Furfural Preparation using $KHSO_4$ as the Catalyst and its Recovery and Reuse

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$KHSO_4$ was used for furfural production, and the catalyst was recovered. The wet solid mixture after reaction was subjected to hot water washing and solid-liquid separation to recover the catalyst into the filtrate. Methods for determination of the catalyst content in both liquid and solid phases were invented. The effect of the mass ratio of hot water to the wet solid mixture, washing time, and number of washing times on the catalyst recovery were investigated. The total recovery of the catalyst into the filtrate was up to 87.7% when using the optimum conditions. The catalyst was reused in laboratory experiments up to 5 successive times. The recovered catalyst had the same activity for furfural production as the fresh catalyst on the same dosage level. Thermal gravimetric and X-ray diffractometer analyses of the catalyst showed that the catalyst was stable and reusable.

Keywords: Furfural; Corncob; Potassium hydrogen sulfate; Recovery

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INTRODUCTION

Furfural is a very useful chemical that has been produced industrially from lignocellulosic biomass since 1921. It has great potential to serve as a precursor for chemical synthesis in industry. However, the level of severity needed for high yields of furfural are not practical. The concentrations of mineral acids and the high process temperatures lead to high costs and adverse environmental impacts. New processing concepts, involving green technology, are needed in order to produce furfural while minimizing the carbon footprint and related waste streams (Marcotullio and Jong 2010). Traditionally, furfural production proceeds *via* hydrolysis of biomass rich in xylan into pentose and then dehydration of C5 sugar in the aqueous phase in the presence of homogeneous catalysts such as H_2SO_4 and HCl. However, these inorganic acids cause environmental pollution, adverse health effects, and corrosion of equipment (Xu *et al.* 2018).

New catalysts such as some organic acids have been explored for furfural preparation. These include glycine betaine hydrochloride (Liu *et al.* 2014), acetic acid (Liu *et al.* 2018), terephthalic acid (Hronec and Fulajtárová 2019), maleic acid (Kim *et al.* 2012), sulfonated sporopollenin (Wang *et al.* 2017), and p-coumaric acid-OHs (Ji *et al.* 2018). Most organic acids are composed of the elements of C, H, and O, and they are free of the element S. So if they are to be used as the catalysts for furfural production in the industry, the reaction solid residue does not contain the element S coming from the catalysts and treatment of the reaction solid residue does not need to consider desulfurization (the content of the element S in the biomass itself is very low).

Solid acids have been used as catalysts for the hydrolysis of biomass or biomass-derived sugar monomers to obtain platform compounds such as furfural. Preyssler heteropolyacid (Pardo Cuervo *et al.* 2020), silicoaluminophosphate (SAPO-44) (Bhaumik and Dhepe 2014), amorphous Nb_2O_5 (Gupta *et al.* 2017), resorcinol-formaldehyde resin carbon (RFC)(Zhu *et al.* 2017), WO_3/TiO_2 (Carnevali *et al*. 2018), HZSM-5 (Jaafari *et al.* 2019), and Ga_2O_3 (Kumar *et al.* 2016) have been shown to be effective. Their application in industrial production is limited especially when the feedstock is the original solid biomass. In this case, two severe defects remain with the solid acid catalysts. One is the easier deactivation by the fine feedstock granule formed during reaction process; the other is the very difficult separation of the catalyst from the reaction residue (solid-solid separation), which hinders the catalyst recovery and reuse. $FeCl_3$ (Marcotullio and Jong 2010), $CrCl_3$ (Wang *et al.* 2018), and $AlCl_3$ (Wang *et al.* 2018) have been used as catalysts for furfural preparation. Chloride ions participate directly in the catalysis, and they have a “salting out effect” in the solution, thus improving furfural yield.

Combined catalysts have been used to enhance preparation of platform compounds such as furfural, 5-hydroxylmethyl furfural (HMF) and levulinic acid (LA). For example, the following combined catalysts were used for furfural preparation. They are acetic acid-seawater-$FeCl_3$ (Mao *et al.* 2013), $CrCl_3$-HCl (Choudhary *et al.* 2012), Sn-beta and the Brønsted-acid (Choudhary *et al.* 2011), and LiH_2PO_4-NaH_2PO_4-$Ca(H_2PO_4)_2$ (Shi *et al.* 2014). In addition, $NaHSO_4$ -$ZnSO_4$ were used for HMF production (Shi *et al.* 2013). The solution of ethanol, H_2SO_4, H_2O_2 and H_2O was designed and used for the dissolution of corn straw to prepare furfural, HMF, and LA (Zhang *et al.* 2016). Hydrochloric acid and sodium chloride in a water/γ-valerolactone solvent system was used for high conversion of glucose to HMF (Li *et al.* 2017). A water-γ-valerolactone-H_2SO_4 combination system was used for conversion of corn stover into furfural and LA (Li *et al.* 2016).

Besides employing new catalysts for furfural production, many researchers have endeavored to investigate new process methods to prepare furfural. In single water phase systems, the furfural yield is usually not high due to possible side reactions leading to loss of furfural, whereas the biphasic system is a very effective method to improve furfural yield through using a co-existing organic phase to extract furfural as soon as it is formed. Thus, the side reactions are greatly avoided. By this technology, the furfural yield can be increased to 60 mol% (Xu *et al.* 2018), 70 mol% (Mittal *et al.* 2017), 80 mol% (Weingarten *et al.* 2010), and 90 mol% (Xing *et al.* 2011; Li *et al.* 2013; Sweygers *et al.* 2018). The membrane pervaporation process was used to remove furfural instantly from the reaction system to improve furfural yield. The SDS membrane (Wang *et al.* 2016) and PDMS membrane (Qin *et al.* 2014) have been tested and they showed even better effect than the biphasic system. New continuous process (Li *et al.* 2015), reactive distillation process (Metkar *et al.* 2015), and microwave heating (Lappalainen and Dong 2019) have been used to intensify the production of furfural. Recently, γ-valerolactone was used as the solvent for furfural preparation and the furfural yield could be higher compared with using water as the solvent (Alonso *et al.* 2013; Li *et al.* 2017; Lin *et al.* 2017).

