第26卷 第4期　　分　子　催　化　　Vol. 26, No. 4
2012年8月　　JOURNAL OF MOLECULAR CATALYSIS(CHINA)　　Aug.　2012

Article ID: 1001-3555(2012)04-0340-07

Effect of Na_2O or K_2O on CoO/SiO_2-Al_2O_3 Catalyst for the Vapor-Phase Synthesis of 1-Phenylazepane

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Abstract: The CoO/SiO_2-Al_2O_3 doped with Na_2O or K_2O for the vapor-phase synthesis of 1-phenylazepane from aniline and 1,6-hexanediol was studied. The catalysts were characterized by XRD, TEM, H_2-TPR and NH_3-TPD. The results indicated that Na_2O not only increased the amount of weak acid sites of the catalyst, but also decreased the amount of the middle-strong acid sites, as a result, Na_2O improved the selectivity of the catalyst. The addition of K_2O took disadvantage of the synthesis of 1-phenylazepane for the amount of weak acid sites decreased remarkably and the CoO particles were sintered easily during the reaction.

Key words: Na_2O; K_2O; CoO/SiO_2-Al_2O_3; 1-Phenylazepane; Vapor-phase synthesis
CLC number: O643.32　　**Document code**: A

Nitrogenous heterocyclic compounds are widely applied in the fields of material chemistry, biology, medicine, analytical chemistry, organic synthesis and so on[1-3]. 1-Phenylazepane, a nitrogenous heterocyclic compound, is not only used as an important organic solvent, but also applied in the manufacture of dyestuff, explosives, pesticide, fertilizer, rubber promoter and many other chemical intermediates[4,5].

Up to now, many routes have been developed for the synthesis of 1-phenylazepane. Among them, liquid-phase method is often considered conventional because it can give the product in a good yield[6-8]. However, many drawbacks existed such as complicated and expensive reagents, a large number of toxic solvents, heavy pollution and rigorous reaction condition, etc[9-12], which limited the further application of 1-phenylazepane. Hence, the development of vapor-phase synthesis of 1-phenylazepane, for economic and environmental aspects, is more attractive.

Although many vapor-phase syntheses of nitrogenous heterocyclic compounds are reported[13,14], only a few are available for the vapor-phase synthesis of 1-phenylazepane. In 1985, Walkup et al. reported the synthesis of 1-phenylazepane from aniline and 1,6-hexanediol over the Al_2O_3 catalyst at 400 ℃, the yield of 1-phenylazepane was 70%[15]. Our latest study found that CoO/SiO_2-Al_2O_3 was an efficient catalyst for the reaction and the yield of 1-phenylazepane reached 80% at 290 ℃[16].

Na_2O and K_2O exhibited the promoting effect on the performance of catalysts in many reactions[17-21]. In this paper, they were introduced into CoO/SiO_2-Al_2O_3 for the vapor-phase synthesis of 1-phenylazepane from aniline and 1,6-hexanediol. XRD, TEM, H_2-TPR and NH_3-TPD techniques were used to investigate and explain the relationship between the structure of CoO-based catalysts and their catalytic performances.

1 Experimental

1.1 Catalyst preparation

The CoO/SiO_2-Al_2O_3 catalyst was prepared by incipient wetness impregnation. First, SiO_2-Al_2O_3(parti-

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Received date: 2012-03-20; Revised date: 2012-07-18

Foundation item: The Education Department of Liaoning Province (2009A421).

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cle diameter 0.900 ~ 0.450 mm) was impregnated with the aqueous solution of cobalt nitrate for 15 h at room temperature, dried at 120 ℃ for 4 h and calcined at 700 ℃ for 4 h to get the catalyst precursor.

