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Cyclization of monoethanolamine to aziridine over Cs_2O–P_2O_5/SiO_2

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Abstract Several commercially available supports were examined for cyclization of monoethanolamine to aziridine, and SiO_2 was found to yield the best results. The obtained results indicated that selectivity of aziridine was mainly influenced by support. The catalysts were characterized by NH_3-TPD and XRD. It was found that SiO_2 with lower acidity could inhibit the intermolecular condensations, and thus favored the formation of aziridine. The $Cs_4P_2O_7$ phase was confirmed as the active site in the supported cesium phosphate catalyst. The reaction parameters were also optimized and a yield of 52% aziridine was obtained over 200 h. Thus, a continuous process for the cyclization of monoethanolamine to aziridine has been established.

Keywords Cyclization · Monoethanolamine · Aziridine · Cs_2O–P_2O_5/SiO_2 catalyst

Introduction

Aziridine is an important intermediate for the manufacture of fine chemicals and pharmaceuticals [1–3]. Nowadays, most aziridine is still manufactured by the Wenker reaction from monoethanolamine (MEA) [4], in which large amounts of sulfuric acid and alkaline substances have to be employed leading to a serious impact on the environment.

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Recently, vapor phase cyclization of MEA to aziridine has been extensively studied. WO_3- and Nb_2O_5-based catalysts have been developed for the reaction [5–7]; however, these catalysts did not exhibit high catalytic performance either on the selectivity or lifetime. Some reports have proved that phosphates, especially cesium phosphate, show a better catalytic performance than the above-mentioned catalyst [8–10]. Even so, the yield of aziridine over the cesium phosphate catalyst was not perfect. Generally, a catalyst support or binder is always used in an industrial process. It has been shown in the literature that these supports or binders could have a key impact on the overall acidic properties of the catalyst and lead to different catalytic performances [11]. So far, the influences of the support on the catalysts for cyclization of MEA to aziridine have seldom been researched.

Thus, in this work, several commercially available supports were examined for cyclization of MEA to aziridine, and the most satisfactory catalytic performance was displayed by SiO_2. The catalysts were studied by NH_3-TPD and XRD, and the process parameters were optimized. Thus, a continuous process for the cyclization of MEA to aziridine has been established.

Experimental

Catalyst preparation

SiO_2 pellets with a diameter of about 3 mm were purchased from Hailang silica-gel drier factory, Qingdao, China. Shaped H-ZSM-5 support with a molar Si/Al ratio of 100 was obtained from Nankai University Catalyst, Tianjin, China. Al_2O_3 pellets with a diameter of about 3 mm were provided by the Aluminum Corporation of China, Zibo, China. The other commercially available reagents were used without further purification.

The catalysts used in this study were prepared by the impregnation method. For example, $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}/SiO_2$ (the suffix = the weight percentage of this component in the catalyst) was prepared as follows. SiO_2 pellets (100 g) were impregnated with 180.0 mL aqueous solution of 5.4 g $(NH_4)_3PO_4{\cdot}3H_2O$ and 8.2 g $CsNO_3$. After being impregnated at ambient temperature for 4 h, the catalyst was dried at 120 °C for 8 h and calcined at 800 °C for 4 h. These catalysts were activated at 400 °C in a stream of nitrogen (0.8 L/min) for 2 h before use.

Catalytic experiments

The reaction was performed in a fixed-bed reactor at atmospheric pressure, which was loaded with 40.0 mL catalyst. MEA was dosed into the reactor with a syringe pump. Nitrogen was employed as the dilution gas. The reaction mixture was condensed in a cold trap (−2 °C) and analyzed without preliminary separation by offline gas chromatograph (SE-30 capillary column: 60 m × 0.32 mm, 1.0 μm film thickness). Moreover, the composition of samples were identified by GC/MS (HP-1 capillary column: 30 m × 0.25 mm, 0.2 μm film thickness) equipped with an ion trap MS detector.

