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- Controllable Multicomponent Co-Assembly Approach to Ordered Mesoporous Zirconia Supported with Well-Dispersed Tungsten Oxide Clusters as High-Performance Catalysts
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Zirconia supported WO_x clusters with high acid strength and good stability are important solid acid 20 catalysts in many reactions. However, conventional synthetic methods such as incipient-wetness 21 impregnation and co-precipitation usually result in the products with low catalytic activity due to low 22 23 surface area, uncontrollable and non-homogeneous distribution of tungsten species. In this study, a facile multicomponent co-assembly approach was utilized to straightforwardly synthesize ordered mesoporous 24 WO_x/ZrO_2 composites (OMWZr) with mesopore size over 17 nm, pore volume of 0.13 - 0.18 cm³/g and 25 surface area of 27.3 - 41.7 m²/g. The materials were composed of robust crystalline ZrO_2 skeleton and 26 27 well-dispersed WO_x clusters (polytungstates) in framework under the optimized conditions. The doped tungsten species were well stabled by the crystallized skeletons of mesoporous ZrO₂, which can inhibit 28 growth of tetragonal ZrO₂ but facilitate crystallization of monoclinic ZrO₂. The states of tungsten species 29 30 (monotungstates, polytungstates and crystalline WO_3) can be precisely adjusted by their doping amount in framework and calcination temperature as well, which can further tune the surface acidity of OMWZr 31 composites. Owing to the existence of numerous active surface WO_x clusters generated over exposed 32 surface of mesoporous ZrO₂, the OMWZr catalysts not only show great spatial homogeneity of accessible 33 34 Brönsted acid sites and feasible mass diffusion during catalytic reactions, but also display outstanding acid-catalytic performance over hydrolysis reactions of benzaldehyde dimethyl acetal. The catalyst can 35 be reused for more than 10 cycles, without reduction of catalytic activity and selectivity to benzaldehyde. 36

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38 1. Introduction

As a kind of important industrial catalysts, solid acids are usually utilized in wide fields including fine chemistry,^[1] pharmaceutical synthesis,^[2] biomass processing,^[3] petrochemical industry,^[4] and so on.

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Compared to conventional homogeneous acid catalysts (HCl, H₂SO₄, p-toluenesulfonic acid, etc.), solid acids possess great advantages such as high safety in transport, outstanding catalytic activity, easy separation and recyclability, no corrosion to reactor, and no discharge of wasted acid solution.^[5-7] Therefore, a large number of new type solid acids, such as zeolites, metal oxides, metal salts, ion exchange resins, have been extensively developed and used as heterogeneous catalysts.^[8-14] Among them, composite metal oxides have attracted more and more attentions because of controllable introduction of acid sites and enhancement of acid amount/strength through a synergistic effect of each component.^[15-17]

48 Through incorporating tungsten on zirconia, the WO_x/ZrO_2 composites were first reported as novel solid superacid catalysts for isomerization of butane and pentane.^[18] Due to high acid strength and good 49 stability in comparison with sulfated zirconia, the WO_x/ZrO₂ composites also enable wide applications in 50 diverse acid-catalytic reactions.^[19-26] Notably, the catalytic activity was demonstrated to be dependent on 51 surface acid density, which was closely associated with the density (W atoms/nm²) and dispersion 52 (electronic structure and domain size) of WOx species supported on ZrO2. Therefore, the surface acid 53 density of WO_x/ZrO₂ can be controlled by tuning tungsten amount, calcination temperature, and surface 54 area of ZrO₂ supports.^[8,27-31] However, conventional incipient-wetness impregnation and co-precipitation 55 methods usually result in WO_x/ZrO₂ composites with low surface area, uncontrollable and non-56 homogeneous distribution of polytungstate species, and low catalytic activity.^[26,32] Therefore, recent work 57 has been devoted to developing feasible strategies, such as microwave-assisted method,^[25] two-phase 58 interface hydrolysis method,^[33] and anionic exchange method,^[34] in order to obtain WO_x/ZrO₂ catalysts 59 with higher specific surface area and desired exposed active sites. The rational design of mesoporous 60 WO_x/ZrO₂ materials with good pore connection and uniform W dispersion has been considered to be an 61 62 effective route, because they can facilitate mass transfer and suppress carbon deposition in catalytic reactions involving large-size organic molecules. By using a one-pot synthesis method with Pluronic P123 63 triblock copolymer as template, tungsten and zirconium precursors were incorporated into the silica 64 framework of ordered mesoporous KIT-6.^[35] The WZr-KIT-6 catalyst possesses strong Lewis/Brönsted 65 66 acid sites, exhibiting improved ethylene yields in ethanol dehydration. The mesoporous ceramic acid was 67 prepared by coating a uniform WZrO_x layer onto the internal surface of mesoporous silica with extralarge pores (such as FDU-12).^[36] This mesoporous silica-supported WO_x/ZrO₂ solid acid exhibited 68 69 ordered mesostructure, strong Brönsted acid sites and high thermal stability, which also performed as a good catalyst in ethanol dehydration. However, most of the reported mesoporous catalysts are supported 70 71 on mesoporous silica through a low-efficiency loading route. To the best of our knowledge, little work has been reported on the direct synthesis of ordered mesoporous WO_x/ZrO₂ solid acids,^[23,37] especially 72 73 those with large ordered mesopores, abundant exposed acid sites and highly crystallized pore walls.

