Preparation of the WO$_x$/MCM-41 Solid Acid Catalyst and the Catalytic Performance for Solketal Synthesis

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ABSTRACT: In the present work, an efficient and stable WO$_x$/MCM-41 solid acid catalyst was prepared by the wet impregnation method. The characterization of powder X-ray diffraction, transmission electron microscopy, ultraviolet-visible, H$_2$ temperature-programmed reduction, X-ray photoelectron spectroscopy, NH$_3$ temperature-programmed desorption, and N$_2$ adsorption-desorption isotherms confirmed that the impregnation amount and calcination temperature of WO$_x$ speciation affected the dispersity and acidity of the resulting catalyst. This WO$_x$/MCM-41 solid acid catalyst was subsequently applied in the ketalization reaction of glycerol and acetone to produce solketal. By catalyst screening and reaction condition optimization, WO$_x$/MCM-41 obtained by impregnating 20 wt % and calcining at 350 °C exhibited the highest solketal yield and catalytic stability.

1. INTRODUCTION

In recent years, with the continuous reduction of fossil fuels such as petroleum and coals in the world, it is inappropriate to use non-renewable sources to produce energy and fuel. Therefore, it is urgent to develop renewable energy which can replace fossil fuels to achieve the sustainable development of the biosphere. Biodiesel has been considered an excellent substitute for fossil fuels since 1988, when Germany’s NieEr company used rapeseed as a raw material to extract clean fuel biodiesel. Biodiesel is a clean oxygen-containing liquid fuel made from natural oil crops, oil aquatic plants, animal fats, and waste catering oil. Compared with petroleum-based diesel, biodiesel has certain advantages such as no pollution to the environment, good lubrication performance, low cost, renewability, and so on. It not only reduces the danger in the transportation and use of raw materials but also extends the service life of the machine. Its low sulfur content also makes it not produce sulfur dioxide and sulfides after combustion. Therefore, biodiesel is a potential alternative to petroleum-based diesel. Indeed, the growth rate of biodiesel production has risen from almost nothing to 20 billion L a year in the past decade. 

At present, there are two main methods to prepare biodiesel: the physical method (direct or mixed use and micro-emulsification) and chemical method (pyrolysis and catalytic transesterification). The former method can reduce the viscosity of animal and vegetable oil, but the problems of oil pollution and carbon accumulation are not well solved. Although the second method can improve the shortcomings of biodiesel production by physical methods, the process produces many byproducts. Especially in the process of preparing biodiesel by the transesterification method, a large amount of glycerol is unavoidably formed, the byproduct of which is expected to be as high as 5.2 million tons by 2020. It is likely to continue to be delivered at a low cost for the foreseeable future, which will significantly affect the cost affordability of the biodiesel process. Therefore, the current research on biodiesel focuses on finding and developing feasible methods to deal with or effectively utilize excess glycerol in order to reduce the production cost of biodiesel and improve the comprehensive economic benefits. There are three hydroxyl groups in the glycerol molecule, so the calorific value of glycerol is low, which leads to its unsuitable direct use as a fuel component. It must therefore look for new forms of the compound to add value. So far, the glycerol conversion technologies that have been implemented or are being developed are esterification, oxidation, dehydration, hydrogenolysis, reforming, and acetalation. Among the derivatives of various glycerol compounds, solketal (4-hydroxymethyl-2, 2-dimethyl-1,3-dioxolane), which is the main product of the ketalization reaction of acetone with glycerol, has attracted special attention. As a useful additive for the preparation of gasoline, diesel, and biodiesel, solketal has some unique advantages, which can effectively reduce viscosity,
enhance cold-flow performance, and achieve flash point and oxidation stability of biodiesel during the extended storage period. In a recent report, it has been determined that the use of fuel additives can significantly increase the viscosity and other properties of biodiesel. In addition, it also has important applications in the fields of disinfectants, cosmetics, flavoring agents, pharmaceuticals, surfactants, food additives, the beverage industry, and the tobacco industry. Therefore, how to efficiently convert glycerol into solketal becomes a challenging work.

