# Preparation of Bifunctional Au-Pd/TiO$_2$ catalysts and research on methanol liquid phase one-step oxidation to methyl formate

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abstract
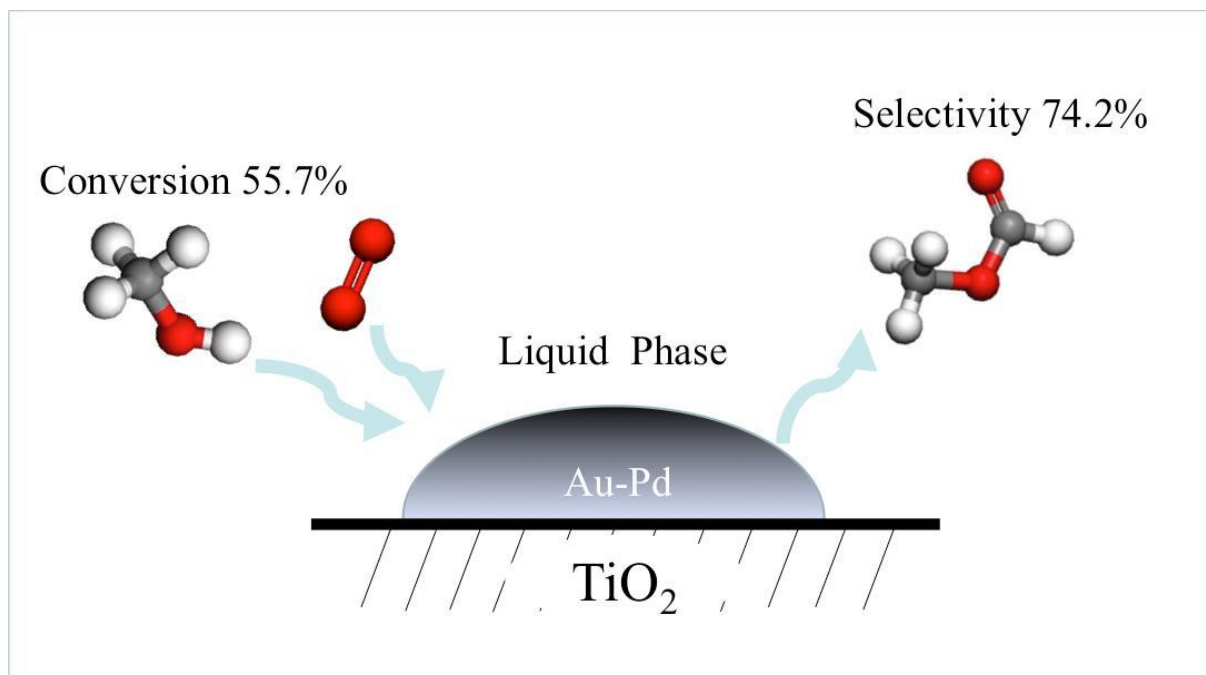
Highlights
1. Bifunctional catalysts supported on titanium were prepared.
2. One step methanol liquid oxidation to formic acid and methyl formate was achieved.
3. Selectivity of products could be tailored through Au and Pd weight percent.

Abstract: A series of Au-Pd/TiO2 bifunctional catalysts with different Au, Pd loading percents have been prepared by sol-immobilization method. The related XRD, HR-TEM and XPS characterizations have been tested for understanding the structure of catalysts. The catalysis activity for methanol liquid phase one-step oxidation to methyl formate have been studied in batch reactor. The results show that the nanoparticles are highly dispersed on TiO2 with 6.4nm mean size. Also, bifunctional catalysts could catalysis transfer methanol to methyl formate with high efficiency. With 1wt%Au-1wt%Pd/TiO2 catalysts, when the molar ratio between active components and methanol is 1/2000, the conversion of methanol is 55.7% for 4h under 100^oC and 25 bar. At the same time, the selectivity of methyl formate is up to 74.2%. The Au-Pd/TiO2 bifunctional catalysts also shows great stability for the reaction with stable conversion and selectivity after 5 cycles.

Keywords： Au-Pd/TiO2 ； Bifunctional catalysts ； Liquid methanol ； One-step catalysis transformation；Methyl formate

1. Introduction

As the simplest alcohol [1], methanol could be the raw material and foundation for C1 chemistry. From methanol, a series of high valuable chemicals could be formed, such as dimethoxymethane, formic acid, methyl formate, dimethyl carbonate and so on [2-4]. The current researches about methanol catalysis transfer to high valuable chemicals mainly focus on methanol gas phase transformation. In this area, the conversion of methanol is low, so plenty of methanol gas need to be recycled during the process with high energy consumption and expenses. Also, the corrosion of equipment could not be ignored [5]. Traditional methanol oxidation to produce methyl formate would add CO in the process and CO is also recycled during the process. At the same time, the selectivity of methyl formate is low [6].

Recent years, some researchers loaded catalysts nanoparticles on the oxides supporters for methanol oxidation reaction in order to improve the conversion and reduce the selectivity of by products [7-8]. R. Wojcieszak [9] used Au/SiO2 as catalysts for methanol oxidation reaction under mild conditions. The conversion of methanol was 88% and the selectivity of methyl formate was 72%. Kaichev[10] prepared a series of V2O5/TiO2 catalysts that could improve the conversion of methanol up to 59.7% without noble metals, but the selectivity of

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methyl formate was 32.8%. Although the conversion of methanol and the selectivity of methyl formate have reached a high level with some catalysts in gas phase reactions, the processing capacity for gas phase is very low. Normally, the volume percentage of methanol is lower than 5% in the reaction system. At the same time, the temperature of the gas phase reaction is not easy to control and the addition products will include poisonous gas such as CO, which will lead to death of catalysts. All of this would increase the costs for reaction system.

Compared with gas phase, the processing capacity in liquid phase is much higher. Also, the temperature for liquid phase is easier to be controlled without addition or production of poisonous gas such as CO. This could increase the stability and recycle ability of catalysts. However, there are few reported literatures about methanol liquid phase oxidation to high valuable chemicals.

