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Highly selective one-pot continuous synthesis of 2-methoxyethanol via hydrogenation of dimethyl oxalate on Cu/ZrO$_2$ catalysts with balanced acid sites

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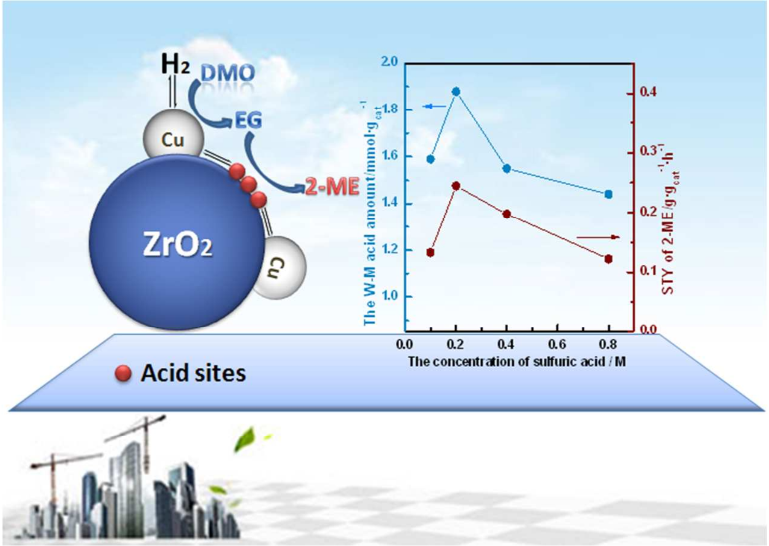

Cite this: DOI: 10.1039/c0xx00000x

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Communication

Highly selective one-pot continuous synthesis of 2-methoxyethanol via hydrogenation of dimethyl oxalate on Cu/ZrO_2 catalysts with balanced acid sites

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Received (in XXX, XXX) XthXXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

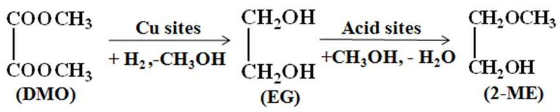
The distribution of 2-methoxyethanol and ethylene glycol can be controlled by regulating the surface acidity of the copper based zirconia catalysts for hydrogenation of dimethyl oxalate. The yield of 2-methoxyethanol can reach 68% due to the synergistic effect of the surface acid site and active copper site.

Considering the depletion of petroleum resources, the transformation of the single-carbon (C1) raw materials carbon monoxide and carbon dioxide into various high-valued-added fine chemicals has emerged as a versatile synthetic tool in organic methodology both on laboratory and industrial scale. [1–3] An efficient production of ethylene glycol (EG) from syngas through a two-step process consisting of the coupling of CO with nitrite esters to dimethyl oxalate (DMO) and heterogeneous catalytic hydrogenation of DMO has been extensively researched and industrialized. [4] Copper-based catalysts with excellent catalytic performance have been extensively explored for the hydrogenation of DMO considering that the Cu active sites are accounting for the selective hydrogenation of the C-O bond, and relatively inactive for the hydrogenolysis of C-C bond**.** [5, 6]

Among the various supports, SiO_2 was found to afford the excellent yield of EG in the hydrogenation of DMO. [7] While as a weakly acidic carrier, silica poorly interacts with metallic Cu, thereby resulting in the coalescence of Cu NPs and the short lifespan of the $Cu\text{-}SiO_2$ catalysts. Some other supports (Al_2O_3, ZrO_2) were once studied. [8] Zirconia has recently emerged as a particularly attractive support material for the activation and stabilization of copper other than ZnO or alumina, which is well documented in the field of methanol synthesis, [9, 10] mainly due to the possession of both amphoteric and redox functions. Previous researches have demonstrated that the surface acidic properties of the support would induce some side reactions. Strong acid sites would induce the intermolecular dehydration of EG, whereas strong basic sites would help to catalyze the Guerbet reaction into the formation of 1,2-butanediol. [11] EtOH might be generated from intramolecular dehydration over weak acidic sites and Cu sites. [12] Zhu et al. proposed that the Cu/ZrO_2 catalyst exhibited different behavior since the etherification to 2-methoxyethanol (2-ME) from EG was found to be the main rival side reaction over the surface $Zr^{4+}O^{2-}$cationic Lewis acid sites when methanol was chosen as solvent, [8] while the yield of 2-ME was below 15% at reaction temperature of 220℃ using Cu/ZrO_2 as the catalyst.

