

Accepted Manuscript

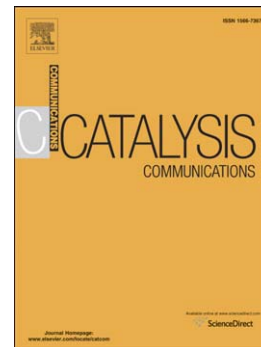
An effective and stable Ni₂P/TiO₂ catalyst for the hydrogenation of dimethyl oxalate to methyl glycolate

Hongmei Chen, Jingjing Tan, Yulei Zhu, Yongwang Li

PII: S1566-7367(15)30105-9
DOI: doi: [10.1016/j.catcom.2015.10.010](https://doi.org/10.1016/j.catcom.2015.10.010)
Reference: CATCOM 4468

To appear in: *Catalysis Communications*

Received date: 7 August 2015
Revised date: 2 October 2015
Accepted date: 5 October 2015



Please cite this article as: Hongmei Chen, Jingjing Tan, Yulei Zhu, Yongwang Li, An effective and stable Ni₂P/TiO₂ catalyst for the hydrogenation of dimethyl oxalate to methyl glycolate, *Catalysis Communications* (2015), doi: [10.1016/j.catcom.2015.10.010](https://doi.org/10.1016/j.catcom.2015.10.010)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

**An effective and stable Ni₂P/TiO₂ catalyst for the
hydrogenation of dimethyl oxalate to methyl glycolate**

Hongmei Chen^a, Jingjing Tan^{b,c}, Yulei Zhu^{a,c*}, Yongwang Li^{a,c}

^a *Synfuels China Co. Ltd., Beijing, 030006, PR China.*

^b *University of Chinese Academy of Sciences, Beijing, 100049, PR China.*

^c *State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China, Fax: +86-351-7560668;
Tel: +86-351-7117097.*

*Corresponding author:

E-mail address: zhuyulei@sxicc.ac.cn

Abstract

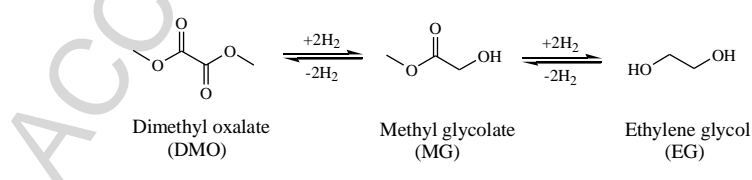
An effective and stable bifunctional Ni₂P/TiO₂ catalyst was proposed for gas-phase hydrogenation of dimethyl oxalate to corresponding alcohols. A 93.0% conversion of DMO with a selectivity of 88.0% to methyl glycolate was observed under 210 °C. Moreover, the catalyst showed an excellent stability which can be performed for 3600 h under the reaction conditions of 230 °C, 3 MPa H₂ and the weight space velocity of 0.1 h⁻¹.

Keywords: Dimethyl oxalate; Methyl glycolate; Hydrogenation; Ni₂P

1. Introduction

Methyl glycolate (MG) is an important fine chemical intermediate, which can be used as a raw material for the synthesis of polyglycolic acid and other organic chemicals [1]. Ethylene glycol (EG) has benign properties and versatile functions, and it has been proposed as a raw material for producing many chemicals, including polyester, dynamite manufacture and antifreeze [2].

Several approaches envisioned for the production of MG have been reported [3,4]. Typically, severe reaction conditions were required to obtain a high yield of MG. For the production of EG, the primary route was the hydration of ethylene or fermentation of sugars [5-7]. However, these routes were limited for the shrinking oil and expensive bioprocesses. In contrast, the hydrogenation of dimethyl oxalate (DMO) to MG or EG is attractive as it is a more efficient and greener catalytic process (as seen Scheme 1) [8].



