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COMMUNICATION

Synthesis of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ and Its Catalytic Performance of Completely Converting Methanol to Ethylene

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A new catalyst $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ was synthesized with perfect catalytic performance of converting methanol to ethylene. Under the optimal conditions, both the conversion of methanol and the selectivity of ethylene are almost 100%, which can avoid product separation process.

At the present time, ethylene has been mainly obtained by stream cracking of naphtha, natural gas liquid and other light fractions of petroleum. Conversion of methanol to light olefins (MTO) is a promising alternative process for the synthesis of ethylene. In the exploration of catalysts used for the conversion of MTO, a wide variety of catalysts were tried for this reaction. As early as in 1977, Chang et al in Mobil Company reported that ZSM-5 molecular sieve¹ could be used as catalyst for MTO reaction. But selectivity of ethylene is a very low and some by-products such as hydrocarbon and wax are produced. In 1984, USA Union Carbide Company synthesized SAPO-34,² which is small pore molecular sieve using tetraethylammonium hydroxide (TEAOH) as template. SAPO-34 consists of four elements Si, Al, P and O and their ratio can change in a certain range. Using SAPO-34 molecular sieve as the catalyst for the MTO reaction, methanol conversion can reach to 100% and $\text{C}_2\sim\text{C}_3$ selectivity is about 80%. What's more, Ni-SAPO-34 had improved ethylene selectivity³ to 88%.

However, SAPO-34 molecular sieve catalyst has its inherent defects. Firstly, rapid carbon deposition makes the reaction cycle

very short and the SAPO-34 catalyst requires frequent regeneration. Therefore, catalyst single-pass lifetime is normally less than 13h according to reported literature.⁴ Secondly, the usage of expensive template greatly increases catalyst manufacturing cost. Furthermore, ethylene selectivity of 50% and propylene selectivity of 30% can not meet the requirement of industrial production.

In this paper, an original catalyst of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ was synthesized and the catalyst was found to show perfect catalytic activity and longer single-pass lifetime for MTO reaction. The preparation process of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ is much simpler than that of SAPO-34.⁵ The $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst can afford the optimal catalytic activity at a very low temperature range of $250^\circ\text{C}\sim 350^\circ\text{C}$, whilst the optimal temperature for MTO reaction using other catalysts normally in the range of $400^\circ\text{C}\sim 600^\circ\text{C}$. Under the optimal conditions, both the conversion of methanol and the selectivity of ethylene are 100%, which can effectively avoid the product separation and purification process.

7.5g (2.205 mmol) $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was dissolved in 200mL deionized water. The $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution was heated up to 80°C and then 0.476g (2.10 mmol) CoCO_3 was added very slowly to the $\text{H}_3\text{PW}_{12}\text{O}_{40}$ solution. The reaction solution was filtrated after stirring for 3h. Then the filter liquor was concentrated and crystals precipitated out upon evaporating. The crystals were dried at 100°C , ground with agate mortar and then sifted with 200 mesh sieve to get the final catalyst $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$. Some preparation steps are referred to literature.⁶

Methanol-to-Ethylene (MTE) reaction was carried out in a continuous tubular fixed-bed micro-reactor at $200^\circ\text{C}\sim 350^\circ\text{C}$ and under 0.1 MPa. Helium was purged into tubular reactor to exhaust the air inside before the catalyst bed was heated up to the set temperature. Methanol was fed in by using helium as a carrier gas, which was saturated by flowing it through a methanol saturator placed in a thermostatic bath. The helium flow rate and methanol container temperature were chosen to give a methanol WHSV of 1.5 h^{-1} . The products of the reaction were identified by GCMS-QP2010 Plus equipped with a capillary column of Rxi-5ms and were real-time detected by GC-7890F equipped with a flame ionization

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† Electronic Supplementary Information (ESI) available: More details of characterization processes, SEM, XRD, TG-DTA, EDS, GC-MS. See DOI: 10.1039/c000000x/

detector (FID) through a six-way valve to connect with the reactor. The used catalyst was regenerated by heating at 350°C for 2 h in fixed-bed reactor with flowing dried air.

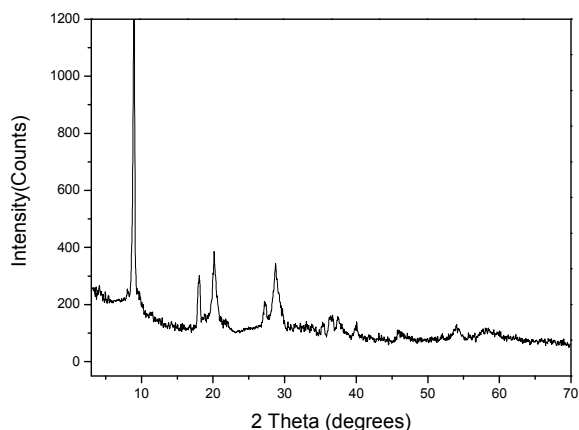


Fig.1 X-ray Diffraction (XRD) patterns of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$

