One-Step Heterogeneous Catalytic Process for the Dehydration of Xylan into Furfural

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Xylan, the major component of hemicellulose in hardwoods and various grasses, has great potential for bio-refinery applications such as the production of energy and high value-added chemicals. A convenient and environment-friendly catalytic process for the conversion of xylan into furfural in ultrapure water using chromium-loaded perovskite-type oxides as the solid catalyst has been investigated. The crystalline and morphologies of the catalysts were studied by X-ray diffraction analysis (XRD) and scanning electron microscope analysis (SEM), and the reactions were optimized by varying different parameters. It was found that $LaCo_{0.8}Cu_{0.2}O_3$ modified with 1.5wt% chromium had the highest catalytic activity in the transformation of xylan to furfural at a temperature of 433 K in a 1:600 weight ratio of xylan to hyperpure water for 10 h; the corresponding yield was 21.2% for furfural. Furthermore, a possible mechanism for the dehydration of xylan to furfural using Cr-$LaCo_{0.8}Cu_{0.2}O_3$ as a catalyst is proposed.

Keywords: Xylan; Furfural; Perovskite-type oxides; Heterogeneous catalysis

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INTRODUCTION

Xylan is the most abundant non-cellulosic component in the secondary cell walls of hardwood species and many other plants, thus constituting a major portion of plant biomass. It is the major component in hemicelluloses, which are generally defined as the non-cellulose polysaccharides in a plant cell wall and represent about 20-40% of the biomass in many plant species. The efficient transformation of xylan into furfural is considered one of the most promising strategies to accommodate the needs for liquid fuel consumption as well as to alleviate the environmental pollution due to its widely available and renewable characteristics. The xylan conversion can contribute to the sustainable and environment-friendly development of processes and products for bio-refinery industries (Balat *et al.* 2008; Kumar *et al.* 2008; Peng *et al.* 2011).

Intensive efforts are being made to use biomass for the production of energy and high value-added chemicals (Chheda *et al.* 2007; Kitchaiya *et al.* 2003; Yemis and Mazza 2011). Several thermochemical approaches for furfural production from biomass have already been reported (Iliopoulou *et al.* 2007; Shi *et al.* 2011; Wei *et al.* 2011). Dhepe and Sahu (2010) developed a process for the conversion of hemicelluloses into pentose (xylose and arabinose) and furfural *via* dilute sulfuric acid at 443 K; 50% pentose and 10% furfural could be obtained in 1 h.

A new route to synthesize furfural from renewable carbohydrates using $CrCl_2$ as a novel catalyst in the *N*, *N*-dimethylacetamide system was brought forward (Binder *et al.* 2010), and a 7 to 8% yield of furfural from the dehydration of xylan at 413 K was achieved. Furthermore, a highly efficient conversion was developed (Zhang and Zhao 2010) by the $CrCl_3$ catalytic process in ionic liquids under microwave-assisted heating at 473 K; the encouraging result of 63% furfural yield from xylan was achieved within 2 min. However, it is still very difficult to overcome the challenges faced in these processes because of the high cost, the toxic solvents, and the corrosion of equipment, which cannot meet the environmental and economical requirements.

A heterogeneous process that is environmentally benign and can be performed in continuous processes is considered a promising pathway for the conversion of biomass using inorganic or hybrid inorganic-organic solid catalysts (Lessard *et al.* 2010). Compared to a homogeneous process, a heterogeneous process has many desirable features including the facile separation of solid catalysts from the reacted systems, the regeneration of catalysts, and eco-friendly systems. The encouraging results can be obtained using solid acid catalysts (zeolites, clays, and metal oxides) for the conversion of hemicelluloses from crop waste into C_5 sugars and furfural (Dhepe *et al.* 2010). Recently, promising results were also reported using HZSM-5 and HUSY zeolites as catalysts in an ultrapure water medium for the production of xylose, arabinose, and furfural. A furfural yield of 18% and 30% pentose yield can be obtained in 6 h at 443 K when using HUSY (Si/Al=15) as the catalyst (Sahu and Dhepe 2012). Therefore, solid catalytic processes offer environmental benefits, which meet the demands of "green" technology (Lin and Huber 2008).

Perovskite-type oxides possess specific physical and chemical properties such as stable crystal structure, unique electromagnetism performance, high activities for oxidation-deoxidization, hydrogenolysis, isomerization, and electro-catalysis, which have a tremendous potential in environmental protection and industrial catalytic areas. Perovskite-type oxides also overcome the disadvantages of novel metal catalysts and recovery issue of homogeneous catalysts (Deng *et al.* 2010). Moreover, chromium-based catalytic processes were found to offer distinct advantages for the selective dehydration of pentose from biomass into furfural (Binder *et al.* 2010; Zhang and Zhao 2010). In order to understand the effect of chromium for the catalytic performance of perovskite-type oxides in the dehydration of xylan into furfural, a convenient and promising strategy for the transformation of xylan into furfural as one of the main products was brought forward using perovskite-type oxides loaded with chromium as a solid catalyst at a low temperature in ultrapure water. The effect of chromium-loaded amounts on the yields of furfural and pentose was investigated in the range from 0.5 wt% to 1.5 wt% and the reaction conditions were optimized to get the maximum yields. A mechanism to account for the catalytic reaction was also proposed.