$KHSO_4$ is easily soluble in water, forming acidic solution and ionizing hydrogen ions, and it is suitable for hydrolysis of biomass. After reactions, the catalyst is transferred into water by washing and solid-liquid separation. It is used as the catalyst for furfural preparation, and its recovery and reuse were investigated in this study. It is not used for furfural production by other researchers except a preliminary study (Wang *et al.* 2020).

EXPERIMENTAL

Feedstock and Catalyst

The corncob used in this study was provided by Furfural Producing Factory of Jilin Woyun Agriculture Co. Ltd. (Changchun, China). The proximate analysis results on an air-dried weight basis were as follows: M_{ad} = 9.5% (moisture), A_{ad} = 3.5% (ash), V_{ad} = 70.1% (volatile), and FC_{ad} = 16.9% (fixed carbon). The corncob was crushed to a size of less than 1.5 mm for use. $KHSO_4$ (GR grade purity, $KHSO_4$ content ≧99.8%) was purchased from Shanghai National Drug Co. Ltd (Shanghai, China).

Experimental Flowsheet

As shown in Fig. S1 (in Supplementary material in the Appendix), the controlled dosage of catalyst was dissolved in 6 g of distilled water. The solution was mixed with 5 ± 0.001 g of dry corncob powder (moisture removed by heating at 100 ℃ for 2 h) in a beaker, and the mixture was subjected to adequate stirring to make the corncob be fully wetted by the catalyst solution. The mixture was transferred to a cylinder reactor with a volume of *ca*. 45 mL (with a height of 6.6 cm and an inner diameter of 3 cm) made of polytetrafluoroethylene. The reactor was sealed and placed in a stainless steel shell with screw threads to get a good grip. The reactor system was put into a heating box set at 190 ℃ for 2 h. After the reaction, the reactor was allowed to cool until its outer shell reached room temperature. The mixture in the reactor was transferred into a beaker, and the controlled amount of distilled water was added to form a suspension. The suspension was stirred adequately, and then it was subjected to suction filtration. The filtrate and filter cake were used for analyses.

Investigation on the Optimum Catalyst Dosage

The reaction temperature was 190 ℃, and the reaction time was 2 h according to the previous study (Wang *et al.* 2020). The effect of the catalyst dosage (0 g, 0.1 g, 0.2 g, 0.3 g, 0.4 g, 0.5 g) on furfural yield was investigated. The dosage percentage based on the weight of the dry corncob was 0%, 2%, 4%, 6%, 8%, and 10%, respectively.

Recovery of the Catalyst

The reaction proceeded as described in Fig. S1 with the catalyst dosage of 0.4 g (8%), and it was conducted repeatedly to obtain wet solid mixture for catalyst recovery experiments. The initial reactants in the reactor were mixtures of 5 ± 0.001 g dry corncob powder and aqueous solution of the catalyst (0.4 ± 0.001 g $KHSO_4$ dissolved in 6 ± 0.001 g distilled water, the mass concentration of the catalyst solution is 6.25% and pH = 0.99 @ 20 ℃). The total mass in one pot was 11.4 g, with water at 52.63% by weight. After the reaction, the total amount of the reactants did not change because the reactor was tightly closed during the reaction process, and the contents in the reactor were called the wet solid mixture (denoted as S). The wet solid mixture was washed by a certain amount of hot water, and the suspension was subjected to suction filtration. Most of the catalyst was transferred into the filtrate together with most of furfural produced and small amounts of other by-products including some organic acids such as acetic acid, some sugar monomers such as xylose and glucose, and some other decomposition components such as HMF and LA. Some trace elements in corncob such as iron, silicon, and aluminum were also transferred into the filtrate. The filtrate was reused for furfural production after concentration. It is not necessary to separate pure $KHSO_4$ from the above mentioned components from hydrolysis of corncob in the filtrate for reuse experiments. During the catalyst reuse process, the acetic acid acts as a cocatalyst for corncob hydrolysis. Xylose is the starting reactant for furfural production. Glucose is dehydrated into HMF and further decomposed into formic acid and LA, which also acts as a cocatalyst. The main goal was to ascertain how much catalyst could be recovered in the filtrate under reasonable conditions.

The washing procedure used an initial hot water temperature of 90 °C, and the wet solid mixture was kept at 55 °C. The wet solid mixture of four pots (whose weight was 11.4 × 4 = 45.6 g), and a certain amount of hot water (denoted as W) were fed to a washing bath together. The washing bath was equipped with an agitator running at 360 rpm to keep constant stirring.

After the first washing operation for a controlled time period, the contents in the washing bath were subjected to suction filtration to realize solid/liquid separation. The filter cake from the first suction filtration was used for the second washing; the filter cake from the second suction filtration was used for the third washing, and so on. The number of washing times was up to 5 in this study. The wet filter cake with the water content of 52.63% was also denoted as S to give the parameter W/S (the mass ratio of hot water to wet solid mixture) as a manipulated variable in the experiments. When the repeating washing was done, the initial temperature of the filter cake from the last washing was the room temperature of 25 °C. All experiments were conducted in triplicate.

Determination of the Catalyst Content in the Filtrate

To obtain the catalyst amount recovered in the filtrate, a method for determination of the catalyst content in the filtrate was invented as shown in Fig. 1. A 15 mL sample filtrate was put into a corundum boat and it was heated on an electric heater to evaporate water and other volatile components in the filtrate, while the leftovers in the boat were the catalyst and other non-volatile components. The boat was heated for 1 h in a muffle furnace at 650 °C, and the catalyst underwent the following reactions in series.