Based on the former research about methanol liquid phase oxidation to formic acid [11], and according to the previous reference, it's reported that TiO_2 showed better catalysis activity in alcohol oxidation compared with other supporters [12]. This paper used TiO_2 as supporter to load Au-Pd nanoparticles by sol-immobilization method to prepare Au-Pd/TiO_2 bifunctional catalysts. This catalyst could transfer methanol to methyl formate in liquid phase under mild conditions. Also, it shows great recycle ability with good application prospect.

2. Experimental Section

2.1 Preparation of Catalyst

This paper chose 25 as supporter, $HAuCl_4$ as gold resource and H_2PdCl_4 as palladium resource, and used sol-gel method as reference [13]. The typical preparation process is as following: certain amount of $HAuCl_4$ and $PdCl_2$ was dissolved into deionized water to prepare solutions of the desired gold concentration (1.26×10^{-4} M) and palladium concentration (1.26×10^{-4} M). Then according to the weight percent of Au and Pd, certain volume of $HAuCl_4$ solution was moved to a beaker with addition of 1wt% equivalent PVA solution (PVA/(Au+Pd) (w/w) = 1.2), and then fresh solutions of 0.1M $NaBH_4$ ($NaBH_4$/Au (mol/ mol) = 5) were added dropwise with stirring 30min to acquire purple sol. Following this, a certain volume of Pd solution was added into the purple sol, and the fresh solutions of 0.1M $NaBH_4$

($NaBH_4$/Pd (mol/ mol) = 5) were added dropwise again and then stir for 30min to acquire a

gray sol. An equivalent of P25 was added into the mixture before adjusting pH to 1-2, and then the mixture was stirred vigorously for 1h. The slurry was filtered, and the resulting solid was washed thoroughly with water. The catalysts were dried under room temperature overnight to produce AuPd/TiO2.

2.2 Characterization

The X-ray diffraction (XRD) pattern was collected on a D/Max 2500 VB 2+/PC diffractometer (Rigaku, Japan) with Cu −Kα irradiation ($\lambda = 1.5418$ Å, 200 kV, 50 mA) in the range of 2θ value between 10° and 80°. Transmission electron microscopy (TEM) was performed with a ZEISS SUPRA55 transmission electron microscope operated at 200 kV accelerating voltage. Scan electron microscopy was operated by ZEISS scan electron microscope. EDS was operated by Oxford instrument. Gold, and palladium contents in the catalysts were determined by inductively coupled plasma analysis (ICP, JY38S). X-ray photoelectron spectroscopy (XPS) spectra was performed at a ESCALAB250, operated with Monochromated Al Kalph at 150W, scanned at 200eV, acquired at 30eV high definition.

2.3 Catalytic Activity Test

All catalytic activity test experiments were conducted in Parr mini batch reactor autoclaves with a total volume of 100 mL. First, 30 mL of 0.3mol/L methanol solution was transferred to the autoclave with the catalyst according to the molar ratio between methanol and metals from 500 to 2000. Then the desired pressure from 10 to 35bar of technical air was applied in the autoclave. he autoclave was heated under stirring and kept at the reaction temperature for the desired reaction time, then cooled in an ice bath to room temperature. The gas phase was collected by collecting bag and analyzed on a Shimadzu GC-9A gas chromatograph equipped with a Nukol capillary column (15 m × 0.53 mm) by TCD detector. The liquid phase was separated by centrifuge and analyzed on Shimadzu Nexera-HPLC (Alltech OA-10308, 300 mm × 7.8 mm). The results of GC and HPLC were calculated based on carbon balance. The conversion of methanol was calculated according to the molar before and after reaction. The selectivity of methyl formate was calculated based on carbon balance results. For the reusability test, after reaction the mixture was filtered and wash by water. Then the catalysts were dried under room temperature overnight and weight it to calculate the desired volume of methanol soloution.

3. Results and Discussion

3.1 Characterization of Catalyst

Fig.1 is the XRD spectrum of prepared samples. Obviously, characteristic peaks of TiO_2 support can be seen from the figure, when the loading amount were lower than 0.6wt%, the peaks of AuPd nanoparticals are weak probably due to its high dispersion (according to TEM results of Fig.2 and Fig.S1) and the low metal weight percent of catalyst [14]. Besides, the Au nanoparticles might be partly covered under Pd ones, and thus, the diffractions of Au nanoparticles were weak. When the weight percent reach above 0.6wt%, diffraction peaks of 200, 220, 311 of AuPd nanoparticles can be seen from the figure [24]. Moreover, the Au and Pd characteristic peaks are relatively close to the alloy nanoparticles in the XRD spectra with overlap of some diffraction peaks as formation of alloy [15]. This is corresponding with the following TEM and XPS results.
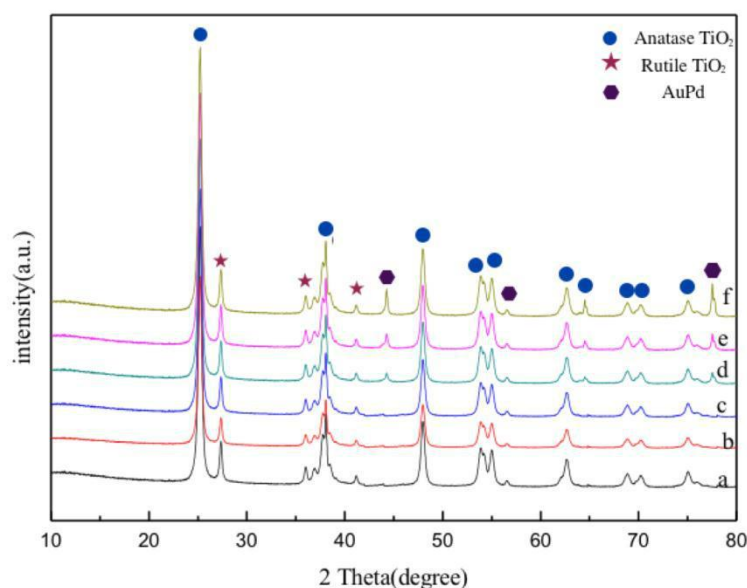

Fig.1 XRD spectrums of Pd1wt%Au/TiO2
（a.TiO2, b-f Pd weight percent:0.2wt%, 0.4wt%, 0.6wt%, 0.8wt%, 1wt%）

