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Clean Synthesis of Ti-MWW by Utilizing the Recycled Mother Liquor

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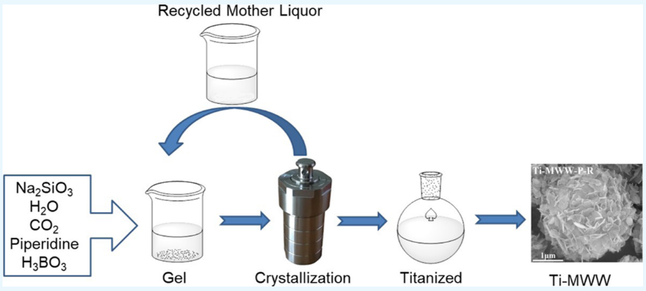
ABSTRACT: This article introduces a clean and efficient method for the synthesis of Ti-MWW by utilizing the recycled mother liquor. The effects of titanium and silicon sources on the synthesis of Ti-MWW and the recycling of the mother liquor are discussed in detail. Precipitated silica prepared with Na_2SiO_3 and CO_2 was selected as the silicon source, and $TiCl_3$ was selected as the titanium source. The mother liquor was recycled five times, and the obtained samples showed good catalytic activity in cyclohexanone ammoximation. This work can be conducive to reducing the influence on the environment and economizing on materials for the industrial production of Ti-MWW.



1. INTRODUCTION

Microporous zeolites have been widely used in petrochemical and fine chemical industries due to their uniform pore size distribution, good thermal stability, and hydrothermal stability.[1−3] A new titanosilicate zeolite with the MWW topology (Ti-MWW) has been successfully synthesized by Wu and Tatsumi and has attracted more attention in clean catalytic oxidation.[4,5] Ti-MWW zeolite has titanium silicate with 10-MR channels and larger 12-MR supercages connected by 10-MR windows.[4] At present, Ti-MWW has been widely applied in various liquid-phase oxidation reactions,[6−8] for instance, olefin epoxidation,[9] phenolic hydroxylation,[10] and ketone ammoximation.[11] Cyclohexanone ammoximation by using the conventional TS-1 zeolite as the catalyst has been commercialized, and product cyclohexanone oxime is an important intermediate in the production of ε-caprolactam (a monomer of nylon-6). The Ti-MWW zeolite has better catalytic selectivity than TS-1 in ammoximation because of its layered structure and higher surface area.[7,11] The hydrothermal synthesis of Ti-MWW usually requires a mass of piperidine (or hexamethyleneimine) and boric acid as the structure-directing agent and structure-supporting agent, respectively, to achieve complete crystallization and produces a large amount of the mother liquor containing borate and organic amine.

An industrial catalyst not only requires high catalytic activity but also needs a clean, efficient, and economical synthesis process. The recycling of the mother liquor is an effective means of clean production. Vinaches et al. studied the effect of the amount of the mother liquor on the synthesis of MCM-22 and found that the spherical amorphous nanoparticles in the mother liquor accelerated the reaction.[12] Nanocrystalline Cs-ABW zeolite with good catalytic performance for the Henry reaction of benzaldehyde and nitroethane was synthesized by utilizing the mother liquor.[13] Yang et al. synthesized pure S-1 from the recycled mother liquor, which not only effectively reduced the cost of S-1 synthesis but also minimized its environmental impact.[14] Liu et al. synthesized hollow TS-1 in a green and efficient way by using recycled mother liquor.[15] The ZSM-5 catalyst was synthesized by using NaY as the seed with the mother liquor and without the organic template.[16]

To the best of our knowledge, although the synthesis of Ti-MWW has been widely studied and this zeolite has been applied in various organic reactions, there are few reports on the synthesis of Ti-MWW by utilizing the recycled mother liquor. In this work, Ti-MWW was successfully synthesized by utilizing the recycled mother liquor, and the effects of titanium and silicon sources on the synthesis of Ti-MWW and the recycling of the mother liquor were studied in detail. The catalytic performances of Ti-MWW in cyclohexanone ammoximation were also investigated.