Scheme 1 The hydrogenation process of the DMO

EG can be achieved efficiently over copper-based catalysts via selective hydrogenation of DMO [9-11]. However, low MG yields (<83%) were obtained over copper-based catalysts [10,12], and the instability of the catalyst limited its further application. To improve the selectivity to MG in hydrogenation of DMO, introducing noble metal to the catalytic system is required, For example, CuAu alloy nanoparticles

and silver-based catalyst were applied for the hydrogenation of DMO to obtain a high yield of MG (>90%) [13-15]. However, the large requirement of noble metal limited its further application in industry. Thus, it is desirable but more challenging to design an efficient non-noble metal catalyst to catalyse the hydrogenation of DMO to MG under mild conditions. As their high catalytic efficiency and stability, the transition metal phosphides have been attracted increasing attentions. Recently, many efforts demonstrated that the transition metal phosphide catalysts showed excellent activities for hydrodesulfurization, hydrodenitrogenation and hydrodeoxygenation owing to its strong noble metallic properties [16-20]. To the best of our knowledge, the transition metal phosphides have scarcely been reported in the hydrogenation of esters to their corresponding alcohols. Based on the above understandings, we hypothesize that it would be a huge breakthrough if the transition metal phosphides could replace the noble metal and be used for the DMO hydrogenation efficiently.

In this work, a bifunctional $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst was proposed. The catalyst exhibited superior catalytic performance for the hydrogenation of DMO to MG. A high selectivity of 88.0% to MG with a 93.0% conversion of DMO was obtained under 210 °C. More importantly, the $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst displayed an excellent stability, which can be successively performed for 3600 h without deactivation under 230 °C.

2. Experimental

The $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst was prepared by temperature-programmedly reducing method. The catalysts were characterized by ICP, XRD, TEM, XPS, BET, H_2 -TPR,

and NH_3 -TPD. The catalytic performance evaluation was performed in a vertical fixed-bed reactor (i.d. 12 mm, length 600 mm) made of a stainless steel tube. Details of catalyst preparation, catalyst characterization, and catalyst evaluation are available in the supporting material.

3 Results and discussion

3.1 Catalyst characterization

The textural properties derived from N_2 adsorption-desorption isotherms of the TiO_2 and $\text{Ni}_2\text{P}/\text{TiO}_2$ catalysts are listed in Table 1. Compared with TiO_2 support, the BET surface area and average pore diameter of $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst decreased while the average pore volume enhanced. To understand the structures of the $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst, XRD, TEM and XPS characterizations were performed. Fig.1A shows the XRD patterns of the TiO_2 support and the as-prepared $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst. For the $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst, the three peaks positioned at $2\theta = 40.8, 44.7, 47.5$ are assigned to the (111), (021) and (210) lattice planes of Ni_2P (JCPDS 65-9706), respectively. Fig.1B (a and c) shows the typical TEM (a) and HRTEM (c) images of the $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst. The HRTEM analysis revealed that the crystal domains within Ni_2P NPs had an interfringe distance of 0.22 nm, which is close to the lattice spacing of the (111) plane in face-centred cubic (fcc) Ni_2P crystal (0.221nm) [21,22]. Fig.1C (a) displays the XPS spectra of $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst. The XPS spectrum for the fresh $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst shows Ni (2p_{3/2}) and P (2p_{3/2}) peaks at 856.5 and 133.3 eV, respectively. The Ni (2p_{3/2}) binding energy is consisted with the range of those reported for Ni (855.6-856.6 eV) in $\text{Ni}(\text{OH})_2$ [23,24] while the P (2p_{3/2}) binding energy is in good

