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Glycerol Catalytic Cyclocondensation with Ethanediamine to Pyrazinyl Compounds over the Modified SiO_2-Al_2O_3

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ABSTRACT: *The Fe, Zn, and Mn-modified SiO_2-Al_2O_3 catalysts for the glycerol vapor-phase cyclocondensation with ethanediamine (ED) to 2-pyrazinemethanol (2-PMol) and 2-methylpyrazine (2-MP) in a fixed-bed system were prepared by coprecipitation and characterized by N_2 adsorption–desorption, X-ray powder diffraction, and NH_3 temperature-programmed desorption (NH_3-TPD) in the present work. The results showed that the Mn-modified SiO_2-Al_2O_3 catalyst with a SiO_2/Al_2O_3 molar ratio 15.84 and 6% Mn gave the highest catalytic activity for formation of 2-PMol (53.1%) and 2-MP (42.9%). Mn species could cause the modulation of the acidic species of catalysts, improving the glycerol cyclocondensation with ED to 2-PMol, and also acted as the catalytic centers for the hydrodehydration of 2-PMol to 2-MP. However, too many strong acidic sites could lead to ED self-cyclocondensation to form a by-product pyrazine. The optimum temperature was tested to be 380°C for the cyclocondensation over a 6%Mn-SiO_2-Al_2O_3 catalyst.* Heteroatom Chem 00:1–6, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21026

INTRODUCTION

With the gradual exhaustion of resources and an increase in demand of oil, human beings are facing a serious energy crisis and the biodiesel as a kind of renewable and clean energy has attracted more and more attention. However, a large quantity of by-product glycerol will come forth during biodiesel manufacturing [1]. Therefore, the reasonable utilization of glycerol is very important to develop the biodiesel industry. It has been reported that glycerol can be catalytically hydrogenated to propanediols [2–5], dehydrated to acrolein [6–9], and converted to hydrogen or syngas through the steam reforming [10–12].

From the recent studies [13–17], it is found that two adjacent hydroxyl groups in glycols such as 1,2-propanediol and glycol can be cyclocondensed with two adjacent amino groups in ethanediamine (ED) to pyrazinyl compounds. Glycerol consists of three adjacent —OH groups; thereby, it can also be cyclocondensed with ED to form 2-pyrazinemethanol (2-PMol) as shown in Scheme 1. Sarkari et al. [18] have studied this reaction over $ZnCr_2O_4$ as a catalyst and discovered that the obtained main product is 2-methylpyrazine (2-MP) due to further hydrodehydration of 2-PMol. Anyway, both pyrazinyl compounds are the key intermediates for pyrazinamide, an effective antitubercular drug. The present work mainly aims to utilize the metal-modified SiO_2-Al_2O_3 mixed oxides as catalysts to carry out the simultaneous synthesis of 2-PMol and 2-MP through the

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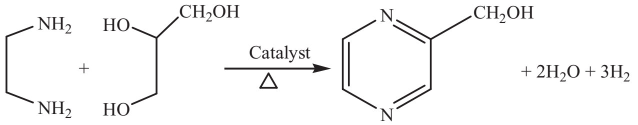
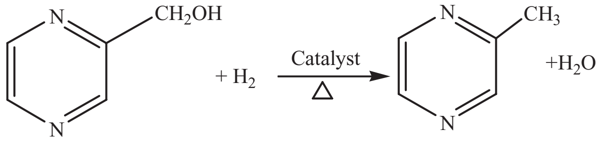


SCHEME 1



SCHEME 2

vapor-phase catalytic cyclocondensation of glycerol with ED. The used typical bifunctional catalysts are characterized by N_2 adsorption–desorption, X-ray powder diffraction (XRD), and NH_3 temperature-programmed desorption (NH_3-TPD). In addition, the effects of catalyst composition and cyclocondensation temperature on the glycerol vapor-phase cyclocondensation with ED in the fixed-bed system are also investigated in detail.