Molecular sieve-type supported catalysts are considered to be better catalysts. However, the mass transfer of macromolecules in the channels of microporous molecular sieves limits their reaction efficiency. ZSM-5 has a high Si/Al ratio, which is a hydrophobic catalyst with a large specific surface area. Theoretical analysis results show that this kind of catalyst is beneficial to the discharge of water during the solketal synthesis reaction so that the reaction yield can be improved. However, studies have shown that the catalytic activity of the ZSM-5 catalyst is not high. It is due to its pore size of only 0.56 nm, which is not conducive to the reactant acetone and glycerol into the pore channel, thus resulting in the condensation reaction which only occurs on the catalytic active center of the outer surface and causing a lower solketal yield. Therefore, the pore size of the molecular sieve is an important factor. Since its discovery in 1992, MCM-41 has become the most popular member of the M41S series of mesoporous silicate and aluminosilicate materials. MCM-41 has a uniform hexagonal straight channel structure, a controllable mesoporous pore size (1.5–20 nm), a large pore volume (>0.6 cm³/g), a high surface area (~700–1500 m²/g), and excellent hydrothermal, chemical, and mechanical stability. This makes MCM-41 widely used in many fields, especially in the catalytic conversion of large molecules. However, the siliceous MCM-41 has a neutral framework. It is especially in the catalytic conversion of large molecules.

2. RESULTS AND DISCUSSION

2.1. Characterization of WOₓ/MCM-41 Catalysts.

2.1.1. Powder X-ray Diffraction. Figure 1 shows the powder XRD patterns of MCM-41 and WOₓ/MCM-41 catalysts. The small-angle XRD patterns in Figure 1 (left) revealed that WOₓ/MCM-41 catalysts maintained the mesoporous structure after loading ammonium tungstate. The large-angle XRD patterns in Figure 1 (right) showed the characteristic peak of tungsten oxide. It revealed that the characteristic peak intensity of tungsten oxide increased with the loading amount. Furthermore, under the same loading amount, the diffraction peak intensity of tungsten oxide decreased obviously with the

Figure 1. Small-angle XRD (left) and large-angle XRD (right) patterns of WOₓ/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) MCM-41, (b) WOₓ/MCM-41-1%-H, (c) WOₓ/MCM-41-5%-H, (d) WOₓ/MCM-41-10%-H, (e) WOₓ/MCM-41-20%-H, (f) WOₓ/MCM-41-30%-H, (g) WOₓ/MCM-41-10%-L, (h) WOₓ/MCM-41-20%-L, and (i) WOₓ/MCM-41-30%-L.
calcination temperature adjusted to 350 °C. It indicated that the dispersibility of tungsten oxide on the MCM-41 substrate obtained by low-temperature calcination was better than that of high-temperature calcination. The possible reason was that ammonium tungstate dispersed on MCM-41 transformed separated \([WO_4]^{2-}\) tetrahedral species and amorphous WO\(_3\) when calcined at a lower temperature. At high temperatures, however, it would lead to the agglomeration of tungsten oxide species to form crystalline WO\(_3\).\(^{23}\)

2.1.2. UV−vis Spectrum. Figure 2 shows the UV−vis absorption spectra of WO\(_x\)/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WO\(_x\)/MCM-41-1%-H, (b) WO\(_x\)/MCM-41-5%-H, (c) WO\(_x\)/MCM-41-10%-H, (d) WO\(_x\)/MCM-41-20%-H, (e) WO\(_x\)/MCM-41-30%-H, (f) WO\(_x\)/MCM-41-10%-L, (g) WO\(_x\)/MCM-41-20%-L, and (h) WO\(_x\)/MCM-41-30%-L.

Figure 2. UV−vis absorption spectra of WO\(_x\)/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WO\(_x\)/MCM-41-1%-H, (b) WO\(_x\)/MCM-41-5%-H, (c) WO\(_x\)/MCM-41-10%-H, (d) WO\(_x\)/MCM-41-20%-H, (e) WO\(_x\)/MCM-41-30%-H, (f) WO\(_x\)/MCM-41-10%-L, (g) WO\(_x\)/MCM-41-20%-L, and (h) WO\(_x\)/MCM-41-30%-L.