2. EXPERIMENTAL SECTION

2.1. Starting Materials. The precipitated silica as the silicon source was prepared as followed: 20 g of sodium silicate ($Na_2SiO_3{\cdot}9H_2O$) and 1 g of polyethylene glycol were completely dissolved in 100 g of water at 60 °C, and then, carbon dioxide was added until pH = 9. The reaction was continued for another 30 min. The product was filtered, washed, and dried to obtain precipitated silica. The precipitated silica was further calcined under 400 °C, and the calcined precipitated silica was obtained. The silica sol

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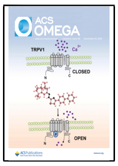

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Scheme 1. Diagram of the Preparation of Ti-MWW with the Recycled Mother Liquor

(SiO_2, 30 wt %) was supplied by Zhejiang Yuda Chemical Co., Ltd. The fumed silica (A-200, SiO_2, 99.8 wt %) was produced from Evonik Industries AG. Other materials were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of Ti-MWW.

The zeolite was prepared with a molar composition of 1.0 SiO_2: 1.4 piperidine: 0.67 B_2O_3: 19 H_2O. The synthetic gel was hydrothermally crystallized at 175 °C for 3 days. After the crystallization, the solid product and mother liquor were separated by filtering. The obtained solid product and titanium source were added into a HCl aqueous solution at a solid−liquid weight ratio of 1:15. The concentration of HCl and the initial concentration of Ti in the solution were 2.0 and 0.042 mol/L, respectively. The mixture was heated to reflux for 8 h. Finally, the Ti-MWW zeolite was obtained by filtering, washing, drying, and calcining at 550 °C.

2.3. Preparation of Ti-MWW with the Recycled Mother Liquor.

The residual piperidine in the mother liquor was determined by acid−base titration with hydrochloric acid (HCl). The concentration of boric acid in the mother liquor was determined by inductively coupled plasma analysis. The recycled mother liquor was used to replace water, part of piperidine, and boric acid. The piperidine, boric acid, and silicon sources were supplemented according to the formula of the initial preparation with fresh raw materials, and the following steps were the same as the initial preparation. The experimental details are shown in the Supporting Information (Pages S2−S6 and Tables S3−S8). The diagram for the preparation of Ti-MWW and the recycling of the mother liquor is shown in Scheme 1.

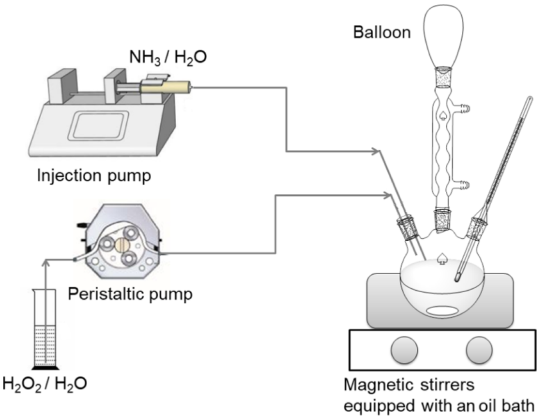
2.4. Characterizations.

Powder X-ray diffraction (XRD) measurements were carried out on a Panalytical X' pert Pro diffractometer using Cu Kα radiation (λ = 1.5406 Å). Using pure $BaSO_4$ as the reference, ultraviolet−visible (UV−vis) diffuse reflectance spectra were obtained on an Agilent Cary 5000 spectrometer. UV Raman spectra were obtained on a LabRam HR Evolution Raman spectrometer using a 325 nm UV laser. Fourier transform infrared (FT-IR) spectra was recorded on a Nicolet Nexus 470 FT-IR spectrometer using the KBr technique ranging from 400 to 4000 cm^{-1}. Nitrogen adsorption−desorption isotherms were obtained on an ASAP 2420 surface area analyzer (Micromeritics, USA), and the total surface area and pore size distributions were calculated by multipoint Brunauer−Emmett−Teller (BET) and Barrett−Joyner−Halenda methods, respectively. The surface area and micropore area were determined by the t-plot method. The scanning electron microscopy (SEM) images were obtained on an S-4800 scanning microanalyzer.