EXPERIMENTAL

Materials

Corn stover xylan with more than 90% xylose residue (M_w=22800 g/mol), L-arabinose (HPLC, ≧99%), and D-(+)-xylose (HPLC, ≧99%) were provided by Qiyun Co. Ltd., (Guangzhou, China). Furfural (99%) and Cu $(NO_3)_2{\cdot}3H_2O$ were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Citric acid (99.5%) and ethylene glycol (99%) were obtained from Lingfeng Chemical Regent Co. Ltd., (Shanghai, China). $Co(NO_3)_2 \cdot 6H_2O$ and $CrCl_3 \cdot 6H_2O$ were purchased from Tianjin Kemiou Chemical Co. Ltd., (Tianjin, China). $LaCl_3 \cdot 7H_2O$ was supplied by Aladdin (Shanghai, China). All reagents were used without any purification.

Preparation of the Solid Catalysts

$LaCo_{0.8}Cu_{0.2}O_3$ was prepared by the sol-gel method of dissolving stoichiometric ration (La/Co/Cu) salts in concentrated nitric acid and water (Deng *et al.* 2010; Dhahri *et al.* 2010). Afterwards, citric acid was added slowly at a molar ratio (total metal ion/citric acid) of 1:1.5 and ethylene glycol was dropped slowly at a molar ratio (ethylene glycol/citric acid) of 1:2. The precipitate was dried overnight at 393 K and calcined at 1073 K for 6 h to yield the desired perovskite structures.

Cr-$LaCo_{0.8}Cu_{0.2}O_3$ samples were prepared by incipient wetness impregnation by various amounts of $CrCl_3$ solution over $LaCo_{0.8}Cu_{0.2}O_3$ powder, respectively (Ammendola *et al.* 2010). The amounts of chromium corresponded to 0.5, 1.0, and 1.5 wt% of the final materials, respectively. The precipitate was then washed with deionized water until Cl^- was no longer detectable with $AgNO_3$ solution, then dried overnight at 393 K and calcined at 1073 K for 3 h.

Characterization of Catalysts

The phase purity of the samples was confirmed by XRD (D8 ADVANCE, Bruker, Germany) with Cu Kα radiation. The tube voltage was 40 kV and the current was 40 mA. The selected 2θ range was 5 to 80°, scanning at a step of 0.02°.

The morphologies of the catalysts were observed on SEM (LEO 1530 VP Field Emission Scanning Electron Microscope, LEO Electron Microscopy Inc., Germany).

The content of chromium was evaluated *via* ICP-AES (SPECTRO CIROS, Germany) instrument. Samples were pretreated with aqua regia before testing.

The NH_3-TPD measurements were performed on an Autochem instrument (Quantachrome, CPB-1). The chemisorbed amount of NH_3 was measured in flowing He gas from 373 K to 1073 K with a heating rate of 10 K min^{-1}.

Typical Procedure for Xylan Conversion

In a typical process, xylan was introduced into an appropriate volume of hyper-pure water, and then catalyst was added. The reaction system was transferred to the autoclave and was subjected under different conditions. After the reaction, the reactor cooled down to room temperature immediately by rushing water. Liquid possessing furfural and pentose was obtained and analyzed by high-performance liquid chromatography (HPLC) and ion chromatography (ICS). All the experiments were performed in duplicate, with 4% standard error.

Catalyst Recycling Study

After the first reaction, the catalyst that showed the best catalytic performance was recovered by centrifugation and then subjected to calcination for the removal of organic materials at 823 K for 4 h. This recovered solid was used as the catalyst for the recycling study and conducted in the optimization conditions to test its recycling ability. The recycling study was done in duplicate, with 4% standard error.

Determination of Furfural and Pentose Yield

The quantitative analysis of furfural was conducted by HPLC (Aglient 1100 series liquid chromatograph with a reversed-phase C18 column) system equipped with a DAD detector at 277 nm. A mixture of 0.1 wt % acetic acid aqueous solution and acetonitrile with a volume ratio of 85:15 was used as the mobile phase, and the flow rate was 1 mL/min. The yield of pentose (xylose and arabinose) was analyzed with ICS (DIONEX INS-3000, PAD detector) with a PA20 column; 96 g furfural may be theoretically obtained from 132 g xylan. Then the yield of furfural can be calculated accordingly by using Eq. 1.

$$\text{Yield}_{\text{(furfural)}} = \frac{\text{weight (HPLC)}}{\text{weight (theoretical)}} \times 100\% \qquad (1)$$