The CoO/SiO_2-Al_2O_3 doped with Na_2O or K_2O was prepared by sequential impregnation. SiO_2-Al_2O_3 (particle diameter 0.900 ~ 0.450 mm) was firstly pre-impregnated with the aqueous solution of sodium nitrate or potassium nitrate for 15 h at room temperature, dried at 120 ℃ for 4 h and calcined at 700 ℃ for 4 h to obtain M_2O/SiO_2-Al_2O_3(M=Na or K). Then M_2O/SiO_2-Al_2O_3 was impregnated with an aqueous solution of cobalt nitrate for 15 h, then dried and calcined as described above to obtain the catalyst precursor of CoO-Na_2O/SiO_2-Al_2O_3 or CoO-K_2O/SiO_2-Al_2O_3. The catalyst with first impregnating CoO, then Na_2O or K_2O was marked as Na_2O-CoO/SiO_2-Al_2O_3 or K_2O-CoO/SiO_2-Al_2O_3. The catalyst with impregnating CoO and Na_2O or K_2O simultaneously was marked as Na_2O+CoO/SiO_2-Al_2O_3 or K_2O+CoO/SiO_2-Al_2O_3.

Prior to the activity evaluation, 3 mL catalyst sample was in situ reduced in a gas mixture composed of N_2(30 mL/min) and H_2(30 mL/min) at 325 ℃ for 0.5 h, then cooled to 290 ℃ in 0.5 h and kept at the temperature for another 0.5 h. The loading of cobal toxide was 0.3 mmol/g.

1.2 Catalytic activity evaluation

The catalytic reaction was carried out in a fix-bed continuous flow glass reactor with inside diameter of 12 mm under normal atmospheric pressure. The reactor was placed vertically inside a tubular furnace and heated electrically. The reactor temperature was monitored by a thermocouple with its tip located at the catalyst bed and connected to a temperature indicator controller. The mixture of reactants (molar ratio of aniline/1,6-hexanediol=3 :1, SV=1 700 h^{-1}, LHSV=0.4 h^{-1}) was pumped through the preheater and vaporized, then entered into the reactor together with N_2(30 mL/min) and H_2(30 mL/min). The reaction was carried out at 290 ℃. The products were analyzed on a gas chromatograph with a mass spectrometer (Shimadzu GCMS-QP2010) using a DB-5 capillary column and a gas chromatograph connected to a hydrogen ame ionization detector (FID-GC, SP-6800A) using OV-17 column. The quantitative analysis of the reactants and products was carried out on the SP-6890A gas chromatograph equipped with an SE-54 capillary column. 1-Hexyl alcohol was used as an interior standard.

1.3 Catalyst characterization

X-ray diffraction (XRD) was recorded using a D8 advance diffraction meter with Cu Kα radiation source at a radiation rate of 0.5 °/min in the 2θ range of 30° ~ 80 °. The voltage and current were 40 kV and 40 mA, respectively.

Transmission electron microscopy (TEM) experiments were done on a JEM-2000EX electron microscope at the accelerating voltage of 50 kV. The samples were crushed and dispersed in alcohol and then spreaded on a holey carbon Cu microgrid. Particle size distribution was evaluated from several micrographs. The average particle size was estimated using the equation $d=\sum(n_i \cdot d_i)/\sum n_i$, where n_i was the number of particles with diameter d_i and $\sum n_i$ was the number of particles used to compute the size distribution.

The temperature programmed reduction (H_2-TPR) experiments were carried out in a quartz reactor with inside diameter of 6 mm and length of 350 mm. A 100 mg sample was pretreated in a flow ultrapure nitrogen gas of 50 mL/min at 100 ℃ for 1 h to remove water and other contaminants. TPR profiles were obtained by heating the sample under a 10% H_2/Ar flow (50 mL/min) from 50 to 700 ℃ at a linearly programmed rate of 10 ℃/min. The hydrogen consumption was recorded with a thermal conductivity detector.

The temperature-programmed-desorption of ammonia (NH_3-TPD) was carried out in a flow apparatus. The sample of 150 mg was pretreated at 500 ℃ for 1 h in a flow of ultrapure helium gas (30 mL/min) to remove water and other contaminants from the catalyst and cooled down to 100 ℃, then saturated with ammonia gas at 100 ℃. After the sample was purged with helium gas (30 mL/min) at 100 ℃ for 2 h to remove the physisorbed ammonia, the TPD was carried out from 100 to 700 ℃ with a temperature ramp of 10 ℃/min.

