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Conversion of 2,3-butanediol to butenes over bifunctional catalysts in a single reactor

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ABSTRACT

In this study, Cu/ZSM-5 catalysts were used to catalyze the hydrodeoxygenation of 2,3-butanediol to butenes in a single reactor in the presence of hydrogen. The carbon selectivity of butenes increased with increasing SiO_2/Al_2O_3 ratio (lowering acidity of zeolite) and $H_2/2,3$ -butanediol ratio. Cu/ZSM-5 with a SiO_2/Al_2O_3 ratio of 280 showed the best activity toward the production of butenes; however, Cu/ZSM-5 with SiO_2/Al_2O_3 of 23 was favorable for the dehydrogenation reaction of 2,3-butanediol even in the excess of hydrogen. On zeolite ZSM-5(280), the carbon selectivity of butenes increased with increasing copper loading and 19.2 wt% of CuO showed the highest selectivity of butenes (maximum 71%). The optimal reaction temperature is around 250 °C. Experiments demonstrated that methyl ethyl ketone (MEK) and 2-methylpropanal are the intermediates in the conversion of 2,3-butanediol to butenes. The optimal performance toward the production of butene is the result of a balance between copper and acid catalytic functions.

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1. Introduction

Because petroleum is a finite resource, there is growing interest in processes that produce hydrocarbons from renewable resources for use as fuels [1–4]. Such processes could produce essentially the same product currently made in petroleum refineries, eliminating the need for modifications to vehicles or to the hydrocarbon distribution infrastructure. A number of routes for producing hydrocarbons from sustainable resources have been proposed [1,5,6]. These routes convert biomass-derived sugars to oxygenated intermediates, which are upgraded to fuel-range hydrocarbons. The key to developing a successful process of this nature is to select intermediate compounds that can be selectively produced from sugars, and can easily be converted to fuel-range hydrocarbons.

A potential intermediate compound that has not previously been considered for the production of hydrocarbons from biomass-derived sugars is 2,3-butanediol (2,3-BDO). 2,3-BDO is an intriguing intermediate because it can be produced via fermentation of sugars with a high productivity at high concentration by using a variety of microorganisms, such as Klebsiella oxytoca [7–10], Enterobacter aerogenes [11], Bacillus licheniformis [12] and Enterobacter cloacae [13]. Ji et al. [7] obtained a maximum 2,3-BDO concentration of 95.5 g/L with productivity of 1.71 g/L/h by fermentation of media containing 200 g/L of glucose in a 3 L batch fermentor using Klebsiella oxytoca. Jansen et al. [14] obtained a final concentration of 2,3-BDO of 12.63 g/L by fermentation of media containing 50 g/L of xylose in a 7-L batch fermentor using Klebsiella oxytoca ATCC 8724. Saha and Bothast [13] obtained a yield of 2,3-BDO of 0.4 g/g arabinose with a corresponding productivity of 0.63 g/L/h by fermentation of media with an initial arabinose concentration of 50 g/L.

Once 2,3-butanediol (2,3-BDO) is produced via fermentation, routes to convert it to hydrocarbons would be needed. However, there is little research in this area. Dehydration of 2,3-BDO to methyl ethyl ketone (MEK) has been well studied, and occurs readily over a number of catalysts [10,15]. Zhang et al. [16] investigated the dehydration of 2,3-BDO over zeolite HZSM-5 and HZSM-5 modified with boric acid, and studied the effect of framework Si/Al ratio and addition of boric acid on 2,3-BDO dehydration. They reported that high Si/Al ratio was beneficial to lowtemperature activation of 2,3-BDO and the methyl migration to 2-methylpropanal, and the addition of boric acid enhanced the catalytic stability. Lee et al. [17] utilized in situ DRIFTS to investigate the dehydration of 2,3-BDO over a series of zeolites ZSM-5, mordenite, β- and Y-type zeolites, and found that dehydration of 2,3-BDO to MEK was favored on ZSM-5. Duan et al. [18] investigated the dehydration of 2,3-BDO over monoclinic ZrO2 and the







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result showed that 3-buten-2-ol was produced with a maximum selectivity of 59.0% along with major byproducts such as MEK and 3-hydroxy-2-butanone. In addition, further dehydration of 2,3-BDO yields 1,3-butadiene [19], which can be dimerized to produce the aromatic intermediate styrene (Diels–Alder reaction) [20] and hydrogenated to butene. Sato and coworkers investigated dehydration of 2,3-BDO to 1,3-butadiene over Sc_2O_3 [21], and dehydration of other diols, such as 1,3-butanediol and 1,4-butanediol over rare earth oxides [22,23], ZrO_2 [24] and Cu-based catalysts [25].

The approach reported here is to convert 2,3-BDO to butene, which is a basic building block of fuels as well as many chemicals. As a precursor, butene can be converted to a variety of oligomers (dimer, trimer, tetramer, etc.) [26,27], which can be further converted to saturated hydrocarbons through hydrogenation reaction. In this way, butene can serve as an intermediate to produce high-grade liquid fuel with specific type of saturated hydrocarbons [6,27].

The major challenge is to remove the two hydroxyl groups of 2,3-butanediol (2,3-BDO) in a single step to produce butene. This process involves a bifunctional pathway, in which 2,3-butanediol is dehydrated on an acid site to methyl ethyl ketone (MEK), 2-methylpropanal, and butadiene, which can be further hydrogenated to butene on the metal sites. Copper is interesting for use as the hydrogenation catalyst. Cu-containing catalysts show high activity for vapor-phase hydrogenation reaction particularly the selective hydrogenation of carbon-oxygen bonds; however, copper catalysts are relatively inactive for hydrogenolysis of carbon-carbon bonds [28]. Guo et al. [29] investigated hydrogenolysis of glycerol to propanediols over Cu catalysts, and found that γ -Al₂O₃ supported Cu catalysts showed excellent performance (selectivity to propanediol, 96.8%) and successfully suppressed the scission of C--C bonds. Sitthisa and Resasco [30] investigated the hydrodeoxygenation of furfural over Cu, Pd and Ni supported on SiO₂, and found that the Cu catalyst mainly produced furfuryl alcohol via hydrogenation of the carbonyl group due to the weak interaction of Cu with C=C. Vasiliadou et al. [31] investigated the hydrogenolysis of glycerol to propylene glycol over highly dispersed Cu/SiO₂ catalyst. The result showed that Cu selectively converted glycerol to propylene glycol with selectivity of 92-97% via consecutive dehydration-hydrogenation reactions. Sato et al. [32] reported that reduced Cu catalyst could effectively catalyze the dehydration of glycerol to hydroxyacetone in N₂, and the hydrogenation of hydroxyacetone followed by hydrogenolysis in H₂ to form ethylene glycol, acetaldehyde and ethanol.

Based on the excellent hydrogenation performance of copper, we have studied a high copper loading catalyst supported on ZSM-5 to convert 2,3-butanediol to butenes in a single reactor. The impact of reaction conditions (temperature and hydrogen to 2,3-butanediol ratio) and the Si/Al ratio of the ZSM-5 catalyst are reported and it is demonstrated for the first time that 2,3-BDO can be converted to butenes in a single reactor at a high yield.

2. Experimental

2.1. Materials

Ammonium-type ZSM-5 with SiO₂/Al₂O₃ ratios of 23, 50 and 280 was obtained from Zeolyst International. ZSM-5 is referred to as ZSM-5(n), where n is the SiO₂/Al₂O₃ ratio. 2,3-butanediol (>97%) was purchased from TCI America. Cu(NO₃)₂·3H₂O (99%) was purchased from Fisher scientific.

2.2. Catalyst preparation

As previously reported, the ion exchange of zeolite ZSM-5 with Cu(II) in ammonia could result in excessively exchanged copper on

zeolites with high copper dispersion [33,34]. The catalysts used in this work were synthesized by the ion exchange method as follows, which is similar to the deposition precipitation (DP) method [35,36] or ammonia evaporation (AE) methods [37,38]. First, the ammonium-type ZSM-5 was calcined at 550 °C for 4 h to convert it to HZSM-5. Then the desired amount of Cu(NO₃)₂·3H₂O was dissolved in 100 mL of deionized water at room temperature. Ammonia was added to the solution until the pH was about 9.1 to form a dark blue cupric ammine complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$, and then water was added to make 250 mL of a copper-ammonia complex solution. 20 g of HZSM-5 zeolite was added to the solution and then the container was capped to avoid the evaporation of ammonia and stirred for 4 h at room temperature. After that, the container was transferred to an oil bath and heated to 60 °C for 2 h. Then the solution was filtered and the precipitate was washed at least five times by water and dried at 110 °C overnight followed by calcination at 550 °C for 4 h. Finally, the calcined catalyst was pelletized, crushed and sieved to obtain a particle size distribution in the range 40-60 mesh. To make 10%CuO/ZSM-5, the amount of $Cu(NO_3)_2$ ·3H₂O added to the solution was 24.16 g. The content of CuO was determined to be 9.5 wt%, 9.7 wt% and 9.2 wt% on ZSM-5 with SiO₂/Al₂O₃ ratios of 23, 50 and 280, respectively, by the inductively coupled plasma (ICP) method. Two Cu/ZSM-5(280) catalysts with high loading of CuO were prepared by increasing the amount of $Cu(NO_3)_2 \cdot 3H_2O$ to 36.24 g, and extending the time of ion exchange in the oil bath to 12 h and 24 h. For these two catalysts, the content of CuO was determined by ICP to be 19.2 wt% and 29.1 wt%, respectively. For the catalyst Cu/ZSM-5(280) with low loading of CuO, the amount of $Cu(NO_3)_2 \cdot 3H_2O$ was decreased to 12.0 g and the time of ion exchange was shortened to about 1 h in the oil bath, and the content of CuO was determined by ICP to be 6.0 wt%.

