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Conversion of Dimethyl Ether to Toluene under O <sub>2</sub> stream over
W/HZSM-5 catalyst
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### 7 Abstract:

The direct conversion of dimethyl ether (DME) to toluene without other aromatics 8 becomes true over W/HZSM-5 catalysts with high W contents. The influence of W content on 9 10 the nature of tungsten species, the distribution of acid sites, the redox properties, and the subsequent catalytic performance of W/HZSM-5 in DME conversion was investigated. The 11 introduction of high content of W in HZSM-5 can bring up some new redox sites and acidic 12 sites associated with W species, although they also cover some acidic sites in HZSM-5. By 13 this way, the introduction of W interrupts the dual cycle of the DME-to-hydrocarbons reaction 14 on HZSM-5, and the formation of higher methylbenzenes is limited effectively. 15

16 Keywords: Dimethyl ether, Toluene, tungsten, HZSM-5

## 17 1. Introduction

Dimethyl ether (DME) can be one-step synthesized from syngas with the elevated maximum conversion, which makes it a promising candidate as clean and high efficiency energy<sup>1-3</sup>. DME can replace liquefied petroleum gas, and it is also an attractive eco-friendly

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fuel for vehicles due to its superior combustion properties<sup>4</sup>. Not only limited to energy 1 products, accompanied with the enlarged DME industry, DME is also an essential starting 2 material or intermediate for value-added chemicals. At present, some catalytic conversion 3 reactions of DME have been explored and progress has been achieved. Generally, DME 4 molecule can be easily activated to form CH<sub>3</sub>-, CH<sub>3</sub>O- and CH<sub>3</sub>OCH<sub>2</sub>- groups. Then the 5 active groups can form hydrocarbons like olefins, gasoline and aromatics<sup>57</sup> through the 6 hydrocarbon pool (HP) mechanism, or they can form oxygenated compounds such as methyl 7 acetate<sup>8</sup>, formaldehyde (FA)<sup>9</sup>, dimethoxymethane (DMM)<sup>10,11</sup>, methyl formate (MF)<sup>12</sup>, and 8 ethanol<sup>13</sup>. 9

Concerning the catalysts, DME catalytic conversion is usually conducted on solid acid 10 11 catalysts like zeolite. In particular, the zeolite ZSM-5, distinguished by shape selectivity and good acid properties, exhibits high activity in conversion of DME to hydrocarbons in a 12 fixed-bed reactor with a slow deactivation rate<sup>14-16</sup>. Moreover, transition metal oxides have 13 usually been used to modify zeolite property to enhance catalytic activity and selectivity, 14 because of the ability of accommodating acidity of zeolite and enhancement of the activation 15 16 of the DME molecule under O<sub>2</sub> atmosphere at lower temperature, thus, adjusting product distribution<sup>17</sup>. Among these transition metals, tungsten oxide gives the strong Brønsted acid 17 sites, either as bulk or supported oxides but their structure and catalytic properties are strongly 18 influenced by the support<sup>18</sup>. Several studies have explored how interactions between support 19 and tungsten oxide domains affect catalytic performance. Indeed, even for a given  $WO_x$ 20 support system,  $WO_x$  domains exhibit a range of surface structures that depend strongly on 21 22 synthetic protocols, such as the  $WO_x$  precursor and content, as well as on the thermal history

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of these materials<sup>19-21</sup>. Yang et al. reported that W/HZSM-5 catalyst was a good dehydroaromatization catalyst in the presence of oxygen<sup>22</sup>. Anyway, Liu et al. obtained trace toluene from DME oxidation to ethanol over HZSM-5 catalysts with low tungsten contents (<23 wt.%) without other aromatic products<sup>23</sup>. Reasonably, it is possible to gain toluene with high selectivity from DME conversion through tuning the synergic effect of tungsten and HZSM-5. However, there have been no reports on direct conversion of DME to toluene over W/HZSM-5 catalysts.

In this work, a novel route for the synthesis of toluene from DME direct conversion over 8 W/HZSM-5 in the presence of oxygen was studied. The catalysts with relative high W 9 contents were prepared and characterized by the X-ray diffraction (XRD),  $N_2$  adsorption, 10 11 ultraviolet visible spectroscopy (UV-vis), X-ray photoelectron spectroscopy (XPS), 12 temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) and temperature-programmed 13 reduction of hydrogen (H<sub>2</sub>-TPR) in details. The influence of W content on the distribution of acid sites, the redox properties, the nature of tungsten species, and the subsequent catalytic 14 performance of W/HZSM-5 in DME conversion to toluene was investigated. 15

16 2. Experimental

## 17 2.1 Catalyst preparation

The W/HZSM-5 catalysts were prepared by a wet impregnation method, as described elsewhere<sup>24</sup>. To obtain the catalysts with different tungsten contents, the HZSM-5 powder (supplied by Shandong Qilu Huaxin High-tech Company) was first infiltrated in thermostat water bath (80 °C) with aqueous solutions of ammonium metatungstate containing the desired amount of  $(NH_4)_6W_{12}O_{40}.xH_2O$ . The resulting material was then dried at 110 °C for 10 h and subsequent calcination at 500 °C for 5 h. The concentration of W was adjusted with the
nominal value of W contents (25, 35, 45, 50 and 55 wt.%). The catalyst obtained was then
expressed as x W/HZSM-5. The actual W contents x were determined by inductively coupled
plasma-atomic emission spectrometry (ICP-AES), as shown in Table 1.