Ordered mesoporous materials (OMMs) are a kind of porous materials with uniform pore diameters
 between 2.0 and 50 nm, displaying unique physical/chemical properties, adjustable pore structure and

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high specific surface area,^[38-44] they thus have been extensively applied in numerous emerging fields. In 76 general, soft-template and hard-template methods are developed for OMMs synthesis.^[45-53] As a typical 77 soft-template approach, the controllable multicomponent co-assembly is flexible and universal for 78 79 synthesis of OMMs with diverse mesostructures and components. However, great challenges still remain 80 in directly synthesizing mesoporous WO_x/ZrO_2 composites by the traditional soft-template approach.^[23] 81 For example, Pluronic F127 was used as template for synthesis, and the product showed high specific 82 surface area but disordered mesopores with confined WO_x clusters, mainly due to mismatch of low glass transition temperature of F127 with high crystallization temperature of ZrO₂.^[47] In past decade, using the 83 lab-made amphiphilic diblock copolymer of poly(ethylene oxide)-b-polystyrene (PEO-b-PS) with rich sp² 84 carbon and high glass transition temperature as template, our group has developed a facile and universal 85 strategy for the synthesis of several highly ordered mesoporous metal oxides with single or multiple 86 components.^[54-62] But until now no work has been reported about the synthesis of ordered mesoporous 87 solid acids based on composite metal oxides.^[19] 88

Herein, by using a high molecular weight amphiphilic diblock copolymer (PEO₁₁₄-*b*-PS₂₂₁) as the 89 soft template, a controllable multicomponent co-assembly strategy was adopted to directly synthesize 90 ordered mesoporous WO_x/ZrO₂ solid acids (OMWZr) with tunable W contents and acid amounts. The 91 WO_x clusters were well restrained as acid sites onto pore walls of mesoporous WO_x/ZrO₂, in which 92 highly-crystallized mesoporous ZrO₂ provided a favorable rigid skeleton for uniform distribution and 93 stabilization of WO_x clusters. The robust ordered mesostructure and acidic polytungstate species on pore 94 walls were well maintained even after calcination at 600 °C. To the best of our knowledge, this is the first 95 report about the successful synthesis of ordered mesoporous WO_x/ZrO_2 solid acids with a soft-template 96 97 method. The OMWZr composites showed ordered mesostructures with pore size over 17 nm, pore volume of 0.13 - 0.18 cm³/g, surface area of 27.3 - 41.7 m²/g and tunable acid sites (0.026 - 0.118 mmol/g). The 98 intrinsic structural characteristics endow the OMWZr compositions with a particular potential application 99 as a high-efficiency solid acid catalyst in hydrolysis reaction of benzaldehyde dimethyl acetal with 100 101 excellent activity and recyclability.

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103 **2. Results and discussion**

Scheme 1 illustrates the procedure of one-pot controllable multicomponent co-assembly for synthesis of ordered mesoporous WO_x/ZrO_2 composites. Amphiphilic diblock copolymer of PEO-*b*-PS and two inorganic precursors were firstly dissolved in THF/EtOH solution. During evaporation of THF/EtOH, spherical composite micelles were gradually formed through aggregation of PEO-*b*-PS, which were composed of cores of hydrophobic PS blocks and shells of PEO blocks associated with uniform inorganic zirconium and tungsten species by hydrogen bonding (Step 1). In order to decrease surface free energy, the spherical micelles tended to closely pack into inorganic-polymer composites

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showing face-centered cubic (*fcc*) ordered mesostructures (Step 2). By calcination in N₂ atmosphere at 350 °C, the polymer as template was partially carbonized, and residual carbon was performed as rigid skeleton to support crystallized composite metal oxides at elevated temperatures. The template and residual carbon were completely removed by calcination in air at 600 °C, and during this process, framework crystallization was promoted to obtain the ordered mesoporous WO_x/ZrO_2 (OMWZr) composites with large mesopores, crystallized pore walls and tunable W/Zr ratios (Step 3).

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Scheme 1. Illustration of the one-pot controllable multicomponent co-assembly pathway for ordered mesoporous WO_x/ZrO₂ composites. Step 1: co-assembly of tungsten precursors, zirconium precursors and PEO-*b*-PS into composite spherical micelles with cores of hydrophobic PS segments and shells of PEO segments during THF/EtOH evaporation; Step 2: the spherical composites further pack into *fcc* ordered mesostructures after complete evaporation of solvent and thermosetting at 100 °C for further solidification; Step 3: carbonization of the ordered mesostructured composites under N₂ atmosphere and pyrolysis in air, resulting in ordered mesoporous WO_x/ZrO₂ composites.

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127 Crystallographic structures of OMWZr composites were identified by using wide-angle X-ray 128 diffraction (XRD) in the range of 20 - $80^{\circ}/2\theta$ (**Figure 1**A). First, the obtained mesoporous ZrO₂ displays 129 four primary diffraction peaks at 30.1, 35.2, 50.1, $60.1^{\circ}/2\theta$ (**Figure S1**A), which are indexed to (111), 130 (110), (112) and (121) reflections of tetragonal ZrO₂ (JCPDS No. 50-1089), respectively. For comparison, 131 two new diffraction peaks appear at 28.2 and $31.4^{\circ}/2\theta$ in OMWZr composites (**Figure 1**A), which are 132 well attributed to (-111) and (111) reflections of monoclinic ZrO₂ (JCPDS No. 37-1484) respectively,