2.5. Cyclohexanone Ammoximation over Ti-MWW.

Cyclohexanone ammoximation over Ti-MWW was carried out in a three-neck round-bottom flask (100 mL) equipped with the magnetic stirrer and reflux condenser. Ti-MWW (0.1 g) and cyclohexanone (5.6 g) were premixed in a solvent (14.5 g tert-butanol). When the temperature of the mixture reached 80 °C, the H_2O_2 solution (8.3 g, 27.5 wt %) and the aqueous solution of ammonia (10.5 g, 25 wt %) were dropwise added into the flask. The NH_3/H_2O_2/cyclohexanone ratio used was 2.7:1.2:1.0 (molar ratio), and the catalyst concentration in the mixture was 0.26 wt %. The reaction lasted for 75 min at 80 °C. The diagram of the experimental device of cyclohexanone ammoximation is shown in Scheme 2.

Scheme 2. Diagram of the Experimental Device of Cyclohexanone Ammoximation



The collected mixture was centrifuged to remove Ti-MWW. The reaction solution was analyzed by a GC-9790 plus gas chromatograph equipped with a flame ionization detector. Ethanol and toluene were used as the solvent and internal standard, respectively. The representative gas chromatograms about the cyclohexanone ammoximation are shown in the Supporting Information (Figures S1−S3). The chromatographic peak located in 4.23−4.28 min is assigned to ethanol and tertiary butanol. The peak located in 4.66−4.69 min represents toluene. The peak located in 5.24−5.35 min represents cyclohexanone, and the peak located in 6.29−6.30 min represents cyclohexanone oxime. The conversion of cyclohexanone, the yield of cyclohexanone oxime, and the selectivity were obtained according to the following equations