RESULTS AND DISCUSSION

X-ray Diffraction Analysis

The X-ray diffraction (XRD) patterns of the catalysts loading with different amounts of chromium on $LaCo_{0.8}Cu_{0.2}O_3$ are displayed in Fig. 1. The patterns of $LaCo_{0.8}Cu_{0.2}O_3$ clearly show characteristic reflections for perovskite–type oxides without other phases, which is consistent with the results reported by Deng *et al.* (2010). Similar peaks of different catalysts indicate that there was no obvious change in phase after the modification. In comparison with the JCPDS charts, the spectra indicates that all the Co-based samples were perovskite-type mixed oxides (JCPDS card 48-0123), but Co_3O_4 (JCPDS card 42-1467) was present in all the Co-based catalysts before being loaded by chromium, indicating that the presence of chromium ions contributes to an improved distribution of cobalt in perovskite-type oxides.

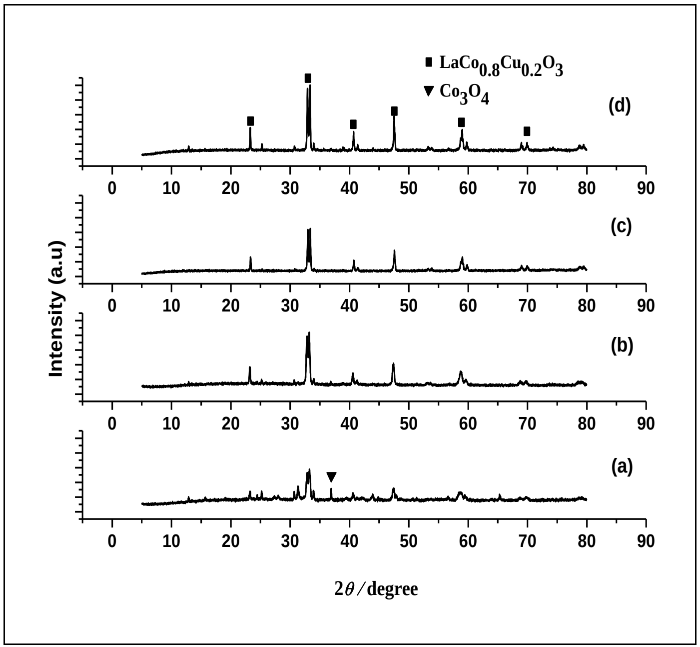


Fig. 1. XRD patterns of various catalysts (a) $LaCo_{0.8}Cu_{0.2}O_3$; (b) Cr- $LaCo_{0.8}Cu_{0.2}O_3$ (0.5 wt%); (c) Cr- $LaCo_{0.8}Cu_{0.2}O_3$ (1.0 wt%); (d) Cr- $LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%)

Scanning Electron Microscope Analysis

The morphologies of the catalysts were observed and compared with each other by scanning electron microscopy (SEM), as shown in Fig. 2. Polyhedral particles can be clearly distinguished in Figs. 2b, 2c, and 2d, while $LaCo_{0.8}Cu_{0.2}O_3$ particles were almost cubic crystals with smooth surfaces (Fig. 2a). The distinct shape change of the catalysts indicates that the shape of $LaCo_{0.8}Cu_{0.2}O_3$ particles was transformed from cubic to polyhedral after the impregnated process. Moreover, many small spherical particles were absorbed on the surface of $LaCo_{0.8}Cu_{0.2}O_3$ (Fig 2c, 2d) after the modification, and the amount increased with the increasing percentage of chromium loaded. That suggests that the presence of chromium ions will endow perovskite–type oxides with an increased surface area and possibly with high catalytic activities in the process of xylan conversion into furfural.

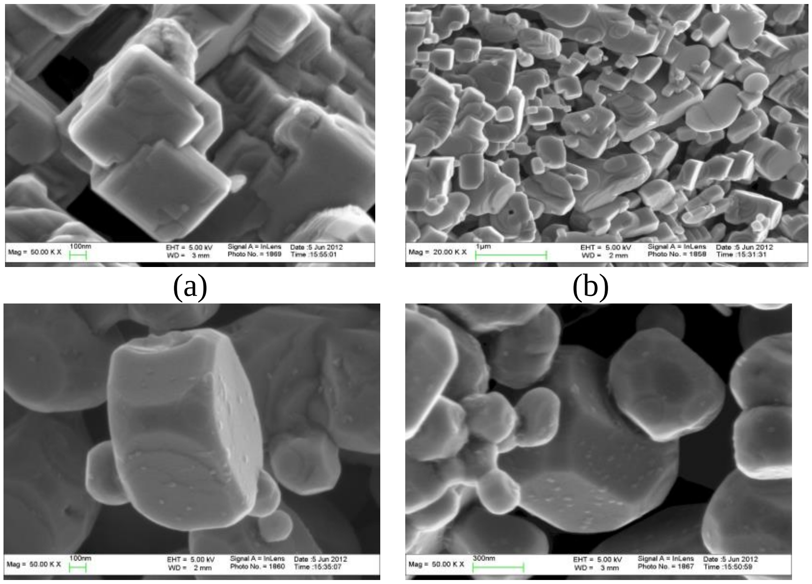

(a) (b)
(c) (d)