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suggesting partial transformation of tetragonal ZrO₂ to monoclinic ZrO₂ caused by in situ insertion of 133 WO_x species into the framework of OMWZr composites. With W/Zr ratios increasing from 0.03 to 0.10, 134 the peak intensity of monoclinic ZrO_2 increases, while that of tetragonal ZrO_2 decreases (Figure 1A-a to 135 c), indicating that introduction of WO_x species can inhibit growth of tetragonal ZrO_2 and facilitate 136 crystallization of monoclinic ZrO₂. Besides, no diffraction peaks belonged to crystalline WO₃ are 137 138 observed in these XRD patterns, demonstrating that WO_x species are well dispersed on pore walls of the OMWZr composites when W content is below 10 mol%. However, diffraction peaks at 22.9, 23.5, 139 140 $24.2^{\circ}/2\theta$ appear in meso-0.15WO_x/ZrO₂ (Figure 1A-d), which are assigned to (002), (020) and (200) 141 reflections of monoclinic WO₃ (JCPDS No. 43-1035, Figure S1-B) respectively, suggesting that the 142 doped WO_x species easily crystallize into isolated WO₃ when W content is over 15 mol%. Raman spectroscopy was applied to further investigate fine structure of the obtained OMWZr composites (Figure 143 **1**B). The absorption peaks at around 469 and 631 cm⁻¹ correspond to tetragonal ZrO₂, while monoclinic 144 ZrO₂ can be well distinguished from the Raman bands at about 273, 331, 378, and 560 cm⁻¹, indicating 145 that all the OMWZr composites show two crystalline phases including tetragonal and monoclinic ZrO₂.^[63] 146 In addition, the Raman spectrum of meso-0.15WO_x/ZrO₂ catalyst displays two additional distinct bands 147 attributed to monoclinic WO₃ at 714 and 808 cm⁻¹ (Figure 1B-d),^[23] in good agreement with its XRD 148 pattern (Figure 1A-d). Each sample of OMWZr composites shows broad bands associated with WOx-O-149 Zr bridging bonds around 920 - 980 cm^{-1.[48]} Moreover, meso-0.03WO_x/ZrO₂ exhibit a band at around 150 1000 cm⁻¹, corresponding to isolated surface monotungstates. Besides of this band, meso-0.07WO_x/ZrO₂ 151 shows an additional band at about 1020 cm⁻¹, attributed to surface polytungstates (WO_x clusters), which 152 are the main sources of acid sites in WO_x/ZrO₂ composites, revealing coexistence of monomeric and 153 polymeric tungsten species in this sample.^[63] The band about monotungstates completely disappears in 154 meso-0.10WO_x/ZrO₂ and meso-0.15WO_x/ZrO₂, but the band about polytungstates can still be observed, 155 indicating that tungsten species in both samples exist as polytungstates. Therefore, the state of WO_x 156 species is closely dependent on the contents of W species in OMWZr composites. When W amount is 157 158 below 3 mol%, it primarily exists as surface monotungstate species. When W amount increases to 7 mol%, 159 both monotungstate species and polymetric WO_x clusters are dispersed in the composites. When W amount is up to 10 mol%, monotungstate species are completely replaced by polymetric WO_x clusters. 160 When W content further increases over 15 mol%, polymetric WO_x clusters and crystalline WO_3 particles 161 coexist in OMWZr composites. 162

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Figure 1. (A) XRD patterns and (B) Raman spectra of ordered mesoporous WO_x/ZrO_2 composites with different W/Zr mole ratios: (a) meso-0.03WO_x/ZrO₂, (b) meso-0.07WO_x/ZrO₂, (c) meso-0.10WO_x/ZrO₂, and (d) meso-0.15WO_x/ZrO₂.

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Transmission electron microscopy (TEM) images of the OMWZr composites taken along [110] 169 170 direction show that meso-0.03WO_x/ZrO₂, meso-0.07WO_x/ZrO₂ and meso-0.10WO_x/ZrO₂ possess ordered face-centered cubic (*fcc*) mesostructure ($Fm\overline{3}m$ symmetry) (**Figure 2A** to **2C**), in which average pore size 171 is estimated to be about 20.0 nm, consistent with the molecular size of PEO₁₁₄-*b*-PS₂₂₁. Field-emission 172 173 scanning electron microscope (FESEM) images further confirm their ordered mesoporous structures over a large domain composed of rigid skeletons in thickness of ~ 4.0 nm (Figure 2D to 2F). Pure mesoporous 174 175 ZrO₂ and WO₃ materials were also synthesized for comparison, exhibiting the same ordered 176 mesostructures with OMWZr composites (Figure S2A and S2B). However, the sample of meso-177 0.15WO_x/ZrO₂ displays worm-like mesostructures with low ordering (Figure 2C), mainly caused by the 178 formation of large WO₃ nanocrystals in WO_x/ZrO₂ composites and collapse of ordered mesopores when W content is as high as 15 mol%. 179

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Figure 2. TEM images of (A) meso- $0.03WO_x/ZrO_2$, (B) meso- $0.07WO_x/ZrO_2$, (C) meso- $0.10WO_x/ZrO_2$; and SEM images of (D) meso- $0.03WO_x/ZrO_2$, (E) meso- $0.07WO_x/ZrO_2$, (F) meso- $0.10WO_x/ZrO_2$.