$$X\ (\%) = (n_0 - n_1)/n_0 \times 100\%$$

$$Y\ (\%) = n/n_0 \times 100\%$$

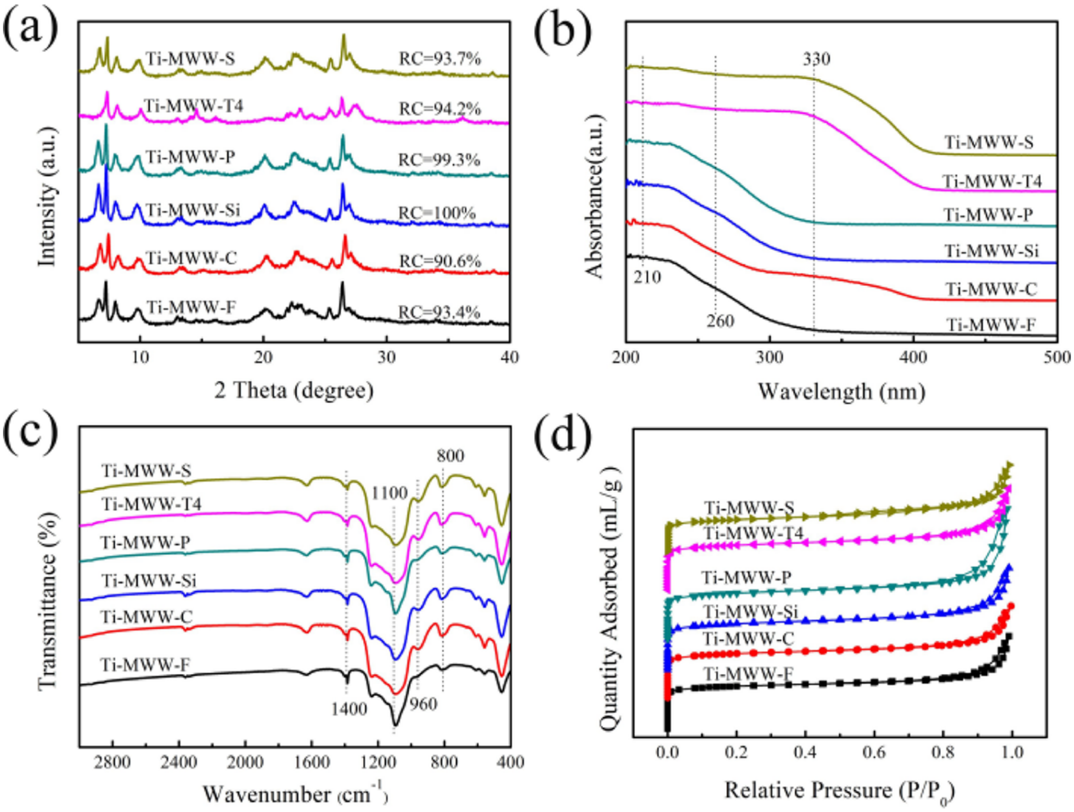


Figure 1. (a) XRD patterns, (b) UV−vis spectra, (c) FT-IR spectra, and (d) nitrogen adsorption−desorption isotherms of samples synthesized with different silicon and titanium sources.

$$S\ (\%) = n/(n_0 - n_1) \times 100\%$$

X, Y, and S refer to the conversion of cyclohexanone, the yield of cyclohexanone oxime, and the selectivity to cyclohexanone oxime, respectively. n_0 is the initial mole of cyclohexanone. n_1 and n are the residual moles of cyclohexanone and the moles of cyclohexanone oxime after the reaction, respectively.

3. RESULTS AND DISCUSSION

3.1. Screening of Silicon and Titanium Sources in Ti-MWW Synthesis. Samples synthesized by using the silica sol, precipitation silica, fumed silica, and calcined precipitated silica as the silicon source ($TiCl_3$ as the titanium source) were correspondingly denoted as Ti-MWW-Si, Ti-MWW-P, Ti-MWW-F, and Ti-MWW-C, respectively. The Ti-MWW synthesized by using $TiCl_4$ and $Ti(SO_4)_2$ as the titanium source (silica sol as the silicon source) were correspondingly named Ti-MWW-T4 and Ti-MWW-S, respectively.

The XRD patterns of the obtained samples are depicted in Figure 1a. All Ti-MWW have peaks at $2\theta = 7.2$, 8.0, 10.1, 14.3, 22.9, and 26.3°, which are in complete agreement with the standard pattern of MWW zeolite.[4,17,18] Ti-MWW-Si is regarded as the reference sample, and its crystallinity is regarded as 100%.

Figure 1b,c presents the UV−vis spectra and FT-IR spectra of these samples, respectively. The absorption band at about 210 nm belongs to framework Ti species.[4,17−19] The band around 260 nm is generally assigned to extraframework Ti species with an octahedral coordination.[4,17−19] It can be seen that extraframework Ti increases in Ti-MWW-S and Ti-MWW-T4. The band at about 330 nm is ascribed to anatase,[4,17−19] which is significant in Ti-MWW-S and Ti-MWW-T4. The reason may be that rapid hydrolyzation of $TiCl_4$ and $Ti(SO_4)_2$ produces anatase, which is difficult to insert into the framework of zeolite.[20,21] Ti-MWW-C also contains anatase. The FT-IR spectra contain a band at 960 cm^{-1}, which is also widely considered to be the evidence of incorporating Ti species into the zeolite framework.[4,22,23]