Fig. 2. SEM images of different samples (a) $LaCo_{0.8}Cu_{0.2}O_3$; (b) Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (0.5 wt%); (c) Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1 wt%); (d) Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%)

NH_3-TPD Characterization

NH_3-TPD profile of Cr-$LaCo_{0.8}Cu_{0.2}O_3$ is depicted in Fig. 3. The peak at 550 K is attributed to the interaction of NH_3 with moderate acid sites, which suggests that the surface of the Cr-$LaCo_{0.8}Cu0._{2}O_3$ catalyst had a broad distribution of moderate acid sites. Many acid sites on the oxides surface may correspond to the catalytic ability for the dehydration of pentose to furfural.

Effect of Perovskite-type Oxides Loaded with Different Amounts of Chromium on the Transformation of Xylan

To understand the catalytic performance of chromium-loaded perovskite-type oxides in xylan transformation, experiments were conducted at a 1:600 weight ratio of reactant to liquid at 413 K using Cr-$LaCo_{0.8}Cu_{0.2}O_3$ containing by 0.0, 0.5, 1.0, and 1.5 weight percentage of chromium as a solid catalysts. In view of the cost and the potential toxicity, higher weight percentage of chromium was not applied in this study. The reaction time was controlled in the range from 10 h to 26 h.

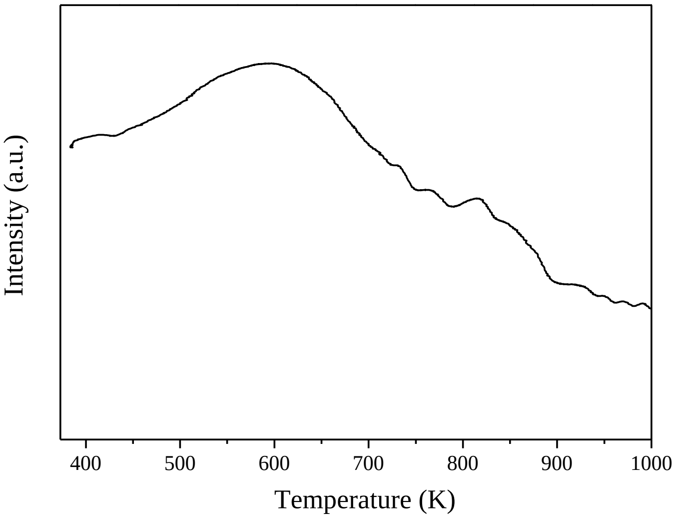
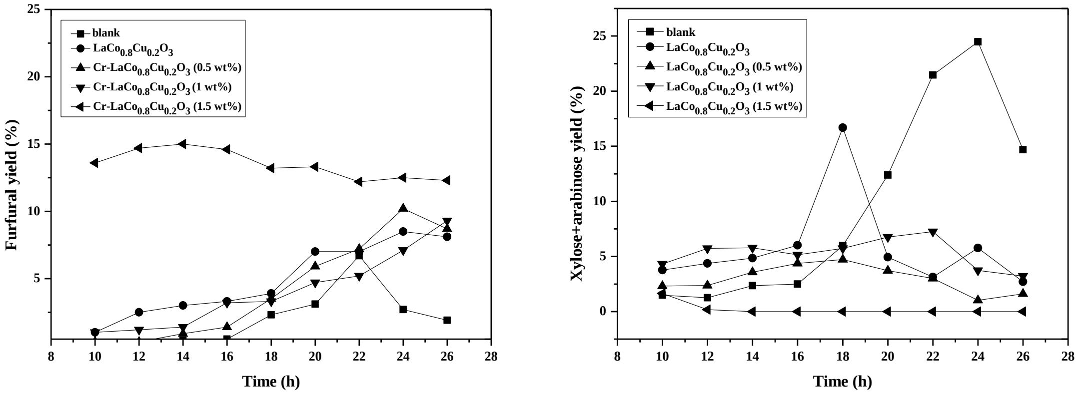


Fig. 3. NH3-TPD profile of Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%)

Figure 4 illustrates the yields of furfural and pentose in the transformation of xylan by varying catalytic conditions. Compared with the non-catalytic process, the yield of furfural increased in the presence of perovskite-type oxides. With an increment in the reaction time from 10 h to 26 h, the increase in the yield of furfural for the transformation of xylan with or without catalysts is clearly present in Fig. 4a. Moreover, the maximum yields of furfural were achieved up to 6.7% within 22 h in the non-catalytic process, and up to 15.0% within 14 h in the catalytic process using Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%). These results indicate that the catalyst plays a significant role in the selective conversion of xylan into furfural. The highest yield of furfural could be achieved within 14 h. With further prolonging of the reaction time, the yields of furfural decreased. Such a decrease can be attributed to carbonization, dimerization, and decomposition (Dhepe and Sahu 2010, 2012).