According to the mapping results of SEM-EDS, Au loading of catalyst is 0.81wt% and Pd loading is 0.95wt%, which is quite close to theoretical loading. The addition of Pd nanoparticles can affect Au nanoparticles through forming core-shell structure and alloy, as a result, the tested Au loading percentage is much lower than theoretical number [16]. In order to

confirm the weight percent of Au and Pd, the related ICP had been tested for 1wt%Au1wt%Pd/TiO$_2$ catalyst. The results show that Au and Pd weight loading are 0.87% and 0.94wt%, which are close to the EDS results. Fig.2 is the TEM image of prepared catalyst sample. Simultaneously, it can be observed from Fig.2 and Fig.S1 that the nanoparticles are highly dispersed on the support surface, which is agree with the results in XRD spectrum of low weight percentage, and no obvious agglomeration was observed. The particles were uniformed with a diameter of 6.4nm, according to the count of 200 nanoparticles. Additionally, the nanoparticles immobilize on the support exist with two forms, one with Au-Pd nanoparticles of high dispersion and one with AuPd alloyed nanoparticles. In comparison, the last ones are with larger diameters but higher catalytic activity [17] that has been approved through the following reaction results.
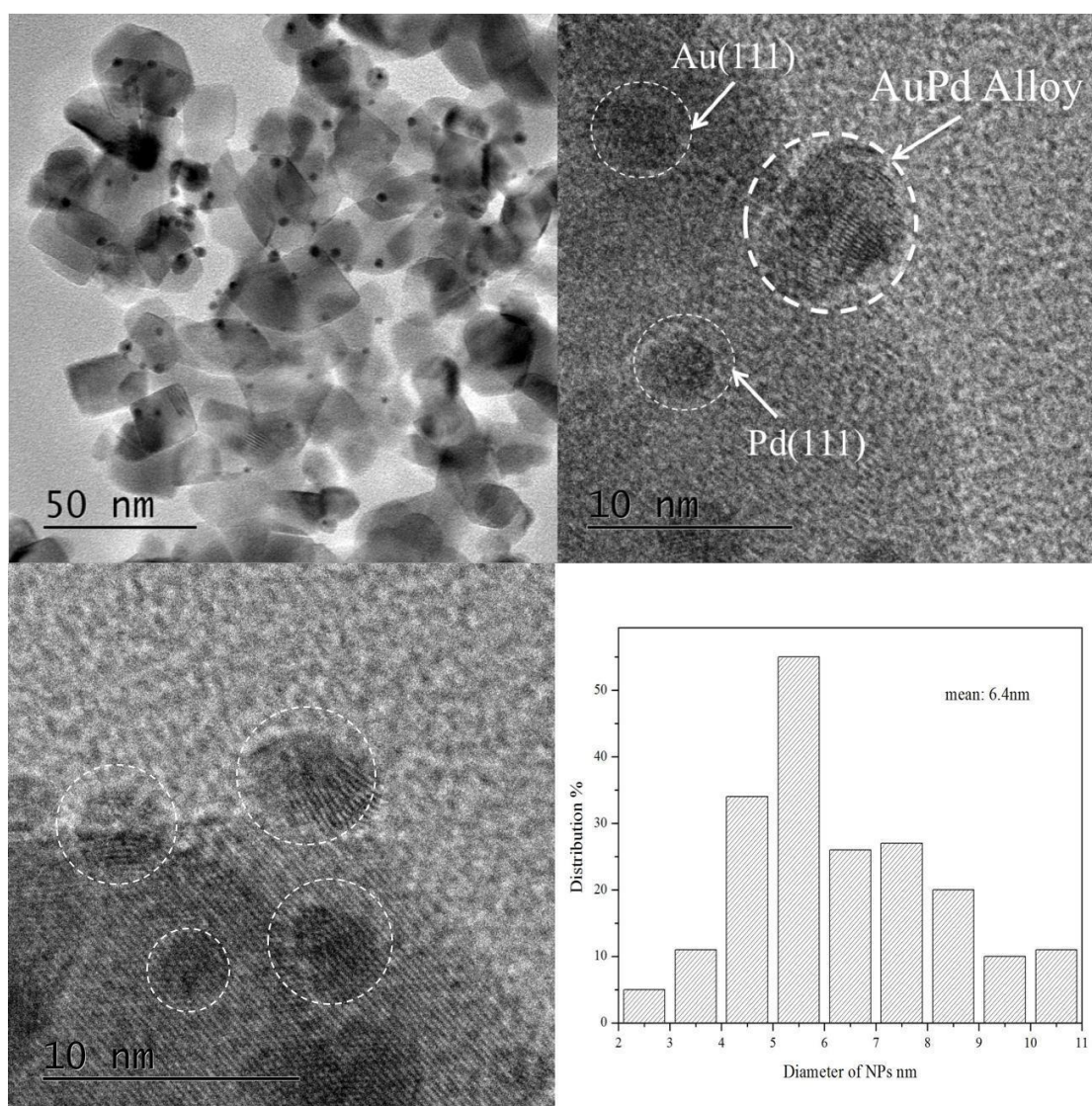
Fig.2 TEM images of 1wt%Pd1wt%Au/TiO$_2$

To further understand AuPd nanoparticles dispersive state on the TiO$_2$ support, the XPS spectrum was performed on the sample. It can be seen from Fig.3 (a), the two peaks of Au of bimetallic catalyst AuPd/TiO$_2$ are shown with binding energy of 83.5eV and 87.3eV assigned to 4f$_{7/2}$ and 4f$_{5/2}$ respectively, the peaks are slightly shifted toward low energy compared to monometallic Au/TiO$_2$[18], which are 84.0eV and 87.7eV. Meanwhile, the study of Pd 3d energy shows that Pd nanoparticles are existed as metallic state, and no Pd oxidation stated was detected [19]. More specifically, the binding energy of Pd 3d$_{5/2}$ and 3d$_{3/2}$ are 335.0 eV and 341.7eV respectively, which indicated peaks shift to low energy compared to monometallic Pd/TiO$_2$[20], which are 335.0eV and 340.3eV. As for AuPd/TiO$_2$, both the Au and Pd binding energy are shifted due to the formation of AuPd alloy with transition of electrons [21].
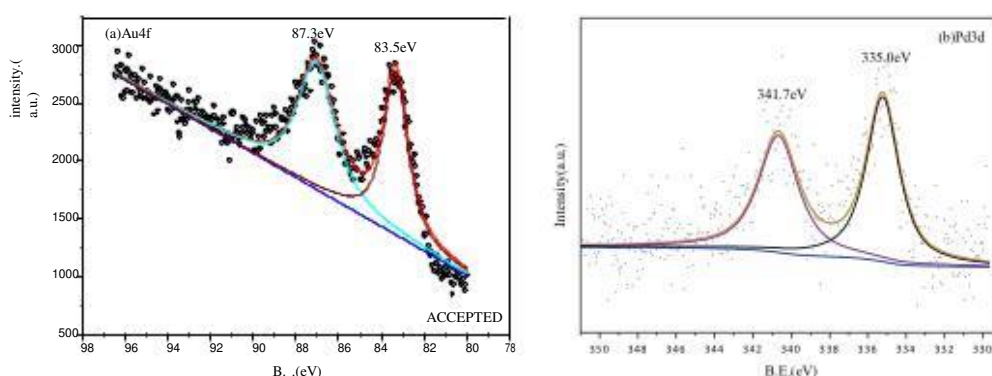