2.2 Catalyst characterization

K-ray diffraction (XRD) analysis was carried out by using Bruker D8 Advance X-ray diffractometer with monochromatic high-intensity Cu Kα radiation ( $\lambda = 1.5418$  Å) in the 20 range of 5-70° operated at 30 kV and 30 mA.

Nitrogen adsorption/desorption isotherms were measured at -196 °C on a Micromeritics ASAP 2020 adsorption apparatus. Before the measurements, the samples were degassed at 300 °C for more than 6 h under high vacuum conditions. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas ( $S_{BET}$ ). The pore size distribution was derived from the adsorption branch by Barrett-Joyner-Halenda (BJH) method. The total pore volumes were estimated from the adsorbed amount at a relative pressure P/P<sub>0</sub> of 0.99.

Diffuse reflectance UV-vis spectra were performed on a Hitachi U-4100 spectrophotometer equipped with a diffuse reflectance attachment. Spectra were recorded at room temperature in the wavelength range 200-800 nm.

18 XPS was obtained on a Quantum-2000 Scaning ESCA Microprobe instrument using Al 19 K $\alpha$  X-ray radiation source. The pressure in the analysis equipment was maintained below 10<sup>-6</sup> 20 Pa during the data acquisition. The passing energy of the experiment was 46.95 eV, and all the 21 binding energy measured was calibrated with contaminated carbon (284.6 eV) as reference. 22 The spectra were decomposed by using XPSPEAK software (Ver. 4.1) after applying a 23 Shirley background subtraction and Gaussian (80%)-Lorentzian (20%) decomposition

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parameters. Atomic ratios were calculated from the peak areas that were calibrated by the
 sensitive factors provided by the equipment manufacturer.

NH<sub>3</sub>-TPD spectra were recorded on Micromeritica Auto Chem 2920. The sample (100 3 mg) was pretreated at 500 °C in an Ar flow of 20 ml/min for 1 h and then cooled down to 100 4 °C to be introduced with NH<sub>3</sub>. The spectra were recorded from 100-700 °C with a rate of 5 5 <sup>o</sup>C/min. The quantities of weak, medium, and strong acid sites are measured by the amounts 6 7 of ammonia desorbed at 100-200, 200-300, and 300-600 °C, respectively, through integrating the NH<sub>3</sub>-TPD profile in each temperature interval. The apparatus and pretreated condition in 8 H<sub>2</sub>-TPR experiment were same with NH<sub>3</sub>-TPD. After cooling down to room temperature and 9 introducing the reduction agent of 10% H<sub>2</sub>/Ar (30 ml/min), the sample was heated up to 10 11 900 °C from room temperature at a rate of 5 °C/min. The amount of H<sub>2</sub> uptake during the 12 reduction was measured by a thermal conductivity detector (TCD), which was calibrated by the quantitative reduction of CuO to the metallic copper<sup>25</sup>. 13

Diffuse reflectance infrared spectra were measured by a Bruker Tensor 27 with a MCT 14 detector (64 scans, 4 cm<sup>-1</sup>). The catalyst was placed in an in situ IR cell equipped with KBr 15 windows (Harrick). After heating at 400 °C for 2 h and evacuating at  $10^{-4}$  bar, the cell was 16 17 cooled down to reaction temperature and the spectrum was recorded. Next, the mixture gas of DME and O<sub>2</sub> (nDME/nO<sub>2</sub>=1:1) was introduced into the cell, and the spectra of catalyst 18 adsorption were recorded. Finally, the catalyst desorption spectra were recorded after 30 min 19 of reaction and the pressure of the cell was evacuated to 10<sup>-3</sup> bar. Thermo 20 gravimetric/derivative thermo-gravimetry TG/DTG was measured on a NETZSCH STA 409 21 22 PC analyser. The sample weight was about 10 mg. The temperature was ramped to 800 °C at

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### 2 2.3 Catalytic tests and analytic procedures