agreement with a value reported for P (133.3 eV) in $\text{Ni}_3(\text{PO}_4)_2$ [24,25]. As a result, the peaks at 856.5 and 133.3 eV are assigned to Ni^{2+} and P^{5+} species in the Ni_2P , respectively. Meanwhile, additional peaks are observed in the Ni (2p_{3/2}) and P (2p_{3/2}) regions at 852.9-853.3 eV and 129.1-129.5 eV, respectively, which are assigned to reduced $\text{Ni}^{\delta+}$ ($0 < \delta < 2$) and $\text{P}^{\delta-}$ ($0 < \delta < 1$) in Ni_2P [26,27]. The XPS for Ni metal and elemental phosphorus are reported to be at (852.5-852.9) and 130.2 eV, respectively [28]. A positive shift of 0.25-0.65 eV to 853.15 eV was observed for Ni (2p_{3/2}) binding energies in Ni_2P catalyst (Fig.1C), while a negative shift of 0.7 eV for the P (2p_{3/2}) signal to 129.5 eV was obtained. These results verified that a few electrons were transferred from Ni to P. These results, combined with the X-ray powder diffraction (XRD) and TEM results further corroborated the formation of Ni_2P NPs. In addition, the accessible surface acidic sites of the catalysts were probed by NH_3 -TPD (Figure S1 in ESI†). Compared with TiO_2 and Ni/TiO_2 , the NH_3 desorption temperature of the $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst shifted toward higher temperature. This result reflected that the addition of P increased the acidity and acid strength of the catalyst, as the formation of P-OH in the surface increasing the Brønsted acid and the formation of electron-deficient state of Ni verified by XPS improving the Lewis acidic [27].

3.2 Catalytic test

Table 2 presents the results of the hydrogenation of DMO over TiO_2 (Entry 1-2), Ni_2P (Entry 3-8), $\text{Ni}_2\text{P}/\text{TiO}_2$ (Entry 9-15) catalysts. As shown in Table 2, the pure support of TiO_2 was inactive towards DMO hydrogenation, while a 38.2% conversion

of DMO was observed with Ni₂P as the catalyst at 200 °C (Entry 3). Therefore, the Ni₂P sites account for the catalytic hydrogenation performance. Additionally, it can be observed that the Ni₂P catalyst exhibited a good selectivity of 90.5% to MG with a conversion of 38.2% under 200 °C. With increasing the temperature from 200 to 280 °C, the conversion of DMO increased from 38.2% to 98.4%, whereas a drastic decrease in the selectivity of MG was found (from 90.5% to 51.0%). The main by-product was MAC, indicating that high temperature was benefit to the dehydration of MG. In comparison, Ni₂P/TiO₂ catalyst displayed higher activity with a high selectivity of 89.7% to MG under 200 °C, implying that the presence of TiO₂ support is important for improving the catalytic efficiency since it can promote the dispersion of Ni₂P active sites. The effect of support on the dispersion of active metal site was also investigated in literature [29-31]. Moreover, the conversion of DMO improved greatly from 84.2% to 100% as the reaction temperature increased from 200 °C to 230 °C while the selectivity of MG decreased slightly. The highest yield of MG was 82% under 210 °C which is close to that of highly active noble-metal catalysts (90%) [14,15]. As a comparison, the silver-based (Ag/SiO₂) catalyst, which was commonly used in the literature [14], was tested for the hydrogenation of DMO to MG under the same conditions, and its catalytic activity was lower than the Ni₂P/TiO₂ catalyst (as seen in Table S1, entries 1-3 in ESI†). Furthermore, the effects of the reaction pressure on the hydrogenation of DMO over the Ni₂P/TiO₂ catalyst (Table 2, entry 12-15) were studied under 230 °C. It can be found that the MG selectivity reduced greatly from 76.0% to 56.3% while the EG selectivity increased gradually from

15.0% to 35.5% with the reaction pressure increasing from 3 to 6 MPa. This result suggested that high pressure was in favour of the hydrogenation for another ester group of MG to EG. Additionally, the generation of dehydration and etherification products (MAC, EtOH, EM, DME) might be resulted from the weak acid sites of the Ni₂P/TiO₂ catalyst (Figure S1 in ESI[†]), which was also reported in the previous work [32,33].