RESULTS AND DISCUSSION

Selection of SiO_2/Al_2O_3 Ratio

The effect of the SiO_2/Al_2O_3 molar ratio on the catalytic properties of SiO_2-Al_2O_3 catalysts (Fig. 1) in glycerol cyclocondensation with ED is investigated under the conditions of liquid hourly space velocity (LHSV) 4.5 h^{-1} and temperature 380°C. It can be found that the glycerol cyclocondensation with ED on the SiO_2-Al_2O_3 catalysts gives two main products including 2-PMol and 2-MP, as well as a small amount of pyrazine (Py). Py is probably generated by the deamination of ED through self-cyclocondensation [19]. 2-PMol is from the cyclocondensation between two adjacent hydroxyl groups in glycerol and two amino groups of ED as described in Scheme 1. Another main product 2-MP is from the hydrodehydration of 2-PMol with active hydrogen produced during formation of 2-PMol as described in Scheme 2.

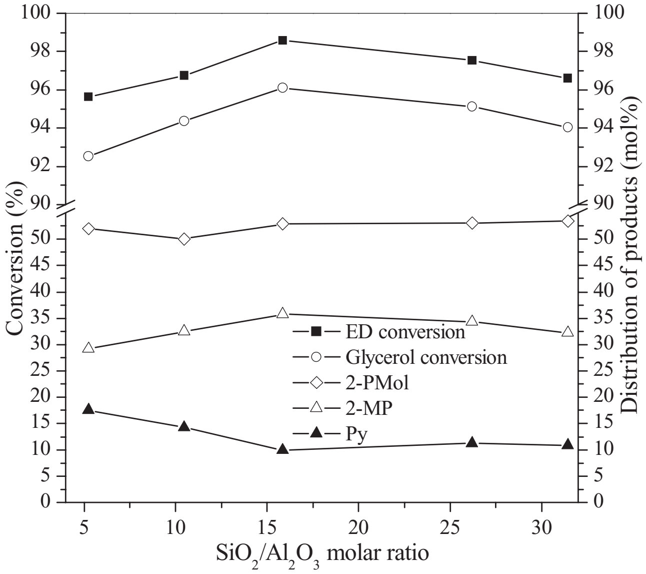


FIGURE 1 Effect of the SiO_2/Al_2O_3 molar ratio on catalytic properties of SiO_2-Al_2O_3 in the glycerol cyclocondensation with ED.

From Fig. 1, it can also be observed that the by-product Py in products is reduced with increasing SiO_2 amount in catalysts. It is probably because that an increase in the SiO_2 amount leads to a decrease in the strong acidic sites provided by alumina species on the catalyst surface, which inhibits the self-cyclocondensation of the strongly adsorbed ED. The NH_3-TPD results of the SiO_2-Al_2O_3 catalysts (Fig. 2a) show that the SiO_2-Al_2O_3 catalyst with a SiO_2/Al_2O_3 molar ratio 10.56 gives two NH_3 desorption peaks at about 90°and 200–450°C, which are assigned to the weak and strong acidic sites, respectively. In addition, it can also be observed that strong acidic site intensities decrease with increasing SiO_2 amount in catalysts. The NH_3 adsorption on the SiO_2–Al_2O_3 catalyst with a higher SiO_2/Al_2O_3 ratio (26.4) mainly occurs on the weak acidic sites, and the NH_3 desorption peak shifts to the high temperature with increasing SiO_2/Al_2O_3 ratio in the catalyst, indicating that they exhibit a stronger acidity. Therefore, the self-cyclocondensation of ED to a by-product Py can be deduced to carry out on the strong acidic sites located on the catalyst surface, which is not helpful to utilization of glycerol.

On the other hand, it is also found from Fig. 1 that the 2-MP formation first increases and then decreases with increasing SiO_2 amount in catalysts and gives the highest value at the SiO_2/Al_2O_3 molar ratio 15.84, and however the 2-PMol content has no obvious change. It is due to the fact that the presence of SiO_2 in the catalyst can provide more surface hydroxyl groups [20], which will probably provide the Brønsted acidic sites. However, a further increase in SiO_2 in the catalyst will excessively decrease the acidic sites and the Lewis acidic sites mainly provided by Al_2O_3 species, which are disadvantageous to the ED adsorption. According to the NH_3-TPD results, it can be concluded that the proper SiO_2/Al_2O_3