2.3. Catalytic reactions

The catalytic reactions were performed in a conventional continuous flow fixed-bed reactor made of stainless steel (id = 8 mm) under atmospheric pressure. Prior to reaction, the catalyst sample (weight = 1.0 g) was reduced in the reactor in the H_2/N_2 flow (flow rate of $H_2/N_2 = 1/5$) at 300 °C for 2 h. The H_2 flow of 24 cm³/min (standard ambient temperature and pressure, SATP) and the N₂ flow of 120 cm³/min (SATP) were controlled with mass-flow controllers (Brooks). 2,3-BDO was fed via a micropump (Eldex 1SMP) at 3 mL/h together with a H₂ flow of 67.2 cm³/min (SATP) and N₂ flow of 15.4 cm³/min (SATP). Reactor temperature was set between 200 and 300 °C. Product compositions were analyzed by an on-line gas chromatograph (SRI 8610C) equipped with an MXT-1 column (nonpolar phase, 60 m, ID 0.25 mm, film thickness 0.25 µm), TCD and FID detectors for the analysis of hydrocarbons and oxygenated chemicals, and quantified by injecting calibration standards to the GC system. The temperature of the tubing from the bottom of the reactor to the inlet of GC was maintained at 230 °C to avoid the condensation of liquid products. The products were injected through the sample loop (0.2 mL), which was controlled by a high temperature ten-port valve. The oven was kept at 40 °C for 5 min, and then raised to 120 °C at a ramp rate of 40 °C/min, finally raised to 250 °C at a rate of 20 °C/min, and held at this temperature for 10 min. As MXT-1 column is not capable of separating some hydrocarbons, such as 1-butene and isobutene, to determine the distribution of butenes (1-butene, isobutene, trans-2-butene and cis-2-butene) over catalysts with different SiO₂/Al₂O₃ ratios, additional experiments were performed where the MXT-1 column was replaced with an MXT-Alumina BOND/MAPD column (30 m, ID 0.53 mm, film thickness $10 \,\mu$ m), which is capable of separating the four isomers of butenes. To ensure the identification of products, GC-MS analyses were also carried out by using an Agilent 7890A GC system equipped with an Agilent 5975C MS detector and HP-1 capillary column. The carbon selectivity [39,40] and conversion of 2,3-BDO were calculated in the following methods.

Carbon selectivity =
$$\frac{\text{Moles of carbon in specific product}}{\text{Total carbon atoms in identified products}} \times 100\%$$

$$Conversion = \frac{(moles of 2, 3-BDO)_{in} - (moles of 2, 3-BDO)_{out}}{(moles of 2, 3-butanediol)_{in}}$$

imes 100%

Two repeat runs were performed at each reaction condition and the two trials were generally within 5% of each other. The relative difference between the sum of butene selectivity from MXT-1 column and MXT-Alumina BOND/MAPD column is about 5–6%. The carbon balances closed with above 90% for all runs in this paper.

2.4. Catalyst characterization

2.4.1. NH₃ temperature-programed desorption (NH₃-TPD)

The surface acidity of catalysts was investigated by temperature programmed desorption of ammonia (NH₃-TPD). NH₃-TPD was carried out in an Altamira AMI-200 system. Prior to adsorption, 0.2 g of copper catalyst was loaded in a quartz U-tube reactor and pre-treated at 550 °C in helium for 1 h followed by cooling to 100 °C. Then the catalyst was reduced in a flow of H₂/Ar (10 v/v%) at a constant rate of 10 °C/min to 300 °C and then maintained for 2 h followed by cooling to 100 °C. 10 mL/min of ammonia (anhydrous, 99.99%) was then introduced at 100 °C for 30 min. Physisorbed NH₃ molecules were removed by flowing pure helium at 100 °C for 2 h. Finally, the temperature was raised to 700 °C at 10 °C/min. Desorbed ammonia was detected with a thermal conductivity detector (TCD).

2.4.2. H_2 temperature-programed reduction (H_2 -TPR)

H₂-TPR was measured in the same system as NH₃-TPD. 0.1 g of sample was loaded in a quartz U-tube reactor and treated at 550 °C in Ar (99.999%) at a flow of 40 mL/min for an hour. After cooling, the temperature was ramped from 50 °C to 900 °C at a ramp rate of 5 °C/min in H₂/Ar flow (10 v/v%, 40 mL/min). H₂ consumption was recorded by a thermal conductivity detector (TCD). H₂ consumption was calibrated by reducing 0.03 g of pure CuO.

2.4.3. Brunauer–Emmett–Teller (BET)

Surface area measurements of catalysts were conducted according to the Brunauer–Emmett–Teller (BET) gas (nitrogen) adsorption method. About 0.06 g of catalyst powder was poured into the sample cell and degassed at 350 °C for 4 h before determining the exact mass of the sample, which was then confirmed after degassing. The adsorption/desorption isotherms were measured using a Quantachrome Autosorb-1 instrument at -196 °C and analyzed with Autosorb-1 software. The total surface area was determined from N₂ adsorption branch in the linear range of relative pressure from 0.007 to 0.03. The micropore surface area and micropore volume were evaluated by the t-plot method [41]. The total pore volume was evaluated by single point pore volume at a relative pressure of 0.95.

2.4.4. X-ray diffraction (XRD)

XRD analysis was conducted using a Rigaku Miniflex II desktop X-ray diffractometer. Scans of two theta angles were from 5° to 90° for all catalysts with a step size of 0.02° and scan speed of 0.75° /min. All samples were well ground before analysis in order to provide a significant number of oriented particles to fulfill the Bragg condition of reflection.

2.4.5. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) experiments were performed on a FEI Nova NanoSEM 430 to identify the morphology of Cu/ZSM-5 catalysts.

2.4.6. X-ray photoelectron spectroscopy (XPS)

XPS data were obtained with a PerkinElmer PHI 5400 using achromatic Al K α radiation (1486.60 eV). The pressure in the analysis chamber was typically 8.0×10^{-8} Torr. Cu $2p_{3/2}$ (932.7 eV) and Au $4f_{7/2}$ (84.0 eV) were used as standards to calibrate the binding energy (BE) range, and the binding energy of carbon 284.6 eV was used as the BE standard to correct for charging on the substrate [42]. XPS spectra were curve fitted by the software CasaXPS based on the centered position, full width at half maximum (FWHM) and peak intensity.

2.4.7. N₂O adsorption

Copper surface area (SA_{Cu}) and dispersion (D_{Cu}) were determined by dissociative N₂O adsorption method at 90 °C [43,44] using the same system as H2-TPR and NH3-TPD. Prior to N2O adsorption, the catalysts (0.1 g) were first treated at 550 °C in Ar at a flow of 40 mL/min for an hour. After cooling, the temperature was ramped from 50 °C to 400 °C at a ramp rate of 5 °C/min in H_2/Ar flow (10 v/v%, 40 mL/min) by the H_2 -TPR procedure described above and decreased to 90 °C in Ar (99.999%, 30 mL/min). In this step, the amount of hydrogen consumption was denoted as X. Then the pre-reduced catalysts were exposed to N₂O/He (5 v/v%, 40 mL/min) isothermally at 90 °C for 1 h to oxidize surface copper atoms to Cu₂O followed by cooling to 50 °C in Ar (30 mL/min). After this process, the second H₂-TPR was carried out on the freshly oxidized catalysts from 50 °C to 400 °C at a ramp rate of 5 °C/min in H₂/Ar flow (10 v/v%, 40 mL/min) in order to reduce Cu₂O back to metallic Cu. The hydrogen consumption in this step was denoted as Y. Copper dispersion (D_{Cu}) is calculated as $D_{Cu} = 2Y/X$, which is defined as the ratio of the surface copper atoms to the total copper atoms present in the catalyst. Copper surface area SA_{Cu} (m²/g_{Cu}) is calculated as described in literatures [43,44] by the following equation:

$$SA_{Cu} = \frac{2 \cdot Y \cdot N_{av}}{X \cdot M_{Cu} \cdot SD_{Cu}} \approx 1353 \text{ Y/X} \text{ } (\text{m}^2/\text{g}_{Cu}),$$

where $N_{\rm av}$ = Avogadro's constant = 6.02×10^{23} atoms/mol, $M_{\rm Cu}$ = atomic weight of Cu = 63.546 g/mol, SD_{Cu} = copper surface density = 1.47×10^{19} atoms/m² (the average value for Cu(111), Cu(110), and Cu(100) crystal surfaces).

2.4.8. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a thermogravimetric analyzer (Shimadzu TGA-50). The used catalyst samples were collected after a specific reaction time (40 min or 280 min). After the feed of 2,3-BDO was stopped, the flow of hydrogen and nitrogen (the same flow rate as reaction) was maintained for about 30 min to remove residual 2,3-BDO in the reactor and the products adsorbed on the catalysts as well. Catalyst was recovered after cooling to room temperature. Prior to TGA analysis, the used catalysts were kept in the oven at 100 °C for 3 days so that the copper in catalysts could be oxidized completely. Typically, about 20 mg of the used catalyst sample was heated in air (air flow: 10 mL/min) from room temperature to 600 °C at a ramp rate of 10 °C/min. The coke content for each sample was then determined from the weight loss between 300 °C and 600 °C [45].