Fig.3 XPS spectra of

Table 1 Data for

	Binding Energy(e.V.)	FWHM(e.V.)	Atomic(%)
Au	86.6	1.09	0.71
Pd	340.5	1.82	0.83

3.2 Catalysis activity for methanol liquid phase oxidation

During the catalysis test, this paper modified the reaction conditions at first and explained the details about the effect for the catalysis activity under various conditions. Through the modification process, the catalyst used was 1wt%Pd1wt%Au/TiO$_2$. Fig.4

exhibits the influence of reaction temperature on catalytic performance. It can be observed from the figure that catalyst perform different catalytic activities along with the changing of temperature. Under low temperature, the methanol conversion is rather low and with temperature increases, methanol conversion rises first and then reaches a platform, with the temperature rises higher, methanol conversion does not increase obviously. As for products, the yields of both formic acid and methyl formate shows clearly increase during 60-100 ^{o}C, when temperature reaches 120 ^{o}C, the yields of both two products doesn`t increase except for methanol conversion, which indicates that selectivity of products decreases. When the temperature reaches 150 ^{o}C, selectivity shows obvious decrease seen from methyl formate decreases with temperature rises. This result shows that though more methanol converted in high temperature, more CO_2 was also formed with reaction proceed [22]. Through studying catalytic performance of different temperature, it can be concluded that this catalyst performs eminent stability under high temperature.
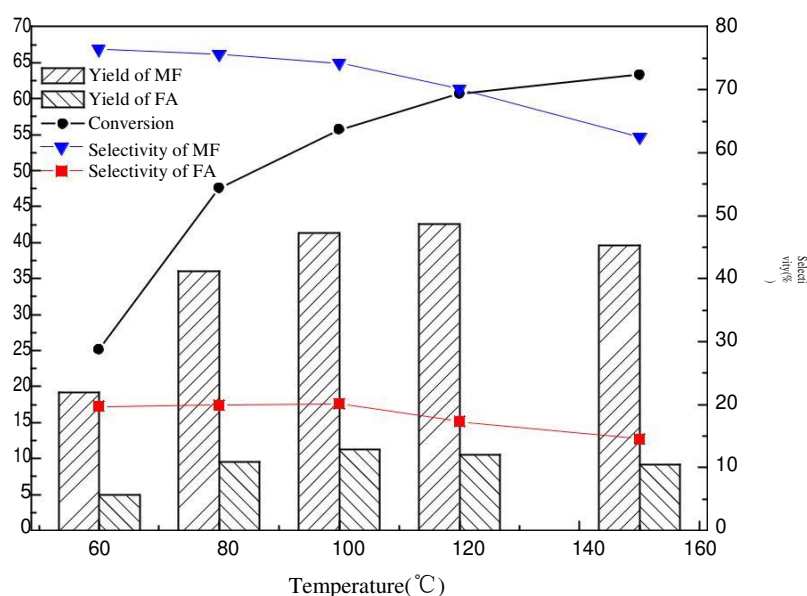

Fig.4 Relationship between reaction temperature and conversion of methanol (reaction conditions: Methanol/PdAu=2000:1 mol/mol, 25bar, 4h)

Fig.5 shows the influence of catalyst amount. With the amount increases, the conversion of methanol is promoted, but when considering catalytic efficiency of single active site, the promotion by increasing catalyst mass does not seem remarkable. Considering from TOF

result, the efficiency of single site is the highest when using the smallest amount of catalyst [23]. While from product perspective, the variety of catalyst amount does not make obvious difference. As for selectivity, however, it decreased with catalyst amount rises. The figure shows that yields of formic acid and methyl formate don't have obvious change with the catalyst mass rises from 1:2000 to 1:500, which shows that when excessive catalyst was added, the active sites were prohibited from reaction and the efficiency was decreased, thus, selectivity and TOF was influenced [24]. More specifically, when the usage of catalysts increases, the conversion grows up. However, from Fig.5, it is shown that the yield of methyl formate and formic acid doesn't change too much, which means the selectivity decreases and more by product produced during the reaction process. Also, through the TOF data, even if the catalyst usage increases to four times from 2000:1(methanol:metals), the TOF decreases. Hence, the increase of conversion is not high enough to match the growing usage, which means some of the active sites don't participate into the reaction. In the following research, the higher molar ration between methanol and metals from 4000:1 to 10000:1 had also been tested and the results showed that there were no obvious increases for both TOF and yield with higher molar ratio. The yield has a plateau after 2000:1. Hence, considering the cost of catalysts and target for the production of methyl formate, 2000:1 is the optical molar ratio.
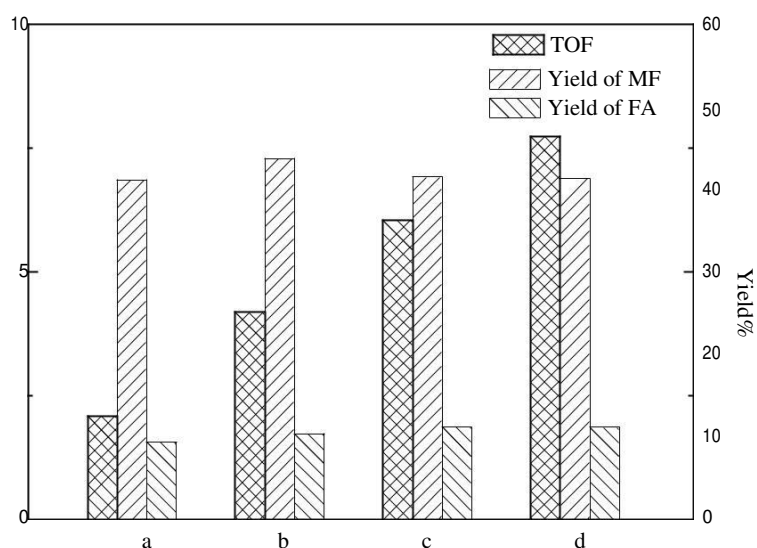