ammonium tungstate loading amounts and calcined temperatures. It is known that MCM-41 does not have a band in UV−vis diffuse reflection.\(^{24}\) Based on the UV−vis spectra results, all WO\(_x\)/MCM-41 catalysts showed two absorption bands in the spectrum: the first peak location is 222 nm and the second peak location is 263 nm. With the reference of Bhuiyan,\(^{25}\) the absorption band at 220 nm indicates the existence of isolated \([WO_4]^{2-}\) tetrahedral species. The second band at 263 nm may be attributed to isolated tungsten species or low-condensed oligomeric tungsten oxide. It was in good agreement with the observations of WO\(_3\) catalysts supported on silica, alumina, and zirconia by other researchers.\(^{25}\) In addition, with the same loading amount of ammonium tungsten but calcined at 350 °C, WO\(_x\)/MCM-41-30%-H calcined at 550 °C had an absorption band at ~380 nm. It revealed that high-temperature treatment could cause the octahedral tungsten oxide species to agglomerate and form additional WO\(_3\) crystals.

2.1.3. H\(_2\) Temperature-Programmed Reduction. The H\(_2\)-TPR results of WO\(_x\)/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures are shown in Figure 3. They revealed that all catalysts had two reduction peaks in the temperature range of 50–880 °C: the first peak appears at 620–660 °C and the second peak appears at 700–775 °C. It was worth noting that the invisible reduction peak of WO\(_x\)/MCM-41-1%-H was attributed to the tiny amounts of loading tungsten oxide. It proposed that the TPR curve of crystalline WO\(_3\) usually has two reduction peaks centered at 650 and 740 °C.

Accordingly, it was speculated that the loading tungsten species was mainly converted to crystalline WO\(_3\) after high-temperature calcination. In addition, the appearance of TPR peaks at higher temperatures is related to the dispersibility of tungsten oxide materials such as polytungstates and WO\(_3\) micro-crystals.\(^{22,23}\)

In this work, it was observed in Figure 3 that the H\(_2\) reduction peaks tend to higher temperature with the increase of ammonium tungstate loading amount. It indicated that the relative content of octahedral tungsten oxide on the MCM-41 substrate increased, which led to the decrease of tungsten oxide dispersion. However, compared with the high-temperature calcined catalysts, the low-temperature calcined catalysts presented better dispersibility. It was consistent with the analysis results of XRD and UV-vis.

2.1.4. X-ray Photoelectron Spectroscopy. Figure 4 shows XPS of WO\(_x\)/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WO\(_x\)/MCM-41-1%-H, (b) WO\(_x\)/MCM-41-5%-H, (c) WO\(_x\)/MCM-41-10%-H, (d) WO\(_x\)/MCM-41-20%-H, (e) WO\(_x\)/MCM-41-30%-H, (f) WO\(_x\)/MCM-41-10%-L, (g) WO\(_x\)/MCM-41-20%-L, and (h) WO\(_x\)/MCM-41-30%-L.

Figure 3. H\(_2\)-TPR of WO\(_x\)/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WO\(_x\)/MCM-41-1%-H, (b) WO\(_x\)/MCM-41-5%-H, (c) WO\(_x\)/MCM-41-10%-H, (d) WO\(_x\)/MCM-41-20%-H, (e) WO\(_x\)/MCM-41-30%-H, (f) WO\(_x\)/MCM-41-10%-L, (g) WO\(_x\)/MCM-41-20%-L, and (h) WO\(_x\)/MCM-41-30%-L.

Figure 4. XPS spectra of WO\(_x\)/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WO\(_x\)/MCM-41-1%-H, (b) WO\(_x\)/MCM-41-5%-H, (c) WO\(_x\)/MCM-41-10%-H, (d) WO\(_x\)/MCM-41-20%-H, (e) WO\(_x\)/MCM-41-30%-H, (f) WO\(_x\)/MCM-41-10%-L, (g) WO\(_x\)/MCM-41-20%-L, and (h) WO\(_x\)/MCM-41-30%-L.

tungstate loading amounts and calcined temperatures. It revealed that all catalysts showed two peaks in the binding energy (BE) region between 34 and 40 eV, which are BE = 36.1 eV and BE = 38.3 eV, corresponding to W 4f\(_{5/2}\) and W 4f\(_{7/2}\) of the W\(^{6+}\) 4f nuclear energy level in the tungsten oxide
species, respectively. It was obvious that all the WOx/MCM-41 catalysts showed similar XPS spectra and the intensity of both peaks increased with the loading amounts of tungsten oxide. The XPS results confirmed that W6+ in tungsten oxide(VI) was well dispersed on the surface of MCM-41, which was consistent with the XRD results.