3. Results and discussion

3.1. Characterization of catalysts

3.1.1. X-ray diffraction

Fig. 1 shows the XRD patterns of the Cu/ZSM-5 catalysts with different SiO₂/Al₂O₃ ratios and those of the parent HZSM-5 calcined at 550 °C, and Figs. S1 and S2 display the XRD patterns and relative crystallinity, respectively, of the calcined catalysts with different CuO loadings on zeolite HZSM-5(280). As seen in these figures, although a slight decrease in the intensity of the main peaks was noticed after the introduction of copper, all the characteristic peaks of the parent HZSM-5 were observed in Cu/ZSM-5 catalysts, which indicated that the introduction of copper did not destroy the structure of the parent HZSM-5. In addition, two characteristic peaks related to CuO (35.7° and 38.55°) were only observed on 9.5%CuO/ZSM-5(23), which indicated that Cu species were well dispersed on HZSM-5(50) and HZSM-5(280). This is in accordance with the SEM result (see Fig. S3), copper clusters were observed only on 9.5%CuO/ZSM-5(23) with the size of 0.5-1.0 µm and the weight percent of CuO in these clusters was estimated at \sim 43% obtained by EDS detector.

3.1.2. H2-TPR

In order to investigate the reducibility of Cu on zeolite ZSM-5, H₂-TPR measurements were performed. Fig. 2 shows the H₂-TPR profiles of Cu/ZSM-5 with SiO₂/Al₂O₃ ratios of 23, 50 and 280. It is reported that Cu/ZSM-5 catalysts undergo a stepwise reduction process [46–49]. Generally, the peak at the low temperature (170-210 °C) may be attributed to the reduction of CuO in one step to metallic Cu⁰, and the reduction of isolated Cu²⁺ ions to Cu⁺ as well; and the high temperature peak (normally > 350 °C) may be ascribed to the reduction of Cu⁺ to metallic Cu⁰. However, in Figs. 2 and 3, the high-temperature peak was not observed. As seen in Fig. 2, catalyst 9.5%CuO/ZSM-5(23) was seen to exhibit two separate reduction peaks. The main peak at low temperature peak (211.4 °C) is assigned to the well dispersed CuO on zeolite ZSM-5 and the small peak at higher temperature (273.2 °C) is assigned to the reduction of bulk CuO. The assignment of the reduction peaks is similar to the catalyst Cu/SiO₂ prepared by ammonia evaporation (AE) method [35,38,50]. The main reduction peaks of CuO/ZSM-5 catalysts with SiO₂/Al₂O₃ ratios of 50 and 280 (see



Fig. 1. XRD patterns of the calcined catalysts with different SiO_2/Al_2O_3 ratios. (a) HZSM-5(280), (b) 9.2%CuO/ZSM-5(280), (c) HZSM-5(50), (d) 9.7%CuO/ZSM-5(50), (e) HZSM-5(23), (f) 9.5%CuO/ZSM-5(23), (g) CuO, and (h) Cu₂O.



Fig. 2. H_2 -TPR profiles of calcined Cu/ZSM-5 with different SiO₂/Al₂O₃ ratios. (a) 9.5%CuO/ZSM-5(23), (b) 9.7%CuO/ZSM-5(50), and (c) 9.2%CuO/ZSM-5(280).



Fig. 3. H₂-TPR profiles of calcined Cu/ZSM-5(280) with various CuO loadings. (a) 6.0%, (b) 9.2%, (c) 19.2%, and (d) 29.1%.

Fig. 2b and c) became sharper than on Cu/ZSM-5(23) and shift to a lower temperature (208.7 °C). The shoulder peak at high temperature for 9.7%CuO/ZSM-5(50) was smaller than that of CuO/ZSM-5(23). For the catalyst 9.2%Cu/ZSM-5(280), only one low-temperature reduction peak was identified. Fig. 3 exhibits the H₂-TPR profiles of catalysts CuO/ZSM-5(280) with various CuO loadings. With increasing CuO loadings from 6.0% to 29.1%, the intensity of the main reduction peak was observed to increase and the temperature was shifted from 208.1 to 218.1 °C. For all trials, the H₂ consumption of catalysts is proportional to the CuO loading and the ratio of H₂/CuO is almost close to 1 (see supplementary information, Table S1), which indicates that Cu is divalent. On the catalysts with CuO loadings of 19.2% and 29.1% (Fig. 3c and d), the shoulder peak at high temperature related to bulk CuO was observed. From the result of TPR measurement, it can be concluded that most Cu species on zeolite HZSM-5 are well dispersed Cu based on the large reduction peak at low temperature.

3.1.3. N₂ adsorption

The structural properties of the zeolites and copper catalysts can be derived from the results of N_2 adsorption–desorption measurements at -196 °C. The surface area and pore volume are summarized in Table 1. As is shown in Table 1, both mesopores

Table 1	1
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Sample	Surface area			Pore volume			NH ₃	SA _{Cu}	$D_{Cu}$
	$\frac{S_{BET}}{(m^2/g)^a}$	S _{micro} (m ² /g) ^b	S _{external} (m ² /g) ^c	V _{total} (cm ³ /g) ^d	V _{micro} (cm ³ /g) ^b	V _{meso} (cm ³ /g) ^e	uptake (mmol/g)	$(m^2/g_{Cu})$	
HZSM-5(23)	431	283	148	0.411	0.212	0.199	1.167	-	-
HZSM-5(50)	447	333	115	0.319	0.169	0.150	0.746	-	-
HZSM-5(280)	437	332	105	0.301	0.180	0.121	0.145	-	-
9.5%CuO/ZSM-5(23)	414	284	130	0.299	0.134	0.165	1.462	20.3	0.03
9.7%CuO/ZSM-5(50)	423	203	220	0.426	0.107	0.319	0.922	155.6	0.23
6.0%CuO/ZSM-5(280)	425	258	167	0.358	0.144	0.214	0.314	209.7	0.31
9.2%CuO/ZSM-5(280)	445	220	226	0.426	0.146	0.280	0.356	162.4	0.24
19.2%CuO/ZSM-5(280)	437	215	222	0.455	0.173	0.282	0.487	148.8	0.22
29.1%CuO/ZSM-5(280)	429	198	231	0.482	0.184	0.298	0.668	67.7	0.10

^a The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was calculated from the linear part of BET plot from 0.007 to 0.03.

^b The micropore area ( $S_{micro}$ ) and volume ( $V_{micro}$ ) were obtained by the t-plot method.

^c The external surface area  $S_{\text{external}} = S_{\text{BET}} - S_{\text{micro}}$ .

^d The total pore volume ( $V_{total}$ ) was evaluated by single point total pore volume at a relative pressure of 0.95.

^e The mesopore volume  $V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$ .

and micropores exist for the zeolites. The external surface area and mesopore volume of HZSM-5(23) (148 m²/g, 0.199 cm³/g) are higher than those of HZSM-5(50) ( $115 \text{ m}^2/\text{g}$ ,  $0.150 \text{ cm}^3/\text{g}$ ) and HZSM-5(280) (105  $m^2/g$ , 0.121  $cm^3/g$ ). It is seen that the introduction of copper into zeolite HZSM-5(23) leads to nearly unchanged micropore area, but lowers both external area and mesopore volume. The external surface area dropped from  $148 \text{ m}^2/\text{g}$  to  $130 \text{ m}^2/\text{g}$  and mesopore volume decreased from 0.199 cm³/g to  $0.165 \text{ cm}^3/\text{g}$ , which indicated that most of the copper species were deposited in the mesopores, reducing the contributions of these pores to the total surface area and total pore volume as a result. However, introduction of copper on zeolite HZSM-5(50) and HZSM-5(280) lowers the micropore surface area (203  $m^2/g$  and 220 m²/g for 9.7%CuO/ZSM-5(50) and 9.2%CuO/ZSM-5(280), respectively), and micropore volume  $(0.107 \text{ cm}^3/\text{g})$ and 0.146 cm³/g for 9.7%CuO/ZSM-5(50) and 9.2%CuO/ZSM-5(280), respectively) (see Table 1). Moreover, as shown in Table 1, when the addition of CuO was increased from 6.0% to 29.1% on zeolite HZSM-5(280), the BET surface area remained almost unchanged; however, the micropore area dropped from 258 to 198  $m^2/g$ , which is assumed to be caused by copper deposition in the micropores of the zeolite. The external surface area increased from 167 to 231 m²/g and the mesopore volume increased from 0.214 to  $0.298 \text{ cm}^3/\text{g}.$ 

## 3.1.4. NH₃-TPD

The acidity of the zeolites and reduced copper catalysts was determined by  $NH_3$ -TPD, as shown in Fig. 4. Fig. S4 displays the  $NH_3$ -TPD profiles of reduced Cu/ZSM-5(280) catalysts with various

CuO loadings. The amount of ammonia uptake is given in Table 1. NH₃-TPD curves with regard to the temperature can provide information of the strength of acid sites of the zeolites. As seen in Fig. 4a, the NH₃-TPD profiles of parent zeolite HZSM-5 with different SiO₂/Al₂O₃ ratios exhibited two distinct desorption peaks centering at around 250 and 450 °C, which are the characteristic peaks of zeolite with MFI structure [51]. However, in Nanba's work, the corresponding two desorption temperature of NH₃ from HZSM-5 was 200 and about 400 °C [52]. The temperature difference (50 °C) was probably due to the different flow rate of carrier gas and different ramp rate of heating when NH₃-TPD was performed (in this work, the flow rate of He is 25 mL/min, ramp rate is 10 °C/min). The peak at low temperature is assigned to ammonia weakly held or physically adsorbed on the Lewis acid sites of zeolite, whereas the peak at high temperature is ascribable to the desorption of ammonia strongly adsorbed on and/or interacting with the dislodged Al, and decomposition of NH₄⁺ on the Brönsted acid sites [53–56]. As is shown, with increasing SiO₂/Al₂O₃ ratios of the zeolite from 23 to 280, the peak intensity of ammonia desorption, especially the peak at low temperature decreased dramatically and the total acid concentration dropped from 1.167 mmol/g_{cat} to 0.145 mmol/g_{cat} (see Table 1), which is consistent with the idea that the acidity of a zeolite is inversely proportional to the SiO₂/Al₂O₃ ratio.

