

Potassium Modified Carbon Nitride as a Highly Efficient and Recyclable Catalyst in Knoevenagel Reaction

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Research Article

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Abstract

A simple calcination method has been developed to prepare potassium-doped carbon nitride (K-CN). The prepared K-CN was characterized and analyzed by fourier infrared spectroscopy (FT-IR), powder X-ray diffraction technology (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and other techniques. It has been proved to be a green and recyclable catalyst for Knoevenagel condensation of benzaldehydes with malononitrile. The reaction system has the characteristics of mild reaction conditions, simple operation, and environmental protection. The catalyst still maintains high catalytic activity and excellent chemical stability after being recycled for six times.

1. Introduction

With the increasing awareness of sustainable development, tremendous efforts have been devoted to the development of green synthetic method so as to minimize chemical waste (Chen et al. 2020). As the core part of various chemical reactions, catalysts play a pivotal role in the reaction process. The appropriate design and careful selection of heterogeneous catalysts can considerably improve the organic transformations (Gao et al. 2020; Paprocki et al, 2020).

The Knoevenagel reaction is the condensation reaction of a methylene compound with aldehyde or ketones to construct C=C bond (Zhang et al. 2016; Gilanizadeh et al. 2018). under weak alkaline conditions, which as leading to α,β -unsaturated compounds. The α,β -unsaturated compounds produced by the reaction have very important applications in many aspects such as medicines (Kraus et al. 1986), cosmetics (Yu et al. 2000), perfumes (Schneider et al. 2015), natural products (Tavakolian et al. 2019) and fine cosmetics (Huang et al. 2020). Traditionally, stoichiometric amounts of homogeneous bases, such as hydroxides and methoxides have been used as catalysts for this conversion. Considering the problems of separation and recycling, compared with homogeneous basic catalysts, heterogeneous basic catalysts are undoubtedly preferred (Wei et al. 2018). Although this reaction has been extensively studied, the reported use of expensive metal catalysts in the catalytic system (Şen et al. 2018). the cumbersome preparation of heterogeneous catalysts (Zhang et al. 2018; Tran et al. 2011; Liu et al. 2016) and the use of non-green solvents have restricted the large-scale application of this reaction (He et al. 2016). Therefore, in line with the concept of green chemistry, it is necessary to a catalytic system using cheap heterogeneous catalysts and green solvents.

Carbon nitride (g-CN), as a new type of carbon material composed of nitrogen and carbon, has attracted the attention of researchers because of its unique and interesting physicochemical properties such as high stability, nontoxicity, metal free organocatalyst, environmentally benign photocatalysts and simple fabrication from cheap raw materials without any additive. It has shown great application prospects in photocatalysts (Khan et al. 2016), degrade pollutants (Pawar et al. 2015) and hydrogen storage materials (Chen et al. 2014). Chemically, carbon nitride itself is an inert material under common acidic or alkaline conditions. The surface basic functions of bare g-CN materials are relatively less and it can not catalyzed Knoevenagel condensation reactions without any modification. Therefore, there has been much effort

devoted to designing and fabricating g-CN materials for improving its catalytic activity. A mesoporous g-CN (MCN) as metal-free base catalyst has been designed with hexagonal platelet morphology by using melamine as C and N source and INC-2 as hard template, wherein MCN materials exhibited efficiently catalytic activity for Knoevenagel condensation reactions under microwave irradiation (Ansari et al. 2012). After the pretreatment of deprotonation by ^tBuOK or KOH solution, the g-CN materials exhibited higher catalytic activity for various Knoevenagel condensation as well as transesterification reactions (Su et al. 2012). It has been demonstrated that the introduction of triazole moieties in the MCN structure significantly enhances the basic catalytic activity (Ruban et al. 2021). However, the reported procedure for Knoevenagel condensation reaction faces the disadvantages of high temperature, long reaction time and most of these catalysts can not be fully recovered. In addition the above fabrication methods are not efficient and not suitable for large-scale industrial applications. However, such materials for Knoevenagel condensation faces the disadvantages of high temperature and long reaction time, and most of these catalysts cannot be fully recovered. In addition, the aforementioned manufacturing methods are not efficient and are not suitable for large-scale applications. From both practical and sustainable points of view, it is highly desired to develop a readily usable, stable and effective g-CN catalyst that can promote Knoevenagel condensation under mild conditions.