2-ME, which can be widely used in printing, coating, ink and many other industries because of the co-existence of the hydroxyl group and ether group in its structure. By 2007 the annual domestic consumption of glycol ethers reached 200 000 tons. Due to rapid development of China's paint industry, water-based paint takes the place of oil-based paint gradually, which means greater demand for glycol ether products. Commercial 2-ME is mainly produced from petroleum-derived ethylene oxide through the reaction of ethylene oxide and methanol. Nevertheless, because of the long-term shortage and the increased price of crude oil, direct synthesis of 2-ME from syngas could complement the existing technologies. Furthermore, products 2-ME and EG are easy to be separated due to the big difference of their boiling points. The objective of this work is to give fundamental insight into the role of acidity on the distribution of 2-ME and EG for the hydrogenation of DMO. Sulfated solid acidic oxides have many applications in acid-catalyzed reactions in industry, such as isomerization, [13] nitration, [14] reduction [15] and Friedel Crafts acylation. [16] Among solid acids and superacids, sulfated zirconia has gained much attention due to its non-toxicity, high strength of acidity and high activity. [17] Li et al. [18] has reported that the catalytic performance of sulfated zirconia depended on the sulfation procedure, sulfating concentration and calcination temperature.

Herein, we demonstrate for the first time that the Cu-based catalysts supported on sulfated ZrO_2 show excellent catalytic activity for the hydrogenation of DMO to EG and 2-ME (Scheme 1). ZrO_2 supports were prepared via the reflux method. [18] The copper supported on zirconia catalysts were labeled as 10Cu/xSZT catalysts, where x and T denote the various concentrations of sulfuric acid solution and the calcination temperature of sulfated supports.



Scheme 1 Reaction pathway for the conversion of DMO

The specific surface areas of the catalysts synthesized under different conditions are shown in **Fig. 1.** The 10Cu–0.2SZ sample with uncalcined sulfated support was found to possess a relatively high BET surface area of 256 m^2/g, whereas further increasing calcination temperature resulted in a gradual decline in surface area. The BET surface area initially increased and reached its maximum at the sulfate concentration of 0.2 M, with value of 170 m^2/g. At higher sulfate content, S_{BET} decreased, very likely due to restricted access to the porosity by pore blockage. [19]

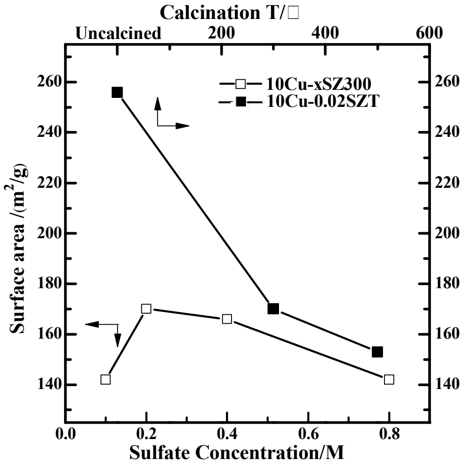


Fig. 1 Specific surface areas of the prepared catalysts.

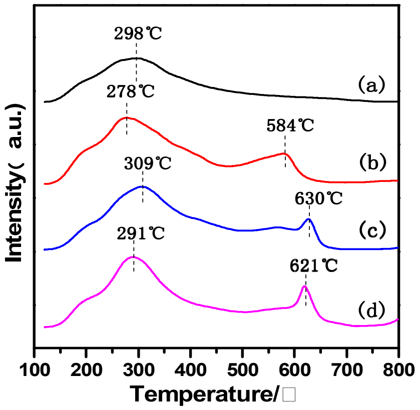


Fig. 2 NH$_3$-TPD of: a) 10Cu-Z500, b) 10Cu-0.2SZ0, c)10Cu-0.2SZ300, d)10Cu-0.2SZ500.