The catalytic test was performed in a continuous flow fixed-bed reactor with an inner 3 diameter of 10 mm. The catalyst (40-60 mesh) was diluted with SiO<sub>2</sub> (20-40 mesh). Before 4 reaction, the catalyst was pretreated in oxygen (99.999%) flow (25 ml/min) at 400 °C for 1 h. 5 The reactant mixture consisted of DME and  $O_2$  (nDME/n $O_2 = 1:1$ ), and the gas hourly space 6 velocity (GHSV) was 800 h<sup>-1</sup>. The outlet stream line from the reactor to the gas 7 chromatograph was heated at 150 °C. The DME, toluene, MF, methanol, DMM, formaldehyde 8 products were analyzed by a gas chromatograph (GC-2060) equipped with a thermal 9 conductivity detector (TCD) and a Porapak Q column (3 m x 3 mm), a gas chromatography 10 11 (Agilent 7890A) with an flame ionization detectors (FID) (HP-PLOT capillary column), and a 12 TCD (5 A molecular sieve) for analyzing alkanes, olefins, H<sub>2</sub>, CO and CO<sub>2</sub>.

13 **3. Results and discussion** 

#### 14 *3. 1 XRD and textural characterization*

XRD patterns of HZSM-5 and W/HZSM-5 catalysts with different W contents are shown 15 in Fig. 1. The parent HZSM-5 sample exhibits the characteristic peaks of MFI structure (at  $2\theta$ 16 of 7.9°, 8.9°, 23.07°, 23.6° and 24.4°) and quartz phase at 20 of 26.6° (PDF number 17 89-1961)<sup>26</sup>. However, with the increase of the W content, these diffraction lines of HZSM-5 18 decrease in intensity. Meanwhile new lines characteristic of cubic WO<sub>3</sub> (at  $2\theta$  of  $23.64^{\circ}$ , 19 33.64°, 41.46° and 54.57°, PDF number 46-1096) and monoclinic WO<sub>3</sub> (at 20 of 23.12°. 20 23.59°, 24.38°, 34.16° and 49.95°, PDF number 43-1035) are observed for the W/HZSM-5 21 22 catalysts. As for the 23.3 and 34.9 wt.% W/HZSM-5 catalysts, the split of the peaks at 23.1°

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and 23.6° are highly likely to be caused by their overlapping with the HZSM-5 zeolite characteristic bands at 23.07°, 23.64° and 24.4°. Moreover, the overlapping peaks become less obvious with the W content increasing from 46.1 to 56.0 wt.%, that is because the crystallinity of HZSM-5 zeolite decrease remarkably, pointing to a possible deterioration effect of tungsten species on the framework of HZSM-5 zeolite. Meanwhile, the intensity of the peaks at 23.6° and 24.4° increase obviously, this suggests that the fraction of the monoclinic phase of WO<sub>3</sub> increases with the W content increasing.

### {Fig. 1}

9 The surface area data of the HZSM-5 and W/HZSM-5 catalysts with different W contents obtained by N<sub>2</sub> adsorption method are shown in the Table 1. Obviously, the 10 introduction of W species leads to the decrease of surface area. With the W content from 23.3 11 to 56.0 wt.%, the surface area decreases from 216.35 to 111.56  $m^2/g$ . The porous structure of 12 the W/HZSM-5 is also affected by introducing different W loadings. In general, the 13 microporous volume of W/HZSM-5 zeolites is decreased by increasing W content. Although 14 most of  $WO_3$  particles located on the surface, as revealed by the XPS results, they still may 15 partially block the HZSM-5 microchannels and reduce the accessibility of micropores (Table 16 17 1). Moreover, the mesoporous volume of W/HZSM-5 increases first and then decreases with 18 the increasing of the W loading. These mesoporous may be some like inter-crystalline 19 mesopores built among the stacked nano-crystals, which is related to the agglomerative morphology<sup>27</sup>. However, with the W content increasing to some extent, the inter-crystalline 20 voids may be reduced, and the mesoporous volume decreases. 21

However, the changes of the surface area and porous structure are more pronounced for the W/HZSM-5 with low W content from 23.3 to 46.1wt.% and the downward trends tend to flat as the W content exceeding 46.1 wt.%. Furthermore, these changes are in agreement with

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the conversion of DME, which may be due to W domains partially covered the acid sites on the surface. To compare the catalysts before and after reaction, BET surface area and micropore volume decreases apparently, which may be a result that the conversion of DME mainly occurs at micropore channel of zeolite, and excessive carbon deposits covers the surface of the catalysts and in turn blocks the pores.