(a) (b)

Fig. 4. The yields of furfural and pentose (xylose and arabinose) for the prepared catalysts

Figure 4 also shows the effects of various catalysts on the yield of pentose (xylose and arabinose) under the same reaction conditions given. The amounts of pentose sharply decreased when using the perovskite-type oxides as catalysts in comparison with no catalyst addition. This was not consistent with the results discussed above, which indicated that the trend of furfural yield increased in the presence of perovskite-type oxides. The disagreement implies that perovskite-type oxides are directly involved in the mechanism of xylan conversion (Binder *et al.* 2010). Furthermore, when utilizing Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%) as a catalyst, almost no pentose was observed after 12 h at a temperature of 413 K, indicating that chromium-loaded perovskite-type oxides can remarkably promote the degradation of xylan to pentose and simultaneously, effectively convert them into furfural.

The main products were pentose (xylose and arabinose) in the non-catalytic process, while the furfural yield was increased by adding perovskite-type oxides into the reaction system. These changes imply that Cr-$LaCo_{0.8}Cu_{0.2}O_3$ has a good catalytic performance for the degradation of xylan to pentose, and further to convert pentose into furfural effectively. Therefore, chromium-loaded $LaCo_{0.8}Cu_{0.2}O_3$ has high selectivity for conversion of xylan into furfural.

Effect of Reaction Temperature on Dehydration of Xylan

The reaction temperature was investigated as an important function in the degradation of xylan in the presence of Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%) with the same reaction conditions (reactant/water weight ratio of 1:600 within 14 h), as presented in Fig. 5. The influence of the four temperatures (393K, 413K, 433K, and 453K) on the yields of furfural and pentose is shown in Fig. 5.

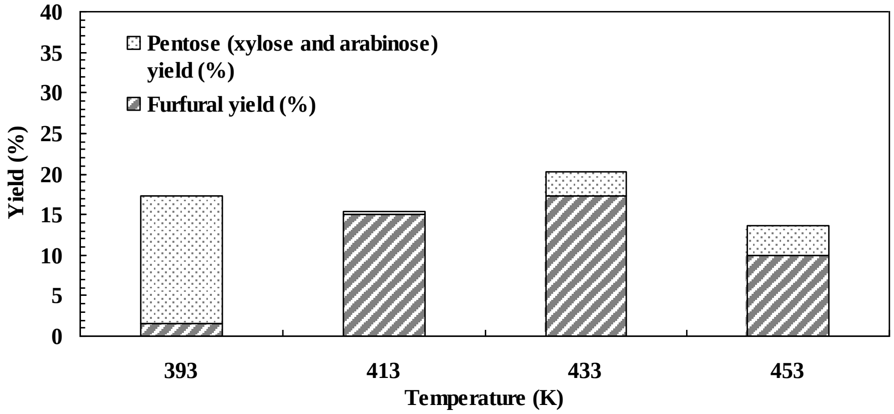


Fig. 5. Effect of reaction temperature on yields of furfural and pentose

Clearly, the transformation of xylan to furfural and pentose by catalytic-assisted reaction was strongly influenced by temperature. In the whole range of the investigated temperatures, the furfural yield increased sharply with the temperature increasing and appeared to be maximized (~17.4%) at 433 K. A significant temperature-dependent decrease in the yield of furfural was observed when the temperature is further elevated to 453 K, implying that the decrease of yield probably resulted from carbonization or repolymerization of monosaccharides at high temperatures (Dhepe and Sahu 2010, 2012). However, the reverse trend occurred for the pentose (xylose and arabinose) yield. Within the temperature range, the pentose yields were 15.7% at 393 K, 0.4% at 413 K, 2.9% at

433 K, and 3.7% at 453 K, respectively. The yield of pentose first markedly decreased and then gradually increased with a further increasing in reaction temperature. The decrease in yield of pentose may be the result of fast conversion of pentose into furfural in the presence of a catalyst. In particular, the total yield of pentose and furfural reached the maximum value at 433 K, which indicates that the most appropriate reaction temperature in the course of dehydration of xylan was 433 K.

Effect of Reactant/Liquid Weight Ratio and Reaction Time on Dehydration of Xylan

In order to understand the optimized reactant/liquid ratio of the reaction, further investigations regarding the effect of operating conditions on the furfural and pentose yields from the degradation of xylan in the presence of Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%) were performed by varying the xylan/hyperpure water weight ratios and the reaction time. These experiments were conducted at the xylan/catalyst weight ratio of 2:1 at 433 K within the time range from 8 h to18 h, and the weight ratios of xylan to hyperpure water were 1:200, 1:400, 1:600, and 1:800, respectively. The furfural yield was found to be dependent of the weight ratio of xylan to hyperpure water and the reaction time, as shown in Table 1. In the experiments on xylan/hyperpure water weight ratio, it was found that when reaction time increased, the yields of furfural increased first and then decreased. The maximum yield of furfural was obtained at 21.2% for 10 h at a weight ratio of 1:600. The decrease in yield of furfural over a long period of reaction time is attributed to the formation of byproducts such as humins by condensation reactions that took place between furfural and intermediates or oligomeric species from furfural (Dias *et al.* 2007).