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \qquad (1)$$

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_3 \qquad (2)$$

Non-volatile organic components in the boat were converted to carbon dioxide and released into the air. Trace elements such as iron and silicon were converted to their corresponding oxides, which were water insoluble and remained in the boat. When the heating process was finished, the boat was cooled to room temperature. Next, 20 mL of distilled water was used to wash the inwall of the boat to transfer the suspension to a beaker. The suspension was filtered to remove the insoluble oxides, while K_2SO_4 was transferred into the filtrate. The filtrate was placed in a clean and dry corundum boat with known net weight. The boat was again heated on an electric heater to evaporate water and then heated again for 1 h in the muffle furnace at 650 °C. Finally, the boat was cooled in a dry box at room temperature, after which, the boat was weighed. After deducting the net weight of the boat, the weight of K_2SO_4 (denoted as M_{K2SO4}) was obtained. The amount of $KHSO_4$ in the filtrate (denoted as $M_{KHSO4,F}$) was calculated using Eq. 3,

$$M_{KHSO4,F} = (M_{K2SO4} / 174) \times 2 \times 136 \times (V_{filtrate} / 15) \qquad (3)$$

where 136 and 174 are the molar mass of $KHSO_4$ and K_2SO_4, respectively, $V_{filtrate}$ is the total volume in milliliters of the filtrate, 15 is the volume in milliliters of the sample taken from the filtrate for analysis, and 2 is the conversion coefficient derived from Eqs. 1 and 2, as 2 moles of $KHSO_4$ result in 1 mole of K_2SO_4. The recovery of catalyst (denoted as R)

was defined in Eq. 4,

$$R = (M_{KHSO4,F} / 1.6) \times 100\% \quad (4)$$

where 1.6 was the total initial catalyst weight in grams.

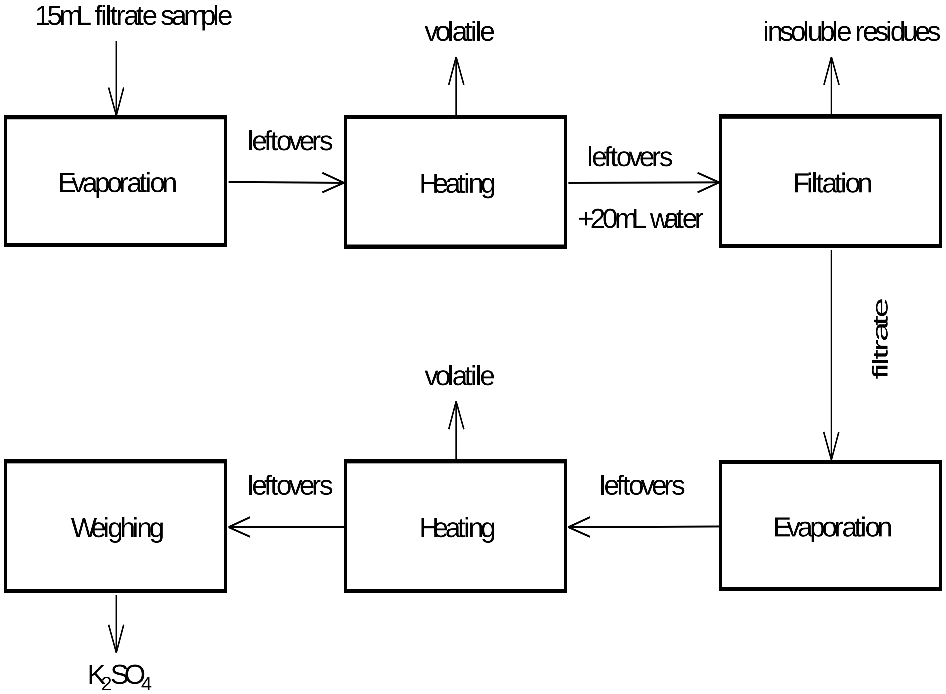

Fig. 1. Flowsheet diagram for determination of the catalyst in the filtrate

Determination of the Catalyst Content in the Filter Cake

The flowsheet diagram for determination of the catalyst content in the filter cake is shown in Fig. S2 (in Supplementary material), which is similar to Fig. 1 except for the first step. A 1 g sample of filter cake (water free) was put into a corundum boat, which was placed on an electric heater in the open air to burn the organic components. The steps were the same as those shown in Fig. 1. The weight of K_2SO_4 (denoted as M_{K2SO4}) converted from $KHSO_4$ in the filter cake sample was obtained. The total catalyst in the filter cake (denoted as $M_{KHSO4,C}$) was determined using Eq. 5,

$$M_{KHSO4,C} = (M_{K2SO4} /174) \times 2 \times 136 \times (M_{cake} /M_s) \quad (5)$$

where M_{cake} is the total weight of the filter cake in grams, from which a sample of M_s grams is taken out for testing the content of $KHSO_4$, and 174, 136, and 2 have the same meanings as defined in Eq. 3. The percentage of the catalyst lost in the filter cake (denoted as L) was calculated by Eq. 6,

$$L = (M_{KHSO4,C} / 1.6) \times 100\% \quad (6)$$

where 1.6 is the total initial catalyst weight in grams.

Verification of the Accuracy of the Catalyst Determination Methods

The method invented for determination of the catalyst content in the filtrate was verified by comparing the determination value of $KHSO_4$ in its water solution with its actual content value. Five solution samples were made by dissolving various amounts of $KHSO_4$ (0.4001 to 2.0003 g) in 20 g of distilled water. These samples were subjected to determination as shown in Fig. 1. The catalyst content determination values and the corresponding errors are shown in Table S1 (in Supplementary material). The results demonstrated that the relative errors were within ± 4%, and the accuracy was acceptable in terms the requirement of the present study.

The method invented for determination of the catalyst content in the filter cake was verified by comparing the determination value of $KHSO_4$ in the original reaction mixture produced as described in Fig. S1 with its actual content value. Five reaction mixture samples were subjected to determination according to the method shown in Fig. S2. The catalyst content determination values and the corresponding errors are shown in Table S2. The relative errors were within ± 3%, and the accuracy was acceptable in terms of the requirement of the present study.

Analysis and Reuse of the Catalyst

pH value of the catalyst solution

The 6.25% $KHSO_4$ aqueous solution had a pH of 0.99 at room temperature (20 °C), as determined with a pH meter (PHS-3E with automatic temperature compensation, (Mike Company, Hangzhou, China). The pH value of the solution was also calculated using Aspen plus V11 software (Aspen Tech, Shanghai, China) selecting ELECNRTL as the property method. The ELECNRTL property method is the most versatile electrolyte property method; it can handle very low and very high concentrations in aqueous and mixed solvent systems. The calculated pH value was 1.05. The difference of 0.06 showed that both methods gave consistent results.

Thermal gravimetric (TG) and X-ray diffractometer (XRD) analyses of the catalyst

To investigate thermal stability of $KHSO_4$ at various temperatures, TG analysis of the pure catalyst was conducted using a METTLER-TOLEDO analyzer (Zurich, Switzerland) with a heating rate of 15 °C/min from 30 °C to 800 °C under 20 mL/min N_2 atmosphere. The recovered catalyst slurries treated at different temperatures were also subjected to TG analyses under the same condition as that for the pure catalyst for comparison purpose.