Fig.5 Relationship between mole of catalysts and conversion of methanol (reaction conditions: a-d,Methanol/PdAu=500,1000,1500,2000:1,25bar,100 ^{o}C,4h)

Fig.6 shows the relationship between reaction time and catalytic performance. In the beginning, with reaction time growing, the conversion and yields of both products increase. When the time exceeds 4h, increase rate of conversion slows down, and when the time reaches 6h, the selectivity remains constant, and the reaction nearly stagnates. This may due to the highly dispersed metal nanoparticles transferred to low surface energy and the metals reunited, and catalytic performance decreased [25]. When reaction time was prolonged to 8h, methanol conversion reaches 63.1%, with methyl formate selectivity of 71.8% and formic acid selectivity of 18.6%. Furthermore, the study of reaction time shows that this bimetallic catalyst possesses prominent stability in liquid-phase-oxidation.
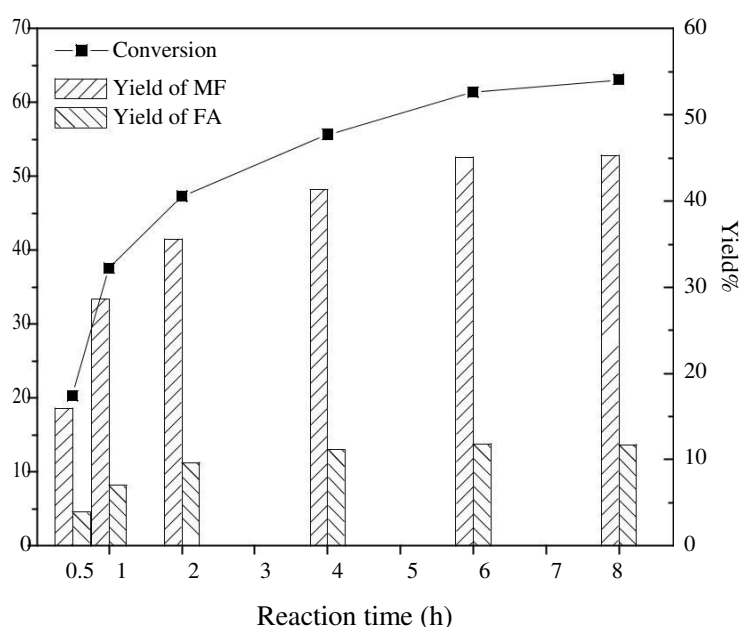

Fig.6 Relationship between reaction time and conversion of methanol
(reaction conditions: Methanol/PdAu=2000:1 mol/mol, 25bar, 100 ^{o}C)

As can be seen from Fig.7, with increase of pressure, methanol conversion increases and then reaches a plateau, simultaneously, the yields of methyl formate and formic acid rise as well. Notably, when considering the selectivity of the two products, the selectivity of methyl formate shows small decrease while selectivity of formic acid keeps stable. More specifically, when the reaction pressure rises from 10bar to 25bar, the conversion increases from 28.1% to 55.7%, the selectivity of methyl formate decrease frome 78.3% to 74.2%, and the selectivity of formic acid maintain around 19%. When the pressure increase from 25bar to 35bar, the

conversion reaches to 56.1% with no obvious change of selectivity. With increasing pressure, the concentration of oxygen would grow. The absorption of oxygen on Au-Pd nanoparticles doesn't reach saturation when the reaction pressure is lower than 25bar. Hence, more oxygen could be decomposed to active oxygen atoms on Au surface [26] when the reaction pressure is growing. At the same time, with boosting dehydrogenation speed on Pd surface, more water produced through combination of hydrogen and oxygen [27], which could improve the reaction efficiency. If the pressure keeps increasing, the decomposition ability of oxygen would reach saturation and the absorption and decomposition of oxygen would reach the balance [28] as to no obvious changes in conversion. At the same time, high oxygen concentration would limit the production of methyl formate, because methyl formate would be oxidized to CO_2 under this kind of reaction conditions [29].
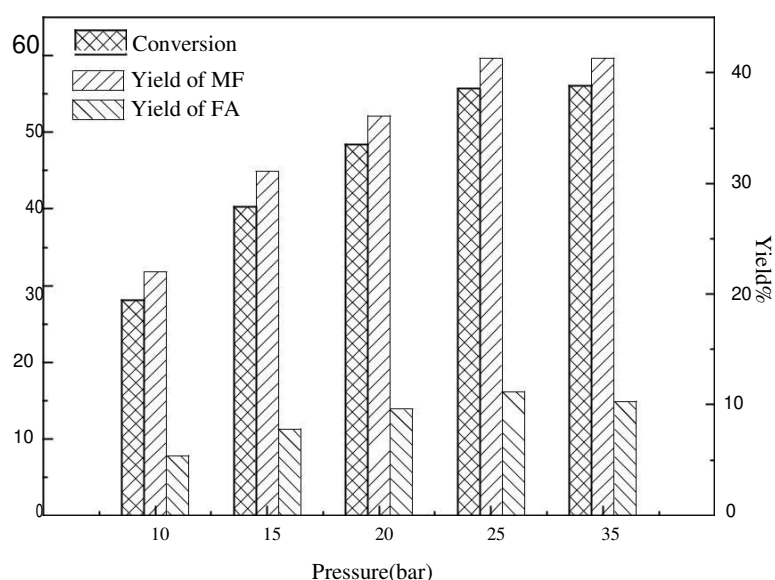

Fig.7 Relationship between reaction pressure and conversion of methanol
(reaction conditions: Methanol/PdAu=2000:1 mol/mol, 100 ^{O}C, 4h)