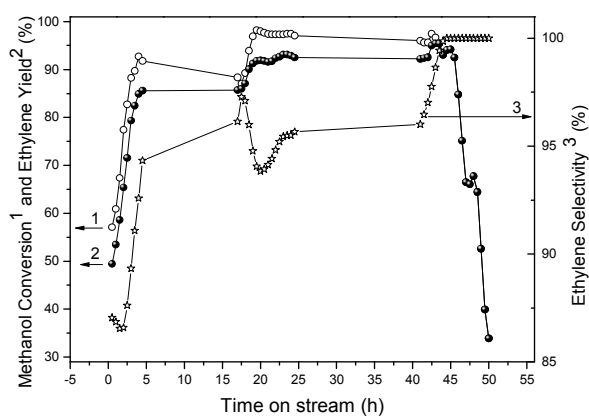


Fig.2 Catalytic performance of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ as a function of time on stream (reaction temperature 35 °C, reaction pressure 0.1MPa, methanol WHSV is 1.5h^{-1} , carrier gas He is 60mL/min)

Fig. 1 shows the XRD patterns of synthesized $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$. The peaks ($2\theta=8.925^\circ$, 28.732°) of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ can be indexed to a well defined Keggin structure of heteropolyanions. **Table 1** shows the effects of reaction temperature on the catalytic performances of Methanol-To-Ethylene reaction over $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst. With increasing reaction temperature, methanol conversion continuously increases and achieves a complete transformation at temperature of 300°C. At lower temperature of 200°C, the main product is dimethyl ether and ethylene is hardly produced. On the contrary, at higher temperature of 300°C, the main product is ethylene and dimethyl ether is hardly yielded. It is obvious that the yield of ethylene dramatically increases and the yield of dimethyl ether rapidly decreases with increasing reaction temperature from 200°C to 300°C. After regeneration, the used catalyst also exhibits nearly 100%

methanol conversion and 85.7% ethylene selectivity with 34 h single-pass longevity in second run.

Table 1 Catalytic performance of different temperatures on Methanol-To-Ethylene reaction^a

Catalyst	Reaction Temperature/°C	Methanol Conversion/%	Product I (CH ₃ OCH ₃) Selectivity/%	Product II (C ₂ H ₄) Selectivity/%
Fresh catalyst	200	60.3%	97.3%	2.70%
	240	84.6%	33.7%	66.3%
	250	92.1%	26.8%	73.2%
	300	100%	2.90%	97.1%
	350	97.3%	1.6%	95.6%
Regenerated catalyst	350	98.5%	14.3%	85.7%

^a catalyst is $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$, reaction pressure 0.1MPa, methanol WHSV is 1.5h^{-1} , carrier gas He is 60 mL/min, methanol conversion and products selectivity were the average data within 12 h

Fig. 2 is the catalytic performance of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ versus reaction time on stream at 350°C. At the beginning stage of reaction, catalyst activity rapidly increases in terms of increased methanol conversion and ethylene selectivity. Thereafter, the catalytic activity almost levels off with a methanol conversion of nearly 100% during a long period. Meanwhile, ethylene selectivity maintains a very high value of about 95% with a slight oscillation. At the end stage of reaction, catalyst starts to deactivate. It is evidenced that the catalytic activity for ethylene formation decreases gradually with dramatically decreasing by-products. During this period, ethylene selectivity is almost 100% with no observation of by-products. Nevertheless, ethylene yield decreases rapidly due to methanol conversion decreases. Consequently, ethylene yield (methanol conversion × ethylene selectivity) keeps higher than 90% for a long period of 27h.

According to literature⁷, ethylene yield was generally less than 60% and single-pass lifetime was normally less than 13h. For example, there was a best record for the same reaction that ethylene yield could reach to 88% with single-pass lifetime of 12h. In this connection, the synthesized catalyst $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ exhibits superior catalytic activity compared to reported catalysts.

Presumably, this is due to that the “Pseudo-Liquid Phase” behavior of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst shows perfect catalytic performance. The “pseudo-liquid phase” behavior is a specific character of polyoxometalate. Alcohols and other polar molecules are very easy to get into the bulk phase of polyoxometalate because heteropoly-anions in the bulk phase of polyoxometalate have a certain gap between them. In bulk phase, the reaction is carried out just like in liquid phase because of reactant molecular diffusion and anionic rearrangement. There are three advantages when

catalytic reaction is carried out in catalyst bulk phase (pseudo-liquid phase). Firstly, active centers in bulk phase and on the surface of catalyst both play catalytic roles. Secondly, the reactant molecules or reaction intermediates in pseudo-liquid phase show coordination state. Thirdly, reaction often has unique selectivity owing to special “pseudo-liquid phase” reaction environment. For $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst, methanol is easy to enter its bulk phase and catalyzed by active centers of bulk phase and surface. Moreover, the special catalytic environment leads to extremely high selectivity of ethylene.

