

Research Article

Zinc Acetate Immobilized on Mesoporous Materials by Acetate Ionic Liquids as Catalysts for Vinyl Acetate Synthesis

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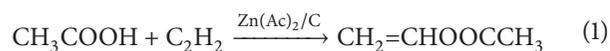
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Ionic liquid containing active ingredient $\text{Zn}(\text{CH}_3\text{COO})_2$ was loaded in mesoporous silica gel to form supported ionic liquids catalyst (SILC) which was used to synthesize vinyl acetate monomer (VAM). SILC was characterized by ^1H NMR, FT-IR, TGA, BET, and N_2 adsorption/desorption and the acetylene method was used to evaluate SILC catalytic activity and stability in fixed reactor. The result shows that 1-allyl-3-acetic ether imidazole acetate ionic liquid is successfully fixed within mesoporous channel of silica gel. The average thickness of ionic liquid catalyst layer is about 1.05 nm. When the catalytic temperature is 195°C , the acetic acid (HAc) conversion is 10.9% with 1.1 g vinyl acetate yield and 98% vinyl acetate (VAc) selectivity. The HAc conversion is increased by rise of catalytic temperature and molar ratio of C_2H_2 : HAc and decreased by mass space velocity (WHSV). The catalyst activity is not significantly reduced within 7 days and VAc selectivity has a slight decrease.

1. Introduction

Vinyl acetate (VAc), an important organic chemical raw material, is widely used in production of polyvinyl acetate emulsion and resin, polyvinyl alcohol, ethylene-vinyl acetate copolymer, vinyl chloride-vinyl acetate copolymer, and polyacrylate plasmodium [1, 2]. Nowadays, ethylene method and acetylene method are used in synthesis of vinyl acetate monomer in industry [3, 4]. In china, coal resource is relatively more abundant than petroleum. As a result, acetylene method is cheaper than ethylene. Therefore, acetylene method has a dominant position in china. In the word, there is about 30% yield of vinyl acetate using acetylene method:



In industry, vinyl acetate (VAc) is synthesized using catalyst of zinc acetate loading activated carbon and synthetic raw materials are acetic acid (HAc) and acetylene [5]. The reaction equation is shown in (1) [6]. In synthesis of vinyl acetate, pore structure of activated carbon supporter has a significant influence on the catalytic activity. Some scholars believe that the catalytic process occurs in mesopore of activated carbon and not in micropore [7]. Although

the surface area of activated carbon is above $1000 \text{ m}^2/\text{g}$ specific surface area and contains rich hole space, the major pore of activated carbon is slim and distortion micro-structure. It is difficult for reactants to enter catalytic pore field and products to leave. The zinc acetate is loaded in carbon pore by physical adsorption. It does likely lead to the loss of zinc acetate during the catalytic reaction.

Ionic liquids (ILs) are ascribed to their distinguished advantages such as chemical and thermal stability, wide liquid phase extent (-40 to 300°C), nondetectable vapor pressure, high dissolvability, great conductivity, and structure adjustment [8]. Ionic liquids can be applied in many areas: liquid-liquid extraction, preparation of nanoparticles [9], environmental protection, chemical catalytic reaction [10], and so on. However, application of ionic liquid is severely suppressed because it is expensive and each experiment costs large amount.

Supported Ionic Liquids Catalyst (SILC) is that ionic liquids containing active center is immobilized in solid supporters [11, 12]. SILC can be used in hydrogenation reaction [11], hydroformylation of propene [13], esterification reaction [14], cyclic carbonate from CO_2 and epoxide [15], and so on. Immobilization can effectively prevent the loss of ionic

liquids in catalytic process and reduce amount of ionic liquids used. SILC can be able to expand the field of catalytic reaction which has the liquid/solid dual catalytic characteristics.

In this study, ionic liquid containing active ingredient, zinc acetate, was loaded in mesoporous silica gel to form SILC which was used to synthesize vinyl acetate monomer (VAM). The $^1\text{H NMR}$, FT-IR, TGA, BET, and N_2 adsorption-desorption were used to characterize ionic liquid and SILC structure. The acetylene method could be used to evaluate SILC catalytic activity and stability in fixed reactor.