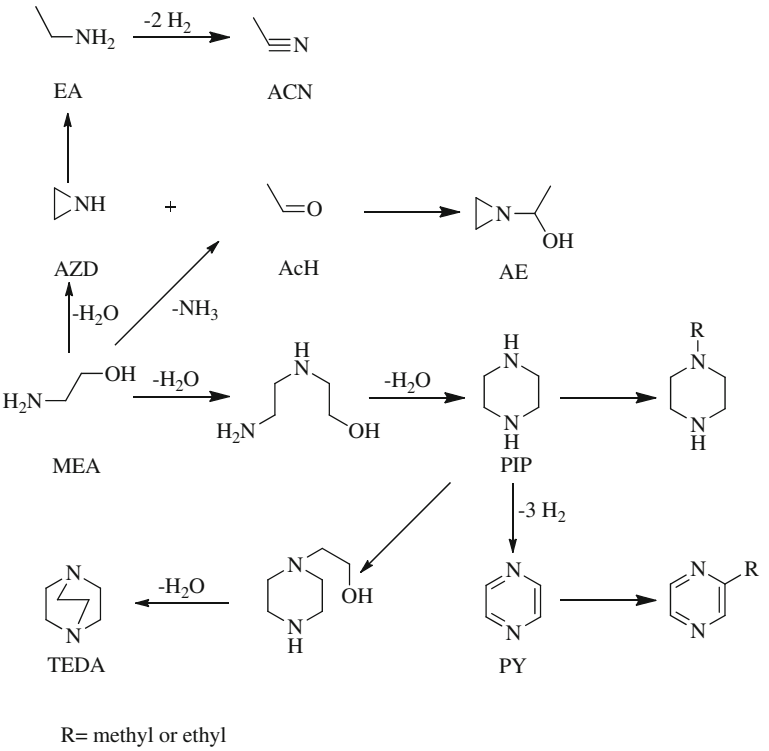
Catalyst characterization

Ammonia temperature programmed desorption (NH_3-TPD) was performed on a TP-5000 instrument with a thermal conductivity detector (TCD). X-ray diffraction (XRD) was recorded on a Rigaka D/max 2500 X-ray diffractometer with Cu-K_α radiation (40 kV, 100 mA) in the range of 5–60°.

Results and discussion

Catalyst activity

As mentioned above, cesium phosphate has been reported to be effective for cyclization of MEA to aziridine, and γ-Al_2O_3 was widely used as support in our previous works [12, 13]. This encouraged us to carry out this reaction over (Cs_2O)–(P_2O_5)/γ-Al_2O_3. The reaction mixture was identified by GC–MS, while aziridine (AZD), piperazine (PIP), pyrazine(PY), triethylenediamine (TEDA), 1-aziridineethanol (AE) and amounts of C_2 chemicals (acetaldehyde, ethylamine and acetonitrile) were also detected. Based on the obtained results and the reported previous work [8, 9], the reaction pathway was deduced and is shown in Scheme 1. It is obvious that the selectivity of aziridine is quite poor due to the complicated reactions.



Scheme 1 The cyclization of monoethanolamine and side reactions

In order to improve the selectivity of aziridine, some commercially available supports, such as HZSM-5 and SiO_2, were examined, and the results are presented in Table 1. The experimental results showed that SiO_2 displayed much better selectivity of aziridine than the other supports. Therefore, SiO_2 was chosen as the support for the following study. To further understand the reasons for these results, the catalysts were studied by NH_3-TPD and XRD.

Catalysts characterization

NH_3-TPD

In this study, extensive TPD of ammonia studies were performed to compare the acidity of different supports and supported catalysts. As shown in Fig. 1, HZSM-5 and γ-Al_2O_3 exhibit both the weak (120–300 °C) and strong acid sites peak (above 450 °C), but for SiO_2, only the weak acid sites peak is observed. These indicated that SiO_2 possess the least acidity in the three kinds of support.

The accurate calculation of total acidity of these catalysts was difficult, since not all TPD profiles displayed distinct NH_3 desorption peaks. However, according to the acidity of the supports, it is clear that the total acidic of the supported catalysts can be deduced as $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2 < $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/γ-Al_2O_3 < $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/HZSM-5. This result implied that. with the decrease of acidity in the catalyst, selectivity of aziridine drastically increased from 0.5 to 51.0%; simultaneously, selectivity of PIP, TEDA, and PP declined sharply (see Table 1).