3. 2 State of tungsten in HZSM-5

7 To determine the structure and coordination states of tungsten species with different contents, UV-vis DRS of W/HZSM-5 catalysts were recorded. As shown in Fig. 2, all the 8 catalysts present three absorption bands at 230, 280 and 380 nm. The peak at 230 nm is 9 associated with tetrahedrally monomeric tungstate species ([WO<sub>4</sub>]<sup>2-</sup>), the band located at 280 10 11 and 380 nm can be assigned to octahedral of polytungstate species ( $[WO_6]^{n-}$ ), and WO<sub>3</sub> crystallites respectively<sup>28</sup>. Therefore, three types of tungsten species exist in W/HZSM-5 12 13 catalysts. With the W content increasing, the intensities of the three bands reinforce. When the content is 23.3 wt. %, the intensity of the band at 230 nm is stronger than that of 280 nm, 14 and while the W content exceeds 34.9 wt.% the peak at 280 nm became the dominant band. 15 16 That is to say the tungsten species for the samples with low W contents (23.3-34.9 wt.%) presents mainly as  $[WO_4]^{2-}$  tetrahedral species, and the tungsten domains for the samples 17 with high content (34.9-56.1 wt.%) are primarily  $[WO_6]^{n-1}$  octahedral polytungstate species. 18 These may be related to the change of the crystallite phase, as demonstrated by XRD. 19

20

#### {Fig. 2}

The XPS survey spectra of W/HZSM-5 with different W contents were carried out. Fig.
3 presents XPS spectra of the W<sub>4f</sub> region for W/HZSM-5 catalysts with different tungsten

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contents. The binding energies of  $W^{6+}$ ,  $W^{5+}$  and  $W^{4+}$  are 37.3, 36.2 and 35.2 eV for  $4f_{5/2}$  and 35.1, 33.6, and 32.9 eV for  $4f_{7/2}$ , respectively<sup>29,30</sup>. In the 23.3 wt.% W/HZSM-5 catalyst, the W species with about 93.5%  $W^{6+}$  and 6.5 %  $W^{5+}$  atoms detected. With the increasing of the W content, the amount of  $W^{6+}$  increases and the  $W^{5+}$  decreases, when the W content reaches 56.0 wt.%, the WO<sub>3</sub> becomes be completely oxidized with 100 %  $W^{6+}$ , as shown in Table 2. It was reported that the structure of monoclinic WO<sub>3</sub> tended to be completely oxidized<sup>29</sup>, hence the change in chemical states is related to the change of WO<sub>3</sub> phase, as indicated by XRD.

The XPS spectra of O 1s shown in Fig. 4 show two BE peaks for all of the W/HZSM-5 8 catalysts with different tungsten contents. The lower BE band at about 530.3 eV corresponds 9 to  $O^{2}$  anions of tungsten oxide, and the higher BE band at 532.5 eV corresponds to  $O^{2}$  anions 10 11 associated with the HZSM-5 and surface hydroxides on the W/HZSM-5 both in physically adsorbed and chemically bonded forms<sup>29,31</sup>. With the increasing of W content, the amount of 12 the O<sup>2-</sup> anions of tungsten oxide increases to the maximum (38.04%) in 51.1W/HZSM-5 and 13 then decreases to 31.03 % in the 56.0 W/HZSM-5. As for the O<sup>2-</sup> species 532.5 eV, the 14 relative amount decreases from 82.72 % in 23.3W/HZSM-5 to 61.96 % in 51.1 W/HZSM-5 15 16 and then increases to 68.96 % in 56.0 W/HZSM-5 catalyst. It is reasonable that the amount of O<sup>2-</sup> anions associated with the HZSM-5 decreases, because the content of HZSM-5 decreases 17 with the increasing of the W content, and the later increase should be ascribed to the surface 18 hydroxides on the W/HZSM-5, because the monoclinic WO<sub>3</sub> contains more surface OH 19 groups and water molecules on the surface, compared with other WO<sub>3</sub> phase, as reported by 20 Firkala<sup>29</sup>. This means that the surface OH species associated with tungsten oxide increases 21 22 with the increasing of the W contents, which can influence the acidic properties of the

1 W/HZSM-5 catalyst.

In summary, the results of UV-vis DRS and XPS demonstrate that the chemical state of W species changes with the W content increasing. The tetrahedral  $[WO_4]^{2-}$  species changes to  $[WO_6]^{n-}$  octahedral polytungstate species, the W<sup>6+</sup> is the main chemical state of tungsten in all the W/HZSM-5 catalysts. However there is more surface OH species appear on the W/HZSM-5 with higher W content, which can influence the acidic properties of W/HZSM-5.

