production of cyclohexane-1,2-diol. The selectivity to 2-cyclohexene-1-one decreased with

increasing H_2O_2 molar ratio of hydrogen peroxide to cyclohexene. Excess amount of H_2O_2 did not significantly cause formation of diol and other byproducts.

 V_2O_5 -MoO₃@SiO₂ and V_2O_5 -MoO₃@(TiO/SiO₂) catalysts were then evaluated using the optimized reaction conditions determined by the controlled experiments. The results are shown in Figure 4. The presence of TiO₂ significantly suppressed the epoxidation reaction and the formation of cyclohexene oxide, leading to decrease in selectivity from 21% to 1.7%. The lowering of cyclohexene oxide selectivity results in an increase in the selectivity to unsaturated alcohol and ketone from 48% to 79% at similar cyclohexene conversion. The presence of TiO₂ also decreases the selectivity to diol from 22% to 15% and selectivity to other byproduct from 9.2% to 4.0%.

The reusability of the V₂O₅-MoO₃@(TiO/SiO₂) catalysts were tested for five times. The conversion of cyclohexene gradually decreases from 63% at the initial entry to 46% at the fifth recycle, and the selectivity to cyclohexane oxide increases from 2% to 13%. This is probably due to the leaching of active components such as TiO₂ during the reaction and recycling process, which was observed in previous studies. [14, 25] Because of the possible TiO₂ leaching during each entries, the composition of V₂O₅-MoO₃@(1cTiO₂/SiO₂) catalyst gradually became similar to the unmodified V₂O₅-MoO₃@SiO₂ catalyst, causing the reaction pathway shifted from allylic oxidation to epoxidation.

The behavior of V_2O_5 -MoO₃@SiO₂ catalyst with and without TiO₂ ALD coating is very different. According to these preliminary results, it appears that the TiO₂-modified V₂O₅-MoO₃@SiO₂ catalyst does not alter the reactivity but significantly suppresses the epoxidation

reaction pathway. Work is in progress to elucidate these differences and overcome the challenge of materials leaching during the reaction.



Figure 4. Catalysts performance (left) and reusability (right). (Reaction conditions: Cyclohexene 5mmol, the molar ratio of hydrogen peroxide to cyclohexene is 1.5, catalyst 10 mg, acetonitrile 10 mL, 55 °C, 10 h. The catalyst was separated by centrifugation after the previous run, dried at 100 °C under vacuum and then subjected to the following run under the same conditions.

4. Conclusions

Selective oxidation of cyclohexene was investigated for SiO₂ supported V₂O₅-MoO₃ mixed oxide catalysts. It is feasible to tune the reaction pathway between epoxidation and allylic oxidation by the choice of solvents. Under the conditions studied in this work, low temperature, low H₂O₂/cyclohexene ratio, and small amount of catalyst in use favors allylic oxidation pathway. Upon modification of the SiO₂ surface with one ALD cycle of TiO₂, the V₂O₅-MoO₃@(1cTiO₂/SiO₂) catalyst showed good activity in allylic oxidation of cyclohexene compared with its unmodified counterpart V₂O₅-MoO₃@SiO₂. The epoxidation pathway is

largely suppressed with the presence of TiO_2 on the SiO_2 surface, resulting in increased selectivity to the unsaturated alcohol and ketone, namely 2-cyclohexene-1-ol and 2-cyclohexene-1-one. Catalyst leaching from V_2O_5 and TiO_2 decreases both the conversion and the selectivity to the allylic oxidation products.

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Appendix A. Supplementary Data

Supplementary data to this article can be found online at http://dx.doi.org/xx.xxxx/j.catcom.2017.xx.xxx.

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Graphical abstract



Keywords: cyclohexene, allylic oxidation, epoxidation, atomic layer deposition, mixed metal oxides, zeolite

Cr.

Highlights

- V₂O₅-MoO₃ mixed oxides are effective catalysts for selective oxidation of cyclohexene ۰
- Atomic layer deposition was used to precisely deposit a uniform layer of TiO₂ •
- The presence of TiO₂ significantly suppressed the formation of byproducts •
- The reaction pathways can be controlled by tuning reaction conditions •

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