Nitrogen adsorption−desorption isotherms are illustrated in Figure 1d. The isotherms display a hysteresis loop in the range of relative pressure (P/P_0) of 0.8 to 1.0, indicating the existence of mesopores in the samples,[22,24] and the isotherm of Ti-MWW-P shows a larger hysteresis loop than that of other samples. The mesopore volume and the BET surface area of Ti-MWW-P are larger than that of others (listed in Table S1). The formation of mesopores may be attributed to the polyethylene glycol in the precipitated silica. The increase in the surface area and mesopores in zeolite can improve the mass transfer performance of reaction species in the channel.[25−27]

The morphology of the sample is observed by SEM. As illustrated in Figure S4, the crystallites of all samples appear as thin platelets. The crystallites of Ti-MWW-Si and Ti-MWW-P reunite into a sphere, while the sheets of Ti-MWW-T4 and Ti-MWW-S appear to be more disordered. Besides, the size of the crystal plate of Ti-MWW-C is larger than that of other samples.

Catalytic performances in cyclohexanone ammoximation over these Ti-MWW samples are listed in Table 1. When Ti-MWW-F, Ti-MWW-Si, or Ti-MWW-P is used as the catalyst, the conversion of cyclohexanone and yield of cyclohexanone oxime are above 99.0%. However, the conversion of cyclohexanone over the sample of Ti-MWW-C, Ti-MWW-S, or Ti-MWW-T4 is only 19−40%, which may be due to the high content of extraframework titanium and anatase.[20,21]

Table 1. Cyclohexanone Ammoximation over Ti-MWW Synthesized with Different Silicon and Titanium Sources

samples	*X* (%)	*Y* (%)	*S* (%)
Ti-MWW-F	99.8	99.8	100.0
Ti-MWW-C	36.4	35.6	97.9
Ti-MWW-Si	99.8	99.8	100.0
Ti-MWW-P	99.9	99.9	100.0
Ti-MWW-T4	40.0	39.1	97.8
Ti-MWW-S	19.7	19.4	98.4

In the acidic solution, $TiCl_3$ exists in the state of titanium ions (Ti^{3+}) and Cl^-. The polymerization of titanium(IV) occurs at [Ti (IV)] > 10^{-3} mol/L and [H^+] > 0.5 mol/L with an increase in the length of the —Ti—O—Ti—O— chains as the titanium concentration increases.[28,29] Therefore, the titanium(IV) species of $TiCl_4$ and $Ti(SO_4)_2$ in hydrochloric acid mainly exists in the state of polymerized $(TiO)_n^{2n+}$. Due to the fact that the Ti^{3+} ion is smaller than $(TiO)_n^{2n+}$, the Ti^{3+} ion is more easily inserted into the framework of zeolite than $(TiO)_n^{2n+}$. Therefore, the samples synthesized with $TiCl_3$ have better catalytic activity.

According to the above, the Ti-MWW samples synthesized with the silica sol, precipitation silica, or fumed silica have better catalytic activity than that with the calcined precipitated silica as the silicon source, and the samples synthesized with $TiCl_3$ have better catalytic activity than that with $TiCl_4$ or $Ti(SO_4)_2$ as the titanium source. Therefore, $TiCl_3$ is selected as the titanium source, and the mother liquor of Ti-MWW-P, Ti-MWW-Si, and Ti-MWW-F are recycled in further research.

3.2. Recycling of the Mother Liquor. The Ti-MWW samples synthesized by using the mother liquor of Ti-MWW-Si, Ti-MWW-P, and Ti-MWW-F were named as Ti-MWW-Si-R, Ti-MWW-P-R, and Ti-MWW-F-R, respectively.

The XRD patterns of these samples are presented in Figure 2a. All samples contain a typical MWW topology structure, suggesting that the zeolite can be successfully synthesized by using the recycled mother liquor.

Figure 2b,c shows the UV−vis and FT-IR spectra of these samples, respectively. All samples have characteristic peaks at about 210 nm in the UV−vis spectra and 960 cm^{-1} in the FT-IR spectra, which are proofs of the introduction of Ti into the framework. As shown in Figure 2b, there is a small absorption band at about 330 nm, which is assigned to anatase.