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High-resolution TEM (HRTEM) image of meso-0.10WO_x/ZrO₂ (Figure 3A) clearly displays crystal 184 185 lattice of tetragonal ZrO_2 ((011) lattice plane) and monoclinic ZrO_2 ((111) and (-111) lattice plane) within mesopore walls, and no crystalline WO₃ phase appears around mesopore skeletons, in good consistence 186 187 with the XRD and Raman results (Figure 1). Owing to serious effect of tungsten precursors in large 188 amount on the co-assembly process, disordered mesopores and highly-crystallized ZrO₂ walls are formed 189 in meso-0.15WO_x/ZrO₂ (Figure S2C and S3A). The regular spotted diffraction rings in selected area 190 electron diffraction (SAED) patterns further confirm polycrystalline walls of meso- $0.10WO_x/ZrO_2$ and 191 meso-0.15WO_x/ZrO₂ (Figure 3B and S3B), containing both tetragonal and monoclinic ZrO₂. Moreover, 192 high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images show 193 ordered mesoporous structures with average pore size of 17.7 nm and wall thickness of 4.2 nm (Figure 194 3C). The corresponding energy dispersive X-ray (EDX) element mappings prove uniform distributions of 195 W, O and Zr elements over large domains (Figure 3D). The W/Zr mole ratio of meso- $0.10WO_x/ZrO_2$ is 196 calculated to be about 0.17, slightly higher than its chemical mole ratio (0.10), indicating that WO_x species

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as acid sites show an enrichment potential on surface of the OMWZr composites. Small-angle X-ray 197 198 scattering (SAXS) patterns of the OMWZr composites (Figure 4A) display scattering peak assigned to 111 reflection of ordered *fcc* mesostructure with space group of $Fm\overline{3}m$.^[58] In contrast, well-dispersed 199 WO_x species in monotungstate or polytungstate states are very small, in consequence, they have almost 200 201 no effects on unit cell parameters of OMWZr composites when W content is below 10 mol% (Figure 4A-202 a to c), which show ordered mesostructures and uniform dispersion of WO_x species. Nitrogen adsorptiondesorption isotherms of the OMWZr composites display type-IV curves with H1-type hysteresis loops 203 204 and sharp capillary condensation at high relative pressure (**Figure 4B**), suggesting that all the samples 205 possess uniform and large ordered mesopores. In addition, meso-0.03WO_x/ZrO₂, meso-0.07WO_x/ZrO₂ and meso-0.10WO_x/ZrO₂ present relatively narrow pore size distribution derived from the adsorption 206 207 branches, showing mean pore size centered at about 17.6, 17.1 and 23.8 nm, respectively (Figure 4C and Table 1). However, doping excessive tungsten species in framework gives rise to formation of crystalline 208 WO₃ and partial collapse of mesostructures, exhibiting wider pore size distribution and larger pore size 209 210 (27.5 nm) in meso-0.15WO_x/ZrO₂. Brunauer-Emmett-Teller (BET) surface area and pore volume of OMWZr composites are in the range of 27.3 - 41.7 m²/g and 0.133 - 0.182 cm³/g, respectively, and the 211 relatively low surface area of OMWZr materials is mainly due to the large mesopore size (> 17 nm) and 212 213 the high density of ZrO₂ skeletons and WO_x species. (Table 1). Meso-0.15WO_x/ZrO₂ owns the lowest 214 BET surface area among the OMWZr composites, further proving collapse of ordered mesopores during 215 calcination process.

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Figure 3. (A) HRTEM image, (B) SAED pattern, and (C) HAADF-STEM image of meso-0.10WO_x/ZrO₂,

and (D) the corresponding elemental mapping images of Zr, W and O elements.

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Figure 4. (A) SAXS patterns, (B) nitrogen sorption isotherms, and (C) pore size distribution curves of
 ordered mesoporous WO_x/ZrO₂ catalysts. (a, b, c and d represent meso-0.03WO_x/ZrO₂, meso 0.07WO_x/ZrO₂, meso-0.10WO_x/ZrO₂ and meso-0.15WO_x/ZrO₂, respectively.)

226 X-ray photoelectron spectroscopy (XPS) was conducted to capture detailed information about 227 surface elements of mesoporous WO_x/ZrO₂ composites (Figure 5). Taking meso-0.10WO_x/ZrO₂ as an 228 example, the Zr 3d XPS spectrum shows two well-resolved peaks at 182.6 and 185.0 eV (Figure 5A), which are assigned to $Zr^{4+} 3d_{5/2}$ and $Zr^{4+} 3d_{7/2}$,^[64] respectively. In addition, valence states of W species in 229 230 meso-0.10WO_x/ZrO₂ are analysed by the W 4f XPS spectrum (Figure 5B), where peaks at 38.0 and 35.9 eV are assigned to $W^{6+} 4f_{5/2}$ and $W^{6+} 4f_{7/2}$ respectively,^[57] demonstrating the existence of hexavalent 231 232 tungsten in polytungstates of WO_x clusters that perform as acid sites in catalytic reactions. The results 233 further indicate that introduction of W species in mesoporous skeletons does not affect the valence states of Zr species. However, they greatly influence the crystallization behaviour of ZrO₂ with a partial 234 transformation from tetragonal phase to monoclinic phase. Meanwhile, the presence of ZrO₂ does not 235 236 affect the valence states of W species, which performs as an appreciate support for uniform dispersion 237 and stabilization of WO_x clusters under an appropriate doping amount. Although crystalline WO₃ is formed from excess doped W precursors in meso-0.15WO_x/ZrO₂, the Zr 3d and W 4f XPS spectra of the 238 239 sample are quite similar with those of meso-0.10WO_x/ZrO₂ (Figure S4).



Figure 5. XPS spectra of meso-0.10WO_x/ZrO₂ in the vicinity of (A) Zr 3d, and (B) W 4f.