Considering these points and based on our research interest in the development of environmentally friendly synthetic methodologies (Zhang et al. 2017; Han et al. 2018; Di et al. 2021), herein, we report on the preparation of a potassium-doped C₃N₄ (K-CN) basic catalyst and its application as a catalyst for the Knoevenagel condensation of benzaldehydes with malononitrile at room temperature.

2. Experimental

2.1 All chemicals and solvents were obtained commercially and were used without further purification.

The reactions were monitored by thin layer chromatography (TLC) using silica gel GF₂₅₄. Melting points were determined on an X-5 melting point apparatus and were uncorrected. IR spectra were recorded on Thermo Fisher iS50 spectrometer with KBr pellets in the range of 400–4000 cm⁻¹. NMR spectra were recorded on a Zhongke Niujin AS 400 spectrometer using TMS as an internal standard. Mass spectra were performed on a 3200 Qtrap instrument with an ESI source. Column chromatography was performed on silica gel (200 – 300 mesh).

2.2 Synthesis of carbon nitride

Carbon nitride was obtained by directly heating dicyandiamide in an alumina crucible with a cover at a rate of 5°C/min to 550°C and keeping it in an air atmosphere for 4 h. After cooling to room temperature, the obtained light yellow solid was uniformly ground in an agate mortar.

2.3 Synthesis of K-CN

The mixture of 10.0 g dicyandiamide and 1.0 g KI was grounded in an agate mortar and then transferred to an alumina crucible with a cover. The temperature was raised to 550°C at a heating rate of 5°C/min and kept in an air atmosphere for 4 hours. After cooling to room temperature, the resulting bright yellow solid was ground into a powder with an agate mortar. The powder was washed with a large amount of distilled water to remove unreacted KI. Then the pure K-CN was dried overnight at 80°C.

2.4 General procedure for Knoevenagel condensation reaction

In a reaction tube equipped with a magnetic stir bar, 1 mmol aldehyde, 1 mmol malononitrile and 10 mg K-CN were added to ethanol/water (1:1, 3 mL). The reaction mixture was stirred at room temperature for an appropriate time. After the reaction was completed (monitored by TLC), the formed product was filtered off and washed with ethanol. The product obtained from the above reaction also contained some amount of K-CN catalyst which was separated by dissolving the product in ethyl acetate and followed filtration. Pure products were obtained by evaporation of the solvent, followed by column chromatography on silica gel using ethyl acetate/hexane as the eluent.

3. Results And Discussions

Solid basic K-CN catalyst is formulated by a facile hydrothermal route using dicyandiamide and KI precursors. The obtained solid in pale yellow color K-CN was thoroughly analyzed by physicochemical characterization techniques.

Through the infrared spectrum, the g-CN samples doped with potassium was found to have peaks related to the typical C_3N_4 heterocyclic skeleton vibration. This shows that doping will not cause changes in its chemical structure. As shown in Fig. 1. The breathing mode of the tri-s-triazine system exhibits a sharp peak at 812 cm^{-1} corresponding to the breathing mode of the tri-s-triazine units (Fang et al. 2015). The stretching vibration mode of C-N/C = N in the tri-s-triazine heterocyclic rings results in an obvious strong absorption peak at $1160\text{--}1648\text{ cm}^{-1}$ (Gao et al. 2017). The terminal amino group and the absorbed water result in the formation of a wider energy band between $3300\text{--}3600\text{ cm}^{-1}$, which is caused by N-H and O-H (Guo et al. 2017). It is worth noting that, unlike the usual g-CN, due to the introduction of KI, there is a very obvious peak at 992 cm^{-1} , which can be attribute to melem (Zhang et al. 2015). In addition, the energy band formed between N and the doped metal K causes the tensile vibration of the azide group, which makes K-CN have a very obvious absorption peak at 2179 cm^{-1} (Guo et al. 2016).

The C_3N_4 and K-CN were characterized by powder ray diffraction (XRD). The result is shown in the Fig. 2. There is a strong diffraction peak at 27.6° , which is caused by the stacking of the (002) plane. The weak diffraction peak caused by the repeating unit of the heptane ring is also found at 13.2° (Han et al. 2015).

The above results show that when potassium is doped, the structure of g-CN does not change significantly.

The structure of the prepared K-CN was further observed by scanning electron microscope. As shown in the Fig. 3, the doping of potassium element did not cause the morphology of g-CN to change, and K-CN still had a typical layered structure. Even after several cycles of reused, the morphology has not changed significantly. This shows that the prepared K-CN has good chemical stability.