The superior hydrogenation activity of Ni₂P/TiO₂ catalyst possibly resulted from the physicochemical properties of Ni₂P. XPS characterizations verified that the Ni atoms in Ni₂P structure possess a small positive charge, which can promote the adsorption of Ni₂P sites to C=O (the electron donor) in DMO and decrease the interaction between OH (the electron acceptor) in MG and Ni₂P. Additionally, the P atoms in Ni₂P catalyst might have the same effect as the additives in bimetallic catalyst, including Ru-Re or Ru-Sn, which is called ensemble-effect in catalysis [34]. The ensemble-effect of P in Ni₂P can lower the number of exposed Ni atoms and the interaction between the electron acceptor (OH) and Ni₂P sites, consequently, enhancing the selectivity of MG.

3.3 Stability test

Since Ni₂P/TiO₂ catalyst presented super activity and high selectivity in hydrogenation of DMO to MG, the long-term performance over this sample was conducted to explore the stability at 230 °C. The decline in the catalytic activity of the catalyst did not appear after operating for 3600h time-on-stream (Fig.2). Concurrently, the product distribution did not show obvious fluctuation during the

complete test, suggesting that the catalyst was rather robust under these conditions. Furthermore, a comparison of the TEM (Fig.1B (b and d)), BET, ICP (Table 1) and the XPS spectra (Fig.1C (b)) of the spent catalyst with that of the fresh one suggested that no evident change in the structure of the catalyst during the reaction. These results reflect the high stability and reusability of the catalyst. The high stability of the catalyst can be ascribed to the strong interaction between Ni₂P and the support, which was confirmed by the characterization of TPR (Figure S2 in ESI†). Moreover, the small positive charge of Ni and the ensemble-effect of P in Ni₂P can also prevent the sintering of Ni₂P crystallites to enhance the stability at higher temperatures.

4 Conclusions

In summary, a bifunctional Ni₂P/TiO₂ catalyst which was prepared by H₂-temperature programmed reduction was developed for the high selectivity hydrogenation of DMO to MG for the first time. The Ni₂P/TiO₂ catalyst exhibited a substantially high catalytic activity and selectivity under 210 °C. A conversion of 93.0% to DMO and a high selectivity of 88.0% to MG were observed. In addition to the strong noble metallic properties, the super catalytic properties were attributed to the electron-deficient of Ni and the ensemble-effect of P in Ni₂P. Moreover, the catalyst displayed an unexceptionable stability. It was performed successively for 3600 h in the gas-phase hydrogenation of DMO under 230 °C without any evident deactivation. It is thus reasonable demonstrated that the Ni₂P/TiO₂ catalyst is promising and good potential for producing MG from DMO on a large scale.

Acknowledgements

This work was supported by the Major State Basic Research Development Program of China (973 Program) (No.2012CB215305).

Notes and references

- [1] Y. Sun, H. Wang, J. Shen, H. Liu, Z. Liu, *Catal. Commun.* 10 (2009) 678-681.
- [2] J. Lin, X. Zhao, Y. Cui, H. Zhang, D. Liao, *Chem. Commun.* 48 (2012) 1177-1179.
- [3] D. He, W. Huang, J. Liu, Q. Zhu, *J. Mol. Catal. A: Chem.* 145 (1999) 228-335.
- [4] Y. Sun, H. Wang, J. Shen, H. Liu, Z. Liu, *Catal. Commun.* 10 (2009), 678-681.
- [5] C. Wen, A. Yin, Y. Cui, X. Yang, W. Dai, K. Fan, *Appl. Catal. A: Gen.* 458 (2013) 82-89.
- [6] X. San, Y. Zhang, W. Shen, N. Tsubaki, *Energy Fuels* 23 (2009) 2843-2844.
- [7] J. Dexter, P. Fu, *Energy Environ. Sci.* 2 (2009) 857-864.
- [8] Z. He, H. Lin, P. He, Y. Yuan, *J. Catal.* 277 (2011) 54-63.
- [9] L. Chen, P. Guo, M. Qiao, S. Yan, H. Li, W. Shen, H. Xu and K. Fan, *J. Catal.* 257 (2008) 172-180.
- [10] A. Yin, C. Wen, W. Dai, K. Fan, *J. Catal.* 280 (2011) 77-88.
- [11] S. Zhao, H. Yue, Y. Zhao, B. Wang, Y. Geng, J. Lv, S. Wang, J. Gong, X. Ma, *J. Catal.* 297 (2013) 142-150.
- [12] C. Wen, Y. Cui, X. Chen, B. Zong, W. Dai, *Appl. Catal. B: Environ.* 162 (2015) 483-493.

