

Vapour phase dehydration of glycerol to acrolein over solid acid metal phosphate catalysts

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Introduction

The valorization of glycerol obtained from biodiesel production is a big challenging task in recent years. An effective usage or conversion of crude glycerol to specific products will further reduce the cost of biodiesel production. Therefore, new uses of glycerol need to be explored for its valorization. Glycerol can be converted to acrolein, which is an important chemical intermediate for the production of acrylic acid, acrylic acid esters, super absorbers, polymers and detergents [1]. Compared with petroleum-based processes, the dehydration of glycerol to acrolein has attracted a great deal of attention as a significant route by virtue of its being an environmentally benign process.

In the present investigation we report the catalytic behavior of metal phosphate (MP : M= Al, Zr, Ti, Nb) catalysts during vapour phase glycerol dehydration. Aluminium phosphate (AIP), zirconium phosphate (ZrP), Titanium phosphate (TiP) and Niobium phosphate (NbP) samples were synthesized and characterized by physico-chemical methods. The acidic properties of these catalysts were determined by ammonia TPD and Py FT-IR spectroscopy. Our results provide a basis mainly for correlating the acidic properties of catalysts with the catalytic performance, and the effect of various reaction parameters on the catalytic functionalities during the glycerol dehydration reaction.

Materials and Methods

The MP catalysts were prepared by the different procedures reported Elsewhere [2, 3]. The gas-phase dehydration of glycerol in presence of water was investigated at 300°C, under atmospheric pressure in a vertical fixed-bed quartz reactor using 0.2g of catalyst. An aqueous solution containing 20 wt% glycerol was fed into the reactor by a micro-syringe pump at a flow rate of 0.5 mL/h (WHSV-2.6 h⁻¹). The reaction products were condensed in an ice-water trap and collected hourly for analysis using a gas chromatograph GC-2014 (Shimadzu) equipped with a DB-wax 123-7033 (Agilent) capillary column (0.32 mm i.d., 30 m long) and a flame ionization detector (FID).

Results and Discussion

The surface acidity is an important characteristic property of a solid acid catalyst to assess its dehydration functionality during glycerol to acrolein. The ammonia TPD profiles of different MP catalysts are presented in Figure 1.

The experimental results of vapour phase dehydration of glycerol at 300°C by various MP catalysts were reported Table. 1. The NbP sample showed high selectivity to acrolein with total a conversion of glycerol, compared to the corresponding other metal phosphate catalysts. During the dehydration reaction deactivation was found to be for all tested

catalysts. The degree of the deactivation depends on the surface acid density and pore diameter of catalyst.

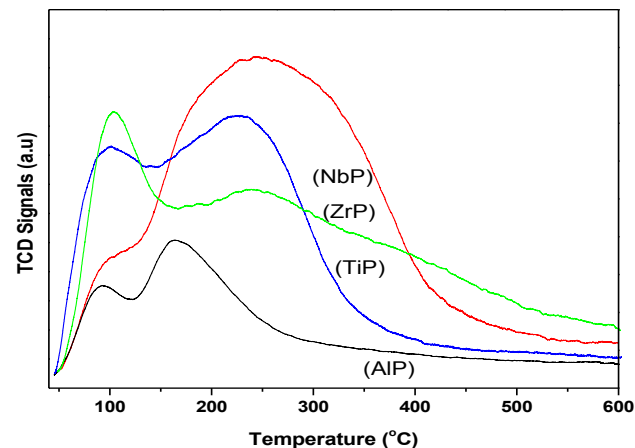


Figure 1. NH₃-TPD profiles of various MP catalysts.

Table 1. Effect of various MP catalysts on product distribution at TOS=10 h.

Catalyst	Con. of glycerol	Selectivity of reaction products					
		Acrolein	Hydroxy acetone	Allylic alcohol	Acetaldehyde	Hydrogenolysis products	Others
AIP	68	40	16	4	10	6	24
ZrP	80	46	15	10	6	5	18
TiP	90	60	12	5	5	4	14
NbP	100	80	4	1	4	2	9

Significance

Glycerol conversion and acrolein selectivity was mainly depends on the fraction of moderate acid sites with majority of them are due to Brønsted acidic sites. The TiP sample showed long catalyst life during vapour phase dehydration of glycerol due to its proper amount of the surface acidic density and large pores on the surface

References

1. Katryniok, B.; Paul, S.; Capron, M.; Dumeignil, F. *ChemsusChem*. **2009**, 2, 719.
2. Ren, T.Z.; Yuan, Z.Y.; Su, B.L. *Chem. Commun.* **2004**, 2730.
3. Sun, Q.; Fang, D.; Wang, S.; Shen, J. Auroux, A. *Applied Catalysis A: Gen.* **2007**, 327, 218.