Table 1. Effect of Reactant to Liquid Weight Ratio on the Yields of Furfural and Pentose

Time (h)	1:200		1:400		1:600		1:800	
	Furfural yield (%)	Pentose yield (%)	Furfural yield (%)	Pentose yield (%)	Furfural yield (%)	Pentose yield (%)	Furfural yield (%)	Pentose yield (%)
8	4.0	-	9.3	8.6	13.7	9.1	10.5	-
10	17.2	-	17.9	9.9	21.2	8.0	14.4	-
12	9.3	-	15.1	-	16.5	9.2	17.7	-
14	9.0	-	9.2	-	17.4	2.0	15.5	-
16	8.0	-	8.5	-	12.8	9.3	11.3	-
18	4.2	-	7.1	-	10.5	9.8	11.2	-
-Pentose was not detected.								

Initial substrate concentration had a remarkable effect on the furfural yield, which was obtained from the transformation of xylan. The highest furfural yield that was obtained was 21.2% in 10 h when a 1:600 weight ratio of xylan to hyperpure water was applied in the experiments. Water when heated under pressure at 433 K acquires the properties of subcritical water and weakens the glycosidic bonds of xylan through binding with a glycosidic oxygen atom (Yemis and Mazza 2011). Herein, the metal ions in perovskite-type oxides may replace the function of subcritical water by forming coordinate bonds with oxygen atoms, thereby promoting the furfural formation. Large amounts of hyperpure water were added in the reaction, which was not favorable for the accessibility of the catalyst for xylan conversion. This may be due to the water molecules competing with the hydroxyl groups on xylose for available protons, leading to catalytic ability decrease (Kristopher and Alexis 2012).

The yield of monosaccharides (xylose and arabinose) showed independence relative to the weight ratio of reactant to liquid and the reaction time. As presented in Table 1, at a low weight ratio of 1:200, no xylose and arabinose were observed, probably due to the enhanced formation of byproducts in the high initial concentration reaction system. These byproducts were mainly from consecutive condensation reactions between furfural and intermediates of the xylose-to-furfural conversion (Yemis and Mazza 2011; Dias *et al.* 2006). Moreover, no pentose appeared at a high weight ratio of 1:800. Such a weight ratio may contribute to the competitive coordination of oxygen atoms in hyper-pure water and glycosidic with metal ions in perovskite-type oxides.

The experiment at the xylan/hyperpure water weight ratio of 1:600 showed the better results in furfural formations versus other weight ratios. The total yield of furfural reached its maximum (~21.2%) within 10 h at the weight ratio of 1:600 at 433 K. Then these parameters such as a temperature of 433 K and the 1:600 weight ratio of xylan to hyperpure water were optimal for the production of furfural.

Study on Catalyst Recycling

Catalyst recycling studies were carried out with Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt% Cr) as the catalyst at 433 K. The reactant to liquid weight ratio was 1:600, and the reaction time was 10 h. After the first reaction, the solids were recovered, containing catalyst, unconverted xylan, and water-insoluble oligomers (Sahu and Dhepe 2012). Moreover, some byproducts may be adsorbed on the catalyst surface. The solids were subjected to calcinations to burn off the organic materials at 823 K for 4 h. As shown in Fig. 6, a decrease in catalytic activity was clearly observed after the first recycling run, which may result from poisoning or the decomposition of the catalyst (Dias *et al.* 2006). The data obtained by ICP-AES measurements showed that the amount of chromium in solid catalyst decreased from 1.26% to 0.38% before and after the catalytic process. Such a decrease can explain the low catalytic activity for Cr-$LaCo_{0.8}Cu_{0.2}O_3$ after one recycling run. The decrease in furfural yield can have the same explanation. However, the catalyst showed almost the same activity (~12.8%) for the transformation of xylan into furfural in the following three consecutive recycling runs. Importantly, the pentose yield had no obvious decline after the first recycling run, which indicates that the catalytic activity for pentose formation of the catalyst had no obvious change after three consecutive recycling runs.