The recovered catalyst slurries were obtained by evaporating most water and volatile organic components in the filtrate of 18 mL obtained by adding 20 mL water in the process shown in Fig. S1. Approximately 60% (0.24 g) of the initial 0.4 g catalyst was recovered in the filtrate and finally in the slurry. The slurry was heated at different temperatures for 2 h, and the corresponding samples were named slurry@30 °C, slurry@ 80 °C, and slurry@180 °C. Each sample used for analysis was *ca*. 4 mg.

XRD analyses of the pure catalyst and the recovered catalyst slurries treated at different temperatures were tested on a Smartlab diffractometer (Smartlab-SE, Tokyo, Japan) with CuKa radiation. The tube voltage was 40 kV, and the current was 40 mA. The selected 2θ range was 10° to 80°, with scanning at a step of 0.02°. Each sample used for analysis was 5 mg.

Reuse of the Catalyst

A certain amount of dilute filtrate obtained was collected in a beaker, and then it was heated on an electronic furnace. The solution was kept boiling for a certain time to concentrate the catalyst until the pH value of the recovered catalyst solution reached 0.99

at room temperature (20 °C). This recovered concentrated catalyst solution has the same pH value as the initial fresh catalyst solution shown in Fig. S1 when 0.4 g (8%) catalyst was used. The recovered concentrated catalyst solution was reused for furfural preparation. Successive recovery and reuse of the catalyst was conducted up to 5 times to investigate the activity of the recovered catalyst compared with fresh pure catalyst. Specifically, at 0th experiments, 20 pots of reaction were carried out and the fresh catalyst used was 20 × 0.4 = 8 (g), twice washing all the reaction mixtures after reaction recovered *ca*. 8 × 87.71% = 7.0618 (g) catalyst into the filtrate of 2400 mL, the recovered 7.0618 (g) catalyst could be used to carried out 7.0618 / 0.4 = 17.6545 ≈ 17 pots of reaction; then, this 2400 mL catalyst solution was concentrated to *ca.* 102 mL(pH=0.99) and 17 pots of reaction were carried out for the 1st reuse. Similarly, 14 pots of reaction were carried out for 2nd reuse, 11 pots for the 3rd reuse, 8 pots for the 4th reuse, and 5 pots for 5th reuse.

Analyses of the liquefied products of furfural, HMF, LA, and liquefied fraction of corncob were described elsewhere (Li M. H. *et al.* 2016; Wang *et al.* 2020). Furfural and HMF were determined using HPLC (America, Waters 2489) with a Waters Sysmmetry-C18 column and an Ultraviolet Detector. The retention times are about 7.4 min and 9.2 min for furfural and HMF, respectively. An Aminex HPX-87H column and a Refractive Index Detactor (America, Waters 2414) were used to detect LA with the retention time about 16.4 min). The definition of the liquefied fraction of corncob and the yield of furfural, HMF, and LA are shown below, in which the weight of the feedstock and the reaction residue was on dry basis.

$$\text{Liquefied fraction} = (\text{feedstock (g)} - \text{reaction residue (g)}) / \text{feedstock (g)} \times 100\% \tag{7}$$

$$\text{Furfural yield} = \text{furfural detected (g)} / \text{corncob feedstock (g)} \times 100\% \tag{8}$$

$$\text{LA yield} = \text{LA detected (g)} / \text{feedstock (g)} \times 100\% \tag{9}$$

$$\text{HMF yield} = \text{HMF detected (g)} / \text{feedstock (g)} \times 100\% \tag{10}$$

The yield of furfural was based on weight. This furfural yield definition has the advantage of easy calculation, and it also gives straight forward comparison with the industrial furfural yield.

RESULTS AND DISCUSSION

The Effect of Catalyst Dosage on Liquefied Fraction and Product Yield

Figure 2 shows the effect of catalyst dosage on the liquefied fraction and the product yield. As the catalyst dosage increased uniformly from 0% to 6%, the liquefied fraction of corncob increased very slowly from 38.6% to 41.7%, whereas the furfural yield increased relatively quickly from 2.5% to 10.8%. When the catalyst dosage increased from 6% to 10%, both furfural yield and liquefied fraction had no apparent change. The catalyst might play a greater role in furfural formation from dehydration of xylose than in liquefaction of corncob since the liquefied fraction was already very high even without the catalyst loading. When the catalyst dosage increased from 8% to 10%, the furfural yield had no apparent change, which indicates that the catalyst dosage of 8% is enough for furfural production. The catalyst activity stabilizes in this dosage range might be due to that the concentration of the precursor of the furfural (*i.e.*, xylose) stabilizes. Therefore, the catalyst dosage was fixed at 8% in all reactions for the study of catalyst recovery and reuse. The by-products HMF and LA were also detected, but the yield was very low.

The furfural yield achieved with the catalyst dosage of 8% was 11.2%, which is similar to that from the industry using H_2SO_4 as catalyst since most furfural factories generally consume 10 tons corncob (on dry basis) to produce 1 ton furfural.