- [13] A. Yin, C. Wen, W. Dai, K. Fan, *J. Mater. Chem.* 21 (2011) 8997-8999.
- [14] A. Yin, X. Guo, W. Dai, K. Fan, *Chem. Commun.* 46 (2010) 4348-4350.
- [15] A. Yin, C. Wen, W. Dai, K. Fan, *Appl. Catal. B: Environ.* 108-109 (2011) 90-99.
- [16] W.R.A.M. Robinson, J.N.M. van Gastel, T.I. Koranyi, S. Eijsbouts, J.A.R. van Veen, V.H.J. de Beer, *J. Catal.* 161 (1996) 539-550.
- [17] S.T. Oyama, *J. Catal.* 216 (2003) 343-352.
- [18] H. Zhao, D. Li, P. Bui, S.T. Oyama, *Appl. Catal. A: Gen.* 391 (2011) 305-310.
- [19] L. Ding, A. Wang, M. Zheng, T. Zhang, *ChemSusChem.* 3 (2010) 818-821.
- [20] S.T. Oyama, *Catal. Today* 15 (1992) 179-200.
- [21] Y. Lu, X. Wang, Y. Mai, J. Xiang, H. Zhang, L. Li, C. Gu, J. Tu, S. Mao, *J. Phys. Chem. C.* 116 (2012) 22217-22225.
- [22] J. Chang, L. Feng, C. Liu, W. Xing, X. Hu, *Angew. Chem. Int. Ed.* 53 (2014) 122-126.
- [23] P. Dufresne, E. Payen, J. Grimblot, J.P. Bonnelle, *J. Phys. Chem.* 85 (1981) 2344-2351.
- [24] S.J. Sawhill, D.C. Phillips, M.E. Bussell, *J. Catal.* 215 (2003) 208-219.
- [25] R. Franke, T. Chasse, P. Streubel, A. Meisel, *J. Electron Spectrosc. Relat. Phenom.* 56 (1991) 381-388.
- [26] S.J. Sawhill, K.A. Layman, D.R. Van Wyk, M.H. Engelhard, C. Wang, M.E. Bussell, *J. Catal.* 231 (2005) 300-313.
- [27] K. Li, R. Wang, J. Chen, *Energy Fuels* 25 (2011) 854-863.
- [28] D. Briggs, M.P. Seah, Wiley, New York, 1983.

- [29] J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu, Y. Li, *ChemCatChem*, 7 (2015) 508-512.
- [30] A. Khodakov, B. Olthof, A. T. Bell, E. Iglesia, *J. Catal.* 181 (1999) 205-216.
- [31] N. Perkas, Z. Zhong, L. Chen, M. Besson, A. Gedanken, *Catal. Lett.* 103 (2005) 9-14.
- [32] P. Guan, Beijing Light Industry Press, 1990, pp. 226-228.
- [33] Y Cui, C Wen, X Chen, W Dai, *RSC Adv.* 4 (2014) 31162-31165.
- [34] J. Li, Y. Chai, B. Liu, Y. Wu, X. Li, Z. Tang, Y. Liu and C. Liu, *Appl. Catal. A: Gen.* 469 (2014) 434-441.

Table 1 The physicochemical properties of TiO₂ and Ni₂P/TiO₂ catalysts

Catalyst	S _{BET} (m ² g ⁻¹)	D _{pore} (nm)	V _{pore} (cm ³ g ⁻¹)	Ni content ^a (mol/g)	P content ^a (mol/g)	Ni:P ^a (mole/mole)
TiO ₂	24.64	0.120	17.41	-	-	-
Ni ₂ P/TiO ₂ -fresh	15.43	0.097	22.65	1.62 × 10 ⁻³	1.0 × 10 ⁻³	1.62
Ni ₂ P/TiO ₂ -spent	16.35	0.106	22.02	1.33 × 10 ⁻³	0.85 × 10 ⁻³	1.56

^a Determined by ICP.