2 Results and discussion

2.1 The performance of CoO/SiO_2-Al_2O_3 doped with Na_2O or K_2O

For the reactions of aniline and 1,6-hexanediol over CoO-based catalysts, 1-phenylazepane was the main product from the results of GC-MS, oxacycloheptane was the primary by-product, besides, small amount of other by-products such as 2,3-dimethyl-1-phenylpyrrolidine, 2,3-dimethyl-3-ethyl-indoline, 4-methyl-2-anilino-cyclo-pentanone, etc, existed. Table 1 and 2 exhibit the activity and selectivity over CoO-Na_2O/SiO_2-Al_2O_3 and CoO-K_2O/SiO_2-Al_2O_3 with different Na_2O and K_2O amount. It can be seen that the conversion of 1,6-hexanediol was 100% over all CoO-based catalysts, but the selectivity of 1-phenylazepane was quite different. The selectivity of 1-phenylazepane increased after adding Na_2O to CoO/SiO_2-Al_2O_3, however, the selectivity of 1-phenylazepane decreased over CoO/SiO_2-Al_2O_3 doped with K_2O. Moreover, the selectivity of 1-phenylazepane first increased, then, decreased with the increase of Na_2O or K_2O amount, while, the selectivity of the by-product of oxacycloheptane increased. The best amount of Na_2O or K_2O was 0.20 or 0.15 mmol/g, respectively. Over CoO-Na_2O/SiO_2-Al_2O_3 with Na_2O amount of 0.20 mmol/g, the yield of 1-phenylazepane was up to 88.4%, whereas, the desired product attained a yield as high as 74.4% over CoO-K_2O/SiO_2-Al_2O_3 when the K_2O amount was 0.15 mmol/g.

Table 1 The activity and selectivity of CoO-Na_2O/SiO_2-Al_2O_3 with different Na_2O amount

Na_2O amount (mmol/g)	1,6-Hexanediol conversion (%)	Product selectivity (%)		
		1-Phenylazepane	Oxacycloheptane	Others
0.00	100	83.8	7.5	8.7
0.05	100	84.3	7.6	8.1
0.10	100	85.7	8.0	6.3
0.15	100	87.1	8.4	4.5
0.20	100	88.4	8.7	3.0
0.25	100	86.2	9.5	4.3
0.30	100	84.5	10.1	5.4

Reaction conditions: 290 ℃, SV = 1 700 h^{-1}, LHSV = 0.4 h^{-1}, aniline:1,6-hexanediol = 3 :1 molar ratio, H_2 = 21 mL/min, steam = 60 mL/min. The results were taken at the third hour.

Table 2 The activity and selectivity of CoO-K_2O/SiO_2-Al_2O_3 with different K_2O amount

K_2O amount (mmol/g)	1,6-Hexanediol conversion (%)	Product selectivity (%)		
		1-Phenylazepane	Oxacycloheptane	Others
0.00	100	83.8	7.5	8.7
0.05	100	69.3	15.9	14.8
0.10	100	71.5	16.6	11.9
0.15	100	74.4	17.1	8.5
0.20	100	72.0	18.3	9.7
0.25	100	69.3	19.4	11.3
0.30	100	66.1	20.3	13.6

Reaction conditions: 290 ℃, SV = 1 700 h^{-1}, LHSV = 0.4 h^{-1}, aniline:1,6-hexanediol = 3 :1 molar ratio, H_2 = 21 mL/min, steam = 60 mL/min. The results were taken at the third hour.

Table 3 shows the activity and selectivity of CoO/SiO_2-Al_2O_3 and Na_2O or K_2O doped- CoO/SiO_2-Al_2O_3 with different impregnation sequence when the amount of Na_2O or K_2O was 0.2 mmol/g or 0.15 mmol/g respectively. Among the CoO-based catalysts, the selectivity over the catalyst with first impregnating Na_2O or K_2O, then CoO was higher, whereas the selectivity over the catalyst with first impregnating CoO, then Na_2O or K_2O was lower.