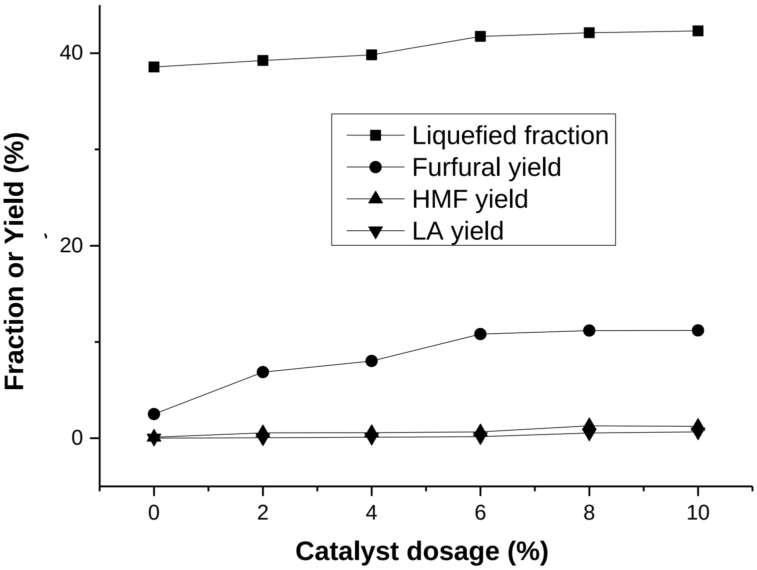

Fig. 2. The effect of catalyst dosage on liquefied fraction and product yield

The Effect of Main Factors on Recovery of the Catalyst

Many factors influence the recovery of catalyst. The ratio of hot water to wet solid mixture (W/S), washing time, and number of washing times are the three most important variables. The temperature of the water used for washing and the temperature of the wet solid mixture are also important factors. To obtain the experimental results on the same basis when varying the manipulated variables, the initial temperature of the washing water and the wet solid mixture was fixed at 90 °C and 55 °C, respectively. The selection of the water temperature level of 90 °C was due to that there are plenty of wasting water of *ca.* 90 °C from the furfural distillation tower that could be utilized for the potential application of this catalyst for the industrial furfural production. The selection of wet solid mixture level of 55 °C was based on two considerations. One is that the mixture was still hot enough, which was instrumental in catalyst dissolving in the first time washing operation. The other is that the temperature level is not too high and it is convenient to open the outside metal shell of the reactor.

The Effect of Washing Time on Recovery of the Catalyst

The effect of washing time on the catalyst recovery of the first washing operation is shown in Fig. 3 by fixing the W/S ratio at 1.32 (60 g hot water/45.6 g wet solid mixture = 1.32) and the agitator frequency at 360 rpm. More than 55% catalyst in the wet solid mixture after reaction was transferred to filtrate after merely 5 min of washing. This is because the catalyst solubility is very high in hot water; the solubility of $KHSO_4$ increased from 67.3 g to 112 g when temperature was increased from 40 ℃ to 90 ℃. The catalyst recovery increased from 55.3% to 66.2% as the washing time increased from 5 min to 13 min. The recovery remained nearly constant after 11 min, potentially because an equilibrium state was reached between the dissolving of the catalyst into water and its adsorption by the solid particles. The W/S ratio 1.32 was the desired value adopted according to the wet solid mixture output, and the recycling hot water output in the furfural production factory. Thus, the optimum washing time was 11 min at this W/S ratio.

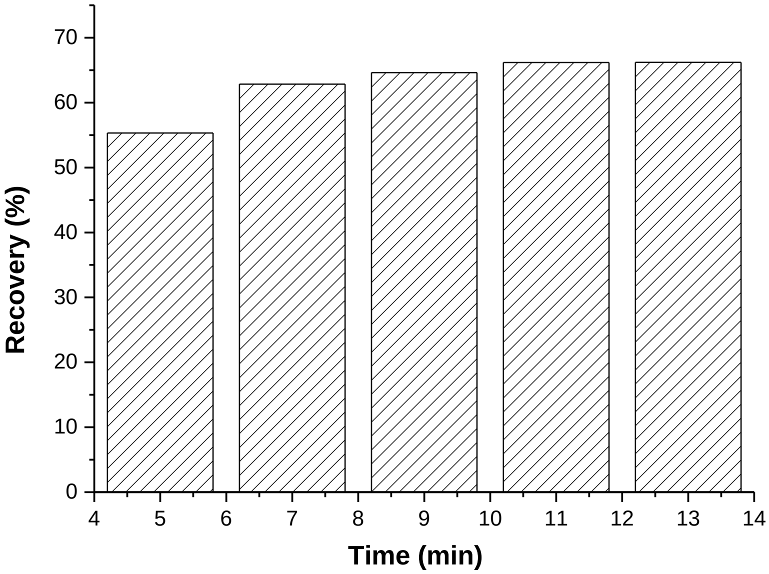

Fig. 3. The effect of washing time on recovery of the catalyst

The Effect of W/S Ratio on Recovery of the Catalyst

At total of 45.6 g wet solid mixture with a temperature of 55 ℃ was added to a certain amount of hot water of 90 ℃ (40, 60, 80, 100, 120, 140, or 160 g), forming the suspension for washing *via* agitation. Seven couples of the suspension were named as follows: (40, 45.6), (60, 45.6), (80, 45.6), (100, 45.6), (120, 45.6), (140, 45.6), and (160, 45.6). The corresponding *W*/*S* ratios were 0.88, 1.32, 1.76, 2.19, 2.63, 3.07, 3.52, respectively. The effect of *W*/*S* on the catalyst recovery is shown in Fig. 4, where the washing time was fixed at 11 min and the agitator frequency was 360 rpm. More water led to higher catalyst recovery. More water could form a greater concentration gradient of the catalyst between the interface of the solid particles and the main water phase. Thus, the mass transfer force increased, and more catalyst was transferred into the main water phase. However, when the *W*/*S* ratio was increased further, the catalyst recovery rate slowed. It could be predicted that an infinite amount of hot water might transfer nearly all the catalyst in the solid into the water, such that the recovery would be near 100%. However, the optimum *W*/*S* ratio was set to be 1.32 through comprehensive consideration of many factors such as the hot water amount that could be utilized in the factory and the concentration of the recovered catalyst in the filtrate. It is obvious that using more water results in a very dilute catalyst solution. Thus, the concentration process will require more heat and increased costs.