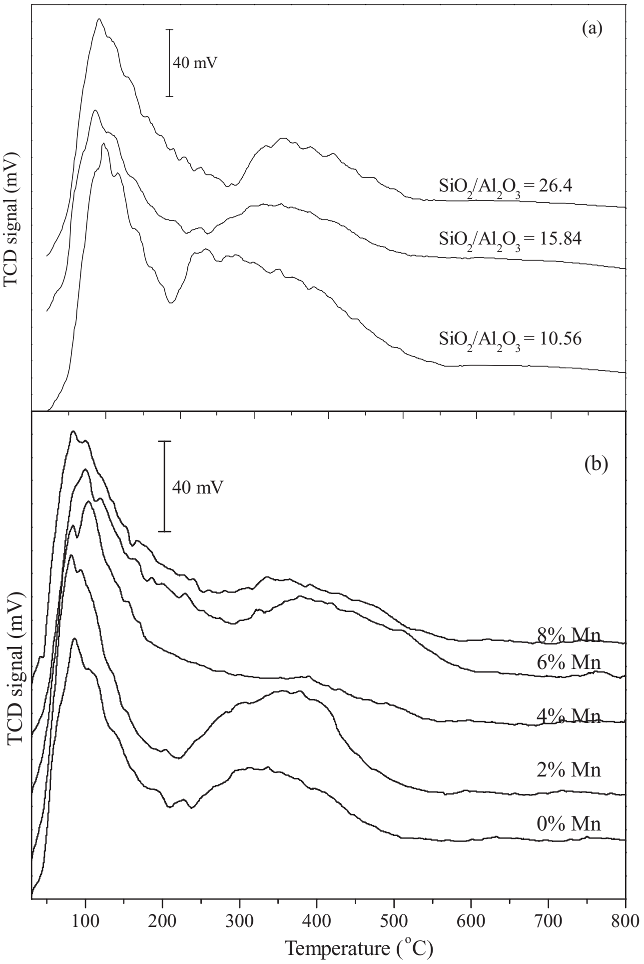
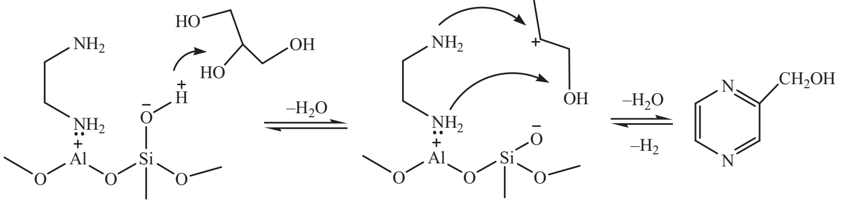


FIGURE 2 NH_3-TPD curves for SiO_2-Al_2O_3 with a different SiO_2/Al_2O_3 molar ratio (a) and Mn-SiO_2-Al_2O_3 ($SiO_2/Al_2O_3 = 15.84$) catalysts with a different Mn amount (b).

ratio will give rise to the simultaneous production of a proper number of Brønsted and Lewis acidic sites on the surface of catalyst. It will be helpful to the simultaneous adsorption of ED and glycerol, and the presence of the Brønsted acidic sites can also lead to the dehydroxylation on 2-C sites of glycerol to carbocation. A slight decrease in 2-MP formation over the catalysts with a higher SiO_2/Al_2O_3 ratio is probably due to a decrease in the absolute 2-PMol amount from cyclocondensation. Therefore, during the glycerol cyclocondensation with ED, the Lewis acidic sites of catalyst first adsorb one of the amino groups in ED molecules, the Brønsted acidic sites give rise to dehydroxylation of glycerol to produce carbocation, which can attack another amino group of ED to carry out the nucleophilic reaction, resulting in cyclocondensation of glycerol with ED to 2-PMol (Scheme 3).