Table 3 The activity and selectivity of CoO-based catalysts

Catalyst	1,6-Hexanediol conversion (%)	Product selectivity (%)		
		1-Phenylazepane	Oxacycloheptane	Others
CoO/SiO_2-Al_2O_3	100	83.8	7.5	8.7
CoO-Na_2O/SiO_2-Al_2O_3	100	88.4	8.7	3.0
CoO-K_2O/SiO_2-Al_2O_3	100	74.4	17.1	8.5
Na_2O-CoO/SiO_2-Al_2O_3	100	64.2	24.4	11.4
K_2O-CoO/SiO_2-Al_2O_3	100	52.6	28.6	18.8
Na_2O+CoO/SiO_2-Al_2O_3	100	67.8	21.7	10.5
K_2O+CoO/SiO_2-Al_2O_3	100	60.4	23.1	16.5

Reaction conditions: 290 ℃, SV = 1 700 h^{-1}, LHSV = 0.4 h^{-1}, aniline:1,6-hexanediol = 3 :1 molar ratio, H_2 = 21 mL/min, steam = 60 mL/min. The results were taken at the third hour.

2.2 Catalyst characterization

For the activity and selectivity over CoO/SiO_2-Al_2O_3 and Na_2O or K_2O doped-CoO/SiO_2-Al_2O_3 with first impregnating Na_2O or K_2O, then CoO were higher, the CoO-based catalysts were characterized to investigate and explain the relationship between the structure of the catalysts and their catalytic performances. Fig. 1 shows the XRD patterns of the fresh and the used catalysts when the amount of Na_2O or K_2O was 0.20 or 0.15 mmol/g, respectively. Three small CoO crystal diffraction peaks at 2θ of 36.5°, 42.4° and 61.5°, assigned to (111), (200) and (220) respectively[22], existed on the fresh catalyst of CoO/SiO_2-Al_2O_3. The same diffraction peaks were observed on the fresh CoO-Na_2O/SiO_2-Al_2O_3 or CoO-K_2O/SiO_2-Al_2O_3 and the intensity of the diffraction peaks increased a little.

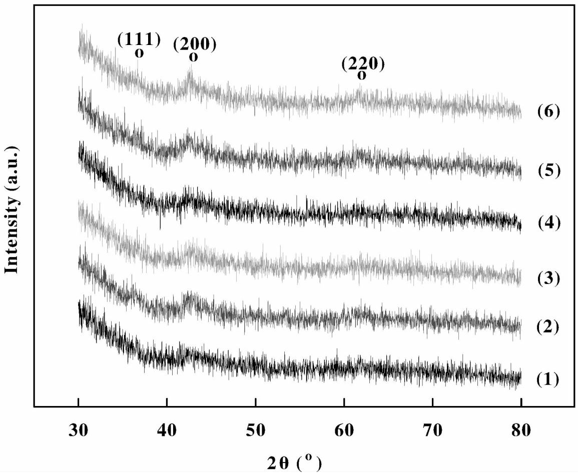

Fig. 1 XRD patterns of the fresh catalysts with CoO/SiO_2-Al_2O_3 (1), CoO-Na_2O/SiO_2-Al_2O_3 (2), CoO-K_2O/SiO_2-Al_2O_3(3) and the used catalysts with CoO/SiO_2-Al_2O_3 (4), CoO-Na_2O/SiO_2-Al_2O_3(5), CoO-K_2O/SiO_2-Al_2O_3(6)

On the used CoO-based catalysts, the intensity of CoO crystal diffraction peaks became stronger compared with the fresh catalyst. Moreover, the intensity of CoO crystal diffraction peaks on the used CoO-Na_2O/SiO_2-Al_2O_3 or CoO-K_2O/SiO_2-Al_2O_3 was stronger than that on the used CoO/SiO_2-Al_2O_3 and the intensity of CoO diffraction peaks on the used CoO-K_2O/SiO_2-Al_2O_3 was strongest.