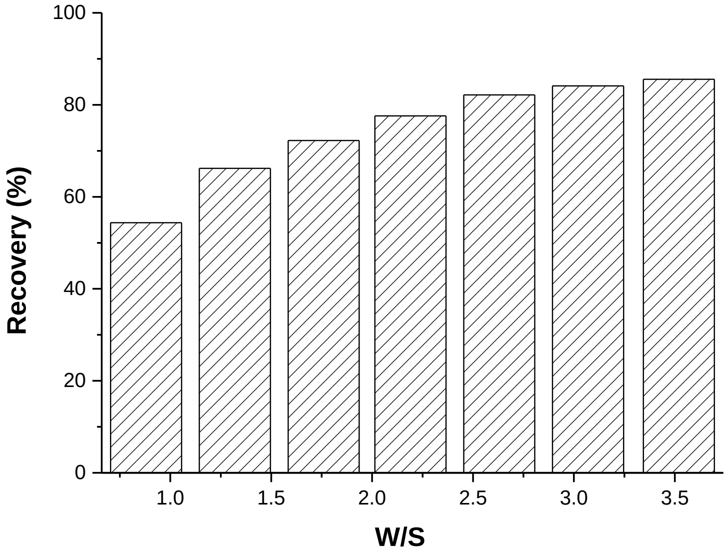

Fig. 4. The effect of W/S on recovery of the catalyst

The Effect of Number of Times of Washing Operation on Recovery of the Catalyst

Figure 5 shows the total recovery and the recovery per-pass (*W*/*S* = 1.32, washing time = 11 min, and agitator frequency = 360 rpm). When the number of times of washing operation was 5, the total recovery was near 100%. Two washes led to a total catalyst recovery up to 87.71%. Therefore, the optimum number of times of washing operation should be 2 considering the high total recovery obtained, the hot water required, and the cost of recovery. The recovery per-pass was very low for the third through fifth washing.

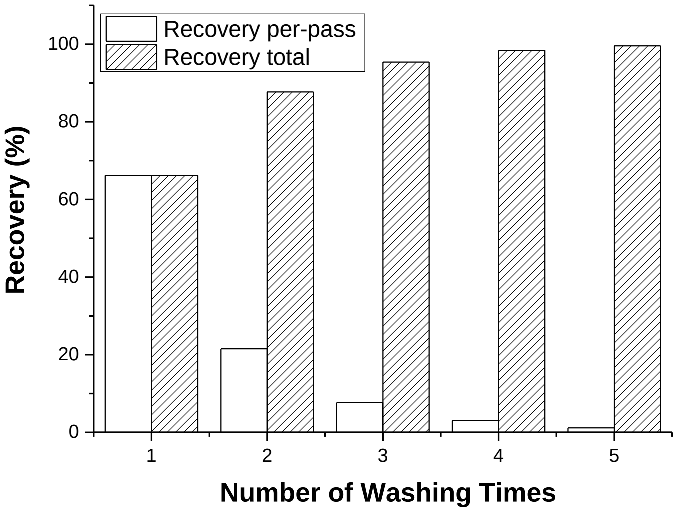

Fig. 5. The effect of number of times of washing operation on recovery of the catalyst

The Property and the Activity of the Recovered Catalyst

TG curves of the fresh catalyst and the recovered catalyst slurries are given in Fig. S3 (in Supplementary material). For the pure catalyst, from 30 °C to 200 °C, the catalyst showed very little weight loss, which demonstrated that it was stable in this temperature range. From 200 °C to 403 °C, a flat slope appeared, and a corresponding weight loss of 6.62% was recorded due to the dehydration reaction shown in Eq. 1. From 403 °C to 650 °C, a steep slope appeared and a corresponding weight loss of 23.71% was recorded, which was due to SO_3 loss reaction shown in Eq. 2. From 650 °C to 800 °C, a weight loss of 1.54% was recorded, which was the continuing loss of SO_3. TG analysis of the pure catalyst showed that the reactions shown in Eqs. 1 and 2 could occur and finish completely if the reaction temperature was kept at 650 °C for a long enough period of time. Thus, the heating temperature was set at 650 °C for determination of the catalyst content in the filtrate and in the filter cake.

The lines of the recovered catalyst slurries @ 30 °C, 80 °C, and 180 °C approached the pure catalyst line gradually. This is due to the further loss of water and other volatile non-catalyst components as the treated temperature was increased. It could be predicted that if all the non-catalyst components were separated and removed from the catalyst slurry, the pure catalyst could be recovered, and the line of it should overlap with that of the pure catalyst. Unfortunately, it was very difficult to purify the catalyst slurry because there were complex non-volatile components present. However, these components did not hinder the reuse of the catalyst as mentioned before. Therefore, obtaining pure recovered catalyst for TG analysis was not expected.

Figure S4 (in Supplementary material) shows XRD patterns of the pure catalyst and the recovered catalyst slurries treated at different temperatures. The strongest characteristic peaks of the pure catalyst in the range of $10^\circ < 2\theta < 20^\circ$ also appeared in the XRD patterns of all recovered slurries. However, the weaker characteristic peaks of the pure catalyst did not appear in the slurries treated at lower temperatures. This might be due to masking by impurities. As the treated temperature was increased, more characteristic peaks of the pure catalyst were revealed, and the XRD pattern of the catalyst slurry treated at 180 °C had the highest similarity to that of the pure catalyst. Similarly, if the recovered catalyst slurry was purified further, the XRD pattern would approach and finally overlap that of the pure catalyst.

The catalyst content of the recovered concentrated filtrate with pH = 0.99 at 20 °C was *ca.* 6.25%, as determined using the method described in Fig. 1, and the values are shown in Table S4 (in Supplementary material). During heating of the dilute filtrate, the furfural in the solution was evaporated with water because furfural and water forms the low boiling azeotrope of 97.9 °C at normal pressure. Most low boiling point organic acids such as formic acid were also evaporated with water. The recovered concentrated filtrate was mainly composed of the catalyst, water, and some non-volatile components such as xylose and glucose. These components do not influence the catalyst activity. It could be expected that the recovered concentrated filtrate has the similar activity for furfural preparation to that of the fresh pure catalyst solution when the content of the catalyst is the same. This could be further demonstrated by repeating recovery and reuse of the catalyst for furfural preparation, as shown in Fig. 6. The liquefied fraction of corncob and the yield of furfural, HMF, and LA for the five successive reusing experiments were very similar to those from the experiments using fresh catalyst at the same dosage level. These results demonstrated that the recovered $KHSO_4$ had the same activity as the fresh $KHSO_4$. Thus, it is a stable catalyst that could be used repeatedly without decreased activity.