Metal Modification

As described in Schemes 1 and 2, the cyclization, dehydrogenation, and hydrodehydration are mainly involved in the glycerol cyclocondensation with ED to 2-PMol and 2-MP. It has been reported that some transition metal species (such as Fe, Mn, Zn, and Cu) exhibit a good catalytic activity on glycol cyclocondensation with ED to pyrazinyl compounds [13,16]. Therefore, the effect of the modification with transition metal ions (such as 5% of Fe^{3+}, Zn^{2+}, or Mn^{2+}) on the catalytic properties of SiO_2-Al_2O_3 (SiO_2/Al_2O_3 molar ratio 15.84) catalyst in glycerol cyclocondensation with ED is also investigated under the conditions of reaction temperature 380°C and LHSV 4.5 h^{-1}. The results (Fig. 3) show that the modification of Zn^{2+} and Fe^{3+} will lead to a little decrease in 2-PMol formation along with 2-MP increase over SiO_2-Al_2O_3 catalysts. It indicates that Zn^{2+} and Fe^{3+} exhibit a catalytic reducibility, resulting in the 2-PMol hydrodehydration to 2-MP, which is consistent with the results in the cyclization of propylene glycol with ED to 2-MP as reported [15–17]. However, glycerol conversion decreases significantly, which is probably because the Zn^{2+} and Fe^{3+} ions are located on the silica species leading to the attenuation of glycerol dehydroxylation to carbocation. In addition, it is also found from Fig. 3 that the Mn modification can result in an obvious increase in the 2-PMol formation (61.0%) with a slight decrease in 2-MP, indicating that the Mn^{2+}modification is



SCHEME 3

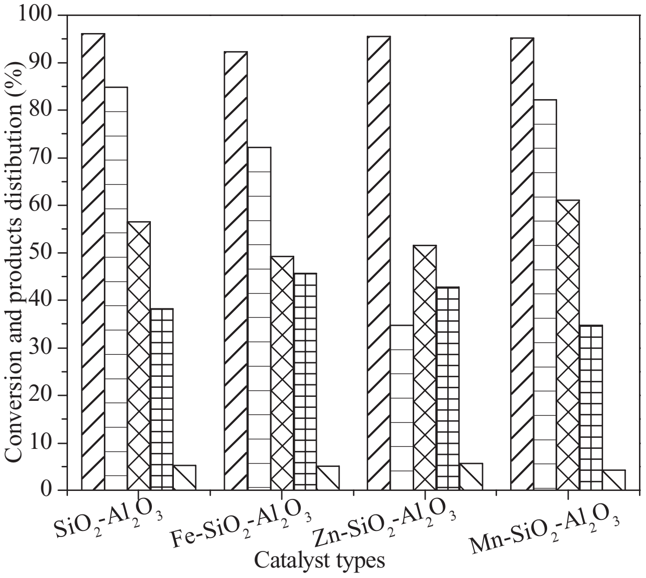


FIGURE 3 Effect of metal ion modification on catalytic properties of SiO_2-Al_2O_3 ▨ ED conversion, ▤ Glycerol conversion ▩, 2-PMol ▦, 2-MP, ▧ Py.

helpful to the glycerol cyclocondensation with ED to 2-PMol over SiO_2-Al_2O_3.

Selection of Mn-Modified Amount

The effects of Mn-modified amount on the catalytic properties of the Mn-SiO_2-Al_2O_3 catalysts (SiO_2/Al_2O_3 molar ratio 15.84) are investigated in detail. The results (Fig. 4) show that the 2-PMol content in products first decreases and then increases with increasing Mn amount, which is opposite to the change in trend in 2-MP. It indicates that the Mn species in catalysts also exhibit a catalytic activity on the hydrodehydration of 2-PMol to 2-MP. In addition, the conversions toward both glycerol and ED increase to some extent with increasing Mn amount and reach up to the highest values at the Mn-modified amount of 6%. It adequately shows that the Mn species in catalysts play an important role in glycerol catalytic cyclocondensation with ED.

The N_2 absorption–desorption results (data omitted here) reveal that the surface area (213 m^2 g^{-1}) of the SiO_2-Al_2O_3 catalyst (SiO_2/Al_2O_3 molar ratio 15.84) is decreased to 170–190 m^2 g^{-1} after the Mn modification. From the XRD patterns (Fig. 5) of Mn-SiO_2-Al_2O_3 catalysts, it can be observed that the Mn-SiO_2-Al_2O_3 catalysts with a low Mn amount give some distinct AlOOH characteristic diffraction peaks (Pdf no. 17-940) at $2\theta = 14.5^\circ$, 28.2°, 38.5°, 49.0°, 65.1°, and 73.2°, respectively. However, with an increase in Mn amount (>3%), the AlOOH species in catalysts generates a crystal-phase transformation to γ-Al_2O_3 (Pdf no: 1-1303) along with the generation of a small amount of new species such as $Mn_7O_8(SiO_4)$ (Pdf no. 89-5664). And, no apparent SiO_2 characteristic diffraction peaks are observed for all the catalysts, indicating that the SiO_2 species in the catalysts were amorphous.