In addition, elemental analysis of the prepared K-CN showed that the catalyst contained three elements of K, C, and N (Fig. 4). The test results of mapping further confirmed this conclusion (Fig. 5).

The microstructure of K-CN was further observed by transmission electron microscope (TEM). The result is shown in Fig. 6. It can be seen from the TEM image that the potassium-doped carbon nitride has a layered structure similar to that of pure g-CN.

In order to test the catalytic activity of the prepared K-CN, the Knoevenagel reaction between benzaldehyde and malononitrile was tested as a model reaction. As illustrated in Table 1, various solvents including CH_2Cl_2 , CH_3CN , ethyl lactate (EL), MeOH, H_2O , EtOH and EtOH/ H_2O were screened (Table 1, entries 1–7). Among them, a mixed solvent of EtOH/ H_2O gave the best result for achieving a maximum yield of product **3a** (Table 1, entry 7). Subsequently, the reaction temperature was screened, and it was found that the increase of the reaction temperature was only helpful for increasing the reaction rate, but had no effect on the yield (Table 1, entry 8). Furthermore, decreasing the amount of the catalyst to 5 mg reduced the yield to 63% (Table 1, entry 9). Increasing the amount of catalyst has no significant effect on the reaction yield (Table 1, entry 10). In addition, shortening the reaction time was not beneficial to the reaction. It is worth noting that expected product **3a** was obtained with a low yield of 25% when pure g-CN was used as the catalyst (Table 1, entry 13). It was found that almost no target product was detected when the reaction mixture was stirring for 1 h at room temperature in the absence of catalyst (Table 1, entry 14). To evaluate the practicability of this method, we conducted best synthesis conditions of **3a** on a 20-mmol scale and finally obtained 97% yield pure product (Table 1, entry 15).

With the optimal conditions in hand (Table 1, entry 7), the generality of the developed synthetic protocol for various aryl aldehydes was examined. As shown in Table 2, various substituted benzaldehydes bearing electron-donating or electron withdrawing groups reacted with malononitrile, furnishing the desired products in excellent yields. Furthermore, it was observed that the position of the substituent on the benzene ring did not significantly affect the reaction. Additionally, heterocyclic aldehydes such as thiophene-2-carboxaldehyde and 5-methylfurfural were also worked well without any structural damage, affording the corresponding products **3k** and **3l** in high yield. In addition, the reactions worked also well when more bulky 1-naphthyl, 2-naphthyl-derived aldehydes and 9-anthracenealdehyd was used as a substrate.

The recyclability of the catalyst is one of the important indicators for investigating heterogeneous catalysts. In this reaction system, the catalyst can be separated by simple filtration, wash it with EtOH

three times and then dry it, which can be used in the next experiment. The results show that after 6 cycles of testing, the prepared K-CN still maintains high catalytic activity (Fig. 7). After the sixth cycle, the reused catalyst was analyzed by FTIR. The result showed that the catalyst fully maintained its chemical integrity by comparing its FTIR spectra with fresh catalyst (Fig. 1). The above results indicate that K-CN has good chemical stability and catalytic activity, and can be used many times in catalytic conversion.

The comparison of this reaction system and other reported Knoevenagel condensation between benzaldehyde and malononitrile is listed in Table 3. As can be seen in Table 3, the present catalytic system is an equally or more efficient to those previously reported for this reaction in respect of the reaction time and yield.

4. Conclusion

In conclusion, potassium modified carbon nitride (KCN) has been prepared and characterized using a variety of different techniques, including FT-IR, XRD, EDX, TEM and SEM. A. The KCN exhibits high catalytic activity toward Knoevenagel condensation with a broad substrate under mild reaction condition. This method avoids the use of expensive catalysts or strong bases. Furthermore, the catalyst is very stable under the reaction conditions and can be easily recovered and reused for six cycles without any decrease in the catalytic activity. This new approach meets the requirements of green chemistry and opens a new avenue for the development of more sustainable organic reactions.