Figure 2d exhibits the nitrogen adsorption−desorption isotherms of all obtained samples. All samples exhibit a large BET surface area and mesopore volume (listed in Table S2), which is conducive to the contact of reactants and active sites, can improve the catalytic activity, and is consistent with that of the initial samples synthesized with different silicon and titanium sources. SEM images of the samples are demonstrated in Figure S5, and the crystallites of all samples appear as thin platelets and reunite into a sphere.

Catalytic performances in cyclohexanone ammoximation over Ti-MWW are listed in Table 2, and all obtained samples present good catalytic performance.

The precipitated silica can be prepared simply from minerals with lower cost and lower energy consumption. Therefore, in consideration of the environmental and economic factors, the precipitated silica is chosen as the silicon source.

The Ti-MWW samples were synthesized by repeatedly using the recycled mother liquor and named in turn as Ti-MWW-P (sample of the initial synthesis), Ti-MWW-P-R, Ti-MWW-R2,

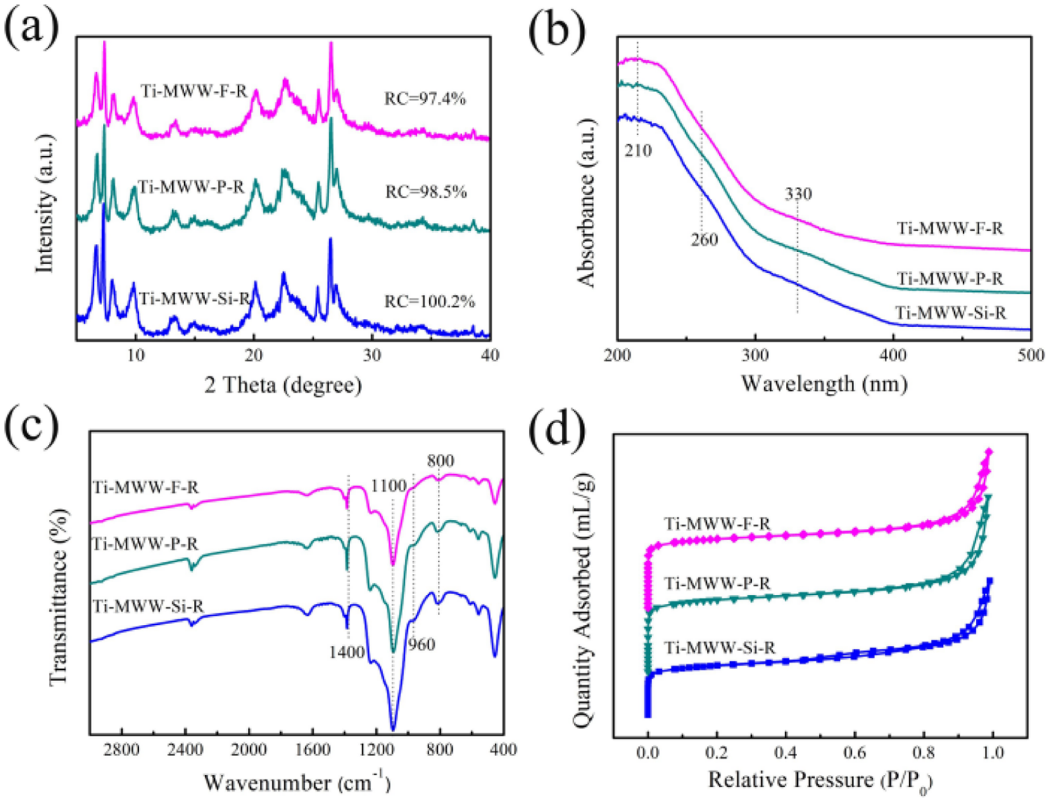


Figure 2. (a) XRD patterns, (b) UV−vis spectra, (c) FT-IR spectra, and (d) nitrogen adsorption−desorption isotherms of samples synthesized with the recycled mother liquor.