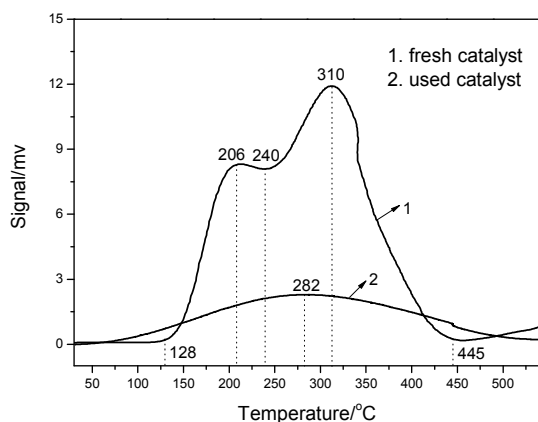


Fig.3 TPD- NH_3 profile of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$

In order to investigate the acid nature of catalyst, the NH_3 adsorption on $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst is shown in **Fig. 3**. Two peaks of NH_3 desorption are observed in the TPD- NH_3 profiles for fresh $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst. One peak appears at relatively lower temperature range (128-240°C) and another at relatively higher temperature range (240-445°C). However, there is only a very weak and broad peak for used catalyst, suggesting that the amount of acid sites drop to a very low level after catalyst deactivation. Bronsted acid sites generally play the major role because H_2O is needed to be introduced during the reaction. Prior to using $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst, it was completely dried at 100°C. Moreover, methanol ionization was also difficult in the reaction process. Therefore, $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ does not have hydron and it belongs to Lewis acid with relatively stronger acid sites.

Fig.4 shows thermal weight loss of used catalyst in N_2 and air, respectively. Under the N_2 atmosphere, total weight loss is less than 3%. In air atmosphere, there is about 11% total weight loss. The catalyst decreases rapidly at temperatures higher than 400°C, because carbon deposition on the catalyst surface is rapidly combusted. There is about 10% carbon deposition on the catalyst's surface.

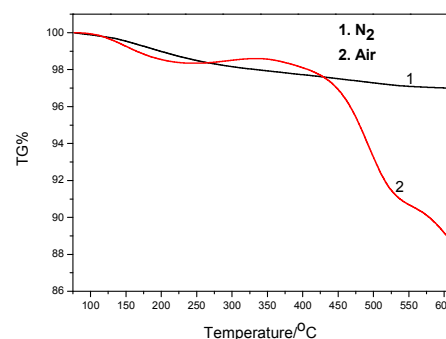


Fig. 4 Thermogravimetric analysis (TG) of used $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst

In summary, a novel catalyst of $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ that can be readily synthesized by crystallization method is firstly reported. The synthesized catalyst shows extremely high catalytic activity for the transform reaction of methanol to ethylene at a relatively lower temperature compared with literature. Under the optimal conditions, a complete transformation from methanol to ethylene can be achieved with almost no by-product formation. Compared to the disclosed catalysts for the reaction of methanol to ethylene, the $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst shows attractively much higher ethylene selectivity and catalyst lifetime. Owing to these advantages, the synthesized $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ catalyst shows potentially industrial application for the transformation reaction of methanol to ethylene.

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Notes and references

- 1 C. D. Chang and A. J. Silvestri, *J. Catal.*, 1977, 47, 249.
- 2 B. M. Lok, C. A. Messina, R. L. Patton, R. T. Gajek, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1984, 106, 6092
- 3 I. Tomoyuki and K. Misook, *Appl. Catal.*, A, 1997, 164, 211
- 4 (a) W. G. Song, H. Fu and J. F. Haw, *J. Am. Chem. Soc.*, 2001, 123, 4749; (b) Q. M. Sun, N. Wang, D. Y. Xi, M. Yang and J. H. Yu, *Chem. Commun.*, 2014, 50, 6502;
- 5 (a) X. S. Han, C. D. Williams, D. F. Lee and C. I. Rounda, *Chem. Commun.*, 2002, 166; (b) L. X. Zhang, J. F. Yao, C. F. Zeng and N. P. Xu, *Chem. Commun.*, 2003, 2232
- 6 (a) Ahmed Aouissi, Allen W. Apblett, Zeid A. AL-Othman, Amro AL-Amro, *Transition Met Chem*, 2010, 35, 927 (b) Ahmed Aouissi, Salem S. Al-Deyab, Ahmad Al-Owais, Amro AL-Amro, *Int. J. Mol. Sci.*, 2010, 11, 2770 (c) Ahmed Aouissi, Zeid Abdullah Al-Othman, Amro AL-Amro, *Int. J. Mol. Sci.*, 2010, 11, 1343.
- 7 (a) X. C. Wu, M. G. Abraha and R. G. Anthony, *Appl. Catal.*, A, 2004, 260, 63; (b) I. Svetlana, L. Charline, V. Estelle, P. H. Cuong, L. Benoit, *J. Catal.*, 2009, 265, 1; (c) G. J. Yang, Y. X. Wei, S. T. Xu, J. R. Chen, J. Z. Li, Z. M. Liu, J. H. Yu and R. R. Xu, *J. Phys. Chem. C*, 2013, 117, 8214