Table 4 exhibits the average sizes of cobalt particles of the fresh and the used CoO-based catalysts tested by TEM technique. It can be seen that the average size of CoO particles became bigger after adding Na_2O

or K_2O to the fresh CoO/SiO_2-Al_2O_3, indicated that Na_2O or K_2O did not promote the dispersion of CoO particles on the support. On the used CoO-based catalysts, the average size of CoO particles became bigger compared with that on the fresh catalysts, revealed that there existed the sintering of CoO particles during the reaction. Furthermore, the average size of CoO particles on the used CoO-Na_2O/SiO_2-Al_2O_3 or CoO-K_2O/SiO_2-Al_2O_3 was bigger than that on the used CoO/SiO_2-Al_2O_3, revealed that Na_2O or K_2O did not inhibit the sintering of CoO particles. For the average size of CoO particles on the used CoO-K_2O/SiO_2-Al_2O_3 was bigger than that on CoO-Na_2O/SiO_2-Al_2O_3, it can be obtained that K_2O resulted in the sintering of CoO particles more easily.

Table 4 The average size of CoO particles on the CoO-based catalysts

Catalyst	The average size of CoO particle (nm)	
	Fresh sample	Used sample
CoO/SiO_2-Al_2O_3	12	14
CoO-Na_2O/SiO_2-Al_2O_3	14	16
CoO-K_2O/SiO_2-Al_2O_3	15	19

The reduction behavior of the calcined Co_3O_4/SiO_2-Al_2O_3 and the sample doped with Na_2O and K_2O was investigated by H_2-TPR and the profiles are shown in Fig. 2. No hydrogen consumption peak can be seen on the sample of Na_2O/SiO_2-Al_2O_3 or K_2O/SiO_2-Al_2O_3, indicated that the Na_2O or K_2O was not reduced during the temperature range. On the sample of Co_3O_4/SiO_2-Al_2O_3, two reduction peaks were observed, which was attributed to the reduction of Co_3O_4 to CoO[23]. From Fig. 1(1) it can be seen that the intensity of CoO diffraction peaks on CoO/SiO_2-Al_2O_3 was weak, it can be deduced that the reduction peak at lower temperature was the reduction of the bulk Co_3O_4 species and the peaks at higher temperature were attributed to the reduction of the dispersed Co_3O_4 particles. On the sample of Na_2O or K_2O doped-Co_3O_4/SiO_2-Al_2O_3, only one reduction peak existed, assigned to the reduction of bulk Co_3O_4 phase. The reduction peak of Co_3O_4 shifted towards the low temperature after adding Na_2O and K_2O to CoO/SiO_2-Al_2O_3, suggested that the interaction between Co_3O_4 and the support became weaker, as a result, Co_3O_4 particles were reduced and got together easily.

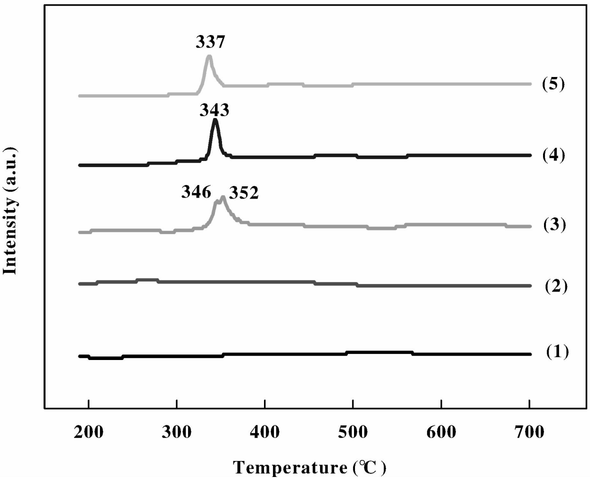

Fig. 2 H_2-TPR profiles of Na_2O/SiO_2-Al_2O_3 (1), K_2O/SiO_2-Al_2O_3 (2), Co_3O_4/SiO_2-Al_2O_3 (3), Co_3O_4-Na_2O/SiO_2-Al_2O_3(4) Co_3O_4-K_2O/SiO_2-Al_2O_3(5)