The morphologies and structural details of the catalyst were examined using TEM **(Fig. S1)**. HR-TEM images of 10Cu-0.2SZ300 sample clearly showed the copper particles located at the support surface with the crystalline phase of CuO (111) (0.209 nm). In addition, EDS data showed that sulfur appeared along with copper clusters on the samples. The presence of sulfate on the surface was also confirmed by XPS (**Fig. S2**).

XRD patterns of 10Cu-Z500, 10Cu-0.2SZT and 10Cu-xSZ300 samples were measured and recorded in **Fig. S3**. The sample 10Cu-Z500 was observed to be predominantly tetragonal phase in nature, while the sulfated catalysts has transformed from monoclinic phase and tetragonal phase to amorphous. This finding is explained in terms of the presence of SO_4^{2-} ions, which necessitate into higher thermal energy of SO_4^{2-} for the crystallization of ZrO_2. Similar mechanism was also proposed by Scurrell. [20] A decrease in surface area is observed when the calcination process of the sulfated support was introduced, which could contribute to the emerging of CuO peak. The low intensity of the XRD peaks for the catalysts suggested that CuO supported on sulfated zirconia mainly consisted of small crystallites.

As surface acidity plays critical roles on reaction route and product distribution in DMO hydrogenation, [21] NH_3-TPD experiments were performed to measure the acidity of the catalyst samples. TPD profile based on desorption temperature maxima is divided into three regions corresponding to (i) weak (100–200℃), (ii) medium or intermediate (200–450℃), and (iii) strong acid strengths (>450℃). [22] The 10Cu-Z500 catalyst exhibits one peak in the intermediate range (296℃), while for the sulfated catalysts, peaks in the range of strong acid strength emerged **(Fig. 2)**. The total amount of acid sites was about 2.18 mmol/g for 10Cu-0.2SZ500 catalyst higher than that 1.29 mmol/g for 10Cu-Z500 **(Table S1)**. The results showed that the total amount of acid sites increased from 1.35 mmol/g to 2.36 mmol/g then decreased to 2.18 mmol/g corresponding to the uncalcined sulfated supports, calcined at 300℃ and 500℃, respectively.

It's obvious that the calcination temperature of support had great influence upon the catalyst acidity. At a lower calcination temperature the acid site did not completely form. Therefore the desorption temperature of ammonia (~584℃) of the 10Cu-0.2SZ0 catalyst is lower than the 10Cu-0.2SZ300 and 10Cu-0.2SZ500 (both above 620℃) catalysts. However, when the calcination temperature was increased to 500℃, the slightly decreased amount of strong acid site could be due to the inevitable initial decomposition of sulfate groups. In agreement with previous reports, [23] the activation of sulfate species in these samples can be understood according to the following sequence. Firstly, after drying at 100℃, the sulfate groups replace hydroxyl groups to form bidentate chelation or bridging sulfate groups. Secondly, after calcination at a relatively low temperature, these species are inclined to migrate to the surface and create potentially active sites. Thirdly, these surface species start to decompose and evolve as SO_x around high temperature. Based on

Table 1. The catalytic performance of different catalysts[a]

Catalysts	Conversion (%)	Selectivity (%)	
		2-ME	EG
10Cu-Z500	100	9	91
10Cu-0.2SZ	100	56	44
10Cu-0.2SZ500	100	40	60
10Cu-0.1SZ300	100	37	53
10Cu-0.2SZ300	100	68	32
10Cu-0.4SZ300	100	55	45
10Cu-0.8SZ300	100	34	66

[a] Reaction conditions: T = 220 ℃, $LHSV$ = 0.4 h^{-1}, $P(H_2)$ = 3.0 MPa, H_2/DMO=150.

the above discussion, the calcination temperature for sulfated zirconia was determined as 300℃.