Declarations

Acknowledgements

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Tables

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Figures

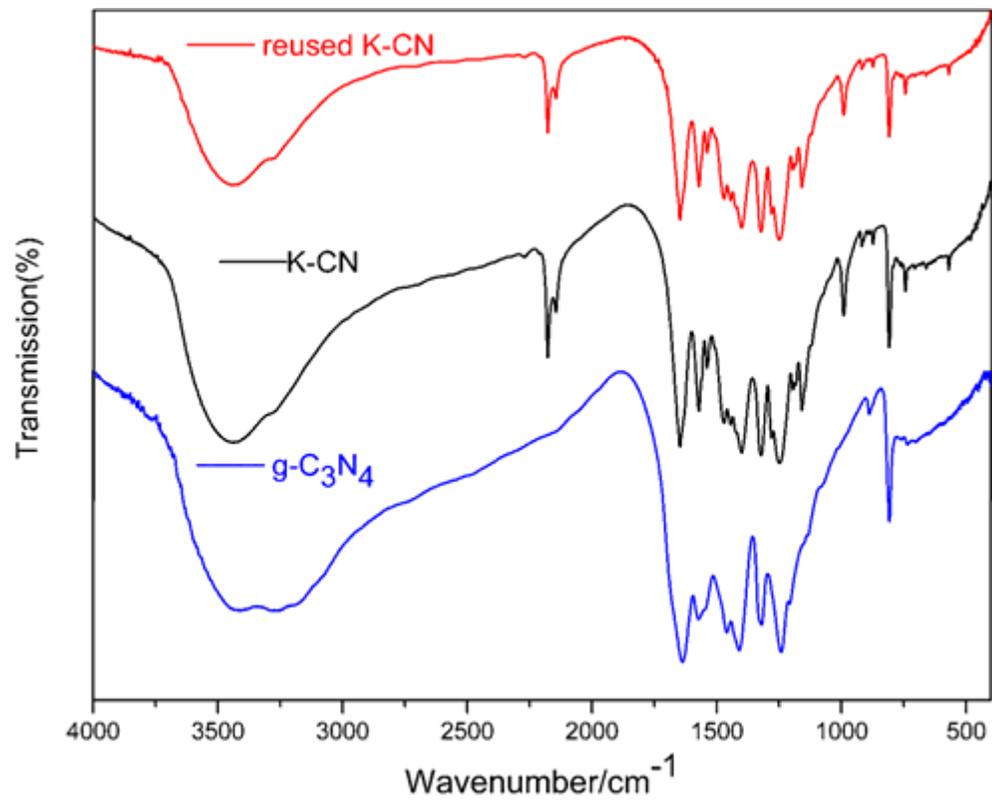


Figure 1