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Figure 6. (A) NH₃-TPD curves of (a) meso-0.10WO_x/ZrO₂, and (b) bulk-0.10WO_x/ZrO₂, (B) total acidity
of WO_x/ZrO₂ composites with different amount of W species, (C) pyridine-adsorbed DRIFT spectra of
(a) meso-0.10WO_x/ZrO₂, and (b) bulk-0.10WO_x/ZrO₂.

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NH₃-TPD profiles are used to compare the acid density and strength of meso-0.10WO_x/ZrO₂ and 247 248 bulk-0.10WO_x/ZrO₂ composites (Figure 6A). From the integration areas it can be observed that meso-0.10WO_x/ZrO₂ possesses higher acid amount than bulk-0.10WO_x/ZrO₂. Meanwhile, each sample shows 249 250 one broad NH₃ desorption peak centered at about 120 °C, belonged to weakly bounded NH₃, suggesting 251 that mesoporous and bulk WO_x/ZrO_2 composites possess the acid sites with similar acid strength. 252 Moreover, through calibrating the integration areas of NH₃ desorption peaks, the acid amount of OMWZr 253 composites increases from 0.026 to 0.118 mmol/g when W content increases from 3 to 10 mol%, and then decreases to 0.098 mmol/g when W content is up to 15 mol% (Figure 6B and Table 1), due to formation 254 of crystalline WO₃ of excess tungsten species in meso-0.15WO_x/ZrO₂, further proving that polymeric 255 256 WO_x clusters supported on ZrO₂ are the acid sites of OMWZr composites. In order to understand better the relationship between acid property and tungsten content, WO_x density (W per nm²) was calculated by 257 the equation as follows:^[65] 258

Promoter loading (wt.%)/100 \times N_A

W surface density =

Formula weight of promoter \times S_{BET} $(m^2g^{\text{--}1}) \times$ 1 \times 10^{18}

The W surface densities of OMWZr catalysts were 2.23, 5.53, 8.03 and 13.78 W/nm², respectively (**Table** 1), demonstrating that isolated monotungstates species existed in meso-0.03WO_x/ZrO₂ and the formation of polytungstates occurred in OMWZr catalysts with W content over 0.03. Notably, crystalline WO₃ coexisted with polytungstates species in meso-0.15WO_x/ZrO₂ with a tungsten density (13.78 W/nm²) over 8 W/nm², according to the growth mode of tungstate species over zirconia, which has been previously studied in depth.^[28] Moreover, the W density of meso-0.10WO_x/ZrO₂ was calculated as 8.03 W/nm²,

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indicating the saturation of polytungstate over meso-0.10WO_x/ZrO₂, therefore, meso-0.10WO_x/ZrO₂ 266 267 owns the highest acidity of OMWZr catalysts. The existence form of tungsten species in OMWZr composites inferred from tungsten density is in good agreement with the results of Raman analysis, which 268 269 well explains the acidity change of OMWZr catalysts with the increase of W content. Pyridine-adsorbed 270 DRIFT spectra captured at 100 °C of bulk-0.10WO_x/ZrO₂ and meso-0.10WO_x/ZrO₂ show bands around 1449, 1490 and 1545 cm⁻¹ (Figure 6C). The band at 1449 cm⁻¹ is attributed to molecular pyridine 271 coordinated to Lewis acid (L acid) sites, and peak at 1545 cm⁻¹ is responsible for Brönsted acid (B acid) 272 sites, while the band at 1485 cm⁻¹ is a combined one originating from pyridine bonded to both B and L 273 acid sites.^[29] The results suggest that both meso-0.10WO_x/ZrO₂ and bulk-0.10WO_x/ZrO₂ composites 274 possess L and B acid sites. While the 1545 cm⁻¹ band of bulk-0.10WO_x/ZrO₂ is weaker than that of meso-275 0.10WOx/ZrO2, indicating that meso-0.10WOx/ZrO2 possesses more B acid sites than bulk-276 0.10WO_x/ZrO₂, because WO_x clusters mainly bring B acid sites to the catalyst,^[29] which are very stable 277 278 and difficult to migrate and crystallize into large particles on the surface of meso-0.10WO_x/ZrO₂ with 279 mesostructure of three-dimensional connected spherical pores. Moreover, peak areas at 1545 cm⁻¹ of both 280 meso-0.10WO_x/ZrO₂ and bulk-0.10WO_x/ZrO₂ change little with purge temperature increasing from 100 281 to 400 °C (Figure S6), revealing high stability of B acid sites in WO_x/ZrO₂ composites. Considering the 282 unique mesostructures and surface acid properties, the obtained OMWZr composites were used as heterogeneous catalysts for deprotection of benzaldehyde dimethyl acetal (BDA), a typical acid-catalytic 283 probe reaction and an important step for protection amd deprotection of aldehyde groups (Figure 7A).^{[66-} 284 67] 285

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Figure 7. (A) Reaction equation of hydrolysis of benzaldehyde dimethyl acetal to benzaldehyde catalyzed by Brönsted acid, (B) conversion of benzaldehyde dimethyl acetal, and (C) selectivity to benzaldehyde over ordered mesoporous WO_x/ZrO_2 catalysts and bulk-0.10 WO_x/ZrO_2 at the reaction time of 2 h (a, b, c, d, e and f represent blank system (without catalyst), meso-0.03 WO_x/ZrO_2 , meso-0.07 WO_x/ZrO_2 , meso-0.10 WO_x/ZrO_2 , meso-0.15 WO_x/ZrO_2 and bulk-0.10 WO_x/ZrO_2 , respectively), (D) conversion of

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benzaldehyde dimethyl acetal and selectivity to benzaldehyde over meso- $0.10WO_x/ZrO_2$ calcined at different temperatures (500, 600 and 700 °C) for 2 h.

