Direct synthesis of ethylene glycol by C–C coupling of methanol under visible light

Shunji Xie,[a] Zebin Shen,[a] Jiao Deng,[b] Pu Guo,[a] Qinghong Zhang,[a] Haikun Zhang,[a] Chao Ma,[c] Zheng Jiang,[d] Jun Cheng,[a] Dehui Deng,[b] Ye Wang[a]*

[a]*State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.*

[b]*State Key Laboratory of Catalysis, Collaborative Innovation Center of Chemistry for Energy Materials, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.*

[c]*Center for High Resolution Electron Microscopy, College of Materials Science and Engineering, Hunan University, Changsha 410082, China.*

[d]*Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201204, China.*

**Corresponding author: 0592-2183047, shunji_xie@xmu.edu.cn; wangye@xmu.edu.cn*

Abstract: Here we report a new route for the direct synthesis of ethylene glycol from methanol by C-C coupling. We found that the dehydrogenative coupling of methanol into ethylene glycol could occur under visible light irradiation using MoS_2 nanofoam-modified CdS nanorod catalyst. Ethylene glycol was formed with 90% selectivity together with hydrogen. Mechanistic studies reveal a unique activation of C−H bond instead of O−H bond in methanol by photoexcited holes on CdS via a concerted proton-electron transfer mechanism, forming hydroxylmethyl radical ($\bullet CH_2OH$) that can readily desorb from catalyst surfaces for subsequent coupling.

Keywords: C−H activation, Methanol, C–C coupling, Ethylene glycol.

1. Introduction

Methanol can be derived from a variety of carbon resources, such as natural gas or shale gas, coal, biomass and carbon dioxide, and is an abundant and renewable one-carbon (C_1) building block.[1] Several processes such as methanol-to-olefins (MTO) and methanol-to-gasoline (MTG) have been developed for the C-C coupling of methanol into chemicals, but these processes usually show limited selectivity to a specific product.[2] Traditionally, the conversion of methanol involves the activation of its O−H or C−O bond. The system that can selectively activate the unreactive C–H bond of methanol with hydroxyl group intact and form C–C bond is rare.[3,4] Here, we present the first visible-light-driven dehydrogenative coupling of methanol into ethylene glycol (EG) (Eq. 1).

$$2CH_3OH \rightarrow HOCH_2CH_2OH + H_2 \qquad (1)$$

2. Experimental

Photocatalytic reactions were carried out in a sealed quartz reactor. Reaction conditions: solution, 76 wt% CH_3OH + 24 wt% H_2O, 5.0 cm^3; atmosphere, N_2; light source, 300 W Xe lamp; UV-Vis light, λ = 320-780 nm; visible light, λ = 420-780 nm. Selectivity was calculated on a molar carbon basis.

3. Results and discussion

Eq. 1 cannot proceed via conventional catalysis because of the thermodynamic limitation. Photocatalysis is a promising strategy for C-C coupling reactions, but the efficient visible-light-responsive catalyst for C-C coupling of CH_3OH has not been reported so far.[3,4] We investigated many typical semiconductor photocatalysts for the conversion of CH_3OH. However, over most semiconductors examined, instead of EG, HCHO was formed as a major carbon-based product (Table 1), suggesting that the O−H bond in CH_3OH is easier to be activated. We discovered that a few metal sulfides such as ZnS and CdS could catalyze the formation of EG, and CdS showed better selectivity under visible-light irradiation. Then, we investigated the effect of various co-catalysts. We found that the loading of MoS_2 nanofoam onto CdS nanorods could remarkably enhance the formation rate of EG. The rates of EG and H_2 formations over MoS_2-foam/CdS were about 24 and 16 times higher than those over CdS alone (Table 1). We performed characterizations and found that MoS_2 nanofoam with abundant edge sites accelerates the photocatalytic activity for EG formation by both providing H_2-evolution active sites and enhancing the transfer of photogenerated electrons and hole (Figure 1). The mechanistic studies reveal that CdS-based photocatalyst is quite unique in the preferential activation of the C−H bond in methanol without affecting the O−H group, forming EG via •CH_2OH radical intermediate. High selectivity (90%) and yield (16%) of EG were obtained by designing a process-intensified reactor with EG separation capability.