2. Experimental

2.1. Materials. 1-Allyl-3-acetic ether imidazole acetate ionic liquid (98%) and 3-mercaptopropyl trimethoxysilane (MPTMS, 97%) were purchased from J&K Scientific Ltd. Mesoporous silica gel (MSG), azodiisobutyronitrile (AIBN), and zinc acetate were purchased from Beijing Chemical Co. All the reagents were used in experimental process without purification. Acetylene gas (99%) was purified by NaOH (20%), silica gel, and activated carbon to remove impurities and H_2O before catalytic reaction.

2.2. Supported Ionic Liquids Catalyst (SILC) Preparation. Supported ionic liquids catalyst (SILC) was prepared following methods reported in the literature [16, 17]. 1-Allyl-3-acetic ether imidazole acetate ionic liquid (IL) and zinc acetate were mixed at 50°C for 12 h. When all the zinc acetate was dissolved in IL, the IL containing active ingredient, $[\text{Zn}(\text{Ac})_2\text{-IL}]$, was acquired. Mesoporous silica gel (MSG) and 3-mercaptopropyl trimethoxysilane (MPTMS) were mixed at 80°C for 24 h. After reaction, the yellow MPTMS/MSG was obtained. The MPTMS/MSG, $\text{Zn}(\text{Ac})_2\text{-IL}$, azodiisobutyronitrile (AIBN), and acetonitrile were added in 200 mL round bottom flask with magnetic stirring at 50°C for 48 h. After linking reaction, the supported ionic liquids catalyst (SILC) was obtained to apply for synthesis of vinyl acetate.

2.3. SILC Characterization. Fourier transform infrared spectrophotometer (FT-IR) analyses were carried out on a NEXUS-670 Fourier transform infrared spectrophotometer (Thermo Nicolet, USA) in a frequency range of $400\text{--}4000\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} , a scanning number of 100, and KBr as a reference. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a STA-409 PC TG-DSC/DTA thermal analyzer (NETZSCH-Gerätebau, Germany), with a heating rate of $15^\circ\text{C}/\text{min}$ from 50 to 800°C . Nitrogen adsorption-desorption isotherms were determined at 77 K using an Autosorb iQ porosimeter. Prior to measurement, the sample was degassed at 200°C for 2 h. Specific surface areas and pore distributions were calculated using the BET (Brunauer-Emmett-Teller) and NLDFT (nonlocal density functional theory) methods, respectively. The products were analyzed by gas chromatogram (Techcomp Chromatogram Co., China).

2.4. Catalytic Performance. Vinyl acetate was synthesized using $\text{Zn}(\text{Ac})_2\text{-IL}/\text{MSG}$ catalyst at microfixed bed reactor.

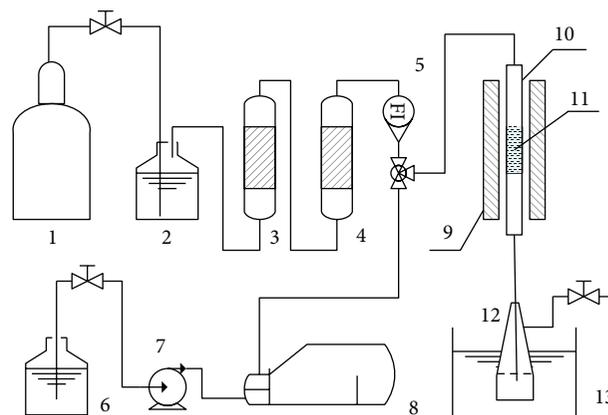


FIGURE 1: Schematic diagram of vinyl acetate synthesis. 1: acetylene gas; 2: 20% NaOH solution; 3: silica gel; 4: activated carbon; 5: gas flowmeter; 6: acetic acid; 7: dual piston metering pump; 8: gasifier; 9: heating device; 10: reaction tube; 11: catalyst layer; 12: collector; 13: ice-water bath.