Table 2. Cyclohexanone Ammoximation over Ti-MWW Synthesized with the Recycled Mother Liquor

samples	*X* (%)	*Y* (%)	*S* (%)
Ti-MWW-Si-R	99.8	99.7	99.9
Ti-MWW-P-R	99.9	99.8	99.9
Ti-MWW-F-R	99.8	99.7	99.9

Ti-MWW-R3, Ti-MWW-R4, and Ti-MWW-R5. The experimental details and the recoveries of boric acid and piperidine are listed in Tables S3–S8. It indicates that the utilization of piperidine and boric acid could be significantly improved via the recycling of the mother liquor.

From the XRD patterns (Figure 3a), all samples show the MWW phase with similar relative crystallinities. The UV–vis spectra of these Ti-MWW samples are displayed in Figure 3b. A small characteristic peak at about 260 and 330 nm appeared in the UV–vis spectra of the samples synthesized with the recycled mother liquor, indicating the presence of a small number of extraframework Ti and anatase. It may be due to the accumulation of some impurities in the mother liquor which obstructs titanium from incorporating into the zeolite framework weakly. It can be clearly observed that all samples show the characteristic IR band around at 960 cm^{-1} in IR spectra (Figure 3c). This peak has been widely acknowledged as the evidence of the incorporation of Ti species into the zeolite framework.[4,22,23] The 325 nm excited UV resonance Raman spectra of Ti-MWW are shown in Figure S6. All samples synthesized with the recycled mother liquor have weak peaks at 394, 512, and 635 cm^{-1}, which are attributed to the anatase TiO_2 species, which is consistent with the results of UV–vis spectroscopy.

The nitrogen adsorption–desorption isotherms are illustrated in Figure 3d. The isotherms, BET surface areas, and pore volumes (Table S9) of all samples are similar.

The SEM images are shown in Figure S7. The crystallites of all samples appear as thin platelets and reunite into a sphere. This indicates that the repeated use of the recycled mother liquor has an insignificant effect on the morphology of synthesized samples.

These samples are used as catalysts in the cyclohexanone ammoximation (shown in Table 3). The recycled mother liquor was repeatedly reused five times in the synthesis of Ti-MWW, and all obtained samples show good catalytic activity. The conversion of cyclohexanone and the yield of cyclohexanone oxime are above 99.0%. Despite the UV resonance Raman spectra showing the presence of a small amount of anatase TiO_2 in the samples synthesized with the recycled mother liquor, the results of ammoximation indicates that the presence of a small amount of anatase TiO_2 has no obvious negative effect on the catalytic performance of zeolite. The reason may be that the framework Ti (catalytic active site) and

Table 3. Cyclohexanone Ammoximation over Ti-MWW Synthesized with the Sustainable Recycled Mother Liquor

samples	*X* (%)	*Y* (%)	*S* (%)
Ti-MWW-P	99.9	99.9	100.0
Ti-MWW-P-R	99.9	99.8	99.9
Ti-MWW-R2	99.9	99.8	99.9
Ti-MWW-R3	99.9	99.8	99.9
Ti-MWW-R4	99.7	99.6	99.9
Ti-MWW-R5	99.8	99.8	100.0