From NH_3-TPD curves (Fig. 2b) of Mn-SiO_2-Al_2O_3 catalysts, the Mn-SiO_2-Al_2O_3 catalysts with Mn amount of 2% is found to give two strong NH_3

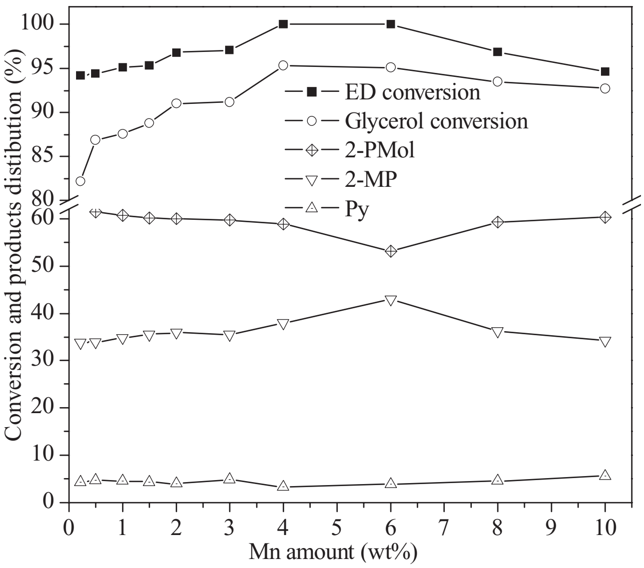


FIGURE 4 Effect of Mn-modified amount on catalytic properties of Mn-SiO_2-Al_2O_3 in glycerol cyclocondensation with ED.

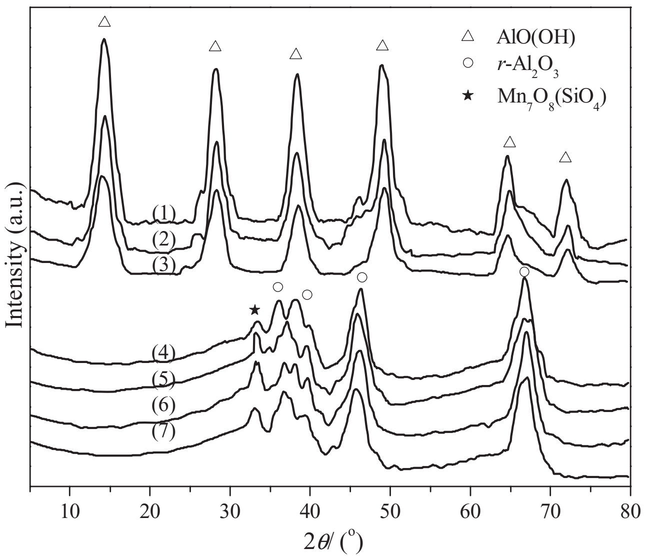


FIGURE 5 XRD patterns of Mn-SiO_2-Al_2O_3 with a different Mn amount of (1) 0.2%; (2) 1.0%; (3) 2.0%; (4) 3.0%; (5) 4.0%; (6) 6.0%; and (7) 8.0%.