Schematic diagram of vinyl acetate synthesis was shown in Figure 1. From Figure 1, acetic acid was pumped to heating device by dual piston metering pump which could measure liquid flow rate. The acetylene gas which had been purified was mixed with acetic acid vapor into microfixed bed reactor. The gas flow of acetylene was controlled and measured by gas flow meter. The fixed bed reactor was a stainless steel tube with an inner diameter of 8 mm and a length of 400 mm. The 1 g $\text{Zn}(\text{Ac})_2\text{-IL}/\text{MSG}$ catalyst and 4 g quartz sand were uniformly mixed and filled in the middle of fixed bed reactor. The quartz sand is an inert media. The vinyl acetate synthesis is an exothermic reaction and quartz sand can dilute catalyst to prevent catalyst local overheating and deactivation. The reaction temperature was controlled by the heating device and thermocouple inserted in the middle of fixed bed reactor. After reaction, the gas products were cooled from gas phase to liquid in ice-water bath. The liquid products were measured using chromatography to determine the content of vinyl acetate. The column was PEG-20M ($\Phi 0.32 \times 20\text{ m}$) with FID detector. The expression of conversion and selectivity of VAc are as follows:

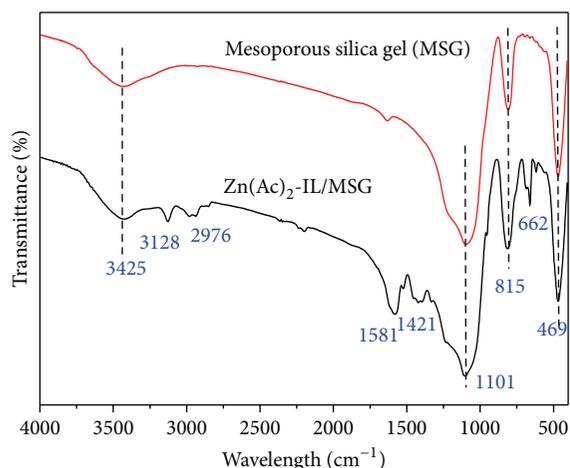
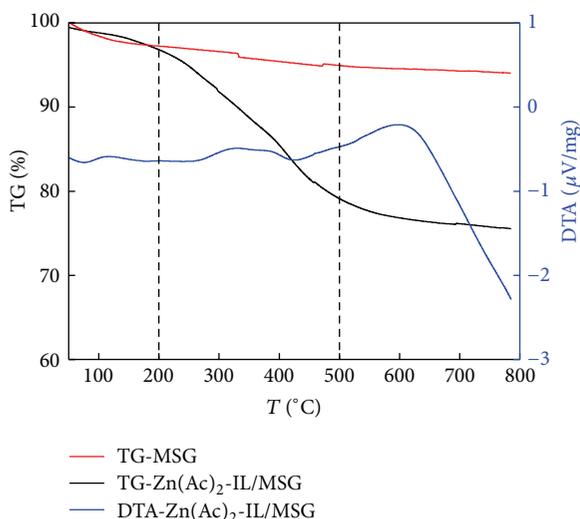
$$X_{\text{HAc}} = \frac{m_{\text{VAc}}}{m_{\text{HAc}(i)}} \times 100\% \quad (2)$$

$$S_{\text{VAc}} = \frac{m_{\text{VAc}}}{(m_{\text{HAc}(i)} - m_{\text{HAc}(o)})} \times \frac{M_{\text{HAc}}}{M_{\text{VAc}}} \times 100\%.$$

From (2), m_{VAc} is vinyl acetate cumulative mass within 24 hours in liquid products. $m_{\text{HAc}(i)}$ is HAc feed mass dosage within 24 hours. $m_{\text{HAc}(o)}$ is acetic acid cumulative mass within 24 hours in liquid products. M_{HAc} is the molecular weight of HAc. M_{VAc} is the molecular weight of vinyl acetate.