As is reported, copper catalyst exhibits a strong capability of oxidizing NH₃ to NO or N₂ [57,58]. However, Nanba et al. demonstrated that only N₂ was formed over  $Cu^{2+}$  species, which was accompanied by the reduction of  $Cu^{2+}$  to  $Cu^+$  [52]. Therefore, to reduce the possibility of oxidization of NH₃ prior to an NH₃-TPD



Fig. 4. NH₃-TPD profiles of (a) HZSM-5 with different SiO₂/Al₂O₃ ratios and (b) reduced Cu/ZSM-5 with different SiO₂/Al₂O₃ ratios.

experiment, all copper catalysts in this work were reduced by H₂ at temperature of 300 °C for 2 h. As seen in Fig. 4b, NH₃-TPD profiles of reduced Cu/ZSM-5 with various SiO₂/Al₂O₃ ratios also exhibited two distinct peaks, both of which shifted to higher temperatures (about 300-350 °C and 600-650 °C) compared to characteristic peaks of the parent zeolites; meanwhile, the peaks of low temperature became larger and broader, which can be ascribable to the combination of NH₃ desorption from both Lewis acid sites of zeolites and copper sites on the surface. The higher temperature peak above 600 °C is not shown in the NH₃-TPD profiles of parent zeolites, which indicates that some copper species strongly adsorb NH₃, and is probably due to NH₃ adsorbed on Cu that only binds to one Al [58]. The high temperature peak exhibits a slight shift to lower temperature from 650 to 600 °C with increasing SiO₂/Al₂O₃ ratios from 23 to 280. In addition, the total acid concentration of Cu/ZSM-5 catalyst is higher than that of the corresponding parent zeolite and decreases with increasing SiO₂/Al₂O₃ ratio (from 1.462 mmol/g_{cat} to 0.356 mmol/g_{cat}, see Table 1).

## 3.1.5. X-ray photoelectron spectroscopy

XPS analysis was employed to elucidate the chemical states of copper on the Cu/ZSM-5 catalysts. The Cu 2p photoelectron spectra of the calcined Cu/ZSM-5 with various SiO₂/Al₂O₃ ratios are shown in Fig. 5. The asymmetric peaks of Cu  $2p_{3/2}$  were deconvoluted into two peaks centering about 935.2 and 933.2 eV. It is seen from Fig. 5 that the Cu 2p_{3/2} peak of CuO/ZSM-5(23) is centered around 933.2 eV; however, the peaks of the other two catalysts CuO/ZSM-5(50) and CuO/ZSM-(280) are at 935.2 eV. Typically, peaks observed at 935.2 eV are assigned to well dispersed Cu(II) species [59]. The binding energy of the bulk CuO species is 933.6 eV (Cu  $2p_{3/2}$ ), and the shift to higher binding energy of well dispersed Cu(II) species is indicative of a charge transfer from the metal ion to the support oxide [59]. The presence of the Cu 2p shake-up satellite peak (942-944 eV) is characteristic of Cu²⁺ with electron configuration of  $(d^9)$  [38]. However, the Cu  $2p_{3/2}$  at about 933.2 eV is difficult to discriminate between Cu(I) and Cu(II). It was reported that X-ray irradiation from XPS could cause the reduction of the CuO particles [42] and X-ray sensitivity to metal ion reduction depends strongly on the chemical environment of the metal ion [60]. Gervasini et al. [59] suggested that the peak of lower binding energy (Cu 2p_{3/2} 933.15 eV) could be attributed to Cu(I) when they compared the valence state of Cu on the catalysts Cu/Al₂O₃ and Cu/SiO₂-Al₂O₃. Interestingly, one peak at 933.15 eV was observed on Cu/SiO₂-Al₂O₃, which is similar to our Cu/ZSM-5(23)



**Fig. 5.** XPS spectra of the calcined CuO/ZSM-5 with different  $SiO_2/Al_2O_3$  ratios. (a) 9.5%CuO/ZSM-5(23), (b) 9.7%CuO/ZSM-5(50), (c) 9.2%CuO/ZSM-5(280). Spectra were curve fitted by the software CasaXPS.

(see Fig. 5a) and two peaks (932 and 935.3 eV) were displayed on Cu/SiO₂, which is analogous to our Cu/ZSM-5 catalysts with SiO₂/Al₂O₃ ratios of 50 and 280 (Fig. 5b and c). Contarini and Kevan [60] reported that the lower binding energy peak (933– 934 eV) and the higher binding energy peak (935-936 eV) were assigned to the tetrahedrally and octahedrally coordinated Cu²⁺, respectively, and the shake-up satellites have a stronger correlation with the octahedrally species when they studied the valence state of Cu on dehydrated and hydrated copper-exchanged Xand Y-zeolite. In addition, they pointed out that different Si/Al ratios in zeolites might affect the symmetry and water coordination around the exchanged Cu ion. Espinós et al. [61] pointed out that, for the same oxidation state of Cu, the binding energy can change depending on the dispersion degree. They suggested that the higher binding energy (935.4 eV) and lower binding energy (933.6 eV) were related to the dispersed and bulk Cu species, respectively. Böske et al. [62] investigated the binding energy of various cuprate crystals by high-resolution XPS and found out that the Cu  $2p_{3/2}$  peak varied due to the changes with the linking arrangement of Cu-O networks within the lattice, such as linear chain, zigzag chain and CuO₂ plane, which resulted in the shifts in the position of binding energy and the relative intensity between the satellite and the main peak.

In this work, if the peak at 933.2 eV is ascribable to Cu(I), the H₂ consumption of catalyst 9.5%CuO/ZSM-5(23) should be much smaller than the other two catalysts (9.7%CuO/ZSM-5(50) and 9.2%CuO/ZSM-5(280)). However, from the TPR results, it is clearly seen that the H₂ consumption area of catalyst 9.5%CuO/ZSM-5(23) is very close to the other two catalysts and the molar ratio of H₂/Cu is close to 1 (see Table S1). Based on the results of XPS, TPR and XRD, we can safely conclude that the difference between the binding energy of Cu on HZSM-5 with various SiO₂/Al₂O₃ ratios is due to the dispersion of Cu or the structural environment where Cu is located. The binding energy of Cu on ZSM-5(23) tends to shift to the lower energy level (see Fig. S6a for 18.6%CuO/ZSM-5(23)); however, the binding energy of Cu on ZSM-5 with SiO₂/Al₂O₃ ratios of 50 and 280 shifts to the higher energy level.

XPS results for Cu/ZSM-5(280) with higher CuO loadings (see Fig. S5) show no significant change in the Cu binding energy. Fig. 6 displays the XPS spectra of reduced and used 19.2%CuO/ZSM-5(280) compared to the fresh one. The satellite peaks (943.2 eV) disappeared for the reduced and used catalyst. For the used catalyst, the peak of Cu  $2p_{3/2}$  was symmetric and found at 932.4 eV, which is assigned to Cu⁰ species [38]. This



**Fig. 6.** XPS spectra of 19.2%CuO/ZSM-5(280) catalyst. (a) Without reduction, (b) after reduction, and (c) after reaction. Spectra were curve fitted by the software CasaXPS.

indicates that the valence state of Cu on the catalyst did not change during reaction.

## 3.1.6. N₂O adsorption

Copper surface area (SA_{Cu}) and dispersion ( $D_{Cu}$ ) were calculated by the N₂O decomposition method [43,44]. As is shown in Table 1, the catalyst 9.5%CuO/ZSM-5(23) has the worst copper dispersion (0.03) and lowest copper surface area (20.3 m²/g_{Cu}), which is in agreement with the results of H₂-TPR, SEM (Fig. S3) and XPS. On ZSM-5(280), the dispersion of copper decreases slightly from 0.31 to 0.22 with increasing CuO loadings from 6.0% to 19.2%, and the copper surface area decreases from 209.7 to 148.8 m²/g_{cu}. However, when the CuO loading was increased to 29.1%, the copper dispersion and the copper surface area drastically decreased to 0.10 and 67.7 m²/g_{Cu}, respectively. This is in accordance with the result of H₂-TPR (Fig. 3). High loading of copper is not favorable for the copper dispersion [63].

# 3.2. Reaction of 2,3-but anediol over catalysts with different $SiO_2/Al_2O_3$ ratios

Experiments were performed on the parent zeolites HZSM-5 with different SiO₂/Al₂O₃ ratios (23, 50 and 280) in the absence of hydrogen (N₂ flow: 82.6 cm³/min, SATP) and the presence of hydrogen (H₂: 67.2 cm³/min, SATP; N₂: 15.4 cm³/min, SATP), respectively, at temperature 250 °C. The conversion of 2,3-butanediol and selectivities of the main products taken at 40 min and 100 min are shown in Table 2. As is reported [15-18], the dehydration reaction of 2,3-butanediol occurs readily on acid catalysts. As seen in Table 2, the conversion of 2,3-butanediol over HZSM-5 under all conditions is very high (>99.0%), and the main products are MEK, 2-methylpropanal and 1,3-butadiene, which is in accordance with the result reported in the literature [16]. Minor products including 2-methyl-1-propanol, 3-hydroxy-2-butanone and 2-ethyl-2,4,5-trimethyl-1,3-dioxolane were detected, but the selectivities were much lower than the main products mentioned above (see Table 2). 3-hydroxy-2-butanone was produced via dehydrogenation of 2,3-butanediol, while 2-methyl-1-propanol was from hydrogenation of 2-methylpropanal. The formation of the cyclic ketal 2-ethyl-2,4,5-trimethyl-1,3-dioxolane was reported from the intermolecular condensation of 2,3-butanediol and MEK [64]. However, the selectivities of butenes, which are of interest, are negligible for conversion of 2,3-butanediol over HZSM-5. Moreover, it can be seen that running the reactions of 2.3-butanediol over each HZSM-5 in the absence or presence of hydrogen led to almost the same result, which indicates that hydrogen is not involved in the conversion of 2,3-butanediol over HZSM-5.