The FT-IR spectra of C₃N₄, K-CN and reused K-CN

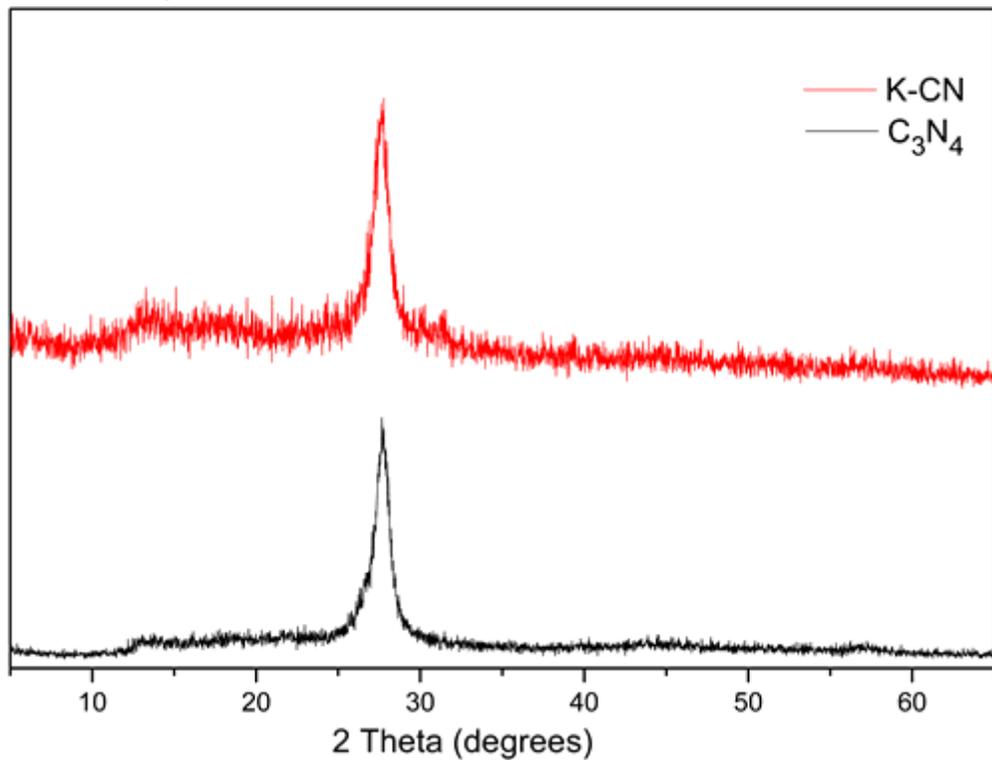


Figure 2

The XRD patterns of g-CN and K-CN

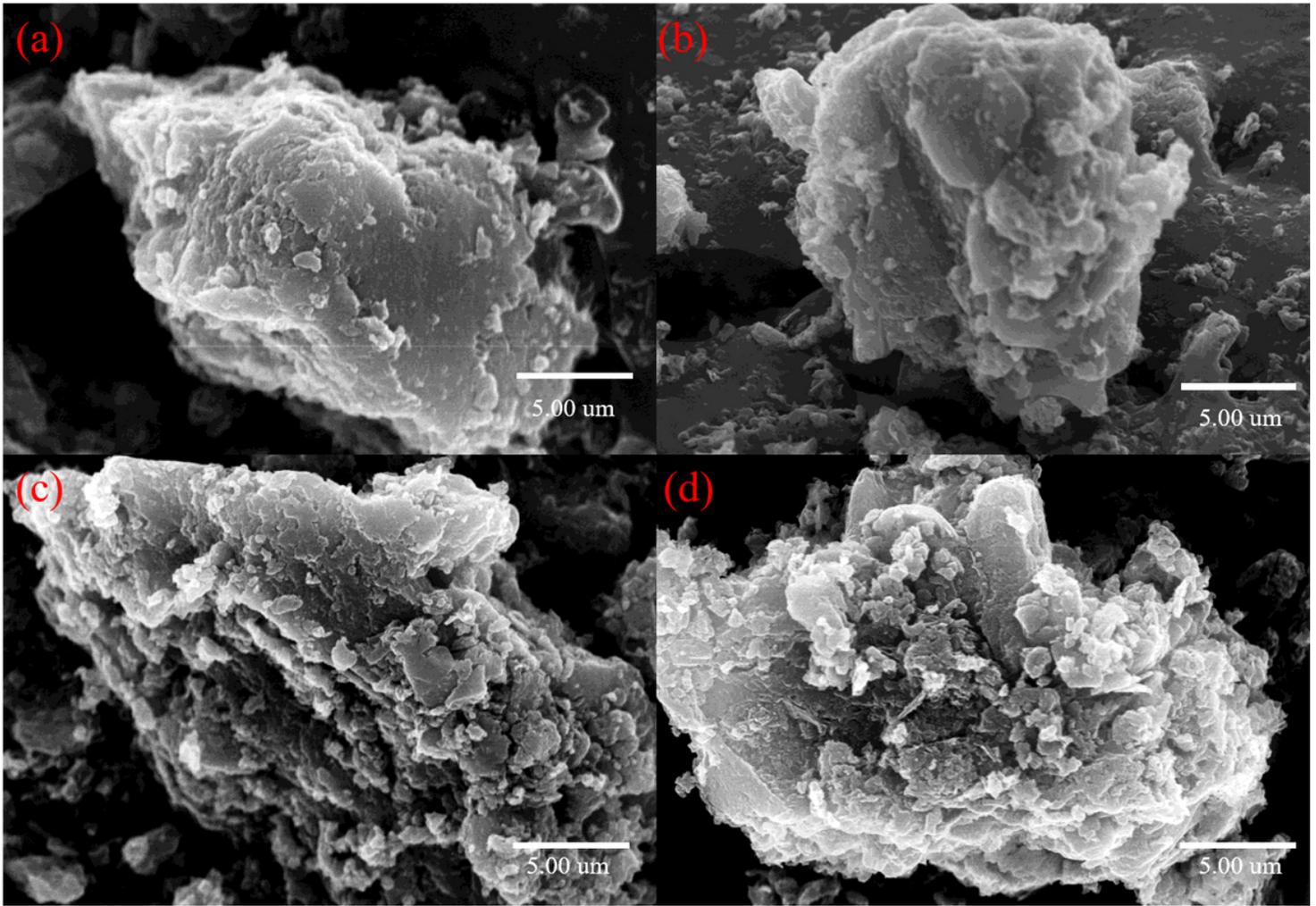


Figure 3

SEM images of K-CN (a, b) and reused K-CN(c, d)