desorption peaks at 90° and 250–350°C, respectively. They are assigned to the weak and strong acidic sites. No obvious change in the peak intensity of NH_3 desorption occurred on the weak acidic sites, which can be observed after the SiO_2-Al_2O_3 catalyst is modified by Mn. However, when Mn amount is increased from 2% to 6%, the intensities of the NH_3 desorption peak are weakened at about 250–350°C. In combination with the XRD results, it can be concluded that the acidic sites are mainly provided by AlOOH or γ-Al_2O_3 species and the Mn oxide species are probably located on the surface of aluminum oxide species, resulting in a slight decrease in Lewis acidic sites and can provide Brønsted acidic sites similar to the Si-OH groups, which are helpful to glycerol conversion. However, the presence of excessive Mn leads to formation of $Mn_7O_8(SiO_4)$ composite oxides in catalyst, probably resulting in a decrease in the Brønsted acidic sites. From the catalytic results (Fig. 4), the SiO_2-Al_2O_3 catalyst with Mn amount of 6% exhibits the best catalytic property; it is mainly because of the simultaneous existence of proper Brønsted and Lewis acidic sites. In other words, the modification with a proper Mn can modulate the acidic species over the surface of catalysts. The glycerol catalytic cyclocondensation with ED occurs between the carbocations from glycerol and the adsorbed ED on Lewis acidic sites to 2-PMol and H_2, and whereafter the 2-MP formation will be carried out by the hydrodehydration of 2-Pmol, which can be improved by the presence of Mn in catalysts.

Effect of Reaction Temperature

The effect of reaction temperature on the catalytic property of 6%Mn-SiO_2-Al_2O_3 in the glycerol cyclocondensation with ED is investigated under LHSV 4.5 h^{-1}. From Fig. 6, the by-product Py in products increases gradually with increasing reaction temperature, it indicates that the high temperature is helpful to ED self-cyclocondensation on the catalyst surface. The product 2-PMol first decreases and then increases; however, 2-MP formation gives an adverse trend with increasing reaction temperature. It is mainly because the increase in temperature is advantageous to the hydrodehydration of 2-PMol; however too high a temperature can make the produced 2-PMol escape from the catalyst surface quickly. As far as conversions toward glycerol and ED are concerned, they increase first and then decrease with the increasing reaction temperature and the highest conversions come forth at 380°C. Moreover, a decrease in the glycerol conversion in the high-temperature region is also found to be much more than that of ED, which is mainly because of ED self-cyclocondensation and the difficulty in glycerol conversion on Brønsted acidic sites of the catalyst surface. 380°C should be the optimum reaction temperature for the glycerol cyclocondensation with ED in the fixed-bed system, which is the same as that for the synthesis of the other pyrazinyl compounds as reported [17]. The investigation on the catalytic stability of 6%Mn-SiO_2-Al_2O_3 in the glycerol cyclocondensation with ED (Fig. 7) shows that the conversions of glycerol and ED are at the stable levels of about 95% and 97%, respectively. And the content of 2-PMol (~60%) and 2-MP (~35%) in products also has not decreased after 48 h. It indicates that this catalyst displays a stable catalytic property in the glycerol cyclocondensation with ED.

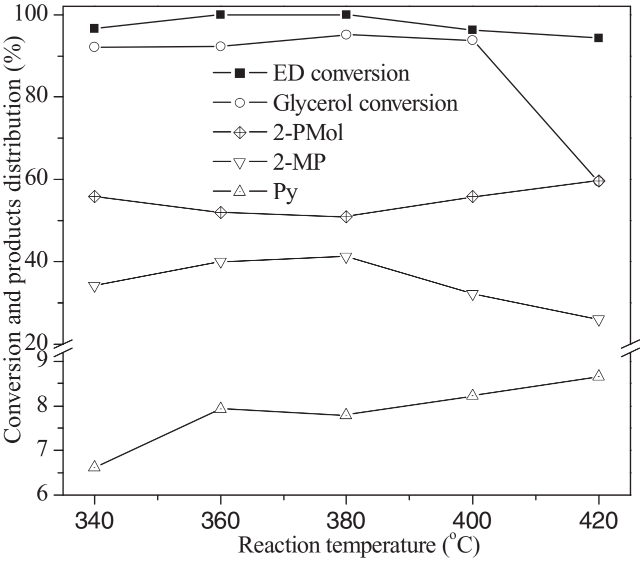


FIGURE 6 Effect of reaction temperature on catalytic properties of 6%Mn-SiO_2-Al_2O_3 in glycerol cyclocondensation with ED.