Next, reactions were performed over reduced catalysts with ~10 wt% of CuO loaded on ZSM-5 zeolites with silica to alumina  $(SiO_2/Al_2O_3)$  ratios of 23, 50 and 280 at the same reaction conditions (feed rate of 2,3-butanediol of 3.0 mL/h, hydrogen to 2,3-butanediol molar ratio of 5, and a reaction temperature 250 °C). The selectivities of the major reaction products as a function of time on stream for the catalysts with different  $SiO_2/Al_2O_3$  ratios are shown in Fig. 7, and the conversion of 2,3-butanediol and selectivities to the products taken at 40 min and 280 min are shown in Table 3.

It can be seen in Table 3 that the conversion of 2,3-butanediol on all three catalysts was extremely high, especially in the beginning of the reaction, because the dehydration reaction of 2,3-butanediol occurs readily on acid catalysts [15–18]. It has been reported that dehydration of diols will occur on silica-supported copper catalysts since Cu is a Lewis acid [63]. Hence, Cu is active for both hydrogenation [28–32] and dehydration reactions. Interestingly, it is observed that the conversion of 2,3-butanediol on 9.5%CuO/ZSM-5(23) is 98.95% at 40 min, which is lower than that of the other two catalysts (almost 100% at 40 min) and the control data of HZSM-5(23) as well (see Table 2). This is probably due to the deactivation of the Cu/ZSM-5 catalyst.

It can be observed that the selectivities of MEK (Fig. 7b) and 2-methylpropanal (Table 3), both of which are the main products from dehydration reaction of 2,3-butanediol (see Table 2) by a pinacol rearrangement [15-18,65], decreased with increasing  $SiO_2/Al_2O_3$  ratio in the beginning of reaction (40 min), which is inconsistent with the report that high SiO₂/Al₂O₃ ratio is favorable for the high yield of MEK and high selectivity of 2-methylpropanal [16]. As we can see, on the catalyst with a  $SiO_2/Al_2O_3$  ratio of 23, the MEK (Fig. 7b) selectivity decreased slightly from 35% to 27% over time and the selectivity of 2-methylpropanal (Table 3) was extremely high (10.65% at 40 min, 9.03% at 280 min); however, on catalyst with SiO₂/Al₂O₃ of 280, the selectivity of MEK was found to be about 20% and the selectivity of 2-methylpropanal was negligible even at 280 min of time on stream. In addition, as seen in Fig. 7a, the catalyst with SiO₂/Al₂O₃ of 280 was found to have significantly higher butene selectivity, which is the sum of the selectivities of 1-butene, cis-2-butene, trans-2-butene and isobutene, than the other two catalysts; butene selectivity increased from 48% during the initial 10 min to 65% at 100 min and then tended to be relatively stable. However, the highest butene selectivity over catalysts with SiO₂/Al₂O₃ ratios of 50 and 23 was approximately 50% and 40%, which dropped slightly to 45% and dramatically to 10%, respectively, in 280 min of time on stream.

Table 3 also shows the distribution of the different butene isomers made over all catalysts. All four isomers of butene (1-butene, trans-2-butene, cis-2-butene, and isobutene) were detected. The

Table 2

Conversion of 2,3-butanediol (%) and carbon selectivity of main products (%) on the parent HZSM-5 with different  $SiO_2/Al_2O_3$  ratios in 40 min and 100 min (shown in parentheses).

	Zeolite (without	H ₂ ) ^a		Zeolite (with H ₂ )		
	HZSM-5(23)	HZSM-5(50)	HZSM-5(280)	HZSM-5(23)	HZSM-5(50)	HZSM-5(280)
1,3-Butadiene (C ₄ H ₆ )	10.05 (10.42)	11.11 (11.32)	13.87 (15.36)	10.61 (11.06)	10.42 (12.08)	14.00 (14.48)
Butenes (C ₄ H ₈ )	0.85 (0.65)	0.64 (0.51)	0.80 (0.50)	0.85 (0.67)	0.67 (0.48)	0.81 (0.48)
MEK $(C_4H_8O)$	55.30 (54.69)	56.21 (54.36)	52.77 (49.87)	56.32 (55.1)	56.13 (53.65)	53.69 (51.51)
2-Methylpropanal (C ₄ H ₈ O)	27.95 (27.30)	29.25 (28.21)	29.38 (26.00)	28.79 (28.62)	29.80 (28.44)	28.41 (25.59)
2-Methyl-1-propanol (C ₄ H ₁₀ O)	0.53 (1.23)	0.68 (0.98)	0.68 (1.02)	0.77 (1.24)	0.71 (1.02)	0.67 (0.95)
3-Hydroxy-2-butanone (C ₄ H ₈ O ₂ )	0.71 (1.68)	0.60 (1.04)	0.76 (1.30)	0.64 (1.37)	0.62 (1.01)	0.81 (1.27)
2-Ethyl-2,4,5-trimethyl-1,3-dioxolane (C ₈ H ₁₆ O ₂ )	0.36 (0.62)	0.24 (1.71)	0.38 (3.39)	0.10 (0.53)	0.29 (1.36)	0.36 (3.24)
Others ^c	4.25 (3.41)	1.27 (1.87)	1.36 (2.56)	1.92 (1.41)	1.36 (1.96)	1.25 (2.48)
Conversion	100 (99.65)	100 (99.70)	100 (99.50)	100 (99.71)	100 (99.81)	100 (99.00)

^a Reaction condition: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g; temperature, 250 °C; N₂ flow, 82.6 cm³/min.

^b Reaction condition: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g; temperature, 250 °C; H₂ flow, 67.2 cm³/min; N₂ flow, 15.4 cm³/min.

^c Other products: acetone, tetramethylfuran, 3,4,5-trimethyl-2-cyclopentenone and aromatics.



**Fig. 7.** Catalytic results as a function of time on stream for the conversion of 2,3-butanediol over reduced copper supported on ZSM-5 with different SiO₂/Al₂O₃: (■) 9.5%CuO/ZSM-5(23), (○) 9.7%CuO/ZSM-5(50), (▲) 9.2%CuO/ZSM-5(280). Carbon selectivity to main products (a) butene, (b) MEK, (c) 3-hydroxy-2-butanone, and (d) 2-methyl-1-propanol. Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g; H₂/2,3-butanediol (molar ratio), 5:1; temperature: 250 °C.

Table 3

Conversion of 2,3-butanediol (%) and carbon selectivity of the products (%) on reduced Cu/ZSM-5 with different SiO₂/Al₂O₃ ratios in 40 min and 280 min (shown in parentheses).^a

	Catalysts				
	9.5%CuO/ZSM-5(23)	9.7%CuO/ZSM-5(50)	9.2%CuO/ZSM-5(280)		
Ethylene ( $C_2H_4$ )	0.04 (0.01)	0.36 (0.13)	0.21 (0.15)		
Propylene $(C_3H_6)$	0.38 (0.13)	2.80 (0.79)	1.90 (0.75)		
Isobutane and butane $(C_4H_{10})$	0.04 (0.03)	0.32 (0.09)	0.18 (0.11)		
Butenes ( $C_4H_8$ )	24.30 (7.23)	44.13 (42.41)	58.65 (62.84)		
$C_5$ olefins ( $C_5H_{10}$ )	0.16 (0.02)	6.02 (0.66)	3.74 (0.79)		
$C_6$ olefins ( $C_6H_{12}$ )	0.05 (0.02)	0.16 (0.34)	2.10 (0.12)		
C ₇ olefins (C ₇ H ₁₄ )	0.10 (0.02)	0.52 (0.19)	0.38 (0.19)		
$C_8$ olefins ( $C_8H_{16}$ )	0.62 (0.27)	3.37 (1.61)	1.24 (0.72)		
MEK ( $C_4H_8O$ )	33.07 (26.31)	25.62 (32.52)	19.06 (24.30)		
2-Methylpropanal (C ₄ H ₈ O)	10.65 (9.03)	0.03 (4.21)	0 (0.17)		
2-Methyl-1-propanol ( $C_4H_{10}O$ )	10.23 (11.40)	0.80 (3.46)	0 (0.46)		
2,3-Butanedione $(C_4H_6O_2)$	0.21 (1.41)	0.35 (0.02)	0.14 (0.01)		
3-Hydroxy-2-butanone ( $C_4H_8O_2$ )	5.14 (24.53)	1.24 (0.20)	0.22 (0)		
2-Butanol (C ₄ H ₁₀ O)	0.87 (1.64)	1.00 (0.41)	0.57 (0.22)		
2-Ethyl-2,4,5-trimethyl-1,3-dioxolane (C ₈ H ₁₆ O ₂ )	1.84 (3.52)	0.05 (0.03)	0.15 (0.01)		
Ethylbenzene (C ₈ H ₁₀ )	0.45 (0.79)	1.07 (0.71)	0.55 (0.57)		
p-Xylene (C ₈ H ₁₀ )	0 (0)	1.12 (0.58)	0.72 (0.43)		
Tetramethylfuran (C ₈ H ₁₂ O)	9.36 (8.37)	2.75 (7.25)	0.98 (3.43)		
1-Ethyl-3-methyl-benzene (C ₉ H ₁₂ )	0.03 (0.88)	0 (0.10)	0.19 (0.08)		
1,3,5-Trimethyl-benzene ( $C_9H_{12}$ )	0.12 (0.07)	0.42 (0.15)	0.19 (0.09)		
Conversion of 2,3-butanediol	98.95 (91.69)	100 (99.80)	100 (99.67)		
Distribution of butenes					
1-Butene (C ₄ H ₈ )	3.85 (2.40)	4.61 (3.67)	7.62 (7.97)		
Isobutene (C ₄ H ₈ )	6.82 (0.43)	11.03 (10.90)	11.54 (12.80)		
Trans-2-butene (C ₄ H ₈ )	7.58 (2.27)	14.45 (13.17)	20.22 (21.43)		
Cis-2-butene (C ₄ H ₈ )	5.97 (1.80)	12.20 (12.95)	16.91 (18.12)		