It has been reported that the desorption of amino compounds from the surface of catalyst could be restrained by the strong acidity sites [14], and this may be the reason why the multi-molecular condensation products such as PIP and TEDA were readily formed over the strong acidity HZSM-5 and γ-Al_2O_3-supported catalyst, and aziridine was smoothly obtained over the weak acidity SiO_2-supported catalyst. In

Table 1 Effect of different supports on the catalytic performance

Catalyst	Conversion/%	Selectivity/%						
		Aziridine	1-Aziridine-ethanol	C_2^a	PIP[b]	PY[c]	Triethy-lenediamine	Unknown
$(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/HZSM-5	97.6	0.5	2.7	2.5	28.0	7.5	18.6	40.2
$(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/γ-Al_2O_3	98.7	2.6	3.7	6.0	22.3	13.0	10.1	42.3
$(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2	84.0	51.0	31.6	6.8	2.2	6.1	0.7	1.6

Reaction conditions: 420 °C; feeding rate: 0.1 mL/min; N_2 flow rate: 0.8 mL/min

[a] The sum of acetaldehyde, ethylamine and acetonitrile

[b] The sum of piperazine and *N*-alkylpiperazine

[c] The sum of pyrazine and *N*-alkylpyrazine

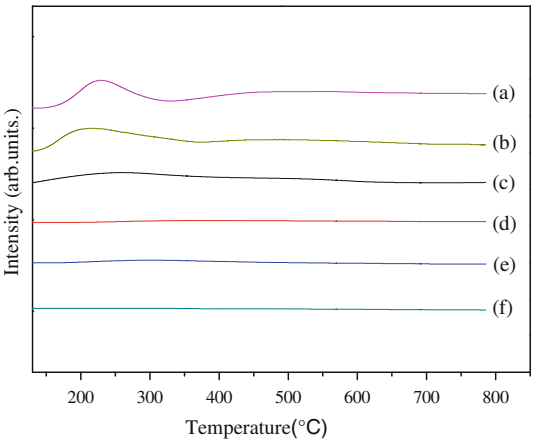


Fig. 1 NH_3-TPD curves for **a** HZSM-5, **b** γ-Al_2O_3, **c** SiO_2, **d** $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/HZSM-5, **e** $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/γ-Al_2O_3, **f** $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2

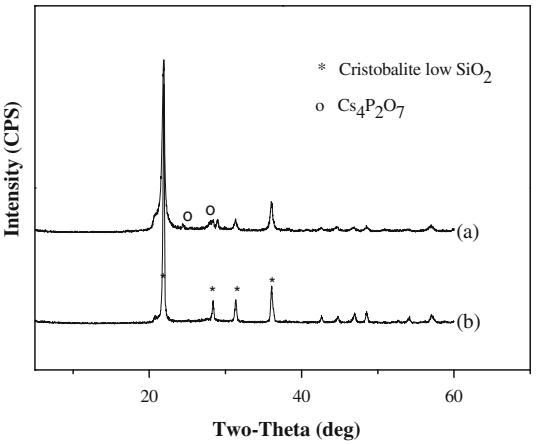


Fig. 2 X-ray diffraction patterns of **a** $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2, **b** SiO_2

other words, the SiO_2 support with lower acidity favored the formation of aziridine more than other supports.

XRD

The XRD patterns for SiO_2 support and $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2 are shown in Fig. 2. The typical diffraction lines at about 22.0°, 28.5°, 31.3°, and 36.1° in both of the XRD curves can be assigned to cristobalite low SiO_2 phase. Only diffraction peaks of pyrophosphate ($Cs_4P_2O_7$) crystals were detected for $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2. This demonstrated that most of the initial impregnated orthophosphate (Cs_3PO_4) was transformed to the more stable pyrophosphate phase during the calcination treatment, and thus pyrophosphate ($Cs_4P_2O_7$) crystals is believed to be the main active species in $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}$/SiO_2. This result was in accordance with a previous report [15].

Optimization of the process conditions

Reaction temperature

The cyclization reaction was examined at a temperature range from 400 to 460 °C and the results are listed in Table 2. As the temperature increased, selectivity of aziridine slightly decreased from 52.2 to 46.4%, but the conversion of MEA increased steadily from 74.4 to 98.0%. It was unexpectedly found that selectivity of 1-aziridineethanol sharply decreased at the same time. This may be because the higher temperatures favor desorption of aziridine from the weak acid sites of catalyst so preventing the unexpected nucleophilic addition of aziridine to acetaldehyde as mentioned in Scheme 1. However, higher temperatures may result in other side reactions, thus 440 °C was chosen to be the reaction temperature.