EXPERIMENTAL

Catalyst Preparation

SiO_2-Al_2O_3 catalysts were synthesized as follows: A desired amount of pseudoboehmite ($AlO(OH)\cdot xH_2O$, 68%–72% Al_2O_3) and tetraethyl orthosilicate was successively added in urea solution under the vigorous stirring for 20 min at room temperature. The obtained white slurry was then heated at 70°C under stirring for another 1.5 h to carry out the homogeneous coprecipitation. The white precipitates were filtrated, washed, dried, and calcined at 500°C for 5 h to obtain the SiO_2-Al_2O_3 catalysts. The metal modification of SiO_2-Al_2O_3 catalysts was carried out by the impregnation using the nitrates of Zn^{2+}, Fe^{3+}, or

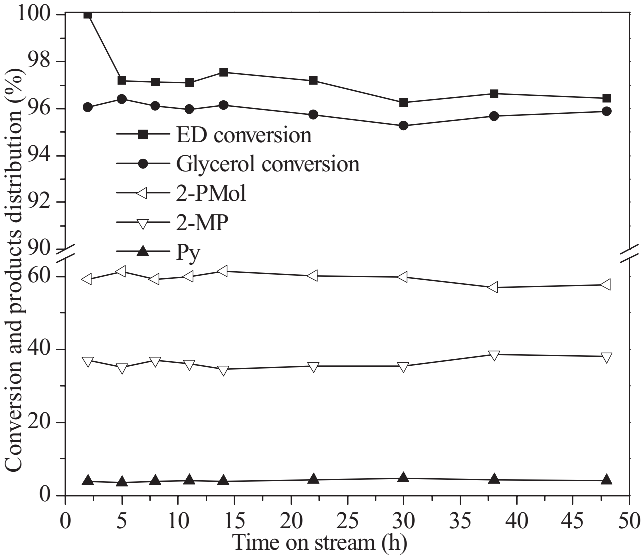


FIGURE 7 Catalytic stability of 6%Mn-SiO_2-Al_2O_3 in glycerol cyclocondensation with ED at LHSV 4.5 h^{-1}, reaction temperature 380°C, N_2 as a carrier gas.

Mn^{2+} as a precursor. After impregnation, the samples were calcined at 400°C for 1 h after drying.

Catalyst Characterization

The specific surface areas of catalysts were measured by the N_2 adsorption–desorption isotherms at –196°C using an SSA-4200 micromeritics instrument (Builder Co., Beijing, China). XRD patterns of catalysts were recorded on a DX-2700 powder diffractometer (Dandong Fangyuan Instrument Co., Dandong, China) operated at 30 kV and 20 mA, using Cu $K\alpha$ radiation. The compositions were determined using a XRF-1800 X-ray fluorescence spectrometer (Shimadzu Co., Japan). The surface acidity of catalysts was tested by NH_3-TPD on a TP-5080 adsorption instrument (Tianjin Xianquan Instrument Co., Tianjin, China): 0.2 g samples (0.38–0.83 mm) was loaded and pretreated with N_2 at 600°C for 1 h to remove the adsorbed water. The adsorption of NH_3 and the removal of the physically adsorbed NH_3 on the catalyst surface were carried out at room temperature. The desorption of the chemically adsorbed NH_3 was carried out by heating it from 20 to 900°C (at a heating rate of 10°C min^{-1}) in 30 mL min^{-1} of Ar gas; the desorbed NH_3 amount was detected by the thermal conductivity detector.

Catalytic Test

Glycerol cyclocondensation with ED was performed in a fixed-bed reactor under atmospheric pressure at the temperature range of 340-420°C. 1.5 g of catalysts (0.38–0.83 mm, apparent volume 2 mL) was sandwiched between quartz wool layers in a quartz tube reactor and was activated in a flow of dry air at 400°C for 4 h prior to catalytic runs. The catalysts were then flushed with 30 mL min^{-1} of dry N_2 and cooled to the desired temperature. The aqueous liquid reactants with a molar composition of 0.1 glycerol : 0.1 ED : 1 H_2O were fed into the reactor by a PDB-FT-2505 syringe feed pump (Jing-Wei Good Friends Beijing, Tech Development Co., Beijing, China) at a rate of 9 mL h^{-1}. The liquid products collected in an ice-cooled condenser were analyzed by a GC-2000 gas chromatograph (Chongqing Chuanyi Analyzer Co., Chongqing, China) equipped an OV-101 column and a flame ionization detector.

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