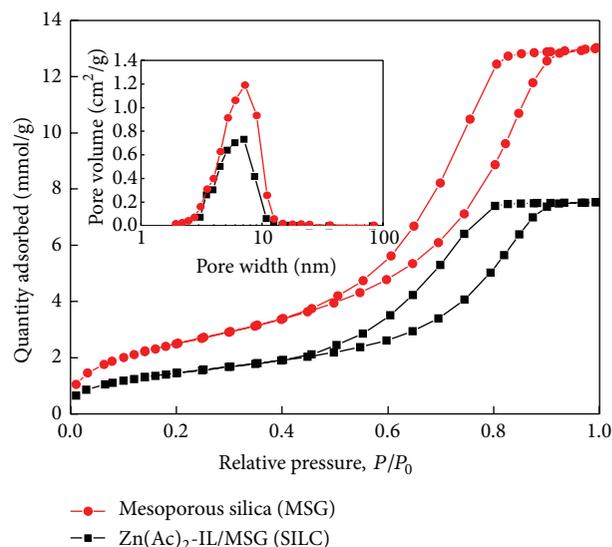
3. Results and Discussion

3.1. Catalyst Characterization. FT-IR spectra of $\text{Zn}(\text{Ac})\text{-IL}/\text{MSG}$ and MSG are shown in Figure 2. The characteristic absorption peaks of MSG at 3425 cm^{-1} , 1101 cm^{-1} , 815 cm^{-1} ,

FIGURE 2: FT-IR of $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ and MSG.FIGURE 3: TG-DTA of $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ and MSG.

and 469 cm^{-1} are assigned to the stretching vibration of surface hydroxyl, stretching vibration of Si-O, bending vibration of O-H, and bending vibration of Si-O, respectively. These characteristic absorption peaks are equally observed in $\text{Zn}(\text{Ac})\text{-IL/MSG}$. The absorption peaks of $\text{Zn}(\text{Ac})\text{-IL/MSG}$ at 3128 cm^{-1} and 2976 cm^{-1} are assigned to the stretching vibration of C-H, and the bands at 1581 cm^{-1} and 1421 cm^{-1} are assigned to the stretching vibration absorption of C=N bond in imidazole ring. The absorption peak at 662 cm^{-1} is bending vibration of C-S bond. From the FT-IR analysis, ILs are successfully loaded in MSG.

TGA curves for $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ catalyst and MSG are shown in Figure 3. From Figure 3, thermal decomposition of $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ catalyst presents three parts. Firstly, $50\text{--}200^\circ\text{C}$ part is the loss of adsorbed water or organic matter. Loss of quality is 3.5%. $200\text{--}500^\circ\text{C}$ part is the loss of ILs in $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ catalyst. The loss of quality is 24%. SILC is severely damaged in this stage. In addition, above 500°C , there is not any loss but there is a great peak due to crystal

FIGURE 4: N_2 adsorption-desorption isotherms and pore diameter distributions of $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ and MSG.

transition of MSG. Based on TG-DTA findings, $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ catalyst can be used below 200°C .

Figure 4 shows the N_2 adsorption-desorption isotherms and pore diameter distributions of $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ and MSG. BJH distributions and BET surface were calculated using N_2 adsorption at 77 K. Both of samples displayed a type IV isotherm with HI hysteresis loop and a sharp increase in pore volume adsorbed above $P/P_0 \sim 0.9$, which is typical characteristic of highly ordered mesoporous materials. Functionalization of basic ionic liquid catalyst significantly affected the surface area and pore distribution of MSG and pore volume is significantly smaller. The MSG sample showed a maximum pore diameter at 9.4 nm and surface area of $329.8\text{ m}^2\text{ g}^{-1}$. After functionalization of basic ionic liquid, the maximum pore diameter and surface area of the sample $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ decreased to 7.3 nm and $121.2\text{ m}^2\text{ g}^{-1}$, respectively. The thickness of ionic liquid catalyst layer is about 1.05 nm in MSG pore.

3.2. Catalyst Activity. The effect of reaction temperature on conversion and selectivity is shown in Figure 5. It can be seen from Figure 5 that, with increasing reaction temperature, HAc conversion and vinyl acetate product increase and VAc selectivity decreases. As the reaction temperature rises up to 195°C , the HAc conversion is 10.9% with 1.1 g of vinyl acetate yield and 98% of VAc selectivity. The VAc selectivity does not reach 100%. This can be ascribed to the fact that a small amount of HAc is not liquefied and is taken away by acetylene gas stream. According to the TG analysis of $\text{Zn}(\text{Ac})_2\text{-IL/MSG}$ catalyst, the catalyst shows serious disaggregation at high temperature. So, the usage temperature of catalyst should not exceed 200°C .

