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Communication

Silica supported potassium oxide catalyst for dehydration of 2-picolinamide to form 2cyanopyridine

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Graphical Abstract



Si-O-K produced by the reaction of loaded K_2CO_3 with Si-OH was found to be the active species for the dehydration of 2-PA to 2-CP over K_2O/SiO_2 catalyst.

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ABSTRACT

The dehydration of 2-picolinamide to produce 2-cyanopyridine was investigated thoroughly using silica supported potassium oxide as a heterogeneous catalyst. Both large specific surface area and pore size of SiO₂ (B) contributed to the favorable catalytic performance for the synthesis of 2-CP. In addition, the yield of 2-CP showed the linear relationship with the amounts of medium basicity of the catalysts, demonstrating that medium basic sites were the active sites of silica supported potassium oxide catalysts. The catalysts were further characterized by XRD and FT-IR to clarify the active species. The results indicated the Si-O-K group produced by the reaction of K₂CO₃ with Si-OH was the active species, which was further evidenced by the adjustment of the amount of Si-OH by silylation and hydroxylation procedure.

The direct synthesis of dimethyl carbonate (DMC) from CO_2 and methanol over the CeO_2 catalyst has attracted wide attention because of its implications in CO_2 utilization and sustainable development [1]. However, the DMC yield is far from satisfactory due to the thermodynamics of the reaction, which is generally unfavorable owning to equilibrium limitation. According to the previous study [2, 3], 2-cyanopyridine (2-CP) can act as efficient dehydration agent by in situ hydrolysis, leading to the improvement of methanol conversion and DMC yield. Meanwhile, in terms of commercialization requirements and atom economy, it is also desirable for the recyclability of the 2-cyanopyridine by dehydrating 2-picolinamide (2-PA) back to 2-cyanopyridine.

As for the dehydration of primary amides to nitriles, classical dehydrating agents such as acidic (*e.g.*, P_2O_5 , $POCl_3$, $SOCl_2$) [4-6] and basic reagents (*e.g.*, NaBH₄) [7] are known to be effective. In addition to these dehydrating agents, many catalysts have also been reported to be applied for dehydration of amides to nitriles. For example, Stephan Enthaler reported various homogeneous catalysts such as Cu [8], Zn [9] and Fe ion for dehydration of amides to nitriles [10]. On the other hand, Kiyotomi Kaneda proposed V/HT catalyst [11] and Noritaka Mizuno applied lacunary silicotungstate as the efficient heterogeneous catalysts for the dehydration of amides [12].

However, there have been few papers reported on the dehydration of 2-picolinamide to 2-cyanopyridine [3, 9, 13-15]. Moreover, in most of these work, excess amount of dehydrating agents which are expensive and nonrenewable have been used for the dehydration of 2-picolinamide to 2-cyanopyridine, such as ethyl dichlorophosphate [13], *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide [9], trifluoromethane sulfonic acid anhydride and trimethylamine [14]. Although there was a report on U ion catalyzing the dehydration of 2-cyanopyridine, it has inevitably utilized dehydrating agents [15]. If catalytic dehydration of 2-picolinamide could be performed without any additives, it would be a green procedure for 2-cyanopyridine synthesis due to its high atom efficiency (only water is formed as a byproduct).

In this work, silica supported potassium oxide acting as a heterogeneous catalyst was developed for the dehydration of 2picolinamide to produce 2-cyanopyridine without any additives. The effect of catalyst preparation conditions on the catalytic activity was studied. XRD and FT-IR was employed to clarify the active sites of the catalyst. To gain the further insight into the importance of Si-OH to the formation of the active species, the adjustment of the amount of Si-OH was carried out by silylation and hydroxylation procedure.