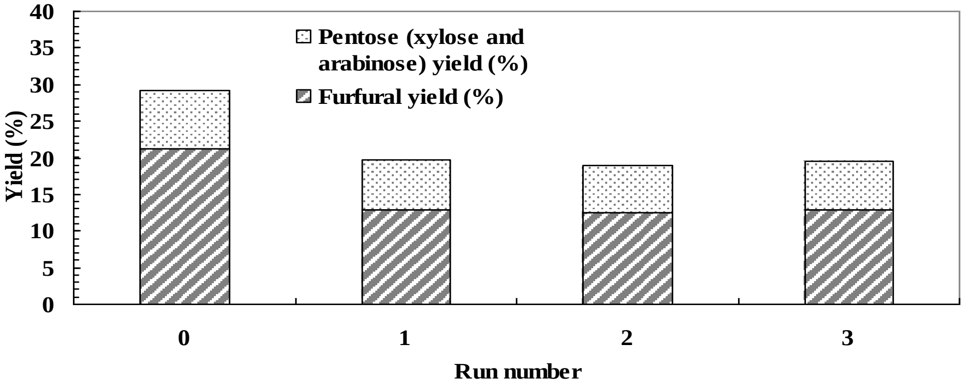


Fig. 6. The catalyst [Cr-$LaCo_{0.8}Cu_{0.2}O_3$ (1.5 wt%)] recycling study

Proposed Mechanism of Xylan Conversion into Furfural and Pentose

A possible mechanism for the conversion of xylan into furfural and pentose under the presence of Cr-$LaCo_{0.8}Cu_{0.2}O_3$ can be proposed in Fig. 7. The reaction of xylan conversion can be divided into two stages. One is the degradation of xylan into monosaccharides (xylose and arabinose) and the other is the conversion of them into furfural, acid, and other chemicals. The cyclodehydration of pentose involves the liberation of three molecules per monosaccharide molecule converted into furfural (Sérgio *et al.* 2008). The hydrolysis step of xylan mainly depends on the acidity of ultrapure water under high temperature and high pressure, while a catalysis is critical to the conversion process and competed with the degradation of xylan when water was used as the reaction medium, which is consistent with the results of furfural yield and pentose yield with or without the catalyst under the same reaction conditions.

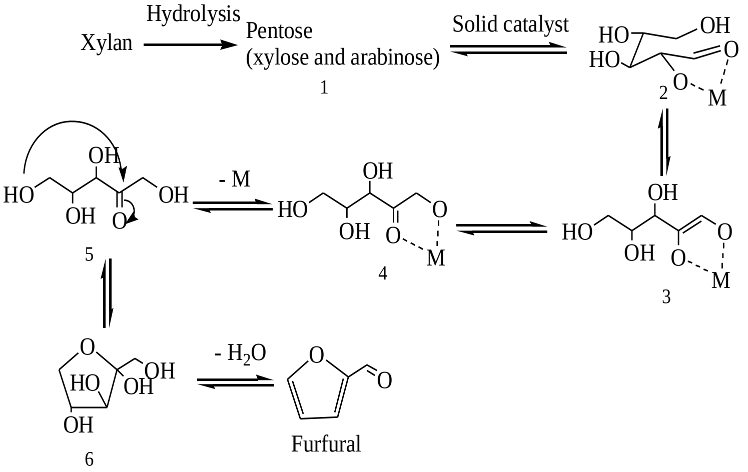


Fig. 7. Proposed mechanism of chromium-loaded catalysts promoted the transformation of xylan into furfural

Increasing the loading weight percentage of chromium, a high yield of furfural can be achieved in the appropriate period. This may be interpreted to mean that the metal ions in perovskite-type oxides play a role in proton transfer, leading to ring opening. These complexes promote rapid conversion of xylan to pentose and furfural through bonds between metal ions and the monosaccharide oxygen atom (as shown in Fig. 7), which may be caused by the incomplete coordination of the exposed metal at the solid surface (Zhang and Zhao 2010; Ding *et al.* 2012).

CONCLUSIONS

1. One-step heterogeneous catalytic process was successfully developed for the conversion of xylan into furfural in hyperpure water using a solid catalyst (Cr-$LaCo_{0.8}Cu_{0.2}O_3$) in this study.
2. The influence of the reaction parameters on the conversion of xylan into furfural was optimized. A furfural yield of 21.2% was achieved through the catalytic process within 10 h in the 1:600 weight ratio of xylan to water at 433K.
3. The catalyst (Cr-$LaCo_{0.8}Cu_{0.2}O_3$) can be regenerated.

4. This catalytic system meets the environmental requirements and will be applied for future utilization of lignocelluloses. Meanwhile, perovskite-type oxides with less toxic transition metals, as well as with higher catalytic capabilities will be investigated for the xylan conversion in further work.

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REFERENCES CITED

Ammendola, P., Chirone, R., Lisi, L., Piriou, B., and Russo, G. (2010). "Investigation of the catalytic activity of Rh–$LaCoO_3$ catalyst in the conversion of tar from biomass devolatilization products," *Appl. Catal. A: General.* 385(1-2), 123-129.

Balat, M., Balat, H., and Cahide, O. (2008). "Progress in bioethanol processing," *Prog. Energy Combust. Sci.* 34(5), 551-573.

Binder, J. B., Blank, J. J., Cefali, A. V., and Raines, R. T. (2010). "Synthesis of furfural from xylose and xylan," *ChemSusChem.* 3(11), 1268-1272.