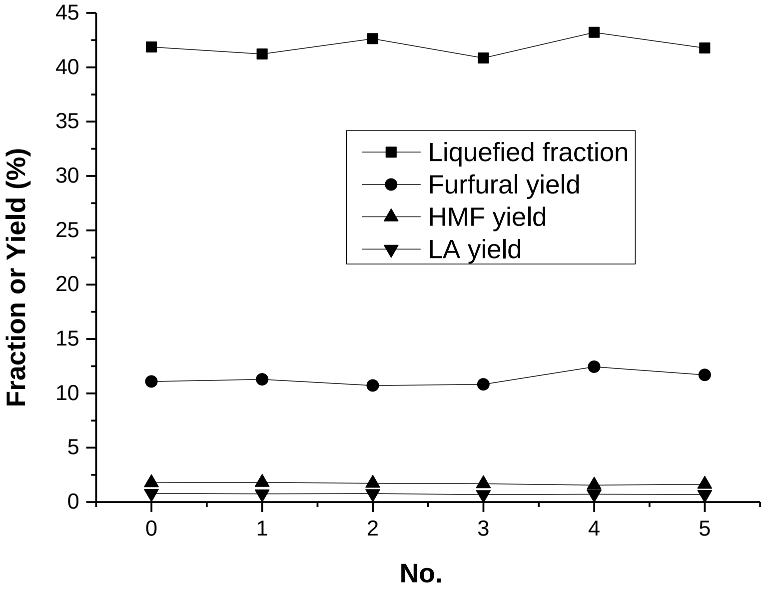

Fig. 6. The experimental results for reusing the recovered catalyst. No. 0 stands for fresh catalyst, No.1-5 stands for the five successive recovered catalyst.

CONCLUSIONS

1. $KHSO_4$ was used as the catalyst and corncob was used as the feedstock for furfural preparation with the catalyst dosage of 8% based on the dry weight of the feedstock to obtain wet solid reaction mixtures for recovery of the catalyst.
2. Recovery of the catalyst could be realized by washing the wet solid mixture after reaction with hot water and subsequent filtrating of the liquid/solid mixture. The optimum condition for recovery of the catalyst was as followed. The washing time was 11 min, the *W*/*S* ratio was 1.32, and the number of washing times was 2. Under this condition, the catalyst recovery reached 87.7%.
3. Thermogravimetric (TG) and X-ray diffraction (XRD) analyses of the pure catalyst showed that it is stable in the reaction temperature range and reuse of the catalyst indicates that it is reusable.

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Conflict of interest statement

There are no conflicts to declare.

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SUPPLEMENTARY MATERIAL

Table S1. $KHSO_4$ Content in Water Solution Determined *vs*. Actual

Sample No.	1	2	3	4	5
$KHSO_{4,AC}$ (g)	0.4001	0.8002	1.2003	1.6002	2.0003
Water (g)	20.003	20.002	20.006	20.004	20.001
$KHSO_{4,DE}$ (g)	0.4116	0.7812	1.1804	1.6201	1.9253
Error (g)	0.0115	-0.0190	-0.0199	0.0199	-0.0750
Error (%)	2.8743	-2.3744	-1.6579	1.2436	-3.7494

Table S2. $KHSO_4$ Content in the Original Reaction Mixture Determined *vs*. Actual

Sample No.	1	2	3	4	5
$KHSO_{4,AC}$ (g)	0.4003	0.4001	0.4002	0.4002	0.4003
$KHSO_{4,DE}$ (g)	0.4103	0.4092	0.3901	0.3887	0.4086
Error (g)	0.0100	0.0091	-0.0101	-0.0115	0.0083
Error (%)	2.4981	2.2744	-2.5237	-2.8736	2.0734

Table S3. The Effect of Catalyst Dosage on Liquefied Fraction and Product Yield

Cat. dosage (g)	0	0.1	0.2	0.3	0.4	0.5
Cat. dosage (%)	0	2	4	6	8	10
Liquefied fraction (%)	38.56	39.23	39.82	41.73	42.12	42.31
Furfural yield (%)	2.51	6.86	8.02	10.82	11.18	11.20
HMF yield (%)	0.11	0.56	0.58	0.66	1.29	1.24
LA yield (%)	0.02	0.05	0.10	0.16	0.54	0.66

Note: Temperature=190 ℃, Time=2 h

Table S4. Experimental Results for the Five Successive Recovery and Reuse of the Concentrated Catalyst Filtrate (pH = 0.99 @ 20 °C)

Repeating No.	0	1	2	3	4	5
$KHSO_4$ (wt.%)	6.25	6.31	6.35	6.22	6.36	6.18
Liquefied fraction (%)	41.86	41.22	42.63	40.85	43.21	41.77
Furfural yield (%)	11.09	11.28	10.72	10.83	12.45	11.69
HMF yield (%)	1.78	1.81	1.72	1.68	1.55	1.63
LA yield (%)	0.79	0.75	0.78	0.69	0.72	0.70

Note: reaction temperature:190 °C, time: 2 h, catalyst dosage: 8% (based on corncob)

Table S5. The Effect of Washing Time on Recovery of the Catalyst (W/S=1.32, rpm=360)

Time (min)	5	7	9	11	13
Recovery (%)	55.32	62.85	64.63	66.18	66.20

Table S6. The Effect of W/S on Recovery of the Catalyst (Washing time = 11min, rpm=360)

Water (g)	40	60	80	100	120	140	160
Wet Solid (g)	45.6	45.6	45.6	45.6	45.6	45.6	45.6
W/S	0.88	1.32	1.76	2.19	2.63	3.07	3.52
Recovery (%)	54.36	66.18	72.23	77.59	82.16	84.12	85.56

Table S7. The Effect of Number of Times of Washing Operation on Recovery of the Catalyst (W/S=1.32, Washing time = 11min, rpm=360)

Number of times	1	2	3	4	5
Recovery per-pass (%)	66.18	21.53	7.69	3.01	1.16
Recovery total (%)	66.18	87.71	95.40	98.41	99.57