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296 The blank system in absence of catalysts shows only 1% conversion of BDA even after reaction for 297 4 h (Figure 7B-a), and similar results appeare when the reaction is catalyzed over mesoporous ZrO_2 298 (Figure S7A), indicating that hydrolysis rate of BDA is very slow under spontaneous reaction and pure 299 mesoporous ZrO_2 provides hardly catalytic active sites. Though mesoporous WO_3 has slight catalytic 300 effect on the hydrolysis of BDA, it exhibits poor selectivity to benzaldehyde (Figure S7B). All the 301 investigated WO_x/ZrO₂ composites display catalytic activity toward the hydrolysis of BDA, and the 302 conversion gradually increases as a function of reaction time (Figure 7B-b to f). Moreover, for the 303 OMWZr catalysts, the conversion of BDA at the same reaction time of 2 h increases in the order as meso-304 $0.03WO_x/ZrO_2 < meso-0.07WO_x/ZrO_2 < meso-0.15WO_x/ZrO_2 < meso-0.10WO_x/ZrO_2$, in consistence 305 with that of the acid amount (Figure 6B), further confirming that the BDA hydrolysis is an acid-catalytic 306 reaction. Meso- $0.10WO_x/ZrO_2$ shows the best catalytic activity, reaching as high as 99.1% conversion of 307 BDA at 2 h (Figure 7B-d). In spite of that meso- $0.03WO_x/ZrO_2$ owns the largest surface area, it shows 308 the lowest acid amount (0.026 mmol/g) and catalytic activity, due to existence of monotungstates but no 309 polytungstates at the surface of mesoporous skeletons.^[29] In addition, although the content of W species in meso-0.15WO_x/ZrO₂ is higher than that of meso-0.10WO_x/ZrO₂, the former catalyst exhibits lower 310 311 catalytic efficiency before 2 h, probably because of partially crystallized WO₃ on ZrO₂ support from excess W species and slightly lower acid amount (0.098 mmol/g) in meso-0.15WO_x/ZrO₂. For comparison, 312 313 the hydrolysis reaction was also conducted over the counterpart sample of bulk- $0.10WO_x/ZrO_2$ with comparable acid amount (0.103 mmol/g) but low specific surface area (9.6 m^2/g) and high tungsten 314 density (13.78 W/nm²), showing lower catalytic activity than meso-0.10WO_x/ZrO₂ (Figure 7B-f). 315 Therefore, under the same W content and close acid amount, meso-0.10WO_x/ZrO₂ presents improved 316 catalytic activity compared to bulk-0.10WO_x/ZrO₂, attributed to faster diffusion of reactants and products 317 318 within well-developed mesopores, more appropriate W density (8.03 W/nm²) and easily accessible acid 319 sites especially rich Brönsted acid in meso-0.10WO_x/ZrO₂. The same conclusion can also be drawn by 320 comparing other mesoporous and bulk WO_x/ZrO_2 catalysts (Figure S8). Furthermore, all the WO_x/ZrO_2 321 catalysts show the selectivity to benzaldehyde higher than 97% (Figure 7C), in which meso-322 0.10WO_x/ZrO₂ owns the highest selectivity of 98.9%, further proving its outstanding catalytic 323 performance in BDA hydrolysis. Meso-0.10WO_x/ZrO₂ with polytungstate species of WO_x clusters on ZrO_2 surface shows the highest TOF value of 1.1×10^{-2} s⁻¹ among all the obtained WO_x/ ZrO_2 composites 324 325 (Table 1), in good agreement with the excellent catalytic performance of meso- $0.10WO_x/ZrO_2$. The influence of calcination temperatures on catalytic performance of meso-0.10WO_x/ZrO₂ solid acids was 326 327 also studied (Figure 7D). The sample calcined at 600 °C shows the highest catalytic activity. The

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conversion of BDA over meso-0.10WOx/ZrO2-500 composed of low-crystallized tetragonal ZrO2 (Figure 328 329 **S5B**) is as low as 59%, due to low content of acid amount and existence of a little of residual carbon on surface after calcination at 500 °C for 2 h (Figure S9A). Once calcination temperature further increases 330 to 700 °C, the conversion of BDA decreases to 91.3% as the acid amount reduced by formation of 331 332 monoclinic WO₃ crystals (Figure S5D). Therefore, the calcination temperature of 600 $^{\circ}$ C favors the 333 formation of polytungstate WO_x species as active acid sites, which further facilitate the improvement of 334 BDA hydrolysis. Moreover, the catalysts calcined at different temperatures show close selectivity to 335 benzaldehyde at about 99%, indicating that calcination temperatures have weak effects on the catalytic 336 selectivity. In addition, the long-term stability and recyclability of meso-0.10WO_x/ZrO₂ were also tested 337 (Figure S10), and the catalytic activity decreased slightly as reaction cycles going on. The XRD pattern 338 and Raman spectrum (Figure S11) of the recycled meso-0.10WO_x/ZrO₂ after 10-cycles catalytic reactions 339 show similar results to those of the fresh catalyst, and no peaks indexed to crystalline WO₃ are observed, 340 suggesting that polymeric WO_x clusters didn't crystallize into WO₃ particles in the mesopore channels 341 during recycling process. The TEM and SEM images of the recycled catalysts (Figure S12) retained 342 ordered mesostructure, indicating that the mesoporous ZrO_2 skeleton can be well maintained during the 343 catalytic reactions. In addition, the average crystallite sizes of the fresh and the recycled meso-344 0.10WO_x/ZrO₂ measured by TEM observation were around 5.5 and 6.5 nm, respectively, agreeing well with XRD results. The recycled meso-0.10WO_x/ZrO₂ possesses surface area of 32.6 m^2/g and pore size 345 346 of 20.2 nm (Figure S13A and B), which were slightly reduced in comparison with that of the fresh catalyst, 347 mainly originated from the slight growth of grain size. The acid amount of the recycled catalyst was calculated as 0.093 mmol/g from NH₃-TPD profile (Figure S13C), lower than 0.118 mmol/g of the fresh 348 catalyst possibly due to the leaching of W species, which is responsible for the decrease of acid-catalytic 349 350 performance. Nevertheless, the conversion was still preserved higher than 85% and the selectivity to 351 benzaldehyde was over 97% even after ten cycles. Therefore, meso-0.10WO_x/ZrO₂ with ordered mesostructure and moderate loading amount of W species calcined at 600 °C exhibits the optimal catalytic 352 353 performance, due to numerous WO_x clusters dispersed on pore walls of rigid mesoporous ZrO₂, which 354 provide a large number of accessible Brönsted acid sites.