Chheda, J. N., Roman-Leshkov, Y., and Dumesic, J. A. (2007). "Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides," *Green Chem.* 9(4), 342-350.

Dias, A. S., Lima, S., Carriazo, D., Rives, V., Pillinger, M., and Valente, A. A. (2006). "Exfoliated titanate, niobate and titanoniobate nanosheets as solid acid catalysts for the liquid-phase dehydration of D-xylose into furfural," *J. Catal.* 244(2), 230-237.

Dias, A. S., Lima, S., Pillinger, M., and Valente, A. A. (2007). "Modified version of sulfated zirconia as catalysts for the conversion of xylose to furfural," *Catal. Lett.* 114(3-4), 151-160.

Deng, H., Lin, L., and Liu, S. (2010). "Catalysis of cu-doped co-based perovskite-type oxide in wet oxidation of lignin to produce aromatic aldehydes," *Energ. Fuel.* 24(9), 4797-4802.

Dhahri, N., Dhahri, A., Cherif, K., Dhahri, J., Taibi, K., and Dhahri, E. (2010). "Structural, magnetic and electrical properties of $La_{0.67}Pb_{0.33}Mn_{1-x}CoxO_3$ ($0 \leq x \leq 0.3$)," *J. Alloys. Compd.* 496, 69-74.

Dhepe, P. L., and Sahu, R. (2010). "A solid-acid-based process for the conversion of hemicellulose," *Green Chem.* 12(12), 2153-2156.

Ding, Z. D., Shi, J. C., Xiao, J. J., Gu, W. X., Zheng, C. G., and Wang, H. J. (2012). "Catalytic conversion of cellulose to 5-hydroxymethyl furfural using acidic ionic liquids and co-catalyst," *Carbohyd. Polym.* 90(2), 792-798.

Iliopoulou, E. F., Antonakou, E. V., Karakoulia, S. A., Vasalos, I. A., Lappas, A. A., and Triantafyllidis, K. S. (2007). "Catalytic conversion of biomass pyrolysis products by mesoporous materials: Effect of steam stability and acidity of Al-MCM-41 catalysts," *Chem. Eng. J.* 134(1-3), 51-57.

Kitchaiya, P., Intanakul, P., and Krairiksh, M. (2003). "Enhancement of enzymatic hydrolysis of lignocellulosic wastes by microwave pretreatment under atmospheric-pressure," *J. Wood Chem. Technol.* 23(2), 217-225.

Kumar, R., Singh, S., and Singh, O. V. (2008). "Bioconversion of lignocellulosic biomass: biochemical and molecular perspectives," *J. Ind. Microbiol Biotechnol.* 35(5), 377-391.

Kristopher, R. E., and Alexis T. B. (2012). "The kinetics of Brønsted acid-catalyzed hydrolysis of hemicellulose dissolved in 1-ethyl-3-methylimidazolium chloride," *RSC Advances.* 2(26), 10028-10036.

Lessard, J., Morin, J. F., Wehrung, J. F., Magnin, D., and Chornet, E. (2010). "High yield conversion of residual pentoses into furfural via zeolite catalysis and catalytic hydrogenation of furfural to 2-methylfuran," *Top Catal.* 53(15-18), 1231-1234.

Lin, Y. C., and Huber, G. W. (2008). "The critical role of heterogeneous catalysis in lignocellulosic biomass conversion," *Energy Environ. Sci.* 2(1), 68-80.

Peng, X. W., Ren, J. L., and Sun, R. C. (2011). "An efficient method for the synthesis of hemicellulosic derivatives with bifunctional groups in butanol/water medium and their rheological properties," *Carbohydr. Polym.* 83(4), 1922-1928.

Sahu, R., and Dhepe, P. L. (2012). "A one-pot method for the selective conversion of hemicellulose from crop waste into C_5 sugars and furfural by using solid acid catalysts," *ChemSusChem.* 5(4), 751-761.

Sérgio, L., Pillinger, M., and Valente, A. A. (2008). "Dehydration of D-xylose into furfural catalysed by solid acids derived from the layered zeolite Nu-6(1)," *Catal. Commun.* 9(11-12), 2144-2148.

Shi, X., Wu, Y., Yi, H., Rui, G., Li, P., Yang, M., and Wang, G. (2011). "Selective preparation of furfural from xylose over sulfonic acid functionalized mesoporous sba-15 materials," *Energ.* 4(4), 669-684.

Wei, L., Shrestha, A., Tu, M. B., and Adhikari, S. (2011). "Effects of surfactant on biochemical and hydrothermal conversion of softwood hemicellulose to ethanol and furan derivatives," *Process Biochem.* 46(9), 1785-1792.

Yemis, O., and Mazza, G. (2011). "Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction," *Bioresour. Technol.* 102(15), 7371-7378.

Zhang, Z., and Zhao, Z. K. (2010). "Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid," *Bioresour. Technol.* 101(3), 1111-1114.

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