The K_2O/SiO_2 catalyst was prepared by incipient wetness impregnation method. SiO₂ (A), SiO₂ (B) and SiO₂ (C) with the different specific surface area and the pore size distribution were adopted as the supports, respectively. Before being impregnated with potassium carbonate, the commercially available silica supports were heated at 700 °C in order to dehydroxylate hydrogen-bonded Si-OH to obtain more free Si-OH group. Then an aqueous solution of K_2CO_3 was slowly added to the support, with rapid stirring at room temperature. Different loadings were achieved by adjusting the amount of K_2CO_3 . After being evaporated and dried at 110 °C for 12 h, the catalyst was then calcined in air at various temperatures for 3 h. The sections of silica surface modification, catalyst characterization and activity tests are presented in Supporting information.

Three kinds of silica were employed as the supports. Fig. S1 (Supporting information) gives the N₂ adsorption–desorption isotherms and pore-size distribution of the different supports. For the mesoporous and microporous supports, the pore sizes were calculated from the desorption branch of the isotherm using the BJH model and HK model, respectively. The specific surface areas were calculated by Barrett-Emmett-Teller (BET) equation. As illustrated in Fig. S1(a) (Supporting information), the type IV patterns of the adsorption curves of SiO₂ (B) and SiO₂ (C) suggested the typical hysteresis loop of mesoporous materials according to the classification of the International Union of Pure and Applied Chemistry (IUPAC) [16]. For SiO₂ (A), at the low pressure, the adsorption–desorption curves showed the existence of microporous structure. The pore size distribution in Fig. S1(b) (Supporting information) verified the different mesopore sizes and micropore sizes for these three kinds of silica [17,18]. SiO₂ (A) and SiO₂ (B) had a narrow Gaussian-like unimodal pore size distribution. Nevertheless, SiO₂ (C) showed a broad distribution.

The pore diameter, specific surface area and pore volume of the different supports were listed in Table S1 (Supporting information). As it showed, the average pore diameters of SiO₂ (A), SiO₂ (B) and SiO₂ (C) were 1.1, 5.5 and 8.7 nm, respectively. And the specific surface areas of SiO₂ (A), SiO₂ (B) and SiO₂ (C) were 479, 578 and 330 m²/g. The specific surface area decreased in the order SiO₂ (B) >SiO₂ (A) >SiO₂ (C). The order of pore size was as following: SiO₂ (C) >SiO₂ (B) >SiO₂ (A). Table S2 (Supporting information) listed the textural information of 0.8K/SiO₂ (B) catalyst calcined at different temperature. As calcination temperature increased, the pore diameter increased and the specific area decreased dramatically.

As shown in Fig. 1(a), He-TPD was performed to examine the amount of residual K_2CO_3 of the 0.8K/SiO₂ (B) catalysts calcined at different temperatures, which was induced by the slow decomposition rate of the catalysts [19]. CO₂-TPD was employed to evaluate the basicity of the samples calcined at different temperatures as illustrated in Fig. 1(b). It was noted from Fig. 1(b) that, desorption peaks were divided into four parts. Peak 1 at around 100 °C corresponded to the physical adsorption of CO₂. Peak 2 centered at approximately 200 °C was attributed to weak basicity of SiO₂ (B) [20,21]. The peaks at around 400 °C and 650 °C, denoted as peak 3 and peak 4, respectively, were attributed to medium and strong basicity. Peak 3 was derived from reactions of basic species with siliceous supports while peak 4 originated from the production of K₂O caused by the decomposition of bulk phase of K₂CO₃ [22].

However, in light of the slow decomposition rate of the 0.8K/SiO₂ (B) catalysts, the catalysts calcined at different temperatures may not decompose completely after calcination. Furthermore, as Yamaguchi reported [18], supported K₂CO₃ can release CO₂ at around 400 °C and 750 °C which were close to the positions of peak 3, and peak 4 of CO₂-TPD. Therefore, it indicated that when calculating the amounts of medium basicity and strong basicity of the catalysts, the amount of CO₂ produced by the decomposition of loaded K₂CO₃ should be subtracted. Hence, decomposition peaks in Fig. 1(a) were divided into four parts in accordance with Fig. 1(b) in order to calculate the amount of basicity. For the peak at around 650 °C, denoted as peak 4 in Fig. 1(a), it corresponded to the decomposition of the bulk phase of K₂CO₃[19]. Moreover, for the two temperature branches from 200 °C to 500 °C, denoted as peak 2 and peak 3, CO₂ was produced by the reaction between K₂CO₃ and Si-OH which gave rise to the medium basic sites [22]. The peak centered at 100 °C was assigned to weak adsorption interaction between CO₂ and the catalyst



Fig. 1. (a) He-TPD profiles of the samples calcined at different temperatures, (b) CO₂-TPD profiles of the samples calcined at different temperatures.