Table 2 Selective hydrogenation of DMO over TiO₂, Ni₂P and Ni₂P/TiO₂ catalysts^a

Entry	T /°C	Conv. /%	Sele./%				
			MG	EG	MAC	EtOH	Others
1	200	0	-	-	-	-	-
2	220	0	-	-	-	-	-
3	200	38.2	90.5	1.9	4.1	3.5	0
4	220	62.8	88.8	2.1	4.5	4.6	0
5	230	81.6	87.8	2.2	4.7	5.3	0
6	240	82.3	83.6	3.9	8.7	3.8	0
7	260	87.3	73.9	6.4	14.6	4.1	1.0
8	280	98.4	51.0	13.3	31.7	1.5	2.5
9	200	84.2	89.7	3.5	6.8	0.0	0
10	210	93.0	88.0	5.3	5.9	0.7	0.1
11	220	97.3	84.0	7.5	5.7	0.9	1.9
12	230	100	76.0	15.0	6.0	1.5	1.5
13 ^b	230	100	71.2	19.8	6.8	1.4	0.8
14 ^c	230	100	64.1	27.0	5.9	1.2	1.8
15 ^d	230	100	56.3	35.5	5.0	1.1	2.1

^aReaction conditions: 0.1h⁻¹, n<sub>(H₂)/n_(DMO)=300, 3 MPa, ^b4 MPa, ^c5 MPa, ^d6MPa.
MAC: Methyl Acetate; Others: EM (2-Methoxyethanol), DME (Dimethoxyethane) et al.</sub>