^a Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g; H₂/2,3-butanediol (mol ratio), 5:1; temperature, 250 °C.

selectivity of 1-butene is much smaller than the other three isomers (isobutene, trans-2-butene and cis-2-butene) in the initial 40 min. In this work, 1,3-butadiene, which is a major product from

dehydration of 2,3-butanediol (see Table 2), was not detected, suggesting that either it is not formed over the Cu/ZSM-5 catalysts, or it was immediately hydrogenated to butenes after forming. In addition, the selectivities of butane and isobutane, which could be produced by further hydrogenation of the butenes, were very small (see Table 3), which indicates that copper catalysts are not favorable for the hydrogenation of butenes to C₄ alkanes in this work.

As discussed above, there is a trend that increasing the SiO₂/Al₂O₃ ratio (lowering acidity of HZSM-5) increases butene selectivity. However, it was also observed that during the first 10 min of reaction, the selectivity of butene over catalyst with  $SiO_2/Al_2O_3$  of 23 (40%) is higher than with a ratio of 50 (25%). This is likely due to the influence of dimerization and cracking reactions that occurred during this period of time. As we can see in Table 3, the catalyst with a  $SiO_2/Al_2O_3$  ratio of 50 showed the highest selectivity of  $C_8$  olefins (3.37%), which is from dimerization of butenes [26], and highest selectivities of propylene (2.80%) and  $C_5$  olefins (6.02%, the sum of the selectivities of 2-methyl-1-butene, 3-methyl-1-butene and 2-methyl-2-butene), both of which are from cracking reactions [26]. It seems that catalyst with modest acidity  $(SiO_2/Al_2O_3 = 50, acidity 0.746 \text{ mmol/g})$  is beneficial for the oligomerization of butenes to form dimers, with subsequent cracking reaction to form ethylene, propylene, C₅, C₆ and C₇ olefins, which reduced the production of butenes especially at the beginning of reaction. It has to be mentioned that the selectivities of products from dimerization and cracking reactions decreased over time due to the deactivation of catalysts.

As mentioned above, a small amount of 3-hydroxy-2-butanone can be seen in the control experiment of conversion of 2,3-butanediol over HZSM-5 (see Table 2), which is a product from the dehydrogenation reaction of 2,3-butanediol [18]. Over Cu/ZSM-5 catalyst, 3-hydroxy-2-butanone was also observed (see Fig. 7c) even in the excess of hydrogen present in the reactor (molar ratio of H₂/2,3-BDO = 5). Over the catalyst with SiO₂/Al₂O₃ of 23, the selectivity of 3-hydroxy-2-butanone increased dramatically with increasing time on stream (increased from almost 0% to about 25%), which is probably due to deactivation of catalyst. However, the catalyst with SiO₂/Al₂O₃ ratio of 50 presented activity for dehydrogenation reaction only in the first 70 min on stream, while the selectivity of 3-hydroxy-2-butanone over the catalyst with SiO₂/Al₂O₃ ratio of 280 was negligible. The reaction mechanism will be discussed later.

Over the catalyst with a  $SiO_2/Al_2O_3$  ratio of 23, the increase of 2-methyl-1-propanol selectivity is a result of the deactivation of catalyst (Fig. 7d). Deactivation of zeolite-based catalysts is mainly



**Fig. 8.** Thermogravimetric profile of catalysts after 280 min of reaction. Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g;  $H_2/2,3$ -butanediol (molar ratio), 5:1; temperature: 250 °C.

due to the formation of coke [66,67], which is a non-desorbed product that prevents access to the acid sites of catalysts. To determine the coke content of the used catalysts, a quantitative analysis of coke formation over the used catalysts after the reaction was investigated by thermogravimetric analysis (TGA). Fig. 8 shows the TGA results of the catalysts after 280 min of reaction. As is shown, the coke content on 9.5%CuO/ZSM-5(23) was 5.81%, which was higher than that on 9.7%CuO/ZSM-5(50) (4.97%) and 9.2%CuO/ZSM-5(280) (2.57%). This indicates that the acidity of catalyst is an important cause in coke formation. Indeed, with more acid sites, the coke formation will occur faster. The coke content on 9.5%CuO/ZSM-5(23) was 4.29% after 40 min of reaction, which was much higher than the other two catalysts (see Fig. S7). Hence, the catalyst will deactivate sooner as a result. For this reason, the catalyst with a SiO₂/Al₂O₃ ratio of 23 deactivated faster than the other two catalysts. As is shown in Table 3, the conversion of 2.3-butanediol over 9.5%CuO/ZSM-5(23) decreased from 98.95% at 40 min to 91.69% at 280 min, while conversion over the other two catalysts remained above 99.0% even after 280 min. In addition, deactivation of catalysts results in the loss of acid sites, decreasing the possibility of dehydration reaction over acid sites; therefore, the selectivity of MEK over the catalyst with a SiO₂/Al₂O₃ ratio of 23 decreased over time. Meanwhile, the selectivity of 2-methyl-1-propanol increased dramatically from 3.5% to 12.0% with time on stream (Fig. 7d), which was accompanied by the decrease of isobutene selectivity from 6.82% at 40 min to 0.43% at 280 min (see Table 3). Consequently, the selectivity of butenes on 9.5%CuO/ZSM-5(23) showed a decreasing trend over time. It has been reported that copper catalysts are also active in dehydrogenation [25]. Hence, as is seen in Fig. 7c and Table 3, when deactivation occurred, Cu on 9.5%CuO/ZSM-5(23) turned into the active sites in conversion of 2,3-butanediol to 3-hydroxy-2butanone and 2,3-butanedione, both of which showed an increasing trend in selectivity with time on stream.

As is mentioned above, large copper clusters were observed on the surface of 9.5%CuO/ZSM-5(23) (see SEM image, Fig. S3), which is in accordance with the copper dispersion result (0.03) shown in Table 1. It is possible that poor copper dispersion and large Cu particle sizes could affect the catalytic reaction, as shown in the literature [31,68]. However, in this work, we believe that the differences noted for the different SiO₂/Al₂O₃ ratios are due to differences in catalyst acidity rather than Cu dispersion or Cu size, since the activity of catalyst 9.7%CuO/ZSM-5(50) was not as good as catalyst 9.2%CuO/ZSM-5(280) even though it exhibited a good dispersion of Cu on the surface (0.23, see Table 1). Over a catalyst with SiO₂/Al₂O₃ of 280, only a trace amount of 2-methyl-1propanol and 3-hydroxy-2-butanone was found in 280 min of time on stream. Also, it was seen to exhibit the highest selectivity of butenes and lowest selectivities to other byproducts, such as aromatics and tetramethylfuran (Table 3). Based on the discussion above, it can be concluded that zeolite ZSM-5 with SiO₂/Al₂O₃ ratio of 280 can be chosen as the best support for catalyzing the hydrodeoxygenation of 2,3-butanediol to butene in a single reactor. Next, we will focus on this zeolite to examine other reaction parameters.

#### 3.3. Effect of copper content

Fig. 9 shows the impact of copper loading on catalytic conversion of 2,3-butanediol to the main products as a function of time on stream under the same reaction conditions as used in Fig. 7 and Table 3 for ZSM-5(280) with four different CuO loadings: 6.0%, 9.2%, 19.2%, and 29.1%. The conversion of 2,3-butanediol and selectivities to the products are shown in Table S2. As is seen, the conversion of 2,3-butanediol was high (>99%) over all four catalysts.



**Fig. 9.** Catalytic results for the conversion of 2,3-butanediol to butene over different copper loadings on ZSM-5 (SiO₂/Al₂O₃ = 280). ( $\triangle$ ) 6.0%CuO/ZSM-5(280), ( $\square$ ) 9.2%CuO/ZSM-5(280), ( $\blacksquare$ ) 19.2%CuO/ZSM-5(280), ( $\blacksquare$ ) 19.2%CuO/ZSM-5(280), ( $\blacksquare$ ) 29.1%CuO/ZSM-5(280). Carbon selectivity to main products (a) butene, (b) MEK, (c) 3-hydroxy-2-butanone, and (d) 2-methyl-1-propanol. Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g; H₂/2,3-butanediol (molar ratio), 5:1; temperature: 250 °C.

As is shown in Fig. 9a, the selectivity of butene increased with increasing copper loading, and the catalyst with 19.2 wt% of CuO showed the highest catalytic activity toward the production of butene; the selectivity gradually increased from 60% in the initial 10 min to reach a maximum of approximately 71% at 70 min and then dropped slightly to 65% after 310 min on stream. However, it does appear that the catalyst with highest weight loading (29.1 wt%) of CuO deactivated faster than the catalysts with lower loadings of CuO (9.2 wt% and 19.2 wt%). This suggests that it is not necessary to have excessively high loadings of CuO to get high selectivities of butenes.