The total acid amount of 10Cu-xSZ300 catalysts (when x is greater than 0.2) had no obvious change as shown in **Table S2** and **Fig. S4**, which indicated that the sulfate on the surface of zirconia had reached saturated monolayer dispersion. However, the amount of surface weak and medium acid sites on the 10Cu-0.2SZ300 catalyst reached the maxima compared with other catalysts. It was clear that the sulfate content played a key role in the formation of the amount of acid sites and the distribution of acid strength.

The catalytic activities for the hydrogenation of DMO were investigated under the same reaction condition, as presented in **Table 1**. Generally, hydrogen-transfer reactions occur on acid sites, while hydrogenation reactions are greatly accelerated by the existence of a metal. The conversion of the reaction was found all to be 100% under relatively low LHSV (0.4 h^{-1}) for hydrogenation of DMO as a consequence of better Cu dispersion and the appropriate amount of surface acid, which can be proved by XRD and NH_3-TPD. Remarkably, the yield of 2-ME using the 10Cu-xSZT catalyst was obviously higher than that over 10Cu-Z500. Basically, etherification starts from the protonated hydroxyl groups in the presence of heat or catalysts and is likely sensitive to the surface acidity. [24] Thus the observed notable increase could be due to the presence of induced acidity in the catalyst matrix by treatment with sulfuric acid, which is confirmed by NH_3-TPD results. The catalyst with the sulfated support calcined at 300℃ exhibited highest selectivity to 2-ME. It is also worthy to note that the as-prepared 10Cu-0.2SZ500 catalyst was very stable under the reaction conditions. After 100 hours' lifetime test, no obvious deactivation was observed. It is also interesting to find that the sulfur content or surface acid amount and/or strength is all kept constant as confirmed by XPS and NH_3-TPD. This finding is not strange considering the special stability of the ZrO_2 support and the strong interaction between sulfate and the support.

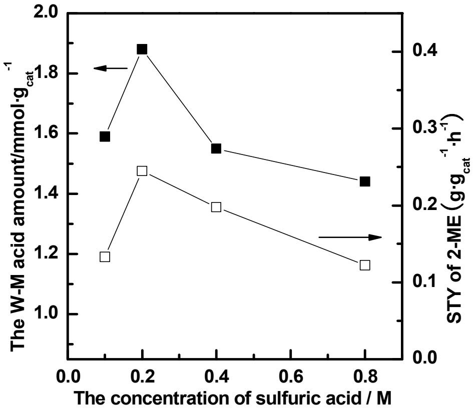


Fig. 3 STY of 2-ME with different weak-medium acid sites on the surface of 10Cu-xSZ300 catalysts

In this study, various treatment conditions of the support influence not only the physicochemical properties but also the surface acidity of the as-prepared catalysts, the former determines the dispersion of copper while the latter affects the etherification process. Although the 10Cu-0.2SZ exhibits the smallest surface acid amount, the small copper particle and the higher S_{BET} value make it be a high-efficiency catalyst. Taken the discussion into consideration, the relatively poor catalytic performance of 10Cu-0.2SZ500 seems much more acceptable. It is interesting to find that the surface weak-medium acid amounts of 10Cu-xSZ300 catalysts were related to the acidification concentration of the support, which was well consistent with the selectivity to 2-ME, as can be seen in **Fig. 3**. These results indicate that the surface weak-medium acid amount has a significant effect on the yield of 2-ME. Through the simple modulation of the acidity on the catalysts, a maximum yield of 2-ME (68%) was obtained. Nevertheless, study to further enhance the product yield needs to proceed.

Conclusions

In summary, the findings in this study show that with the introduction of acidification process, the 10Cu-0.2SZ500 derived catalyst exhibits remarkable enhancement in its catalytic performance for the hydrogenation of DMO to 2-ME. Highly dispersed copper species and appropriate acid sites on the surface mainly contribute the hydrogenation of DMO, while weak-medium surface acid sites of the catalysts promote the generation of 2-ME. The facile synthesis of the low-cost catalysts makes them promising candidates for practical application.

Ackonwledgements

We would like to thank financial support by the Major State Basic Research Development Program (Grant No. 2012CB224804), NSFC (Project 21373054, 21173052), the Natural Science Foundation of Shanghai Science and Technology Committee (08DZ2270500).

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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