From Fig.8, the weight percent of Pd have obvious effect for the catalysis activity as to conversion of methanol and selectivity for the products. In details, the conversion of methanol increases from 40% to 55.7%, when the weight percent of Pd grows from 0.2wt% to 1wt%. At the same time, the selectivity of methyl formate increases from 23.5% to 74.2% with decrease of selectivity of formic acid from 69.3% to 20.1%. Corresponding with the above characterization results, the high dispersity Au-Pd nanoparticles would be alloyed with

increasing Pd weigh percent, which is beneficial for the electrons transfer between two metals and this synergy would improve the conversion of methanol and selectivity of methyl formate [30]. In the reaction system, Au nanoparticles are easy to absorb electrons to improve the decomposition speed of oxygen [31] and Pd would donate electrons and transfer them to speed the dehydrogenation step and ester reaction, in order to improve the reaction efficiency [32].
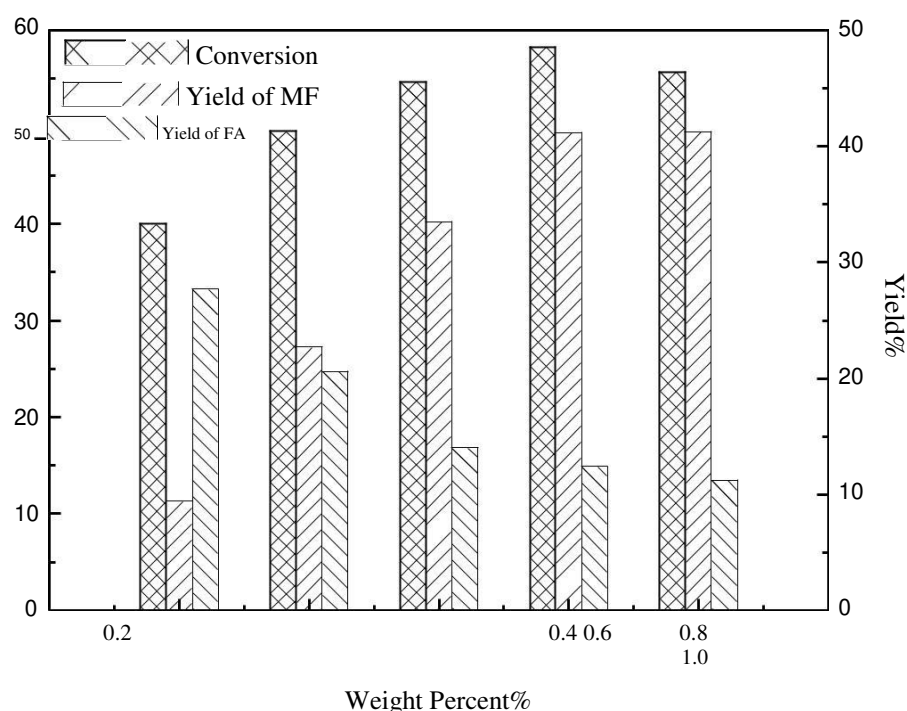

Fig.8 Relationship between Pd loading and conversion of methanol
(reaction conditions: 25bar,100 $^{\circ}$C,4h)

3.3 Reusability of catalysts

In the following research, the reusability of bifunctional catalysts for methanol liquid phase oxidation reaction had also been tested as shown in Fig.9. The results show that catalysts have great stability for the reaction. After 5 cycles, the conversion of methanol and selectivity of methyl formate almost keep the same as the first run. This could be corresponding with the TEM results for used catalysts as shown in Fig.10. From Fig.10, it is clear that the Au-Pd nanoparticles are still remain high dispersity after 5 cycles without agglomeration, which guarantee the catalysis activity.
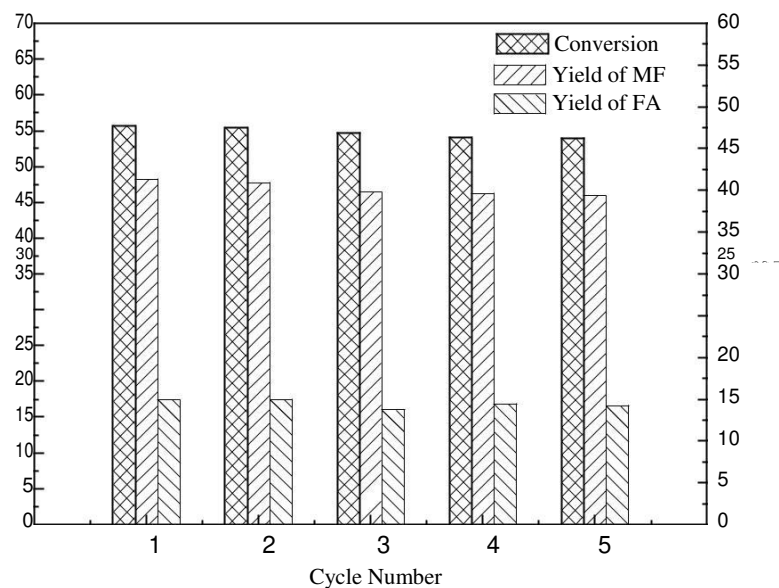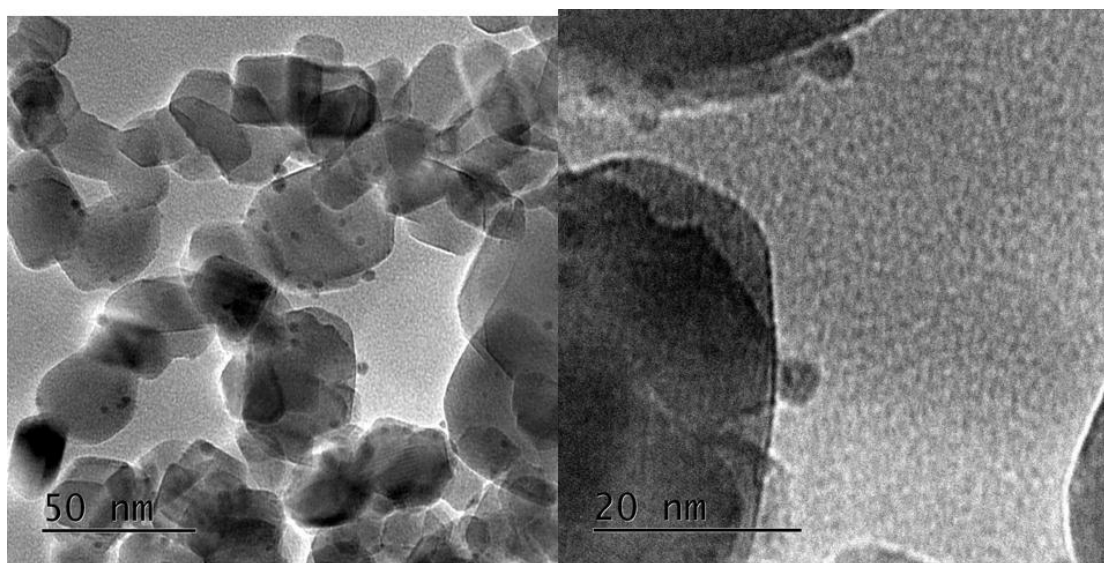
Fig.9 Reuseability of catalysts