#### 7

#### {Fig. 3 and Fig. 4}

### 8 3. 3 Acidic properties

The concentration and strength of acid sites in W/HZSM-5 catalysts are determined by 9 NH<sub>3</sub>-TPD, as presented in Fig. 5. Generally, a NH<sub>3</sub>-TPD profile on HZSM-5 zeolite shows 10 11 two desorption peaks, i.e. the high-temperature one located above 300 °C and the low-temperature one situated below 200 °C, which are ascribed to ammonia adsorbed on the 12 strong and weak acid sites, respectively<sup>27</sup>. In this work, the distribution of the acid sites across 13 the acidic strength is determined by integrating the NH<sub>3</sub>-TPD profiles in different temperature 14 intervals, as listed in Table 2, where the quantities of weak, medium, and strong acid sites are 15 16 measured by the amounts of ammonia desorbed at 100-200, 200-300, and 300-600 °C, respectively. The W content exhibits a significant influence on the distribution of acid sites in 17 W/HZSM-5. With the W content increasing, the total acid quantity decreases. It seems that the 18 amount of the strong acid sites is increased with the W content increasing from 23.3 to 34.9 19 wt.%, and then decreased with the W content increasing to 56.0 wt.%. As for the amount of 20 weak acid sites, it decreased with the W content increasing from 23.3 to 51.1 wt.%, and then it 21 increases from 0.18 to 0.24 mmol g<sup>-1</sup> with the W content increasing to 56.0 wt.%, as shown in 22

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Table 2. Undoubtedly, these are related to the cooperation between tungstate species and
HZSM-5. As the XPS and UV-vis DRS results demonstrate that the octahedral polytungstate
domains could accommodate a proton by electron transfer and charge delocalization across an
extended W-O network and form some acidic sites<sup>32</sup>.

5

### {Fig. 5}

#### 6 3.4 Redox properties

7 H<sub>2</sub>-TPR profiles of W/HZSM-5 with different W contents are shown in Fig. 6, and the quantitative result is listed in Table 2. H<sub>2</sub>-TPR has been extensively used to characterize the 8 reducibility of oxygen species in  $WO_3$  and  $WO_x$  containing materials. It was found that bulk 9 WO<sub>3</sub> can be reduced to W metal at temperatures below 927  $^{\circ}$ C. Three overlapping peaks were 10 11 detected for the reduction of bulk WO<sub>3</sub> samples, which occurs via stepwise reduction:  $WO_3 \rightarrow WO_2 \rightarrow WO_2 \rightarrow W^{32}$ . The reduction profiles for W/HZSM-5 samples have three 12 13 overlapping peaks (Fig. 6) that occur at similar temperatures (about 550, 730 and 810 °C) with all W concentrations. These three peaks correspond to the same three reduction steps 14 found in bulk WO<sub>3</sub> above. While the second peak at about 730 °C becomes obvious with the 15 W concentration increasing. It was reported that the second reduction step (WO<sub>2.9</sub> $\rightarrow$ WO<sub>2</sub>) is 16 sensitive to the dispersion of  $WO_x$  domains<sup>32</sup>. At low W concentration (23.3 wt.%), there are 17 18 not enough  $WO_x$  neighbors in these highly dispersed domains to form the stable intermediate  $WO_2$  species, a large fraction of the  $WO_x$  domains bypass this second reduction step and 19 instead reduce directly to W metal (WO<sub>2</sub>  $\rightarrow$  W) in the third reduction step. With the W 20 21 content increasing from 34.9 to 56.0 wt.%, the WO<sub>x</sub> surface densities become higher, the WO<sub>x</sub> 22 polyhedra are connected by W-O-W bonds, and there are enough  $WO_x$  neighbors to share the

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reduced charge and the H<sub>2</sub>-TPR profiles exhibit obvious reduction step from WO<sub>2.9</sub> to WO<sub>2</sub>.
 Anyway, the amount of redox sites of the W/HZSM-5 catalysts is positive correlated with the
 W content. The amount of redox sites increased from 3.75 to 10.25 mmol g<sup>-1</sup> with W content
 increasing 23.3 to 56.0 wt.%, as shown in Table 2.

5

#### {Fig. 6}

#### 6 *3.5 Catalytic performance*

7 The catalytic performances of W/HZSM-5 with different W contents in DME conversion under O<sub>2</sub> stream are illustrated in Fig.7. As for the conversion of DME, it decreases with the 8 W content increasing. When the W contents are 23.3 and 34.9 wt.%, the DME conversion is 9 above 99.0%. As the W content reaches 46.1 wt.%, the DME conversion decreases to 82.6%, 10 11 and then the conversion is almost unchanged although the W content increasing, DME 12 conversion keeps at 80.8% and 87.0% for 51.1 and 56.0 wt.% W/HZSM-5 respectively. Obviously, the W content has influence on the product distribution. The W/HZSM-5 catalysts 13 with W content from 23.3 to 51.1 wt.% show high selectivity to toluene, however, when the 14 W content becomes 56.0 wt.%, the toluene selectivity decreases to about 29.6%. When the W 15 16 contents are 23.3 and 34.9 wt.%, there is nearly no methanol and CO, the main side-products are DMM, HCHO, MF and  $C_xH_y$  (CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>). With the W content increasing 17 18 from 23.3 to 51.1 wt.%, the selectivity to  $CH_3OH$  increases first and then decreases, and the selectivity to HCHO decreases first and then increases, the highest CH<sub>3</sub>OH and HCHO 19 selectivity is about 23.2% and 24.4 %, which are achieved over the 46.1 wt.% and 56.0 wt.% 20 21 W/HZSM-5 catalysts. Meanwhile, the selectivities to MF and DMM decrease with the 22 increasing of the W content. The 34.9 and 56.0 wt.% W/HZSM-5 catalysts have relative high