Effect of N_2 flow rate

Nitrogen was applied as the dilution gas in this study. The influences of dilution gas on the catalytic performance are listed in Table 3. With an increase of N_2 flow rate from 0.8 to 1.6 L/min, selectivity of aziridine jumped from 50.7 to 59.0%, while conversion of MEA reduced to 78.2 from 90.5%, making it obvious that 1.2 L/min could be selected as the optimum N_2 flow rate.

Lifetime of $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}/SiO_2$

The lifetime test was carried out under the optimum conditions and the results are shown in Fig. 3. During this process, conversion of MEA and selectivity of aziridine remained at about 84.0 and 62.0%, respectively. These results demonstrated that $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}/SiO_2$ showed good stability for the cyclization of MEA to aziridine.

Table 2 Effect of reaction temperature on catalytic performance

Temperature/°C	Conversion/%	Selectivity/%						
		Aziridine	1-Aziridine-ethanol	C_2[a]	PIP[b]	PY[c]	Triethy-lenediamine	Unknown
400	74.4	52.2	33.4	7.2	1.4	4.3	0.3	1.2
420	84.0	51.0	31.6	6.8	2.2	6.1	0.7	1.6
440	90.5	50.7	24.6	14.1	2.2	5.5	0.2	2.7
460	98.0	46.4	16.7	24.7	1.1	6.5	0.9	3.7

Reaction conditions: feeding rate: 0.1 mL/min; N_2 flow rate: 0.8 mL/min

[a] The sum of acetaldehyde, ethylamine and acetonitrile

[b] The sum of piperazine and *N*-alkylpiperazine

[c] The sum of pyrazine and *N*-alkylpyrazine

Table 3 Effect of N_2 flow rate on catalytic performance

N_2 flow rate/L/min	Conversion/%	Selectivity/%						
		Aziridine	1-Aziridine-ethanol	C_2[a]	PIP[b]	PY[c]	Triethylenediamine	Unknown
0.8	90.5	50.7	24.6	14.1	2.2	5.5	0.2	2.7
1.2	83.7	61.8	18.6	9.6	3.1	6.8	0.0	0.1
1.6	78.2	59.0	25.6	9.2	0.0	6.2	0.0	0.0

Reaction conditions: 440 °C; feeding rate: 0.1 mL/min

[a] The sum of acetaldehyde, ethylamine and acetonitrile

[b] The sum of piperazine and *N*-alkylpiperazine

[c] The sum of pyrazine and *N*-alkylpyrazine

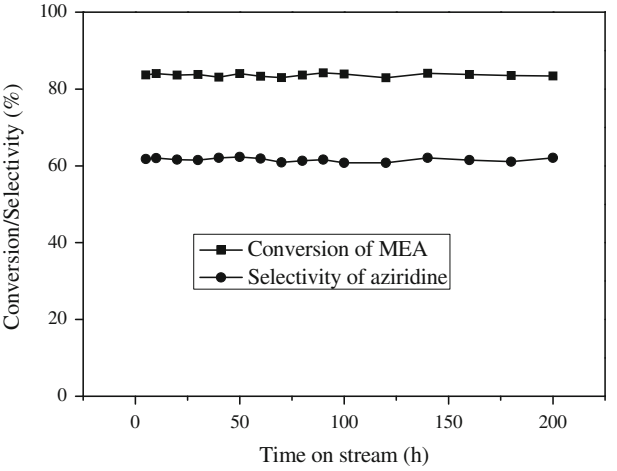


Fig. 3 Service life of $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}/SiO_2$

Conclusion

$(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}/SiO_2$ was certified as suitable for cyclization of MEA to aziridine. It was found that SiO_2 with lower acidity favors the formation of aziridine more than other supports, and that the $Cs_4P_2O_7$ crystal is believed to be the main active species in $(Cs_2O)_{5.5}$–$(P_2O_5)_{1.8}/SiO_2$. Conversion of MEA and selectivity of the aziridine are deeply affected by reaction temperature and N_2 flow rate. The reaction performed well for 200 h. Therefore, this process may offer interesting prospects for large-scale industrial production of aziridine from MEA.

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