The data of He-TPD and CO₂-TPD were demonstrated in Table S3 (Supporting information). The basicity was calculated by eqs. (1) and (2) assuming that the peak area of CO₂ desorption peak in CO₂-TPD was proportional to the basicity amount. As calcination temperature increased from 250 °C to 500 °C, the total peak area of peak 2 and peak 3 and peak 4 in Fig. 1(a) decreased which means the catalysts were decomposed more completely. Meanwhile, when the calcination temperature increased from 250 °C to 300 °C, the amount of medium basic sites of Fig. 1(b) increased because of more K₂CO₃ reacting with Si-OH. Nevertheless, when it increased from 300 °C to 500 °C, the medium basicity decreased. As mentioned in Fig. 1(a), reaction of potassium carbonates species with siliceous supports proceeded from 200 °C to 300 °C to form medium basicity, while above 300 °C more potassium carbonates decomposed into potassium oxide contributing to the increase of the amount of strong basicity. Hence, when the calcination temperature was above 300 °C, more potassium carbonates were decomposed into potassium oxide instead of reacting with Si-OH contributing to the medium basicity. Therefore, the catalyst calcined at 300 °C had the maximum medium basic sites. When the calcination temperature was higher than 300 °C, the amounts of medium basicity decreased.

In order to identify the nature of active sites, the catalysts were characterized in depth. Fig. 2 displays the XRD patterns of the SiO₂ (B) supported potassium oxide catalysts with different loadings. The sample loading K of 0.8 mmol/g had the same XRD patterns as the parent amorphous silica, and neither any characteristic peaks of K₂CO₃ (JCPDS NO. 16-0820) nor any new phase such as K₂O (JCPDS No. 26-1327) was noticed, indicative of finely dispersed active sites on SiO₂. When the loading amount of K increased to 5.1 mmol/g, characteristic peak of K₂CO₃ was observed and the new phase attributed to potassium silicate (Si-O-K) (JCPDS No. 49-0163) appeared. It is likely that on the surface of fully hydroxylated silica, K⁺ ions replaced the protons of isolated hydroxyl groups to form Si-O-K groups (K₂CO₃ + 2Si-OH \rightarrow 2 Si-O-K + H₂O+CO₂) [22-24], which was considered to be the active basic species.



Fig. 2. XRD patterns of the K₂O/SiO₂ catalysts with different loading amounts.

Fig. 3 shows the comparison of FT-IR spectrum of $0.8K_2CO_3/SiO_2$ (B) (without calcination) and $0.8K_2O/SiO_2$ (B) (calcined at 300 °C for 3 h). The existence of the vibration band centered at 3740 cm⁻¹ in the FT-IR spectrum implied that the K_2CO_3/SiO_2 (B) sample possessed abundant free OH groups [25]. And the band at 3650 cm⁻¹ was assigned to non-linearly H bonded vicinal OH groups [26]. The band at 1560 cm⁻¹ referred to the bidentate carbonate species [23]. Obviously, weakened vibration band of free OH groups was observed for K_2O/SiO_2 (B) after calcination. Meanwhile, the decomposition of carbonate occurred with the disappearance of the band at 1560 cm⁻¹ for K_2O/SiO_2 (B). On the other hand, it was noted that the band at 1393 cm⁻¹ appeared. It may be attributed to the newly

generated Si-O-K group of potassium silicate, which may be the active species. It indicated Si-O-K was formed by the reaction between K_2CO_3 and free silanol group on silica surface. In a word, Si-OH played crucial role in the formation of Si-O-K. This point will be further discussed with the surface modification of the support.