The molar ratio of acetylene to acetic acid on catalytic performance is shown in Figure 6 with fixed 1.36 h^{-1} WHSV and 195°C . The increase of acetylene and acetic acid molar ratio

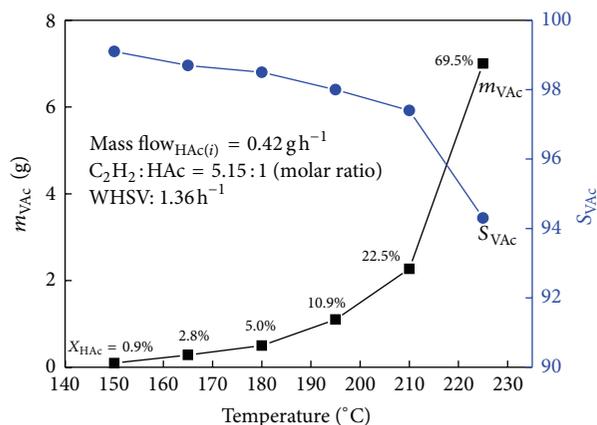


FIGURE 5: Effect of reaction temperature.

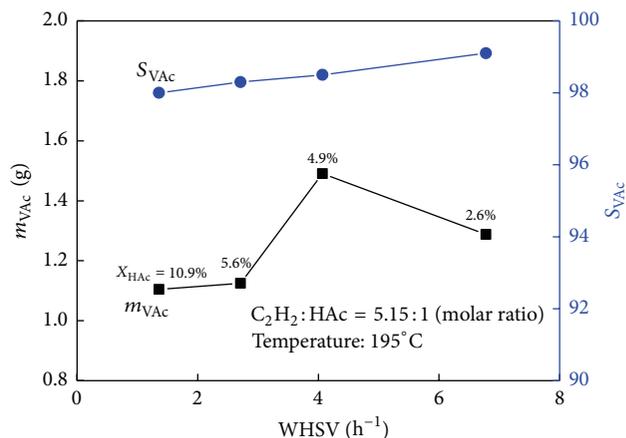


FIGURE 7: Effect of WHSV.

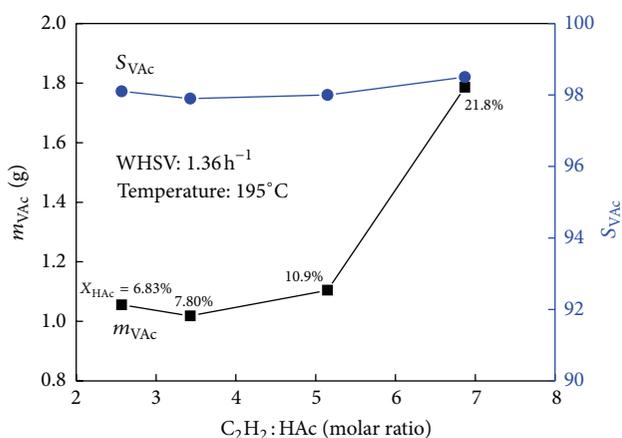
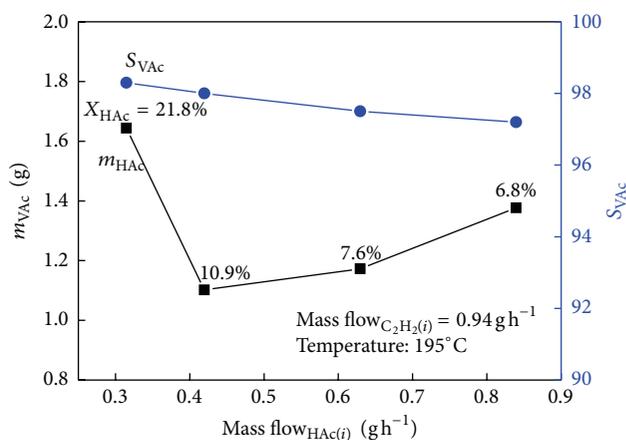
FIGURE 6: Effect of $C_2H_2:HAc$ (molar ratio).