Fig.10 TEM images of reused AuPd/TiO$_2$ catalysts

Considering the leaching of nanoparticles, we used cycled reaction solution to catalyze the fresh reaction. The results showed that there is no activity for the cycled solution, which means the active sites are the heterogeneous catalysts not the homogenous catalyst.

3.4 Comparison between mono- and bi-metalltic catalysts

The catalysis activities of methanol liquid phase oxidation reaction for monometallic and bimetallic catalysts have been shown in Fig.11 and Fig.12. As to conversion of methanol, the

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Au and Pd obviously show lower activity compared with Au-Pd catalysts. The life for Au catalysts is shorter as the conversion keeps stable after 2h and the other two catalysts need more time for reaching stable conversion [33]. For the selectivity of products, bimetallic catalysts also show better activity. For the production of formic acid, it is clear that all the catalyst shows selectivity of formic acid. In more details, although Au catalysts don't have the highest conversion of methanol, the yield of formic acid for Au catalysts is the highest with more than 90% selectivity of formic acid. Compared with Pd catalysts and Au-Pd catalysts, Pd catalysts achieved higher yield of formic acid. Through general consideration for the production of formic acid, the selectivity and yield of formic acid decreases from Au catalyst to Au-Pd catalysts.

On the opposite, the trend of selectivity of methyl formate is different. It is clear that Au catalysts have no production for methyl formate during the reaction. As to the Pd catalysts, methyl formate begins to appear in the distribution of products, but the main product is still formic acid. When we used Au-Pd catalysts for methanol liquid oxidation reaction, it shows great activity for the production of methyl formate with higher conversion of methanol and more than 70% of selectivity.
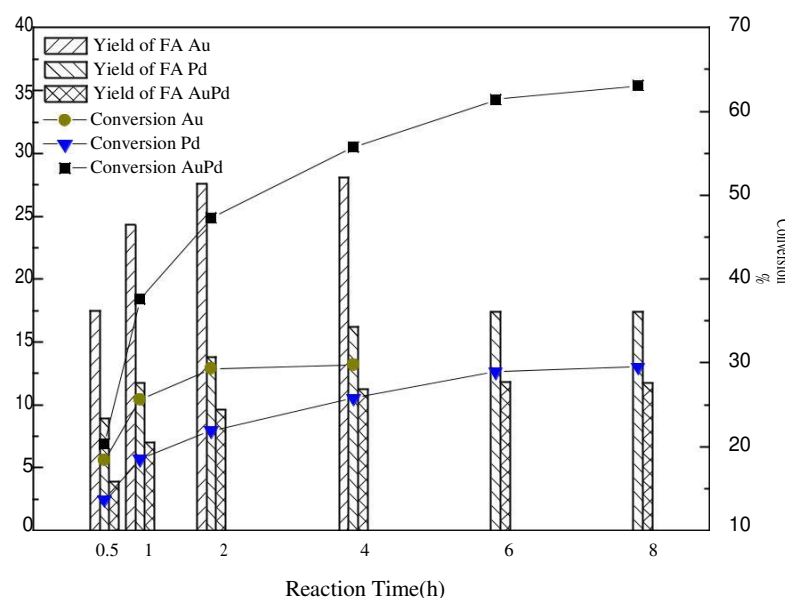

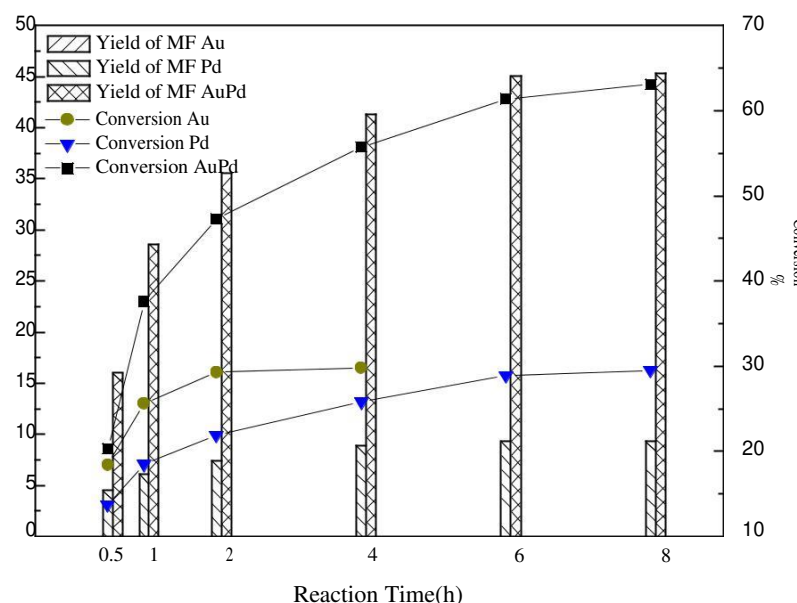Fig.11 Catalysis activity for catalysts in the production of formic acid

Fig.12 Catalysis activity for catalysts in the production of methyl formate

Through the comparison, it can be seen that bimetallic catalysts show higher activity for production of methyl formate because of high dispersity and alloyed status. The previous researchers have already found that Au nanoparticles would absorb electrons that are donated by Pd nanoparticles in Au-Pd catalysts [34], which could improve the conversion and selectivity for alcohols oxidation reactions [35]. In order to confirm if the real key point for high conversion and selectivity is alloy AuPd, we physically mixed 1wt%Au/TiO$_2$ and 1wt%Pd/TiO$_2$ ball mill and used the mixture for the catalysis activity test under optical conditions. The conversion of methanol was 27.3% and the selectivity of methyl formate was only 30.3%, which are much lower than prepared alloy 1wt%Au1wt%Pd/TiO$_2$ activity with 55.7% of conversion and 74.2% of selectivity of methyl formate. Hence, AuPd alloy plays the key role for achieving high conversion and selectivity for liquid methanol oxidation to methyl formate.