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357 **3. Conclusion**

In summary, a facile and controllable multicomponent co-assembly approach was utilized to successfully synthesize a series of ordered mesoporous WO_x/ZrO_2 (OMWZr) catalysts with tunable W contents for the first time, by which loading-efficiency and dispersion of W species were promoted. The obtained OMWZr catalysts possess robust ordered mesostructures with interconnected large mesopores even after

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362 calcination at 600 °C. Besides, the materials show favorable rigid skeletons composed of highly 363 crystalline ZrO₂ for uniform dispersion and stabilization of WO_x clusters, leading to the production of great numbers of exposed accessible Brönsted acid sites. Consequently, the OMWZr catalysts show 364 365 outstanding acid-catalytic performance for hydrolysis of benzaldehyde dimethyl acetal. Detailed structure 366 characterizations and mechanism analysis reveal that large mesopores and active polymeric WO_x clusters 367 result in rich surface Brönsted acid sites, which contribute to superior acid-catalytic activity and excellent 368 recyclability of the OMWZr catalysts. It is believed that the synthesized OMWZr catalysts can be used 369 for various solid acid-catalyzed reactions, and through the similar controllable multicomponent co-370 assembly, a variety of ordered mesoporous metal oxides with high porosity, rich interfaces, different components and functionalities can be readily synthesized for diverse applications, such as petrochemical 371 372 heterogeneous catalysis, chemical sensing and energy conversion.

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Table 1. Textural and catalytic properties of ordered mesoporous WO_x/ZrO_2 composites with different amount of loaded W species and bulk-0.10WO_x/ZrO₂.

Sample	BET surface area (m²/g)	Pore volume (cm ³ /g)	Pore size (nm)	Acidity (mmol/g)	W density (W/nm ²)	TOF [#] (s ⁻¹)
meso-0.03WO _x /ZrO ₂	41.7	0.182	17.6	0.026	2.23	7.2×10^{-3}
meso-0.07WO _x /ZrO ₂	35.7	0.133	17.1	0.074	5.53	8.7×10^{-3}
meso-0.10WO _x /ZrO ₂	33.7	0.162	23.8	0.118	8.03	1.1×10^{-2}
meso-0.15WO _x /ZrO ₂	27.3	0.161	27.5	0.098	13.78	5.1×10^{-3}
bulk-0.10WO _x /ZrO ₂	9.6	0.032	13.6	0.103	20.60	7.9×10^{-3}

[#] TOF: the conversion mole number of benzaldehyde dimethyl acetal at a single active site per unit time.

4. Experimental section

Chemicals and Materials. Monomethyl poly(ethylene oxide) (M_w: 5000 g/mol) was purchased from Aldrich. N,-N,-N',-N",-N"-Pentamethyl diethylenetriamine (PMDETA) was purchased from Acros Corp. Zirconium(IV) acetylacetonate (Zr(acac)₄), tungsten(VI) hexachloride (WCl₆) and decane were purchased from Aladdin Corp. Benzaldehyde dimethyl acetal (BDA) was purchased from TCI Development Co., Ltd. Other chemicals including tetrahydrofuran (THF), ethanol (EtOH), concentrated hydrochloric acid (HCl, 37 wt.%), acetic acid, pyridine, styrene, toluene, benzaldehyde, ethylether, CuBr, petroleum ether (b.p. 30 - 60 °C) were purchased from Sino-Pharm Chemical Reagent Co., Ltd. All the chemicals were of analytical grade and used as received without further purification.