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selectivity to the  $C_xH_y$ . However, for all of the W/HZSM-5 catalysts with different W contents, 1

- 2 there is no CO<sub>2</sub> detected and small amounts of CO and ethanol formed.
- 3

### {Fig. 7}

These catalytic results suggest that the W content not only influences the selectivity to 4 toluene but also the selectivities to oxygen containing chemicals such as HCHO, DMM and 5 6 MF. It is understandable that the change of DME conversion has similar tendency to the total 7 amount of acid sites of W/HZSM-5 with different W contents, because the acid sites are the main active sites for DME activation. DME molecule could be easily activated to generate 8 9  $CH_3$ ,  $CH_3O$  and  $CH_3OCH_2$  group in the presence of  $O_2$ . Then these active groups can form toluene and C<sub>x</sub>H<sub>y</sub> through acidic catalysis process, meanwhile, they also can form DMM. MF 10 11 and HCHO over redox sites. However, with the W content increasing, the number of the redox sites increases to some extent, the DMM and MF may be oxidized further to CO, hence 12 the selectivities to MF and DMM slightly decrease and small amount of CO produced with 13 the W content increasing to 56.0 wt.%. Meanwhile, with the increasing of W content, the WO<sub>3</sub> 14 15 chemical state change. And when the W content exceeds 46.1 wt.%, monoclinic WO<sub>3</sub> 16 becomes the dominant phase, which makes the nature of the acid sites change, this may be the 17 main reason for the variation in the product slate, especially for the change of CH<sub>3</sub>OH 18 selectivity. As indicated by Table 2, although the total acid sites decreases generally, however 19 the relative ratio of the amount of medium strong acid sites is similar, they are 30%, 30%, 28%, 28% and 28% for 23.3, 34.9, 46.1, 51.1 and 56.0 wt.% W/HZSM-5 respectively. This 20 may be the reason why the former four catalysts have similar toluene selectivity. Moreover, as 21 22 for the 56.0 wt.% W/HZSM-5, the acid sites redistribution cannot be omitted, the ratio of the

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amount of weak acid sites increases and the amount strong acid sites decreases, besides that the amount of redox sites increases to maximum, this kind of chemical environment may be favor for the formation of HCHO and  $C_xH_y$ , therefore, the toluene selectivity decreases and the selectivities to HCHO and  $C_xH_y$  increase in the 56.0 W/HZSM-5 catalyst.

5 3.6 Catalytic mechanism of DME to toluene over W/HZSM-5

Fig. 8 depicts the IR spectra of DME/O<sub>2</sub> adsorption and desorption on the 46.1 wt.% 6 7 W/HZSM-5 catalyst. After purification under vacuum condition, infrared spectra of the catalysts show some bands in the OH stretching region at 3200-3800 cm<sup>-1</sup>. They are 8 associated with the framework aluminum [Si(OH)A1] (3610 cm<sup>-1</sup>), the isolated external 9 silanol groups (3745 cm<sup>-1</sup>), free internal silanol groups (3728 cm<sup>-1</sup>), and delocalized 10 hydrogen-bonded groups (3500 cm<sup>-1</sup>) of lattice defects, partially hydrolyzed framework Al 11 (around 3660 cm<sup>-1</sup>) and the band of 3338 cm<sup>-1</sup> could be ascribed to the OH stretching 12 associated with W species<sup>3334</sup>. As for the adsorption spectra, it shows the typical DME 13 adsorption bands with C-O-C stretching vibration at 1100-1200 cm<sup>-1</sup>, C-H stretching vibration 14 at 2800-3000 cm<sup>-1</sup> and C-H deformation vibration at about 1400-1600 cm<sup>-1</sup>. In addition, the 15 bands at 900-1000 cm<sup>-1</sup> appear which can be ascribed to the heterocyclic -C-O-C- asymmetric 16 stretching<sup>35</sup>. However, in the desorption spectra, the bands at 900-1000 cm<sup>-1</sup> disappear, which 17 suggests that this kind of species should be attributed to the intermediate reactant, formed 18 through the adsorption of DME on the catalyst surface. Meanwhile, the bands of O-H 19 stretching region, which are related with the Brønsted acid groups in W/HZSM-5 reduce 20 greatly, and strong multiple absorption bands at 2800-3100 cm<sup>-1</sup> and 1400-1600 cm<sup>-1</sup> are 21 22 observed. These two bands are related to C-H and C-C stretching of the multisubstituted

