Catalysis Communications 92 (2017) 80–85

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

MoO_3 modified Ni_2P/Al_2O_3 as an efficient catalyst for crude glycerol to propylene

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ARTICLE INFO

Article history:
Received 21 September 2016
Received in revised form 2 December 2016
Accepted 12 January 2017
Available online 12 January 2017

Keywords:
Glycerol
Propylene
Hydrogenolysis
Propanol
Phosphide catalyst

ABSTRACT

The highly selective conversion of glycerol to propylene was performed by coupling the hydrogenolysis of glycerol to propanol and the catalytic cracking of propanol to propylene by using metal and acid catalysts together. The coupling of MoO_3-modified Ni_2P/Al_2O_3 and ZSM-5 catalysts efficiently resulted a high selectivity of propylene (88%) for pure glycerol conversion at 523 K. Such coupling was feasible for the conversion of glycerol/methanol (mainly the refined product of crude glycerol) to propylene by increasing cracking temperature to 723 K. The new system is potential for large-scale production in which crude glycerol and hydrogen are available as feedstock.

1. Introduction

The increased production of ethylene from ethane in Middle East has shifted the need of fundamental chemical feedstock from C_2-C_3 to C_3-C_4 olefins [1–4]. With traditional sources of propylene increasingly unable to meet growing market demands, considerable research efforts have been directed towards the development of new alternatives for the intentional production of propylene, such as the dehydrogenation of propane and methanol to propylene (MTP) process [2–4]. Recently, due to the increasing amount of glycerol produced worldwide, considerable attention has been focused on the conversion of glycerol to olefins (GTO) [5–9] and propylene (GTP) [3,10–13].

In our previous work, we found that a high selectivity of propylene (approximately 76%) can be obtained in a tandem GTP process, involving conversion of glycerol to propanol over metal catalysts and sequential catalytic dehydration/cracking of propanol to propylene over acid catalysts [11,12], which is consistent to the results obtained in literature [3,10]. The tandem process combining hydrogenolysis and dehydration/cracking relies on the formation of propanol as the key intermediate from the hydrogenolysis of glycerol [3]. In fact, propanol is the by-product of excessive hydrogenolysis of glycerol to propanediols [13,14], therefore metal catalysts (i.e., Cu and Ru) with high selectivity of 1,2-propanediol kinetically possess low activity in converting 1,2-propanediol to propanol [14]. At present, the use of metal oxides or acid modification of noble metals (typically Ir, Rh and Pt) catalysts has been shown to be an effective route to promote the formation of propanol [3,14–17]. However, the performance of these catalysts was evaluated in a batch reactor with a high H_2 pressure (5–8 MPa) and low concentration of glycerol solution (i.e., 10 wt.%). In contrast to the liquid hydrogenolysis of glycerol to propanol, there are scarcely any available reports on the gas-phase hydrogenolysis of glycerol to propanol under mild conditions. Yu et al. reported a very high selectivity of 1-propanol (>92%) in glycerol hydrogenolysis over Ir/ZrO_2 and approximately 99% selectivity of propylene in 1-propanol dehydration over ZSM-5 catalysts [3]. However, only 67% selectivity of propylene was obtained in gas-phase GTP reactions over Ir/ZrO_2 and ZSM-5 catalysts. Therefore, it is still necessary to screen suitable metal catalysts for the efficient gas-phase conversion of glycerol to propanol.

Sun et al. found that the WO_3-modified Cu/Al_2O_3 catalysts give high propanol selectivity in the one-step and two-step conversion of glycerol to propylene under mild conditions (1 atm) [10], which are also similar to the result on Cu/ZSM-5 [8]. Cu metal has been regarded as one of the best catalysts for the glycerol hydrogenolysis to propanediols owing to its good activity in C—O bond cracking without any C—C bond cracking

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http://dx.doi.org/10.1016/j.catcom.2017.01.009
1566-7367/

[18]. However, the problem of Cu metal catalysts sintering rendered it not suitable for industrial application. In addition to Cu, Pt-, Rh-, and Ir-based catalysts have been proven to be highly selective for the conversion of glycerol to propanediols [13]. Recently, Ren et al. [19] and Zacharopoulou et al. [20] found that the tungsten carbide and Mo-based catalysts are excellent for the selective conversion of C_3 oxygenates to propylene via deoxygenation/hydrodeoxygenation.

Crude glycerol, which contains 65 to 85% (w/w) glycerol and methanol, is one of the most useful hydrocarbon feedstock [21]. However, inorganic impurities in crude glycerol, such as potassium, often have detrimental effects on the catalysts used. In this study, we report the influences of methanol and potassium on the performance of the chosen catalysts. On the other hand, Stockenhuber et al. observed the promotion of allyl alcohol in dehydration conversion over Al_2O_3 catalysts modified by alkali metals [22]. The addition of alkali base to the metal (Pt and Ru) catalysts could also promote the selectivity of 1,2-propanediols and inhibit the formation of ethylene glycerol in the hydrogenolysis of glycerol [13]. In this work, the Al_2O_3-supported metal catalysts were prepared and modified to obtain a suitable catalyst formulation, which gives a high selectivity to propanol during hydrogenolysis and, thus, enabling an effective overall conversion of glycerol to propylene.

2. Experimental

2.1. Catalyst synthesis

The materials for catalyst synthesis and the synthesis procedures of SiO_2 and Al_2O_3 supported metal catalysts from impregnation methods can be found in the Supplementary materials.