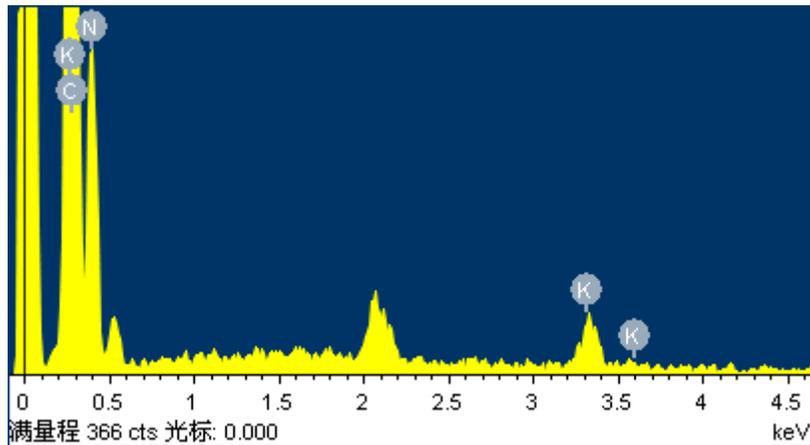


Figure 4

EDX spectra of K-CN



Figure 5

Elemental mapping of K-CN

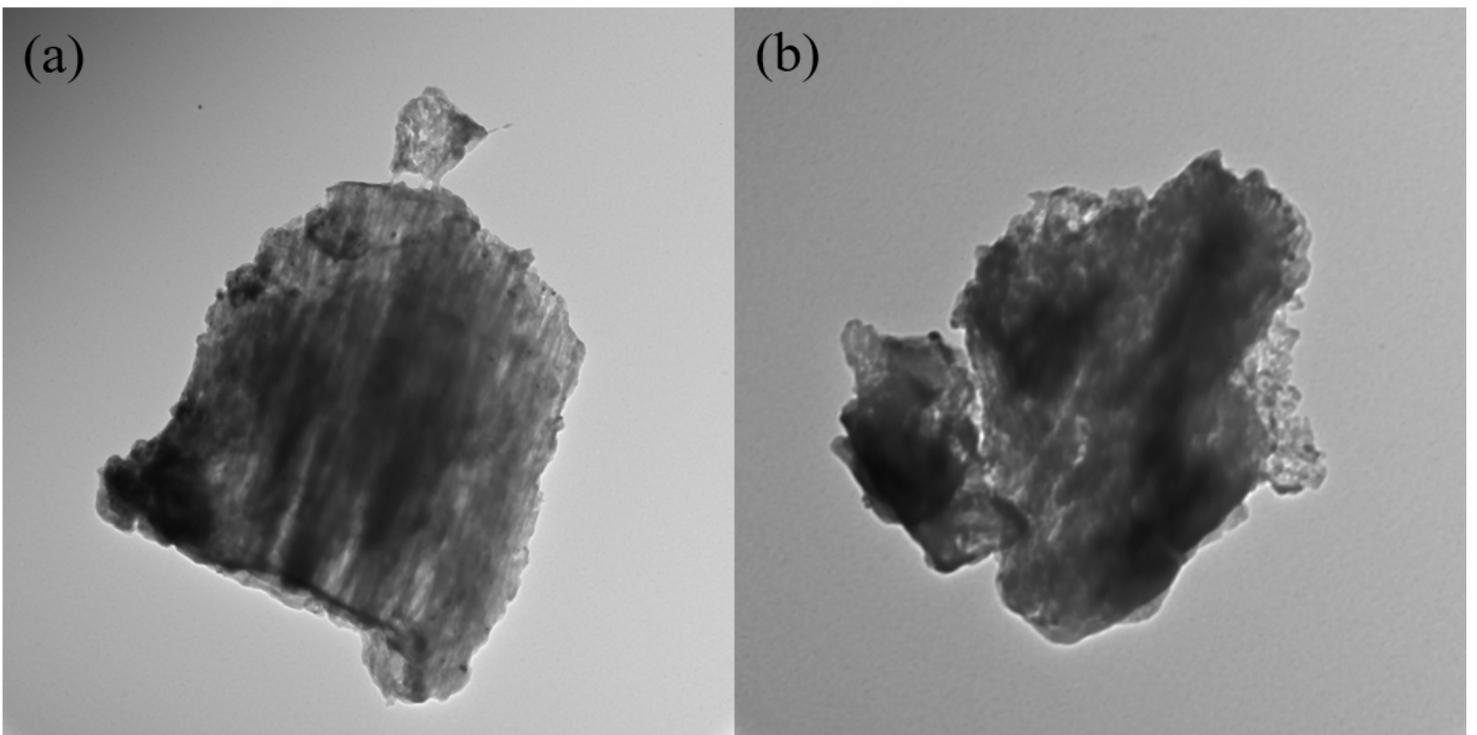


Figure 6