Fig. 3. FT-IR spectra of different samples.

The series of catalysts were tested in dehydration of 2-picolinamide to produce 2-cyanopyridine. Fig. S2 (Supporting information) shows the effect of the loading amount of K_2CO_3 on the yield of 2-CP. Obviously, the optimum K loading amount was found to be 0.8 mmol/g. Initially, the yield increased notably with increasing K loading amount from 0.3 mmol/g to 0.8 mmol/g. About 20.4% yield of 2-CP was observed for 0.8K/SiO₂ (B) at 10 h. However, further increase of K to 2.0 mmol/g lowered the yield of 2-CP. It is probable that for finely dispersed K₂CO₃ on silica support, the interaction between K₂CO₃ and the surface of support weakens the combination of K⁺ and CO₃²⁻ ions, which is helpful to the decomposition of K₂CO₃ and further formation of Si-O-K active sites [27]. At low loading of K₂CO₃, the active basic sites were more finely dispersed on the silica surface but the amount of active sites was limited, resulting in rather low catalytic activity of 0.3K/SiO₂ (B). Thus, with the increase in the loading amount of K₂CO₃ loaded, the K₂CO₃ may not be dispersed well on silica and, consequently, a part of the loaded K₂CO₃ could not be decomposed after calcination. More importantly, the excess K₂CO₃ could cover the active base sites. And for this reason, catalytic activity was lowered with further increase in the loading amount of K₂CO₃ species favors the dehydration of 2-PA. Therefore, based on the superior catalytic activity, 0.8 mmol/g was found to be the optimum K loading amount.

Table S4 (Supporting information) depicts the influence of different kinds of silica supports on catalyst performance. Catalyst loaded on SiO₂ (A) reached the lowest 2-CP yield of 6.9% and catalyst loaded on SiO₂ (C) showed the yield of 18.0%. While the yield of 23.6% was observed for catalyst loaded on SiO₂ (B), showing that SiO₂ (B) was preferred support. Large specific surface area is beneficial for the dispersion of active sites. Consequently, catalyst supported on SiO₂ (B) which had largest specific surface area among these three supports reached the best yield of 2-CP. Although the specific surface area of SiO₂ (A) was larger than SiO₂ (C), the activity of catalyst supported on SiO₂ (A) was lower than catalyst supported on SiO₂ (C) instead. It was assumed that the diffusion of reactant 2-PA and product 2-CP was restricted by the narrow micropores of SiO₂ (A) because of their large molecular diameters. Therefore, both large specific surface area and pore size of SiO₂ (B) contributed to the good catalyst performance, in contrast, small specific surface area (SiO₂ (C)) and narrow micropores (SiO₂ (A)) induced lower catalyst activity for the synthesis of 2-CP.

Particularly, the effect of calcination temperature on the 0.8K/SiO₂ (B) catalyst activity was also investigated in depth. As depicted in Fig. S3 (Supporting information), the catalyst calcined at 300 °C reached the best performance of 23.6%. When the calcination temperature was higher than 300 °C, the catalyst activity decreased. Although the catalysts calcined at 250 °C and 300 °C had almost the same specific area and pore diameter as illustrated in Table S2 (Supporting information), the catalyst calcined at 300 °C had better performance. Hence, it can be deduced that there was other factor determining the catalyst activity. Remarkably, the yield of 2-CP showed linear relationship with amounts of medium basicity expressed by the peak area determined by CO₂-TPD as shown in Fig. 4, indicating that the medium basic sites derived from Si-O-K which was produced by the reactions of loaded K₂CO₃ with siliceous supports were the active sites. Therefore, the uniquely high catalytic activity of the catalyst calcined 300 °C originated from the maximum medium basicity of the catalyst.



Fig. 4. The linear relationship between the amount of medium basicity and catalyst activity.