2.1.5. NH3 Temperature-Programmed Desorption. The acidity of the WOx/MCM-41 solid acid catalysts with different ammonium tungstate loading amounts and calcination temperatures was detected by the NH3-TPD technology. As shown in Figure 5, the NH3 desorption peaks were mainly detected in the range of 100−300 and 400−550 °C, which could be desorbed from the weak and strong acid sites, respectively. All the desorption curves in Figure 5 revealed that the total acid strength was increased with the loading amounts of ammonium tungstate. It was in agreement with the conclusions of Bhuiyan. However, the peak strength of the weak acid and strong acid presented different tendencies (the weak acid peak strength was increased and the strong acid peak strength was decreased) with the loading amounts of ammonium tungstate.

It might be that partial agglomerated WO3 species were formed by calcinating excessive ammonium tungstate and covered the active sites. In addition, with the same loading amounts of ammonium tungstate, the strong acid strength was significantly increased when adjusting the calcination temperature from 550 to 350 °C (c−e vs f−h in Figure 5). This result was consistent with the above inference.

2.1.6. N2 Adsorption–Desorption Isotherms. N2 adsorption–desorption isotherms at 77 K and Barrett–Joyner–Halenda (BJH) adsorption pore size distributions are shown in Figure 6. They revealed that all the prepared WOx/MCM-41 catalysts maintained the mesoporous structure after loading ammonium tungstate, which was in agreement with the XRD results.

Table 1 lists the detailed Brunauer–Emmett–Teller (BET) surface areas, BJH average pore diameters, and pore volumes of all WOx/MCM-41 catalysts prepared with different ammonium tungstate loading amounts and calcined temperatures. It reveals that the BET specific surface area and BJH pore volume decreased with the increase of tungsten content. These results indicated that the calcined tungsten oxide particles were dispersed on the surface and inside of the pores. Based on the UV−vis, H2-TPR, and XPS analyses, it was inferred that the octahedral W(VI) species would enter and partially block the pore channels of MCM-41, thereby reducing the surface area and pore volume of the catalyst. However, the pore diameter of WOx/MCM-41 catalysts did not change significantly with the

Figure 5. NH3-TPD of WOx/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WOx/MCM-41-1%-H, (b) WOx/MCM-41-5%-H, (c) WOx/MCM-41-10%-H, (d) WOx/MCM-41-20%-H, (e) WOx/MCM-41-30%-H, (f) WOx/MCM-41-10%-L, (g) WOx/MCM-41-20%-L, and (h) WOx/MCM-41-30%-L.

Figure 6. N2 adsorption/desorption isotherms (left) and BJH adsorption pore size distributions (right) of WOx/MCM-41 catalysts with different ammonium tungstate loading amounts and calcined temperatures: (a) WOx/MCM-41-1%-H, (b) WOx/MCM-41-5%-H, (c) WOx/MCM-41-10%-H, (d) WOx/MCM-41-20%-H, (e) WOx/MCM-41-30%-H, (f) WOx/MCM-41-10%-L, (g) WOx/MCM-41-20%-L, and (h) WOx/MCM-41-30%-L.

Table 1. BET Surface Area, BJH Average Pore Diameter, and Pore Volume of WOx/MCM-41

| catalyst        | surface area (m²/g) | pore diameter (nm) | pore volume (cm³/g) |
|-----------------|---------------------|--------------------|---------------------|
| MCM-41          | 1513.2078           | 2.52               | 0.8970              |
| WOx/MCM-41-1%-H | 1378.3314           | 2.50               | 0.7870              |
| WOx/MCM-41-5%-H | 1296.4326           | 2.46               | 0.7452              |
| WOx/MCM-41-10%-H| 1088.6299           | 2.60               | 0.6909              |
| WOx/MCM-41-20%-H| 1104.8169           | 2.40               | 0.6449              |
| WOx/MCM-41-30%-H| 903.3235            | 2.65               | 0.5947              |
| WOx/MCM-41-10%-L| 1113.2978           | 2.62               | 0.7229              |
| WOx/MCM-41-20%-L| 1113.8891           | 2.53               | 0.6763              |
| WOx/MCM-41-30%-L| 1063.4701           | 2.50               | 0.6295              |

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increase of ammonium tungstate loading amounts. It indicated that the tungsten oxide deposited in the pore was uniformly dispersed. From the TEM images of Figures S1−S8, there were no obvious agglomerated crystal particles, which could further confirm that the tungsten oxide deposited in the pore was uniformly dispersed.