4. Conclusion

Compared with monometallic catalysts, bimetallic catalysts could improve the catalysis activity, because of high dispersity of nanoparticles, formation of alloyed metals with

synergies through electrons transfer. This paper prepared bifunctional Au-Pd/TiO$_2$ catalysts through sol-immobilization method and characterized the catalysts. The Au-Pd NPs on the supporter have 6.4nm average particle sizes. Through the modification of reaction conditions, the conversion of methanol is 55.7% under 100°C, 25bar after 4h trough treatment of 2000 equivalent methanol and the selectivity of methyl formate could achieve 74.2%, which is higher than monometallic catalysts. Also the catalysts show great stability for the reactions after 5 cycles. The exploitation of Au-Pd/TiO$_2$ bifunctional catalysts provides a new pathway for synthesis of methyl formate from methanol in liquid phase with potential in industrial application. Also, this provides a meaningful method to achieve multi steps reaction in one-step.

Acknowledgement

References ACCEPTED

[1] F. Studt, I. Sharafutdinov, F. A. Pedersen, et al. 6 (2014), 320-324.
[2] M. B. Çelik, B. Özdalyan, F Alkan. Fuel, 90 (2011), 1591-1598.
[3] H. Zhao, S. Bennici, J. Shen, et al. J. Catal., 272 (2010), 176-189.
[4] H. Yang, L. Dai, D. Xu, et al. Electrochim. Acta, 55 (2010), 8000-8004.
[5]   . Chen, A. Grønvold, K. Moljord, et al. Ind. Eng. Chem. Res., 46 (2007), 4116-4123.
[6] R. Wojcieszak, A. Karelovic, E. M. Gaigneaux, et al. Catal. Sci. Tech., 4 (2014), 3298-3305.
[7] G.   . Whiting, S. A. Kondrat, C. Hammond, et al. ACS Catal., 5 (2014), 637-644.
[8] V. V. Kaichev, G. Y. Popova, Y. A. Chesalov, et al. J. Catal., 311 (2014), 59-70.
[9] C. J. Yang, R. B. Jackson. Energy Policy, 41 (2012), 878-884.
[10] G. A. Olah. Angew. Chem. Int. Ed., 44 (2005), 2636-2639.
[11] D. Shi, J.F. Liu, S.F. Ji, Ind. Eng. Chem. Res., 56 (2017), 11028-11033.
[12] J. Ni, W.J. Yu, L. He, et al. Green Chem., 11(2009), 756-759.
[13] A. Rahim, M. Hasbi, M. M. Forde, et al. Angew. Chem. Int. Ed, 52 (2013), 1280-1284.

[14]   D. I. Enache, J. K. Edwards, P. Landon, et al. Science, 311 (2006), 362-365.

[15]   C. Han, L. Wu, L. Ge, et al. Carbon, 92 (2015), 31-40.

[16]   G. Fu, Z. Liu, Y. Chen, et al. Nano. Res., 7 (2014), 1205-1214.

[17]   P. Landon, P. J. Collier, A. J. Papworth, et al. Chem. Commun., 18 (2002), 2058-2059.

[18]   L. Guczi, A. Beck, A. Horvath, et al. J. Mol. Catal. A: Chem., 204 (2003), 545-552.

[19]   S. P. Chenakin, G. Melaet, R. Szukiewicz, et al. J. Catal., 312 (2014), 1-11.

[20]   A. Cybula, J. B. Priebe, M. M. Pohl, et al. Appl. Catal. B: Environ., 152 (2014), 202-211.

[21]   T. Li, H. Zhou, J. Huang, et al. Colloids. Surf. A: Physicochem. Eng. Asp, 463 (2014), 55-62.

[20]   C. Han, L. Wu, L. Ge, et al. Carbon, 92 (2015), 31-40.

[21]   R. Wang, Z. Wu, C. Chen, et al. Chem. Commun., 49 (2013), 8250-8252.

[22]   N. Dimitratos, F. Porta, L. Prati. Appl. Catal. A: Gen.., 291 (2005), 210-214.

[23]   Y. Hou, Y. Wang, F. He, et al. Appl. Catal. A: Gen., 259 (2004), 35-40.

[24]   Y. Sun, Z. Zhang, C. P. Wong. J. Colloid. Interface Sci., 292 (2005), 436-444.

[25]   L. Kesavan, R. Tiruvalam, M. H. Ab Rahim, et al. Science, 331 (2011), 195-199.

[26]   N. Agarwal, S. J. Freakley, R. U. McVicker, et al. Science, 358 (2017), 223-227.

[27]   J. Bao, I. Shalish, Z. Su, et al. Nanoscale Res. Lett., 6 (2011), 404.

[28]   W. Hou, N. A. Dehm. J. Catal., 253 (2008), 22-27.

[29]   F. Gao, D. W. Goodman. Chem. Soc. Rev., 41 (2012), 8009-8020.

[30]   M. Sankar, E. Nowicka, R. Tiruvalam, et al. Chem. Eur. J., 17 (2011), 6524-6532.

[31]   D. Widmann, A. Krautsieder, P. Walter, et al. ACS Catal., 6 (2016), 5005-5011.

[32]   L. T. Murciano, . Villager, D. Chadwick. ChemCatChem., 7 (2015), 925-927.

[33]   P. Stefanov, S. Todorova, A. Naydenov, et al. Chem Eng J., 266 (2015), 329-338.

[34]   Y.Y. Zhang, W. Diao, . . Williams, et al. Appl. Catal. A:Gen., 469 (2014), 419-426.

[35]   H. Y. Kim, G. Henkelman. ACS Catal., 3 (2013), 2541-2546.

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