Table 1. Catalytic performances of typical semiconductor photocatalysts for the conversion of methanol.

Catalyst	Formation rate (mmol g_{cat}^{-1} h^{-1})						e^- / h^{+*}	Selectivity†(%)		
	EG	HCHO	HCOOH	CO	CO_2	H_2		**EG**	HCHO	HCOOH
				UV-Vis light						
TiO_2	**0**	1.6	0.11	0.16	0.042	2.0	0.87	**0**	84	5.6
ZnO	**0**	3.0	0.038	0.23	0.028	3.1	0.87	**0**	91	1.2
g-C_3N_4	**0**	0.79	0.33	0.11	0	1.5	0.89	**0**	64	27
ZnS	**1.3**	2.2	0.067	0.083	0	3.4	0.88	**54**	43	1.3
				Visible light						
ZnS	**0**	0	0	0	0	0	–	–	–	–
Cu_2O	**0**	0.46	0	0	0	0.42	0.91	**0**	100	0
Bi_2S_3	**0**	0.13	0.017	0.023	0	0.19	0.91	**0**	77	10
CuS	**0**	0.11	0.013	0	0	0.13	1.0	**0**	89	11
CdS	**0.46**	0.38	0	0	0	0.75	0.90	**71**	29	0
MoS_2-foam/CdS	**11**	2.5	0	0	0	12	0.92	**90**	10	0

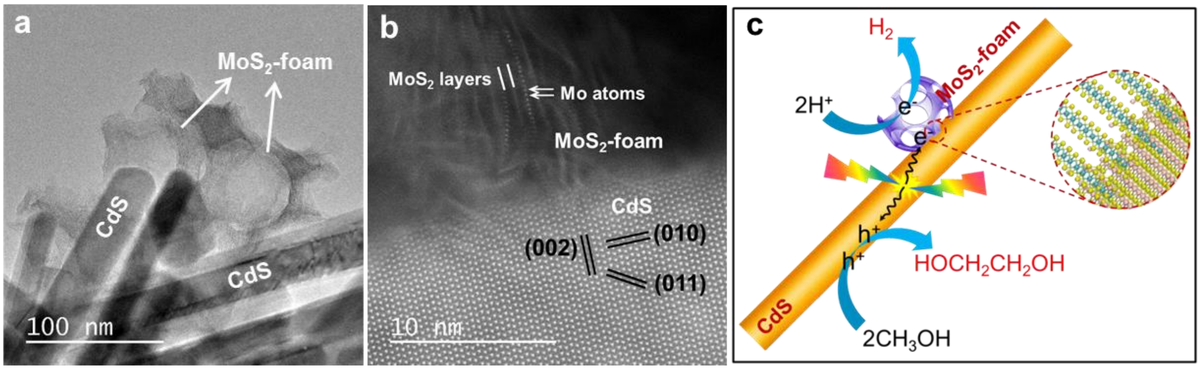

Figure 1. Structural properties of the MoS_2-foam/CdS catalyst. **a.** TEM image. **b.** HRTEM image. **c** Schematic illustration of MoS_2-foam/CdS for photocatalytic synthesis of EG and H_2 from CH_3OH.

4. Conclusions

We have discovered that the CdS-based photocatalytic system is quite unique in the preferential activation of the C−H bond in methanol for subsequent coupling to EG. The loading of MoS_2 significantly improves the formation of EG. The present visible light-driven methanol transformation not only offers an atom-efficient method for the synthesis of EG under mild conditions but also opens up a new avenue for preferential C–H bond activation without affecting other functional groups in the same molecule.

References

1. G. A. Olah, Angew. Chem. Int. Ed. 52 (2013) 104.
2. U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, Ton V. W. Janssens, F. Joensen, S. Bordiga, K. P. Lillerud, Angew. Chem. Int. Ed. 51 (2012) 5810.
3. J. Moran, A. Preetz, R. A. Mesch, M. J. Krische, Nat. Chem. 3 (2011) 287.
4. S. Zhang, F. Zhang, Y. Tu, Chem. Soc. Rev. 40 (2011) 1937.