Synthesis of Ordered Mesoporous WO_x/ZrO₂ Catalysts. In a typical synthesis of mesoporous WO_x/ZrO₂, 37.5 mg lab-made amphiphilic diblock copolymer (PEO₁₁₄-b- PS_{221} , $M_n = 27960$ g/mol) was dissolved in 4 mL THF to obtain solution A. $Zr(acac)_4$ of 0.15 g was dissolved in 1 mL ethanol, in which 75 µL concentrated hydrochloric acid and 75 µL acetic acid were added, and then different amount of WCl₆ was added to form solution B to adjust the content of WOx species. Afterwards, solution A and solution B were mixed under stirring and yellow transparent solution was formed after further stirring for 2 h, which was then poured onto Petri dishes. After slow solvent evaporation under room temperature for 24 h, sequential heating at 40 °C for 24 h to completely remove solvent and aging at 100 °C for another 24 h, the inorganic-polymer composites were formed as a thin film on Petri dishes. The film was scraped off and crushed into fine powder, and then calcined at 350 °C for 2 h in nitrogen (heating rate = 1 °C/min), followed by calcination at 600 °C in air for another 2 h (heating rate = 5 °C/min), resulting in white powder of mesoporous WO_x/ZrO₂ (OMWZr). Pure mesoporous zirconia (ZrO₂) was also synthesized in the same way, during which WCl₆ was not added in solution B. For comparison, bulk WOx/ZrO2 catalysts were synthesized in the same way without addition of PEO₁₁₄-*b*-PS₂₂₁. The final ordered

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mesoporous catalysts and bulk catalysts were denoted as meso- pWO_x/ZrO_2 and bulk pWO_x/ZrO_2 respectively, where *p* stands for feed mole ratio of W to Zr. For instance, meso-0.10WO_x/ZrO₂ means the sample that 10 mol% WCl₆ was added during synthesis. As a note, loading amount of tungsten is defined as mole of nominal W species per mole of ZrO₂ support.

Measurement and Characterization. Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics Tristar 3020 analyzer. Before determination, the samples were degassed in vacuum at 180 °C for longer than 6 h. The Brunauer-Emmett-Teller (BET) method was used to calculate specific surface areas of the samples. By using Barrett-Joyner-Halenda (BJH) model, total pore volume (Vtotal) was calculated from the adsorbed amount of nitrogen at $P/P_0 = 0.995$ and pore size distribution curve was obtained from the adsorption branch of isotherms. Transmission electron microscope (TEM) images were taken on JEM-2100F microscope (JEOL, Japan). Scanning electron microscopy (SEM) images were recorded on Hitachi S4800 FESEM (Japan). High-resolution TEM (HRTEM) images were taken on FEI Field Emission Transmission Electron Microscope (America). Small-angle X-ray scattering (SAXS) patterns were collected on Bruker Nanostar U small angle X-ray scattering system (Germany) using Cu K_{α} radiation (40 kV, 40 mA). X-ray power diffraction (XRD) measurements were carried out on Bruker D4 X-ray diffractometer (Germany) equipped with Ni-filtered Cu K_{α} radiation (40 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) was conducted on RBD 147 upgraded PHI 5000C ESCA system with a dual X-ray source. The pyridine adsorbed Fourier transform infrared (FT-IR) spectroscopy was conducted on NICOLET NEXUS 470 (US THERMO). A certain amount of sample was firstly pressed into in-suit cell and purified at 400 °C for 2 h under vacuum. The saturated pyridine vapor was absorbed on materials at 35 °C for 10 min, and then the spectra was obtained when pyridine was removed by vacuum for 5 min at 100, 200, 300 and 400 °C, respectively. NH₃-temperature programmed desorption (NH₃-TPD) measurement was conducted on Micromeritics AutoChem II 2920 (America) equipped with a thermal conductivity detector (TCD). The catalysts of

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about 100 mg were charged into a quartz U-type tube at ambient temperature and degassed in helium atmosphere at 600 °C for 3 h before test. After cooled to 110 °C, NH₃ gas was poured into the quartz U-type tube immediately, which was held for 2 h to make the sample chemically adsorb NH₃ adequately. Then the temperature was increased from 120 °C to 600 °C at the rate of 10 °C/min to release NH₃. Gas chromatography-mass spectrum (GC-MS) was used to analyze catalytic products and recorded on Shimadzu GCMS-QP2020 (Japan) equipped with SH-Rxi-5Sil capillary.

Acid-catalysis Tests. The acid-catalyzed deprotection of benzaldehyde dimethyl acetal to benzaldehyde was performed to evaluate the activity of mesoporous WO_x/ZrO_2 catalysts. In a typical procedure, the catalytic reaction was carried out in a two-neck round bottom flask, and toluene of 5 mL was used as solvent. Benzaldehyde dimethyl acetal of 150 µL, deionized water of 40 µL and catalyst of 20 mg were charged into the flask, and the mixture was then heated in an oil bath at 90 °C for 4 h. The reaction was performed under vigorous stirring (700 rpm) at atmospheric pressure. Liquid sample of 0.1 mL was withdrawn periodically at 30-minute or 60-minute intervals from the reactor with a syringe in order to separate the solid catalyst from the solution. The withdrawn liquid was cooled down to room temperature and diluted in 1 mL toluene, and the solution was analyzed by GC-MS. In addition, in order to confirm the effect of acid catalysts on conversion of benzaldehyde dimethyl acetal and selectivity to benzaldehyde, a blank experiment in absence of any catalysts was conducted under the same conditions for comparison.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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was utilized to controllably synthesized

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A multicomponent co-assembly approach was utilized to controllably synthesized ordered mesoporous ZrO_2 with stably supported and well dispersed WO_x clusters, which possess easily accessible Brönsted acid sites, and well-connected pore structure and thus exhibit outstanding acid-catalytic performance in hydrolysis of benzaldehyde dimethyl acetal.

Keyword Mesoporous materials, Multicomponent co-assembly, Solid acid, Tungsten oxide, Zirconia

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Controllable Multicomponent Co-Assembly Approach to Ordered Mesoporous Zirconia Supported with Well-Dispersed Tungsten Oxide Clusters as High-Performance Catalysts

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