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benzene<sup>35</sup>. The band at 1739 cm<sup>-1</sup> can be ascribed to the C=O groups, this may be related with 1 the formation of oxygen containing chemicals such as HCHO, DMM and HCOOCH<sub>3</sub>. These 2 results may demonstrate that the formation of toluene over W/HZSM-5 catalyst may be 3 4 accordance with the MTH reaction process on HZSM-5 with the acidic sites involved. 5 Meanwhile, the deactivated catalysts with different W contents were investigated by TG. Fig. 9 shows the profiles of the deactivated catalysts with 34.9, 46.1 and 51.1 wt.% W 6 contents. There are two peaks of weight loss at 150 and 450 °C, which are attributed to the 7 coke formation on the external surface and inside the zeolite voids respectively<sup>36</sup>. Obviously, 8 9 the weight loss of the deactivation catalyst decreased with the W content increasing. The BET 10 results (Table 1) show that the fresh catalyst surface area decreases with tungsten content 11 increasing, which indicates that the W content affects the external surface of the catalyst, the more the W content, the less the coke formation. This may be due to the introduction of 12 13 tungsten covering the surface acid sites, as demonstrated by NH<sub>3</sub>-TPD.

14

#### {Fig. 8 & Fig. 9}

The characteristic pore structure of HZSM-5 zeolite makes it the archetypical catalyst for 15 16 the conversion from methanol/DME to hydrocarbon, hence tremendous efforts have been spent on elucidating the mechanism, varying from autocatalytic mechanism to 17 hydrocarbon-pool mechanism. The dual-cycle concept, first introduced by Olsbye's group<sup>37</sup>, 18 19 demonstrates the formation of ethylene and  $C_{3+}$  olefins more reasonably, being acknowledged 20 as a refinement of hydrocarbon-pool mechanism. It consists of the olefin-based methylations/ 21 interconversions cycle mainly producing  $C_{3+}$  alkenes and aromatic-based cycle involved the formation of ethylene and aromatics. Though it is argued whether the dual cycle operates 22

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independently or mutually dependently, the fact that the aromatics is constantly formed in olefin-based cycle through the aromatization of higher alkenes, and also ethylene is generated from aromatic-based cycle, is proved by numerous kinetic experimental data<sup>38</sup>. Therefore, it can be imagined target product could be obtained through facilitating or suppressing the operation of certain cycle by selecting a catalyst with special topology and acidity.

Combined with the product distribution, high selectivity to toluene was obtained and 6 ethylene occupies the largest proportion among  $C_xH_v$ , and the FT-IR results, the conversion of 7 DME to toluene over W/HZSM-5 should obey to the famous dual cycle of the MTH reaction 8 on HZSM-5, and the aromatic-based cycle may be promoted with the synergistic effect of 9 tungsten and ZSM-5 zeolites in the W/HZSM-5 catalyst. While the introduction of amounts of 10 11 W cover the surface acidic sites may break the cycle at toluene partially, and the formation of 12 higher methylbenzenes is limited effectively. Based on these results, a possible transformation pathway of DME conversion over W/HZSM-5 zeolite is deduced preliminarily, as shown in 13 Fig.10. For one side, the oxygenic groups might be converted to methanol, DMM, ethanol and 14 MF over the redox sites of W/HZSM-5. For the other side, the groups might undergo acid 15 16 catalysis reaction to produce hydrocarbon-pool species under the cooperation of acids site and 17 special pore channel, and toluene obtained.

18

## {Fig. 10}

#### 19 4. Conclusions

A novel synthesis route of toluene from dimethyl ether has been efficiently performed over W/HZSM-5. The nature of tungsten species, the distribution of acid sites, the redox properties, and the subsequent catalytic performance of W/HZSM-5 in DME conversion to

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toluene was influenced by the W content. Obviously, the introduction of W in HZSM-5 can 1 2 bring up new redox sites which are relevant to the formation of the oxygen containing chemicals such as HCHO, DMM and MF and so on. With the W content increasing, the 3 octahedral polytungstate domains become the primary species, which are favor for the 4 formation of new acidic sites associated with W, although the introduction of high content of 5 W can cover lots of acidic sites in HZSM-5. By this way, the existence of W prevents the coke 6 formation and may break the dual cycle of the DME-to-hydrocarbons reaction in HZSM-5 at 7 toluene, and the formation of higher methylbenzenes is limited effectively. When the W 8 content is up to 51.1 wt.% the selectivity of toluene reaches 45% with the DME conversion 9 decreasing from about 99% to about 80%, and the W content increases further, the selectivity 10 11 of toluene decreases to about 29.3%. These may be related with the redistribution of the active 12 acidic sites with the high content of W.