As seen in Fig. 9b, the selectivity of MEK showed a decreasing trend with increasing weight loading of copper. As copper is the active site for hydrogenation, higher copper loading is expected to favor the hydrogenation of MEK to butenes, resulting in a lower selectivity of MEK. It can also be seen that the selectivity of MEK over catalysts showed a general tendency to increase gradually with increasing time on stream, which can be ascribed to the deactivation of catalysts.

Fig. 9d shows the selectivity of 2-methyl-1-propanol over catalysts with time on stream. With the exception of the catalyst with 29.1 wt% CuO, all catalysts showed similar behaviors toward the selectivity of 2-methyl-1-propanol, which increased slightly from 0% to about 0.6% with time on stream. However, over the catalyst with highest loading of CuO (29.1 wt%) in this work, the selectivity of 2-methyl-1-propanol increased dramatically from 0% to 8.5%. In addition, the selectivity of 2-methylpropanal (Table S2) was negligible except on the catalyst with highest CuO loading (29.1 wt%). These trends may be due to the low copper dispersion (0.10, see Table 1) on the catalyst with 29.1% CuO, which is not favorable for dehydration of alcohols to butenes and hydrogenation of

2-methylpropanal, leading to high selectivities of 2-methyl-1propanol and 2-methylpropanal.

The selectivity of 3-hydroxy-2-butanone with time on stream is depicted in Fig. 9c. As seen in Fig. 9c, in the initial 10 min, the catalyst with the lowest CuO loading (6 wt%) exhibited the highest selectivity of 3-hydroxy-2-butanone (1.8%), however, catalyst with 19.2 wt% of copper loading presented the lowest, 0.2%. The selectivities of 3-hydroxy-2-butanone tended to decrease with time on stream, reaching 0 after 100 min, with the exception of the catalyst with 29.1 wt% CuO, on which selectivity was observed to decrease from 0.5% to 0.1% at 100 min, and then increased steadily to 1.2% at 310 min, which probably can be attributed to low copper dispersion. Torresi et al. investigated the conversion of 1,3-butanediol by dehydrogenation and dehydration reactions on CuO/SiO₂, and found that dehydrogenation predominated over catalysts with high copper loading [63], which is similar to our finding in this work.

In addition, over catalysts with different copper loadings, it can be seen that the selectivities of  $C_8$ ,  $C_7$ ,  $C_5$  and  $C_3$  olefins and 2-butanol (Table S2) were higher on the catalyst with lower CuO loadings (6.0% and 9.2%), which indicates that lower copper loadings favored the dimerization of butenes, and subsequent cracking reaction and the formation of 2-butanol (the intermediate to form butenes), especially in the first 40 min of stream. The optimal amount of copper is not yet clear. As discussed in the literature [63], on SiO₂, the copper monolayer surface coverage is about 13.5 wt% of Cu (e.g. 16.9 wt% of CuO), which is close to the CuO loading (19.2 wt%) on the catalyst that gave the highest butene selectivity. The optimal performance is the result of a balance between copper and acid catalytic functions.

#### 3.4. Effect of hydrogen to 2,3-butanediol ratio

The impact of hydrogen to 2,3-butanediol ratio on the catalytic performance of 19.2 wt%CuO/ZSM-5(280) for conversion of 2,3-butanediol to main products with time on stream is depicted in Fig. 10 and the selectivities to all products are shown in Table S3. All conditions exhibit high conversion of 2,3-butanediol, though these is a general increasing trend with increasing hydrogen to 2,3-butanediol ratio.

As expected, the dehydrogenation reaction is an important reaction at low  $H_2/2,3$ -BDO ratio, especially when the ratio is below 2 (see Fig. 10c and 2,3-butanedione in Table S3). The selectivity of 3-hydroxy-2-butanone generally increased with increasing time on stream and decreased when  $H_2/2,3$ -BDO ratio was increased from 0 to 5. The selectivities of 2,3-butanedione at 40 min and 280 min also decreased with increasing  $H_2/2,3$ -BDO ratios. At  $H_2/2,3$ -BDO of 5, it can be seen that the dehydrogenation was suppressed, as indicated by the negligible amount of 3-hydroxy-2-butanone and 2,3-butanedione present.

The main trend of interest is that butene selectivity increases as  $H_2/2,3$ -BDO ratio increases (see Fig. 10a), which is attributed to the fact that hydrogen has a positive impact on catalytic activity toward the hydrogenation reaction. Also, it was observed that the selectivity of butene decreases with increasing time on stream, which is due to the deactivation of catalysts especially with low  $H_2/2,3$ -BDO ratios of 0 and 1. Interestingly, butenes can be formed even in the absence of  $H_2$  ( $H_2/2,3$ -BDO = 0), which are higher than the control data of HZSM-5(280) without  $H_2$  (see Table 2). As mentioned above, the dehydrogenation reaction became the main reaction at low  $H_2/2,3$ -BDO ratios. We suggest that  $H_2$  formed in the process of dehydrogenation of 2,3-BDO is involved in the hydrogenation reactions to produce the butenes.

The impact of  $H_2/2,3$ -BDO ratio toward MEK selectivity is shown in Fig. 10b. It is observed that the selectivity of MEK decreases with increasing  $H_2/2,3$ -BDO ratios from 2 to 5, and  $H_2/2,3$ -BDO ratio of 2 exhibits the highest and most stable selectivity (about 30–34%) of MEK. At  $H_2/2,3$ -BDO ratios of 0 and 1, the selectivities of MEK decreased dramatically over time due to the deactivation of catalysts which lead to decreasing catalytic activity for dehydration. Meanwhile, the selectivities of 3-hydroxy-2butanone and 2,3-butanedione increased dramatically over time in such conditions. This indicates that the dehydrogenation reaction became dominant at the conditions with low hydrogen.

The selectivity of 2-methyl-1-propanol with time on stream is depicted in Fig. 10d. This selectivity increases with decreasing  $H_2/2.3$ -BDO ratio from 5 to 2. It is well known that hydrogen can improve the catalytic stability of zeolite catalysts due to the inhibition effect of the hydrogen on coke formation [69–71] by reacting with carbenium ions to limit the formation of carbonaceous compounds responsible for deactivation, which is in agreement with the TGA results (see Fig. S8). With decreasing H₂/2,3-BDO ratio, more coke is formed (Fig. S8), and faster catalyst deactivation is observed, resulting in increasing selectivity of 2-methyl-1propanol over time. At the  $H_2/2,3$ -BDO ratio of 5, the catalyst exhibited extremely high catalytic activity for hydrogenation and dehydration reactions, resulting in negligible selectivity of 2-methyl-1-propanol, which is expected to be converted to isobutene. As is shown in Fig. 10d, however, when the  $H_2/2,3$ -BDO ratio is decreased from 1 to 0, the selectivity of 2-methyl-1-propanol decreases. This is because dehydrogenation of 2,3-butanediol to 3-hydroxy-2butanone and 2,3-butanedione becomes the dominant reaction pathway under the conditions with low hydrogen. As is seen in Table S3, with different  $H_2/2,3$ -BDO ratios, it can be seen that lower H₂ partial pressures are not favorable for the cracking reaction.



**Fig. 10.** Catalytic results for the conversion of 2,3-butanediol to butene over 19.2 wt% copper supported on ZSM-5 (Si/Al₂O₃ = 280) at a hydrogen to 2,3-BDO ratio of: ( $\Box$ ) 0, ( $\bigcirc$ ) 1, ( $\bullet$ ) 2, ( $\triangle$ ) 3, ( $\nabla$ ) 4, ( $\blacksquare$ ) 5. Carbon selectivity to main products (a) butene, (b) MEK, (c) 3-hydroxy-2-butanone, and (d) 2-methyl-1-propanol. Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst: 19.2 wt%CuO/ZSM-5(280); catalyst weight, 1.0 g; temperature, 250 °C.

Another product from dehydration reaction, 2-methylpropanal, exhibited a decreasing trend of selectivity with increasing  $H_2/2,3$ -BDO ratios from 0 to 5, decreasing from 13.15% to 0% at 40 min, which is the source of 2-methyl-1-propanol and isobutene.

In conclusion, hydrogenation reactions are essential toward getting high butene selectivities. Higher  $H_2/2,3$ -BDO ratios are better for catalyzing hydrogenation reactions because hydrogen can improve catalytic stability of zeolite catalysts.

#### 3.5. Effect of temperature

The impact of temperature on the selectivities of the main products on 19.2 wt%CuO/ZSM-5(280) as functions of time on stream is depicted in Fig. 11. The conversion of 2,3-butanediol and selectivities of all products in 40 min and 310 min are shown in Table S4. All temperatures except 230 °C exhibit stable and high conversion of 2,3-butanediol, with conversions of nearly 100%. However, at lower temperature (230 °C), the conversion is relatively lower at 310 min (93.11%) due to deactivation.

As seen in Fig. 11a, with the exception of 230 °C, the selectivity of butene decreased with increasing temperature, which is mainly due to oligomerization of butenes, and subsequent cracking reactions, resulting in lower selectivity of butene and higher selectivities of  $C_3$ ,  $C_5$ ,  $C_6$ ,  $C_7$  and  $C_8$  olefins (see Table S4). In particular, at a temperature of 250 °C, the catalyst exhibits the highest selectivity of butene. A high butene selectivity (55%) is initially observed for the lowest temperature (230 °C), but it dramatically decreased to 10% over 310 min.