2.2. Catalytic Performances. 2.2.1. Reaction Condition Optimization. With the aim to study the optimal reaction conditions of solketal synthesis by the ketalization reaction of glycerol with acetone, various reaction parameters including the molar ratio of glycerol to acetone, the amount of catalyst, the reaction time, and the reaction temperature were examined.

2.2.1.1. Molar Ratio of Glycerol to Acetone. Based on our previous work,26 the molar ratio of glycerol to acetone plays a vital role in the solketal production. In order to obtain the optimal molar ratio of glycerol to acetone required, molar ratios of glycerol to acetone of 1:1, 1:2, 1:4, and 1:6 were investigated under the other conditions of mass ratio m_catalyst/m_glycerol = 5%, reaction temperature = 50 °C, reaction time = 2 h, and the catalyst being WO_x/MCM-41-10%-H. As shown in Figure 7, the solketal yield was increased with the molar ratio of glycerol to acetone. The results revealed as expected that a higher molar ratio of reactants could be favorable for the solketal production.

2.2.1.2. Mass Ratio of the Catalyst. Based on the WO_x/MCM-41-10%-H catalyst, the mass ratio of the catalyst from 3% m_glycerol to 10% m_glycerol was investigated under the conditions of molar ratio of glycerol to acetone = 1:6, reaction temperature = 50 °C, and reaction time = 2 h. As shown in Figure 8, with the mass ratio of the catalyst increased from 3% m_glycerol to 10% m_glycerol, the solketal yield increased from 66.61 to 78.52%. It revealed that a higher mass ratio of catalysts could provide more catalytic centers and as expected is favorable for the solketal production.

2.2.1.3. Reaction Temperature. Under the conditions of molar ratio of glycerol to acetone = 1:6, mass ratio of m_catalyst = 10% m_glycerol reaction time = 2 h, and the catalyst being WO_x/MCM-41-10%-H, the effect of reaction temperature on the ketalization reaction of glycerol with acetone was investigated. As shown in Figure 9, the solketal yield increased with reaction temperature and reached a maximum of 78.52% at 50 °C. However, with the increase of reaction temperature to 80 °C, the solketal yield will decrease. It might contribute to the violent gasification of acetone reduced the actual molar ratio of glycerol to acetone. Therefore, in this work, 50 °C was selected as the optimal reaction temperature.

2.2.1.4. Reaction Time. Figure 10 shows the effect of reaction time on the ketalization reaction of glycerol with acetone under the conditions of molar ratio of glycerol to acetone = 1:6, mass ratio of m_catalyst = 10% m_glycerol reaction temperature = 50 °C, and the catalyst being WO_x/MCM-41-10%-H. It revealed that the solketal yield could reach 68.92% by 30 min of reaction. With the increase of reaction time, the maximum solketal yield of 78.52% could be obtained when it
was increased to 2 h. Further extension of the reaction time to 6 h could not result in an increase of solketal yield, indicating that there was an optimal reaction time of 2 h for the ketalization reaction of glycerol with acetone.

2.2.2. Screening of Catalysts. The catalytic performance of the series of WO₅/MCM-41 catalysts was analyzed in a conventional glass flask reactor with stirring for catalyst screening. The reaction conditions were as follows: molar ratio of glycerol to acetone = 1:1, mass ratio of catalyst m_catalyst = 5% m_glycerol reaction temperature = 50 °C, and reaction time = 2 h.

Figure 11 shows the solketal yields of pure silicon MCM-41 and WO₅/MCM-41 catalysts with different ammonium tungstate loading amounts (1, 5, 10, 20, and 30%) and a calcination temperature of 550 °C (marked as H). Obviously, the solketal yields were increased from 17.47 to 39.25% with the increase of the ammonium tungstate loading amount (from 1 to 30%), which were all higher than that of pure silicon MCM-41. This revealed that the increase of tungsten oxide loaded on MCM-41 led to the increase of the acidity of the WO₅/MCM-41 catalysts, thereby promoting an increase in the reaction yield.