In order to further clarify the importance of Si-OH to the formation of active species, the surface modification of SiO₂ was performed to alter the amount of Si-OH. The silvlation and hydroxylation of SiO₂ (B) were employed to reduce and increase the amount of silanol groups, respectively. As Table S5 (Supporting information) shows, the activity of the catalysts 0.8K/Sil-SiO₂ (B) was lowered than that of 0.8K/SiO₂ (B) whereas the performance of 0.8K/SiO₂ (B)-OH increased to 26.3%.

It was also noted from Table S5 (Supporting information) that the changes in pore diameter and specific surface area of the 0.8K/SiO₂ (B)-OH catalyst were negligible compared to 0.8K/SiO₂ (B), whereas the specific surface area of 0.8K/SiO₂ (B) was much larger. It is likely that the silylation of SiO₂ (B) prevented the reaction between K₂CO₃ and Si-OH and avoided the structure collapse of SiO₂ (B) [20].

Fig. 5(b) shows the FT-IR spectra of different supports in the range of 4000-2600 cm⁻¹. For silylated silica, a new adsorption band appears at 2960 cm⁻¹ corresponding to the C-H stretching vibration. It implies $-CH_3$ was covalently bonded to silica particles [28]. Moreover, the Si-OH adsorption band at 3740 cm⁻¹ which was of importance to the formation of active species weakened, indicating the reaction between Si-OH and HMDS on the surface of SiO₂(B) occurred [25]. It was proved that the free Si-OH decreased, which was induced by the silylation of SiO₂(B). For hydroxylated silica, comparatively, it is obvious that Si-OH adsorption band at 3740 cm⁻¹ increased dramatically [29], indicating the increase of the amount of free Si-OH.

Fig. 5(a) shows the weight loss curves of the as-synthesized silvlated $SiO_2(B)$ sample. The thermal stability and surface group of the silica were tested in the range of 40 °C to 600 °C. The sample started to lose weight dramatically from 450 °C to 500 °C which corresponded to the oxidation of surface Si–CH₃ groups [30], which is in concordance with the result of FT-IR.



Fig. 5. (a) TG curves of different supports, (b) FT-IR spectra of different supports.

Fig. 6 shows the He-TPD and CO_2 -TPD results of $0.8K/sil-SiO_2$ (B) and $0.8K/SiO_2$ (B)-OH catalysts. The same calculation method as mentioned above was employed to evaluate the medium basicity. The peak areas of medium basicity for $0.8K/sil-SiO_2$ (B) and $0.8K/SiO_2$ (B)-OH were 0.22 and 1.22, respectively. Therefore, it can be deduced that the amount of Si-OH affected the amount of medium basicity of the catalysts. For hydroxylated silica, the free silanol increased causing the increased medium basicity which contributed to the higher catalyst activity. For silylated silica, the decreased Si-OH led to the fewer medium basicity and lower catalyst activity. It can be concluded that the surface Si-OH reacted with K_2CO_3 to form the active species Si-O-K. The catalyst performance was directly related to the amount of free silanol.



Fig. 6. (a) He-TPD profiles of different samples, (b) CO₂-TPD profiles of different samples.

In conclusion, silica loaded with potassium carbonate was demonstrated to be a medium solid-base catalyst for the dehydration of 2-picolinamide to form 2-cyanopyridine. The catalyst prepared by loading 0.8 mmol/g K on SiO₂ (B) after calcination at 300 °C for 3 h was found to be the optimum catalyst, which can give the highest medium basicity and the best catalytic activity reaching 23.6% yield of 2-CP. The catalytic activities of the catalysts showed a striking correlation with their corresponding amounts of medium basic sites. The decomposition products of the loaded K_2CO_3 were either K_2O species or Si-O-K group in the composite. Si-O-K group acting as medium basicity was probably the active basic sites for dehydration of 2-picolinamide to 2-cyanopyridine. The adjustment of the amount of Si-OH by silylation and hydroxylation procedure provided further evidence that Si-O-K was the active species. For hydroxylated silica, the medium basicity increased with the increase of free silanol which contributed to the higher catalyst activity. For silylated silica, the decreased Si-OH led to the fewer medium basicity and hence lower catalyst activity.

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