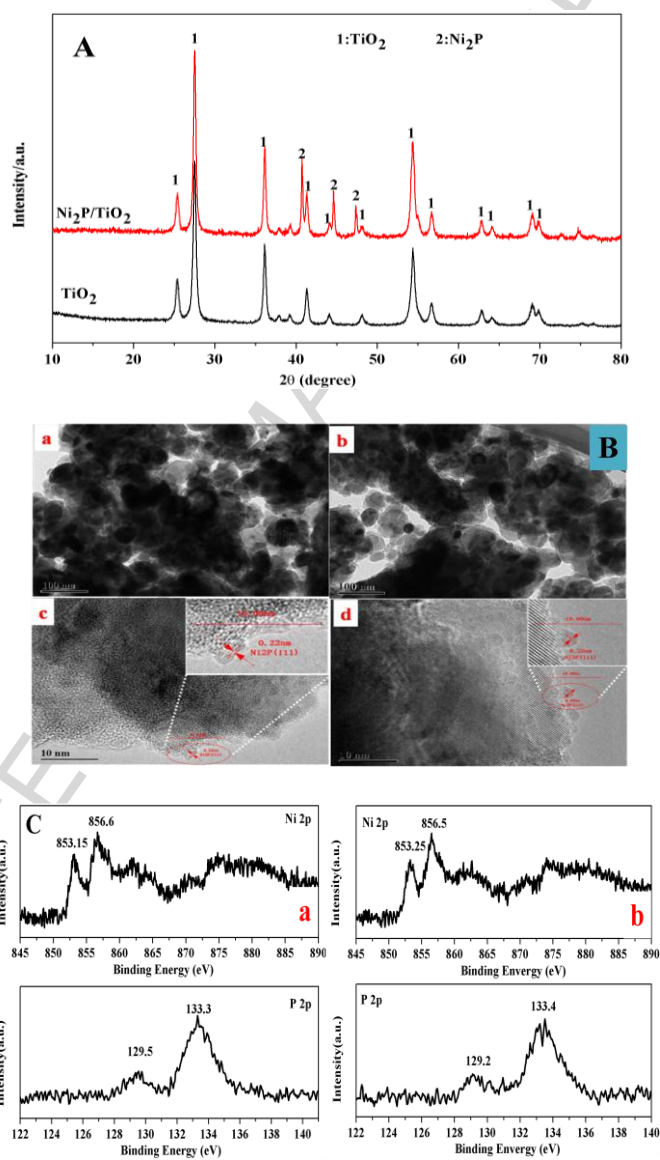


Fig. 1. (A) XRD patterns of as-prepared $\text{Ni}_2\text{P}/\text{TiO}_2$ catalyst and TiO_2 support (B) TEM and HRTEM images of the as-prepared (a and c) and spent (b and d) $\text{Ni}_2\text{P}/\text{TiO}_2$ catalysts (C) XPS spectra in the Ni (2p) and P (2p) regions for the as-prepared (a) and spent (b) $\text{Ni}_2\text{P}/\text{TiO}_2$ catalysts

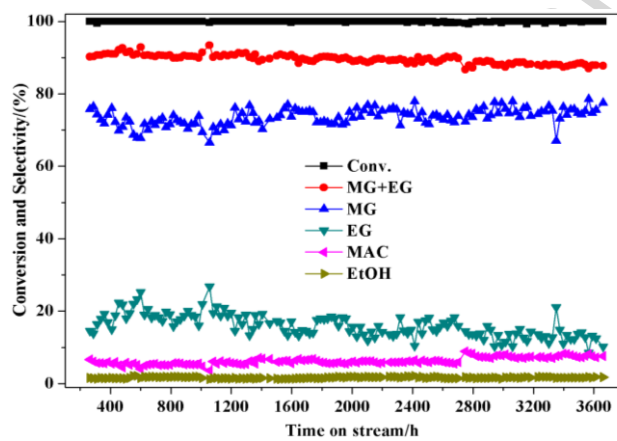
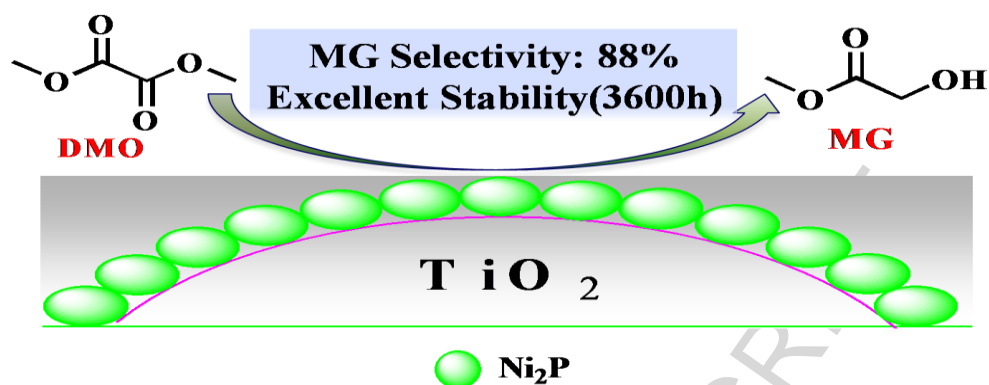


Fig. 2. Stability of Ni₂P/TiO₂ catalyst for DMO hydrogenation
Reaction conditions: 230 °C, 3 MPa, 0.1 h⁻¹, n (H₂):n (DMO)=300



Graphical abstract

An effective and stable Ni₂P/TiO₂ catalyst for the hydrogenation of dimethyl oxalate to methyl glycolate with an excellent stability (3600 h) was proposed.

Highlights

- An effective Ni₂P/TiO₂ catalyst was proposed for dimethyl oxalate hydrogenation.
- A 93.0% conversion of dimethyl oxalate was obtained under 210 °C.
- A selectivity of 88.0% to methyl glycolate was achieved under 210 °C.
- Ni₂P/TiO₂ catalyst showed a superior stability which can be performed for 3600 h.