Figure 12 summarizes the solketal yields of various WO₅/MCM-41 catalysts with different ammonium tungstate loading amounts (10, 20, and 30%) and calcination temperatures (350 °C marked as L and 550 °C marked as H). They revealed that the WO₅/MCM-41-20%-L catalyst (E of Figure 12) had the best catalytic performance and the solketal yield could reach to 47.41%, in which the loading amount of ammonium tungstate was 20 wt % and the calcination temperature was 350 °C.

2.2.3. Leaching Test and Recyclability. The leaching examination was conducted based on the catalyst of WO₅/MCM-41 under the optimal reaction conditions of molar ratio of glycerol to acetone = 1:6, mass ratio of catalyst m_catalyst = 10 wt % m_glycerol and reaction temperature = 50 °C. The fresh catalyst was first used to catalyze the ketalization reaction of glycerol with acetone for 10 min. Then, it was quickly removed by centrifugation, and the filtrate was poured into a new batch reactor to continue the reaction under the same conditions. Tiny products after reaction for 10, 20, 30, and 120 min were suctioned off, and the solketal yield was analyzed by gas chromatography. The results are shown in Figure 13.

In order to confirm the stability of the WO₅/MCM-41-20%-L catalyst, the recyclability examination was carried out under the optimal reaction conditions of molar ratio of glycerol to acetone = 1:6, mass ratio of catalyst m_catalyst = 10 wt % m_glycerol reaction temperature = 50 °C, and reaction time = 2 h. As shown in Figure 14, the solketal yield had an insignificant decrease after three reaction cycles. The observed decrease in activity might be attributable to the partial deactivation of the catalyst due to blockage of acidic sites. Both the leaching and recyclability examination results revealed that the WO₅/MCM-41 catalysts were relatively stable in the ketalization reaction of glycerol with acetone.

3. CONCLUSIONS

In summary, a series of WO₅/MCM-41 solid acid catalysts were prepared by the wet impregnation method. With the characterization of powder XRD, TEM, UV-vis, H₂-TPR, XPS,
NH₃-TPD, and N₂ adsorption–desorption isotherms, it was confirmed that WO₃ species were dispersed uniformly on the surface and the mesopores of MCM-41, which affected the total acidity of the resulting catalyst. By catalyst screening and reaction condition optimization within the ketalization reaction of glycerol and acetone to produce solketal, WOₓ/MCM-41 obtained by impregnating 20 wt % and calcining at 350 °C exhibited the highest solketal yield. It could reach ~87.77% under the optimized reaction conditions of molar ratio of glycerol to acetone = 1:6, mass ratio of catalyst mₓ at 10 wt % m₁, reaction temperature = 50 °C, and reaction time = 2 h. Meanwhile, these WOₓ/MCM-41 catalysts had a low leaching rate and could be reused effectively for continuous catalytic reaction cycles.

4. EXPERIMENTAL SECTION

4.1. Materials and Reagents. The chemical reagents included tetraethyl orthosilicate (TEOS, wt % ≥99.5%), aqueous ammonia (NH₄OH, wt % ≥25%), anhydrous alcohol (EtOH, wt % ≥99.7%), acetone (marked as ACT, wt % ≥99.5%), and glycerol (marked as GCR, wt % ≥99.0%) were purchased from Sinopharm Chemical Reagents Co., Ltd. (Shanghai, China). The used hexadecyl trimethyl ammonium bromide (CTAB, wt % ≥99%) and ammonium tungstate (wt % ≥98.5%) were purchased from Aladdin Industrial Corporation (Shanghai, China). All the above used chemicals were of analytical reagent (AR) grade and used as received without further purification. The used deionized water (DI water, 18.2 MΩ) was homemade.

4.2. Preparation of MCM-41. The MCM-41 support was prepared by a hydrothermal method. According to the procedure described elsewhere, first, 2.5000 g of CTAB was dissolved in 50.0 mL of DI water. After that, 60.0 g of EtOH and 13.2 g of NH₄OH were sequentially added dropwise into the above solution and stirred for 15 min at room temperature. Finally, 4.7000 g of TEOS was added, and a gel with a molar composition of 58EtOH/1TEOS/144H₂O/0.3CTAB/11NH₄ was obtained. After continuous stirring for 2 h, the above mixture was filtered and washed to pH < 8 with amounts of DI water. The resulting powder was calcined for 5 h at 550 °C with a heating rate of 1.5 °C/min.