TEM images of K-CN (a) and reused K-CN(b)

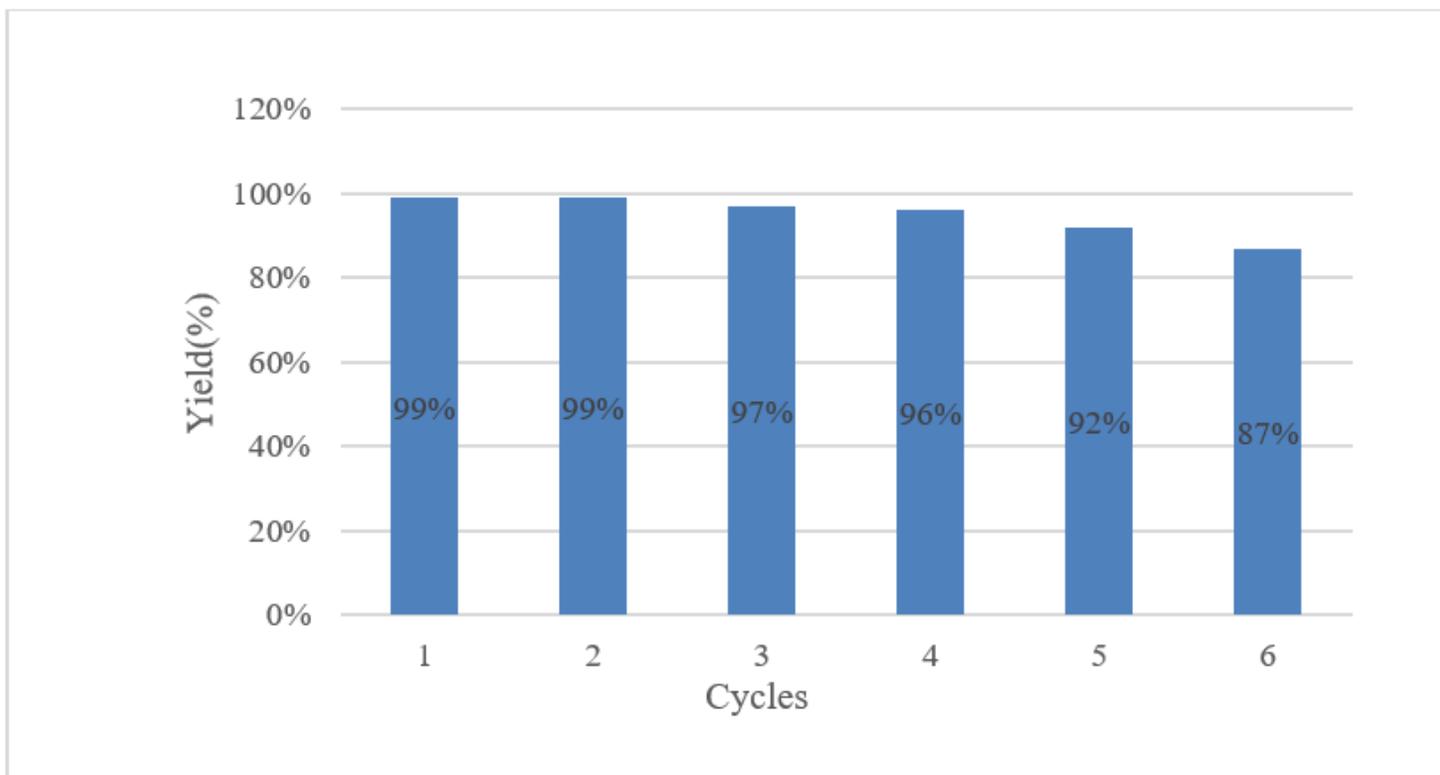


Figure 7

Reusability of the catalyst

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