For the synthesis of supported Ni_2P, nickel precursor (nickel(II)-TPP complex) was prepared by dissolving $Ni(CH_3COO)_2\cdot 6H_2O$ and triphenyl phosphine (TPP) with a molar ratio of 1:2 in ethanol at 333 K [23]. The supported precursor was prepared by impregnation of γ-Al_2O_3 and SiO_2 powders. The sample was dried at 298 K for 24 h and then dried at 333 K for 3 h over a water bath. The supported precursor was then heated at a rate of 5 K min^{-1} to 618 K and kept at that temperature for 2 h under a H_2 flow of 20 mL min^{-1}.

2.2. Characterization

X-ray diffractograms were measured using a Rigaku D/max 2500 X-ray diffractometer (Cu-Ka, $\lambda = 0.154$ nm). The metal compositions of the samples were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) using an IRIS Intrepid spectrometer.

2.3. Catalytic reactions

The conversion of glycerol to propylene was performed in a fixed-bed quartz reactor. The procedures of the reactions and the method for product analysis have been included in the Supplementary materials.

The conversion and selectivity based on carbon were calculated as follows:

$$\text{Conversion }(\%) = \frac{\text{sum of moles of carbon in all products}}{\text{sum of the reactant}} \times 100\%$$

$$\text{Selectivity }(\%) = \frac{\text{moles of carbon in specific products}}{\text{moles of carbon in all products}} \times 100\%.$$

3. Results and discussion

3.1. Synthesis of Ni_2P/Al_2O_3

It is well known that there are strong interactions between Ni species and Al_2O_3 at high temperatures (approximately 873 K) to form $NiAl_2O_4$ compounds, making the preparation of Ni_2P/Al_2O_3 by the conventional temperature-programmed reduction method at 873 K difficult [23]. Instead, we synthesized Ni_2P/Al_2O_3 via the hydrogen-thermal treatment of Ni(II)-triphenylphosphine complexes. Fig. 1 shows the XRD patterns of Ni_2P, Ni_2P/SiO_2 and Ni_2P/Al_2O_3 samples from thermal treatment method at 618 K. The characteristic peaks corresponding to Ni_2P compound (JCPDS 89-4864) were observed in bulk Ni_2P samples. The positions of these peaks did not change after deposition of Ni_2P on SiO_2 and Al_2O_3, but the intensities of diffraction peaks decreased, suggesting formation of smaller Ni_2P particles on supports. Interestingly, the intensities of diffraction peaks on Ni_2P/Al_2O_3 were much lower than those of Ni_2P/SiO_2. This result agreed with the chemisorption results (Table 1), in which a higher Ni metal dispersion was observed on Ni_2P/Al_2O_3 (0.21) than on Ni_2P/SiO_2 (0.12). Fig. 1 shows the successful preparation of Ni_2P/Al_2O_3 with a small particle size (approximately 5 nm calculated from Ni metal dispersion).

3.2. Hydrogenolysis of glycerol to propanol

Fig. S1 shows the performance of metal catalysts in the hydrogenolysis of glycerol. Here, Rh and Ir metal catalysts showed a better performance than Pt, Ru, bulk Mo_2N and Mo_2C catalysts in the conversion of glycerol to propanol. However, the high price of both Rh and Ir active phases is detrimental to the interests of cost-effective products. Therefore, the development of more efficient catalysts for conversion of glycerol to propanol still constitutes a significant challenge, which requires a shift from traditional precious metal catalysts to alternative active phases. Transition metal phosphides show chemical properties similar to noble metals, and they are particularly active for hydrotreating reactions, especially Ni_2P in hydrodeoxygenation [24–26]. Here, Ni_2P/SiO_2 possessed a high conversion (46%) of glycerol and high propanediols (48%) and propanol (38%) selectivities, which are better than Rh metal catalysts and similar to Ir metal catalysts. The results show that Ni_2P presents a significant high conversion and selectivity to propanol, which is the same as typical Rh and Ir metal catalysts in the hydrogenolysis of glycerol to propanol.

Crude glycerol contains 65 to 85% (w/w) glycerol as well as methanol and potassium [12]. Stockenhuber et al. observed the promotion of allyl alcohol in glycerol dehydration over Al_2O_3 catalysts modified with alkali metals [22]. The addition of alkali base to metal (Pt and Ru) catalysts is able to inhibit the formation of ethylene glycerol in the hydrogenolysis of glycerol [13]. Here, Al_2O_3 was considered as a suitable support for the conversion of crude glycerol.

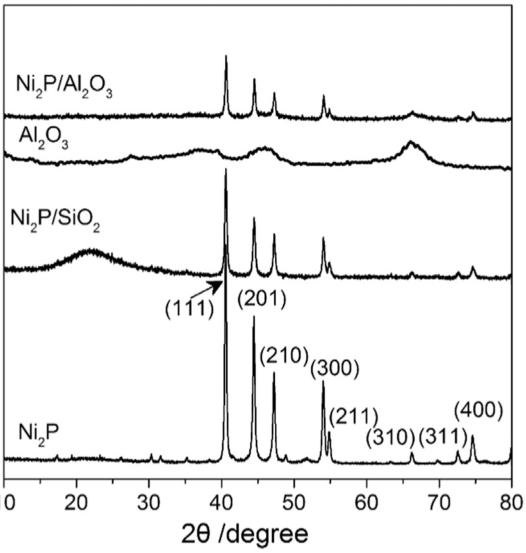

Fig. 1. XRD patterns of the Ni_2P, Ni_2P/SiO_2, Al_2O_3 and Ni_2P/Al_2O_3 samples.