4.3. Preparation of WOₓ/MCM-41 Solid Acid Catalysts. Ammonium tungstate was loaded on MCM-41 by the high-temperature wet impregnation method. Quantitative ammonium tungstate was measured according to a certain mass ratio (mₓ at m₁/MCM-41 = 1, 5, 10, 20, and 30%) and completely dissolved in 10 mL of DI water. A certain amount of MCM-41 powder was slowly added to the above solution. The above mixture was stirred in a 90 °C water bath until DI water completely evaporated. The following solid powder was calcined for 6 h at 350 and 550 °C with a heating rate of 1.5 °C/min. The synthetic catalysts were named according to different mₓ at m₁/MCM-41 ratios and calcination temperatures. Similar to WOₓ/MCM-41-10%-H (L), 10% refers to the ratio of mₓ at m₁/MCM-41 of 10% and H refers to the calcination temperature of 550 °C (L refers to the calcination temperature of 350 °C).

4.4. Characterization. The powder XRD measurements were performed on a Bruker D8 ADVANCE X-ray diffractometer using Cu Kα radiation. The working voltage and current were 40 kV and 40 mA, respectively. The scanning rate was 5°/min. TEM images were inspected with a Talos F200x transmission electron microscope (Thermo Fisher, USA). The working voltage was 200 kV. All samples were coated on a copper mesh before measurements. UV-vis spectroscopy was performed on a PerkinElmer LAMBDA-750 spectrometer with diffuse reflectance attachment by using Spectralon as a reference. The scanning wavelength range was 200–800 nm, and the scanning speed was 120 nm/min. H₂-TPR characterization was performed on a ChemiSorbTM 2720 analyzer. The sample was pretreated in a He atmosphere with 120 °C. Then, it was heated from 50 to 900 °C with a heating rate of 8 °C/min under 10 vol % H₂/Ar flow. During this period, the outlet gas was monitored using a thermal conductivity detector (TCD). The XPS spectra were recorded on a spectrophotometer (Thermo Fisher Scientific ESCALAB 250Xi). The test area was 500 μm on the sample surface, and the excitation light source used was Al Kα. TPD of ammonia (NH₃-TPD) was performed with an AutoChemII chemisorption apparatus. Catalyst samples were pretreated in a stream of He (50 mL/min) at 300 °C for 2 h. Then, NH₃ was adsorbed at 100 °C for 1 h. Catalyst samples were purged with the He stream for 1 h at 100 °C until the baseline was stable to remove physically adsorbed ammonia. Finally, the catalyst samples were heated again from 100 to 650 °C at a heating rate of 10 °C/min, and the desorbed NH₃ was monitored using a TCD. The N₂ adsorption–desorption isotherms at 77 K were measured using an ASAP 2460 Surface Area and Porosity Analyzer (Micromeritics, USA). Before analysis, the catalyst sample was degassed in vacuum at 200 °C for 6 h. The specific surface area of the sample was calculated using the BET model, and the pore size distribution of the sample was obtained using the BJH model.

4.5. Catalytic Performance Test. The catalytic performance of the prepared WOₓ/MCM-41 solid acid catalysts was evaluated by the ketalization reaction of glycerol with acetone. The reaction was conducted in a conventional glass flask reactor with stirring. The products were collected and analyzed by gas chromatography (GC9790, Zhejiang Fuli Analytical Instruments Co., Ltd., China) equipped with an SE-30 column (30 m × 320 μm × 1 μm) and a flame ionization detector. The detection conditions were as follows: the oven temperature was 100 °C, the injector temperature was 260 °C, and the detector temperature was 280 °C. Temperature program: the initial oven temperature was kept at 100 °C for 1 min. After that, the oven temperature was increased to 250 °C at the rate of 10 °C/min and kept for 4 min. Finally, the oven temperature reduced rapidly to 100 °C. The yield of solketal was calculated by an external standard method, in which the...
external standard reagent was DMF. The expression was as follows: 

\[ Y_{SKT} = \frac{A_{SKT}}{A_{DMF}} \frac{M_{DMF}}{M_{GLY}} \times 100\% \]

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