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# Table 1

Textural and structural properties of different catalysts

Catalvat	W conte	nt (wt.%)	$\mathbf{S}_{\text{BET}}$	V <sub>micro</sub>	V <sub>meso</sub>
Catalyst	ICP	XPS	$(m^2/g)$	$(cm^3/g)$	$(cm^3/g)$
23.3W/HZSM-5	23.3	25.4	216.35	0.086	0.054
34.9W/HZSM-5	34.9	36.6	177.88	0.066	0.072
46.1W/HZSM-5	46.1	46.2	121.73	0.048	0.034
51.1W/HZSM-5	51.1	52.7	113.33	0.045	0.032
56.0 W/HZSM-5	56.0	56.9	111.56	0.042	0.022

## Table 2

## NH<sub>3</sub>-TPD, H<sub>2</sub>-TPR and XPS results for the W/HZSM-5 catalysts

		Acid sites <sup>a</sup>			Redox sites <sup>b</sup>				Chemical state <sup>c</sup>			
Catalysts	$(mmol g^{-1})$			$(\text{mmol g}^{-1})$				(%)				
		Weak	Medium	Strong	Total	Low	High	Total	W <sup>6+</sup>	$W^{5+}$	O-W	O-HZSM-5
	23.3W/HZSM-5	0.64	0.63	0.86	2.13	0.55	3.20	3.75	93.5	6.5	17.28	82.72
	34.9W/HZSM-5	0.39	0.59	1.04	2.02	1.0	5.20	6.20	95.9	4.1	19.35	80.65
	46.1W/HZSM-5	0.27	0.43	0.83	1.53	1.44	6.58	8.02	97.6	2.4	32.46	67.54
	51.1W/HZSM-5	0.18	0.28	0.54	1.0	1.75	8.13	9.88	98.7	1.3	38.04	61.96
	56.0W/HZSM-5	0.24	0.27	0.48	0.99	1.77	8.48	10.25	100	0	31.03	68.96

<sup>a</sup> Density of the acid sites, assorted according to the acidic strength, determined by NH<sub>3</sub>-TPD.

<sup>b</sup> "Low" and "High" represent respectively the low temperature and high temperature band in H<sub>2</sub>-TPR profiles shown in Fig. 5, density of the redox sites, determined by H<sub>2</sub>-TPR.

<sup>c</sup> The change of the relative amounts of W and O species of different chemical state, "O-W" and "O-HZSM-5" represent the  $O^{2-}$  anions of tungsten oxide and the  $O^{2-}$ anions associated with the O-Si, O-Al and O-H on the W/HZSM-5.

## **Figure Caption**



Fig. 1 The XRD patterns of catalysts: (a) HZSM-5, (b) 23.3W/HZSM-5, (c) 34.9W/HZSM-5, (d) 46.1W/HZSM-5, (e) 51.1W/HZSM-5, (f) 56.0W/HZSM-5. Crystalline phases detected: •, HZSM-5, •, WO<sub>3</sub>



Fig. 2 UV-vis spectra of W/HZSM-5 catalysts with different W contents: (a) 23.3 wt.%, (b) 34.9 wt.%, (c) 46.1 wt.%, (d) 51.1 wt.%, and (e) 56.0 wt.%.



Fig. 3 XPS spectra of the  $W_{4f}$  region for different W/HZSM-5 catalysts: (a) 23.3 wt.%, (b) 34.9 wt.%, (c) 46.1 wt.%, (d) 51.1 wt.%, and (e) 56.0 wt.%.



Fig. 4 XPS spectra of the O<sub>1s</sub> region for different W/HZSM-5 catalysts: (a) 23.3 wt.%, (b) 34.9 wt.%, (c) 46.1 wt.%, (d) 51.1 wt.%, and (e) 56.0 wt.%.



Fig. 5 NH<sub>3</sub>-TPD spectra of W/HZSM-5 with different W contents (a) 23.3 wt.%, (b) 34.9 wt.%, (c) 46.1 wt.%, (d) 51.1 wt.%, and (e) 56.0 wt.%.



Fig. 6 H<sub>2</sub>-TPR profiles of W/HZSM-5 catalysts with different W contents (a) 23.3 wt.%, (b) 34.9 wt.%, (c) 46.1 wt.%, (d) 51.1 wt.%, and (e) 56.0 wt.%.



Fig. 7 Catalytic performance of DME conversion over W/HZSM-5 catalysts with different W contents.



Fig. 8 DRIFTS spectra of DME/O<sub>2</sub> co-adsorption in (1% DME + 1% O<sub>2</sub>)/Ar flow on the 46.1 wt.%W/HZSM-5 catalyst.



Fig. 9 TG profiles of W/HZSM-5 catalysts with different W contents: (a) 34.9 wt.%, (b) 46.1 wt.%, and (c) 51.1 wt.%.



Fig. 10 Reaction pathway of DME over W/HZSM-5 catalysts in the presence of O<sub>2</sub>.