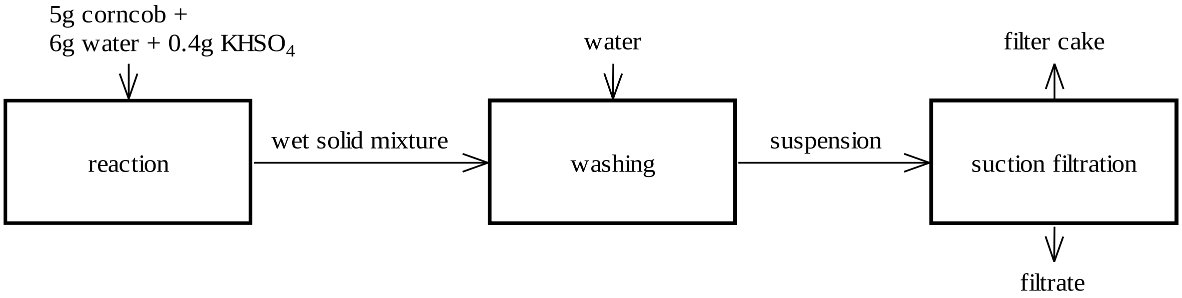

Fig. S1. The experimental flowsheet

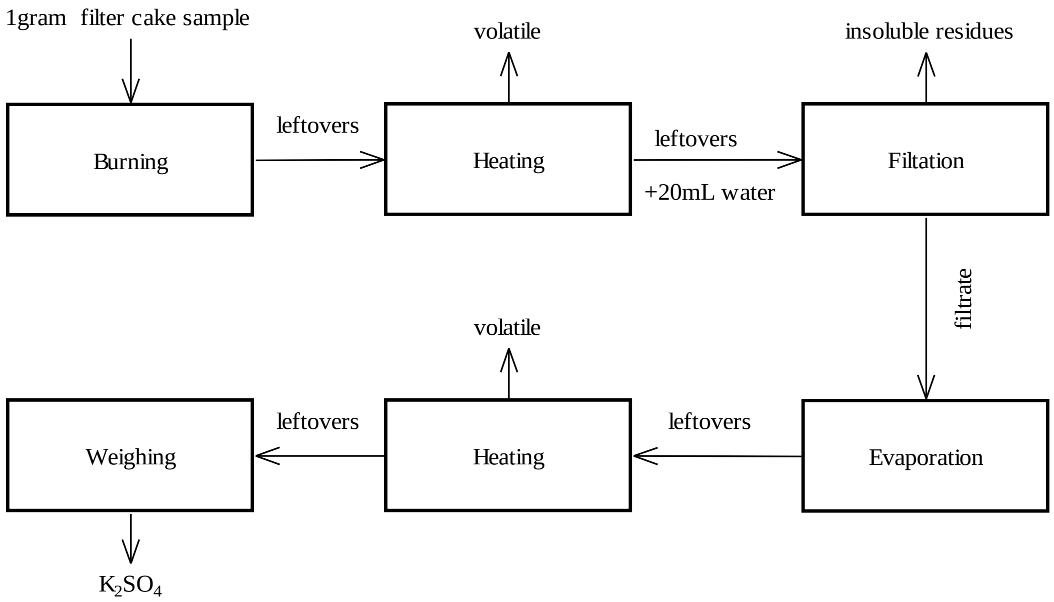

Fig. S2. Flowsheet diagram for determination of the catalyst in the filter cake

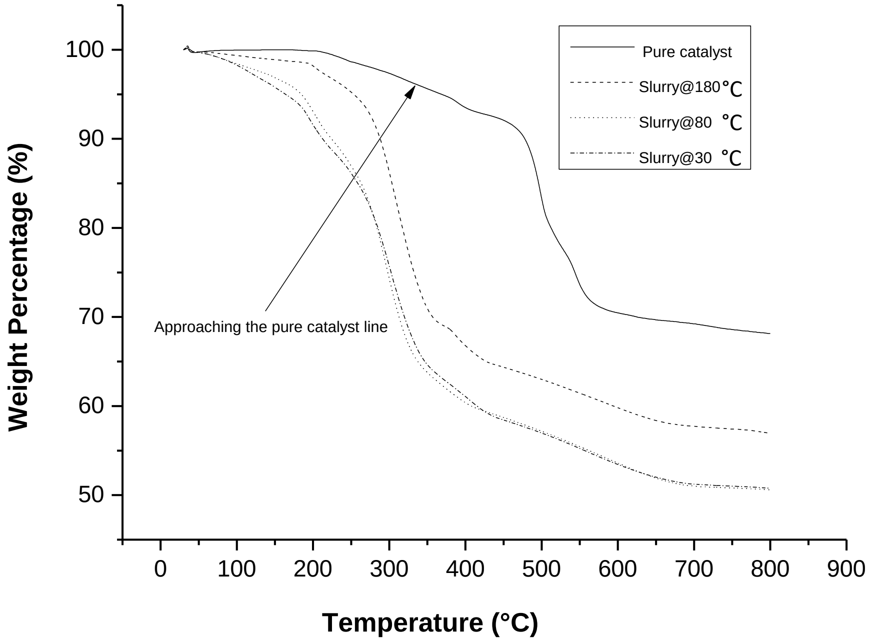

Fig. S3. TG analyses of pure catalyst and recovered catalyst slurries

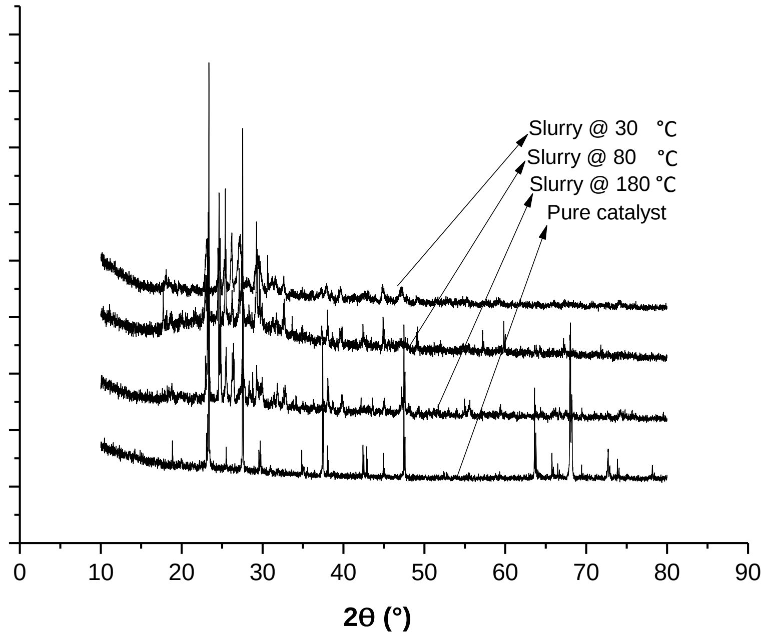

Fig. S4. XRD patterns of pure catalyst and recovered catalyst slurries