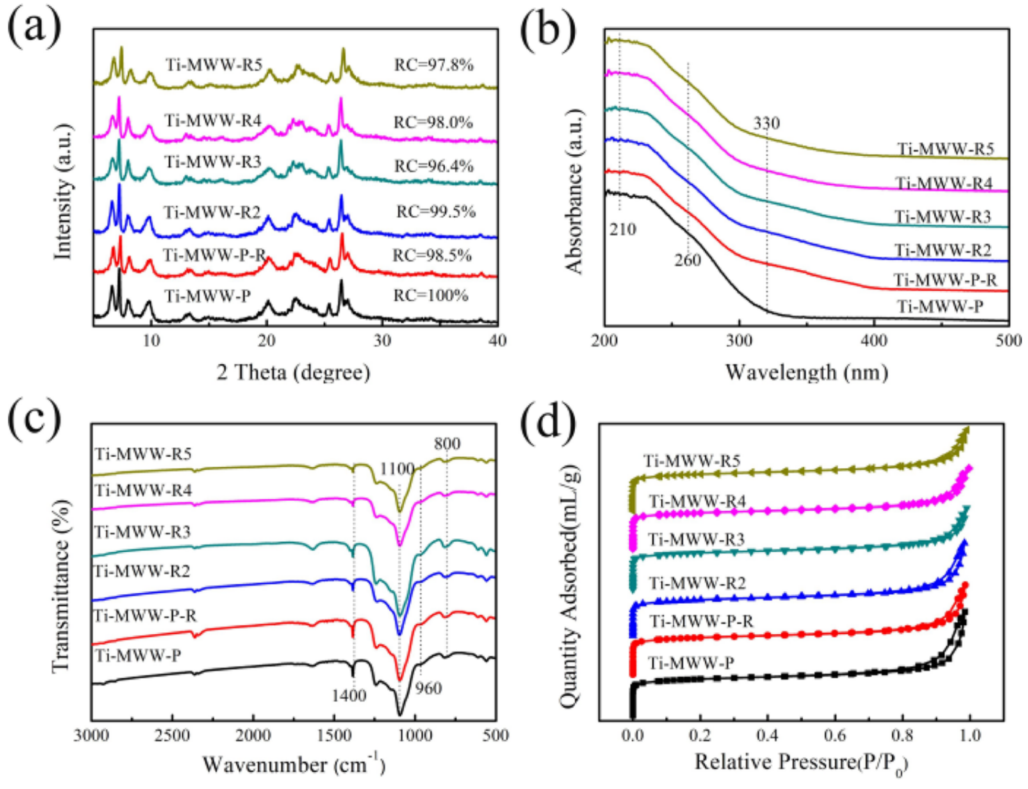


Figure 3. (a) XRD patterns, (b) UV–vis spectra, (c) FT-IR spectra, and (d) nitrogen adsorption–desorption isotherms of samples synthesized with the sustainable recycled mother liquor.

the textural properties of the samples, which are the main factors determining the catalytic activity in ammoximation, show no significant changes. Therefore, all obtained samples show similar catalytic activity. This indicates that Ti-MWW with high catalytic performance can be successfully synthesized by repeatedly using the recycled mother liquor.

4. CONCLUSIONS

In conclusion, an alternative cleaner route to synthesize Ti-MWW by utilizing the recycled mother liquor has been developed. The results of XRD, BET, and SEM analyses indicate that the Ti-MWW samples synthesized by using the recycled mother liquor have a similar crystallinity, surface area, and morphology to the sample synthesized with fresh materials. The recycled mother liquor was repeatedly used five times, and the synthesized Ti-MWW samples exhibited good catalytic performance in the cyclohexanone ammoximation. This work may contribute to reducing the sewage discharge and saving the cost of raw materials for the production of Ti-MWW zeolites.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c04833.

> Textural properties of samples synthesized with different silicon and titanium sources, textural properties of samples synthesized with the recycled mother liquor, recovery of piperidine and boric acid in the mother liquor, textural properties of samples synthesized with the sustainable recycled mother liquor, SEM images of samples synthesized with different silicon and titanium sources, SEM images of samples synthesized with the recycled mother liquor, UV resonance Raman spectra of samples synthesized with the sustainable recycled mother liquor, and SEM images of samples synthesized with the sustainable recycled mother liquor (PDF)

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Notes

The authors declare no competing financial interest.

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