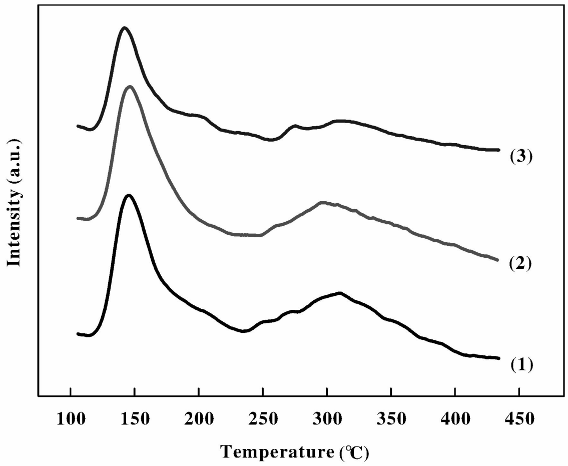

Fig. 3 NH_3-TPD profiles of CoO/SiO_2-Al_2O_3 (1), CoO-Na_2O/SiO_2-Al_2O_3(2) and CoO-K_2O/SiO_2-Al_2O_3(3)

The temperature-programmed-desorption of ammonia is usually used to characterize the acidic property of catalyst surface and the area of desorption peaks corresponds to the amount of acid sites of catalyst. From Fig. 3 it can be observed that two desorption peaks existed on the CoO-based catalyst. The peak at lower temperature (<200 ℃) was assigned to the weak acid sites, while, the other at higher temperature was corresponded to the middle-strong acid sites[24-26]. After adding Na_2O to CoO/SiO_2-Al_2O_3, the amount of weak acid sites increased, whereas, the amount of middle-strong acid sites decreased a little. On the catalyst of CoO-K_2O/SiO_2-Al_2O_3, both the amount of the weak acid sites and the middle-strong acid sites remarkably decreased, which indicated that K_2O could neutralize the acidity of the catalyst effectively.

For the synthesis of 1-phenylazepane from aniline and 1,6-hexanediol, the weak acid sites could facilitate the adsorption of reactants on the surface of the catalyst to synthesize 1-phenylazepane, while, the middle-strong acid sites took disadvantage of the reaction because it was difficult for 1-phenylazepane to desorb from the catalyst, as a result, the yield of 1-phenylazepane decreased. Because Na_2O could increase the amount of weak acid sites and decrease the amount of the middle-strong acid sites, the addition of Na_2O promoter improved the selectivity of the catalyst. Adding K_2O to CoO/SiO_2-Al_2O_3 decreased the amount of the weak acid sites remarkably, as a result, the selectivity of the catalyst was low. Considering the activity and selectivity over CoO/SiO_2-Al_2O_3, CoO-Na_2O/SiO_2-Al_2O_3 or CoO-K_2O/SiO_2-Al_2O_3, it seemed that CoO-based catalyst with small amount of middle-strong acid sites was favorable to the synthesis of the by-product of oxacycloheptane.

3 Conclusions

Na_2O promoter could enhance the selectivity of CoO/SiO_2-Al_2O_3, which the yield of 1-phenylazepane was up to 88.4%. The promoting effect of Na_2O stemmed from its ability to increase the amount of the weak acid sites and decrease the amount of the middle-strong acid sites. Adding K_2O to CoO/SiO_2-Al_2O_3 took disadvantage of the synthesis of 1-phenylazepane because the amount of weak acid sites decreased remarkably. Na_2O or K_2O did not promote the dispersion of CoO particles on the support. The addition of K_2O to CoO/SiO_2-Al_2O_3 resulted in the sintering of CoO particles more easily.

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Na_2O 或 K_2O 对气相合成1-苯基氮杂环庚烷的 $CoO/SiO_2\text{-}Al_2O_3$ 催化剂的作用

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摘 要：研究了 Na_2O 或 K_2O 对苯胺和1，6己二醇气相合成1-苯基氮杂环庚烷的 $CoO/SiO_2\text{-}Al_2O_3$ 催化剂的作用，并采用X射线衍射、透射电子显微镜、H_2-程序升温还原、NH_3-程序升温脱附等技术对催化剂进行了表征. 结果表明，Na_2O 助剂能增加催化剂的弱酸中心数，减少中强酸中心数，使催化剂的选择性得到提高. 加入 K_2O 使催化剂的弱酸中心数显著减少，并使CoO在反应过程中易于烧结，因此不利于1 -苯基氮杂环庚烷的合成.

关键词：Na_2O；K_2O；$CoO/SiO_2\text{-}Al_2O_3$；1-苯基氮杂环庚烷；气相合成