Fig. 11b displays the selectivity of MEK at various reaction temperatures. The initial selectivity of MEK decreases with increasing temperature. However, at 300 °C, the selectivity of MEK increased from 0 during the initial 10 min to 26% at 310 min, indicating catalyst deactivation. As we can see, low temperature (230 °C) favored the production of 2-methyl-1-propanol over time (Fig. 11d) and formation of 2-methylpropanal (Table S4), accompanied by low selectivity of butenes. This is also due to the deactivation of catalyst. From TGA results (see Fig. S9), we can see the sharp weight loss (-0.8%) between 220 °C and 300 °C on the used catalyst after reaction at 230 °C, which is reported due to the formation of heavy oligomers from butenes that do not evaporate on zeolites [26]. However, at higher temperature, the heavy products can evaporate or be cracked into smaller molecules, reducing coke deposition [26]. And at extremely higher temperatures (270 °C and 300 °C), the deactivation of catalyst is due to hard coke formation at high temperature [66]. From the TGA (Fig. S9), we can see the weight loss on the used catalysts after reaction at 270 °C and 300 °C occurs mainly between 400 °C and 600 °C, which are due to the combustion of "hard coke" [72-74].

The selectivity of 3-hydroxy-2-butanone at various temperatures with time on stream is depicted in Fig. 11c. Clearly, low temperatures favor the dehydrogenation reaction of 2,3-butanediol to lose one hydrogen atom from one hydroxyl group, especially after 100 min of stream. However, at higher temperatures such as 270 °C and 300 °C, 2,3-buanediol is likely to lose two hydrogen atoms from both hydroxyl groups to form 2,3-butanedione (see Table S4).

As discussed above, higher temperatures (270 °C and 300 °C) are beneficial for the oligomerization and cracking reactions, resulting in significantly higher selectivities of  $C_3$  and  $C_5^+$  olefins. Moreover, it should be noted that higher temperatures lead to higher selectivities of heavy products, such as aromatic compounds (Table S4) and  $C_4$  alkanes (isobutene and butane, see Table S4).



**Fig. 11.** Catalytic results for the conversion of 2,3-butanediol to butene over 19.2 wt% CuO supported on ZSM-5 (Si:Al₂O₃ = 280) at a hydrogen to 2,3-BDO ratio of 5 at different reaction temperatures: ( $\triangle$ ) 230 °C, ( $\blacksquare$ ) 250 °C, ( $\blacksquare$ ) 270 °C, ( $\blacktriangle$ ) 300 °C. Carbon selectivity to main products, (a) butene, (b) MEK, (c) 3-hydroxy-2-butanone, and (d) 2-methyl-1-propanol. Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst: 19.2 wt%CuO/ZSM-5(280); catalyst weight, 1.0 g; H₂/2,3-BDO (molar ratio)=5.



**Fig. 12.** Catalytic results for the conversion of 2,3-butanediol over reduced catalysts (a) fresh catalyst 19.2%CuO/ZSM-5(280), (b) 19.2%CuO/ZSM-5(280) after first regeneration, (c) 19.2%CuO/ZSM-5(280) after second regeneration. Selectivity to products: ( $\blacksquare$ ) butene, ( $\bullet$ ) MEK, ( $\blacktriangle$ ) 3-hydroxy-2-butanone, ( $\bigtriangledown$ ) 2-methyl-1-propanol, ( $\bigcirc$ ) 2-methyl-1-propanol, ( $\bigcirc$ ) 2-methylpropanal, ( $\square$ ) conversion of 2,3-butanediol. Reaction conditions: feed rate of 2,3-butanediol, 3.0 mL/h; catalyst weight, 1.0 g; H₂/2,3-BDO (molar ratio) = 5; reaction temperature, 250 °C.

## 3.6. Regeneration of catalysts

Since deactivation of the catalyst was shown to be an issue, we have investigated whether the catalyst can be regenerated by heating in air. Deactivation by coke is reversible, because generally coke can be removed by oxidation [75,76]. This would be expected to regenerate the catalyst if coke deposition is the main source of deactivation [77], but not if sintering or other structural rearrangement was responsible. Experiments were run where 19.2% CuO on ZSM-5 (280, Si/Al₂O₃ ratio) was regenerated twice under air with air flow 120 cm³/min at 550 °C for 3 h. Fig. 12a shows the initial catalytic performance, while Fig. 12b and c show the performance after the first and second regenerations, respectively. As seen by comparison of these three figures, regeneration under air is capable to yielding a catalyst with almost identical performance as the initial fresh catalyst. It is remarkable that high conversion of 2,3-butanediol (almost 100%) is exhibited by the catalysts, even ones displaying signs of deactivation. However, after a second regeneration, the catalytic activity, especially the selectivity of butene, is shown to drop faster than the fresh or used catalyst after the first regeneration, which is probably due to the formation of stable or hard coke species agglomerated on the zeolite in the first and second runs which cannot be removed by the regeneration procedure.

# 3.7. Hydrogenation of MEK

As discussed above, the results suggest that MEK and 2-methylpropanal are the intermediates in the conversion of 2,3-butanediol to butene. To explore the roles of the intermediate in conversion of 2,3-butanediol, hydrogenation reactions of MEK and 2-methylpropanal were conducted under similar reaction conditions to those used for 2,3-butanediol conversion. Fig. 13 shows

the catalytic results of conversion of MEK over 19.2 wt%CuO/ ZSM-5(280) with time on stream. As we can see, the selectivity of butene is high (about 50%), although it is not as high as when 2,3-butanediol was the reactant. Interestingly, the results show that the selectivities of  $C_5-C_8$  olefins are significantly higher in comparison with the result from 2,3-butanediol. Similar results are also observed in hydrogenation reaction of 2-methylpropanal, in which, the oligomerization and cracking reactions became dominant catalytic processes (see Fig. S10), with selectivities of  $C_5-C_8$ olefins higher than butenes. The reason why the formation of



**Fig. 13.** Catalytic results for the conversion of MEK over reduced catalyst 19.2%CuO/ ZSM 5(280) with time on stream. Selectivity to products: ( $\blacksquare$ ) butene, ( $\bigcirc$ ) propylene, ( $\triangle$ ) pentene, ( $\nabla$ )  $C_{6}^{-} \sim C_{8}^{-}$ , ( $\bullet$ ) 2-butanol, ( $\Box$ ) conversion of MEK. Reaction conditions: feed rate of MEK, 3.0 mL/h; catalyst weight, 1.0 g; H₂/MEK (molar ratio) = 5.



Scheme 1. Probable reaction pathways in the hydrodeoxygenation of 2,3-butanediol to products.

 $C_6-C_8$  olefins is favorable when MEK and 2-methylpropanal are used as reactants is likely because no acid sites are required to dehydrate 2,3-BDO to MEK and 2-methylpropanal, so more acid sites are available for dehydration of 2-methyl-1-propanol and 2-butanol to butenes, and the subsequent oligomerization and cracking reactions as well.

Based on the results discussed above, we summarize the probreaction pathways in the hydrodeoxygenation able of 2,3-butanediol in Scheme 1. The primary pathways involve dehydration and hydrogenation reactions. Over acid sites (including Cu sites), 2,3-butanediol is dehydrated to form primarily MEK and 2-methylpropanal [16]. MEK and 2-methylpropanal are converted to 2-butanol and 2-methyl-1-propanol, respectively, over copper sites through hydrogenation. Finally, 2-butanol is dehydrated to form 1-butene, trans-2-butene and cis-2-butene and 2-methyl-1-propanol is converted to isobutene through dehydration. 1,3-butadiene, which is a product from dehydration of 2,3-BDO [16], is undetectable in this work. For this reason, a route to butenes via 1,3-butadiene as an intermediate is possible, but likely not very important. Once butene compounds are formed, they can be oligomerized to form dimers, trimers, etc., via a carbenium-ion mechanism [78], which can further be cracked to other olefins such as propylene and pentene. In addition, 2,3-butanediol can be converted to 3-hydroxy-2-butanone and 2,3-butandione via dehydrogenation reactions on copper sites.

## 4. Conclusions

The conversion of 2,3-butanediol to butenes in a single reactor has been demonstrated with a 70% yield over Cu/ZSM-5. Enhanced butene yields were achieved with a high  $SiO_2/Al_2O_3$  ratio, with the best results achieved at  $SiO_2/Al_2O_3 = 280$ . This is attributed to the lower acidity of the high silica catalysts. Increasing copper loading had a relatively minor impact on catalytic results, though in general butene yield increased with copper loading. Deactivation of the catalysts due to coke formation was noted on all catalysts as product selectivities changed over a 5-h run time, but the original activity could be restored by heating the catalyst in air.

The impact of reaction conditions showed that the optimal temperature is around 250 °C. Lower temperature (230 °C) is beneficial for dehydrogenation of 2,3-butanediol; higher temperatures (270 °C and 300 °C) favor the oligomerization and cracking reactions, resulting in significantly higher selectivities of  $C_3$  and  $C_5^+$  olefins. The results show that hydrogenation reactions are essential toward getting high butene selectivities, and higher hydrogen to 2,3-butanediol ratios are favorable for catalyzing hydrogenation reactions. Dehydrogenation reactions become dominant for conditions with low hydrogen, especially when H₂/2,3-BDO ratios are below 2. The reaction mechanism demonstrated that MEK and 2-methylpropanal are the intermediates in the conversion of 2,3-butanediol to butenes. The optimal performance toward the production of butene is the result of a balance between copper and acid catalytic functions.

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#### **Appendix A. Supplementary material**

XRD patterns and XPS spectra of catalysts with different CuO loadings on ZSM-5(280); SEM images; NH₃-TPD profiles of reduced Cu/ZSM-5(280) with different CuO loadings; three TGA figures of used catalysts; a figure presenting catalytic results for the conversion of 2-methylpropanal over reduced catalyst 19.2%CuO/ZSM-5(280); H₂ consumption summarized from TPR; three tables showing the conversion of 2,3-butanediol and selectivities to the products as functions of CuO loading, temperature and H₂: 2,3-butanediol ratio. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10. 1016/j.jcat.2015.07.004.

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