FIGURE 8: Effect of feed mass flowrate.

is an advantage for HAC conversion. With the molar ratio increase, 24-hour cumulative mass of VAc firstly decreases and then increases. The selectivity of VAc stays almost invariable. With the 1.36 h^{-1} WHSV, the increase in molar ratio increases the feed amount of acetylene and reduces HAC. It is favorable for HAC conversion to add C_2H_2 feed and reduce HAC. The tendency of minimum cumulative mass of vinyl acetate with increase of $C_2H_2:HAc$ (molar ratio) is impacted by the decline of acetic acid feed and the improvement of acetic acid conversion.

The effect of WHSV on catalytic performance at given $5.15:1\ C_2H_2:HAc$ (molar ratio) and 195°C is shown in Figure 7. Clearly, as WHSV increases from 1.36 h^{-1} to 6.78 h^{-1} , the HAC conversion drops from 10.9% to 2.6% and the selectivity rises from 98% to 99%. At 4.07 h^{-1} WHSV, the 24-hour cumulative mass of VAc results in maximum yield (1.49 g). Therefore, it is beneficial for VAc selectivity to increase WHSV. The appearance of maximum cumulative mass of vinyl acetate with WHSV increase is the combinative effect of the decrease of acetic acid conversion and the improvement of feeds of C_2H_2 and HAC.

Figure 8 shows the effect of HAC mass flow on catalytic performance at known 0.94 g h^{-1} mass flow of C_2H_2 and

195°C . The selectivity of VAc and conversion of HAC decrease from 98% to 97% and from 21.8% to 6.8%, respectively. The 24-hour cumulative mass of VAc shows minimum value 1.10 g at 0.42 g h^{-1} of HAC mass flow. This is because the increase of HAC mass flow is not beneficial for HAC conversion. However, the increase of HAC mass flow can improve the VAc yield. In influence of the dual role, the minimum yield of VAc occurs.

The lifetime experiment of catalyst is shown in Figure 9. From Figure 9, it is obvious phenomenon that catalyst activity is not significantly reduced with 7 days and VAc selectivity has a slight decrease.

4. Conclusions

Ionic liquid containing active ingredient $Zn(Ac)_2$ was loaded in mesoporous silica gel to form supported ionic liquids catalyst (SILC) which was used to synthesize vinyl acetate monomer (VAM). The 1-allyl-3-acetic ether imidazole acetate ionic liquid was successfully fixed in mesoporous channel of silica gel. The average thickness of ionic liquid catalyst layer is about 1.05 nm. The catalytic temperature should not exceed 200°C . When the catalytic temperature is 195°C , the HAC conversion is 10.9% with 1.1 g vinyl acetate yield and 98% VAc

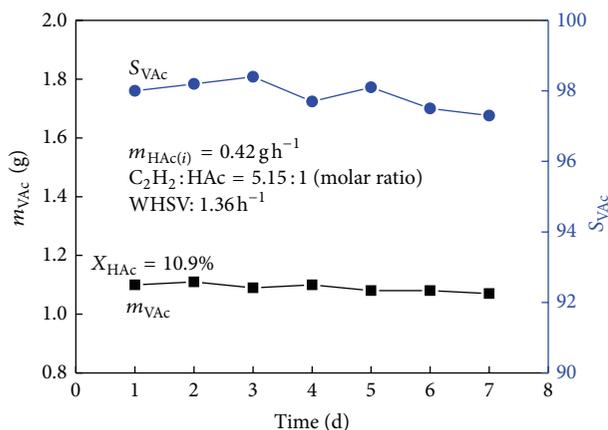


FIGURE 9: Lifetime experiment of catalyst.

selectivity. The HAc conversion is increased by rise of catalytic temperature and molar ratio of $C_2H_2 : HAc$ and decreased by WHSV. The catalyst activity is not significantly reduced with 7 days and VAc selectivity has a slight decrease.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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