**Functional Rice Husk as Reductant and Support to Prepare As-Burnt
Cu-ZnO Based Catalysts Applied in Low-Temperature Methanol Synthesis**

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Abstract

A novel method, that the precursor is burnt in argon without further reduction to directly prepare metallic catalyst, is developed using low-valued by-product. Rice husk not only contributed as catalyst support, but also as reductant and fuel. The XRD, TPR and TG-DTA analysis prove that Cu phase in the as-burnt catalyst is almost reduced to metallic Cu⁰. The as-prepared catalysts exhibit higher activity and methanol selectivity than those prepared by a conventional impregnation method. This method may open a new way to prepare metallic catalysts without further reduction, especially for some catalytic reactions promoted by K, Ca, Mg and Mn.

Key words: Low-temperature methanol synthesis; Rice husk; Rice husk ash; Metallic catalysts; Reduction-free;

1. Introduction

Rice husk (RH), that is mainly composed of cellulose, lignin, pentosans and amorphous silica [1], is an abundant and renewable low-valued by-product in rice-producing countries like China, India, Brazil and US [2]. RH is usually used as direct fuel, pet foods fiber, building materials, and fertilizer. Recently, much attention has been focused on the utilization of RH because of the economic, environmental and social issues [3]. RH can be applied as gasification fuel [4], a kind of sustaining and renewable energy which contributes to the reduction of greenhouse gases. Chemically modified RH can also be used as low-cost adsorbents for the removal of heavy metals [5] and organic compounds [6] from the waste water. In an economic value-added way, rice husk ash (RHA) can be applied to produce advanced materials [3], such as silica [7], activated carbon [8], molecular sieves [9] and so on.

In this study, a novel method is developed to prepare metallic catalyst (Cu-ZnO/RHA) directly without further reduction. Here, RH is not only used as the catalyst support precursor, but also as the reductant and fuel. The as-burnt Cu-ZnO/RHA was directly applied in low-temperature methanol synthesis from CO/CO₂/H₂ using ethanol as a catalyst and solvent [10-13]. The activity of the as-burnt catalyst prepared by this novel method without further reduction is much higher than that prepared by a conventional impregnation method which is already after 10 h reduction at 523 K by 5% H₂.

The advantages of this novel method are as follows: 1) the extra cost for reduction

energy and engineering is saved; 2) low-valued by-product RH is used as the reductant, the fuel and the catalyst support with functional trace elements as promoters; 3) nano-structured Cu-ZnO/RHA (about 15 nm Cu^0) can be prepared; 4) the activity of as-burnt catalyst is much higher; 5) the whole catalyst preparation process is very easy; 6) some catalytic reactions promoted by K, Ca, Mg and Mn are especially suitable for this novel method to prepare their metallic catalysts, as traces of biomass-derived K, Ca, Mg and Mn are left in RHA.

2. Experimental

The details for the preparation of catalysts and the procedure of catalytic activity tests were shown in the Electronic supplementary information (ESI).

3. Results and discussion

The XRD patterns of the catalysts C_{RH} , which were burnt in the argon atmosphere at 523 and 573 K for 1 h respectively, are compared in Fig. S1(ESI). The XRD patterns of $\text{C}_{\text{RH-623}}$, $\text{C}_{\text{RHA-623}}$ and $\text{C}_{\text{SC-623}}$, which were burnt in argon at 623 K for 3 h, are compared in Fig. 1. As displayed in Fig. 1a, only Cu and SiO_2 characteristic diffraction peaks are observed. However, the peaks of $\text{C}_{\text{RHA-623}}$ are attributed to SiO_2 , ZnO, Cu_2O and CuO phases in Fig. 1b, indicating that Cu^{2+} can only be partly reduced to Cu^{1+} but not Cu^0 , by the amorphous carbon left in RHA at 623 K. As shown in Fig. 1c, the peaks of $\text{C}_{\text{SC-623}}$ are corresponded to SiO_2 , ZnO, Cu, Cu_2O and CuO phases, suggesting that CuO phase can be partly reduced to Cu_2O and Cu^0 by activated carbon at 623 K for 3 h.

The XRD patterns of $\text{C}_{\text{RH-623-Reduction}}$, $\text{C}_{\text{RHA-623-Reduction}}$ and $\text{C}_{\text{SC-623-Reduction}}$, which were after 10 h reduction by 5% H_2 at 523 K, are shown in Fig. 2a-2c, respectively. It is

clear that no obvious differences are observed between Fig. 1a and 2a. Cu_2O and CuO phases in $\text{C}_{\text{RHA-623}}$ and $\text{C}_{\text{SC-623}}$ are reduced to metallic Cu^0 in $\text{C}_{\text{RHA-623-Reduction}}$ and $\text{C}_{\text{SC-623-Reduction}}$, respectively.

Cu crystalline sizes of the as-prepared catalysts calculated by Scherrer formula are presented in Table 1. With increasing the calcination temperature from 523 to 623 K, Cu crystalline size of the as-burnt catalyst C_{RH} gradually increases from 13 to 16 nm, and the ZnO phase is not clearly observed. It is inferred that higher calcination temperature leads to the increase of Cu crystalline sizes, but without significant change; ZnO phases are well dispersed on the support when this novel catalyst-preparation method is used. As compared in Fig. 2 and Table 1, Cu crystalline size of $\text{C}_{\text{RHA-623-Reduction}}$ and $\text{C}_{\text{SC-623-Reduction}}$ is nearly the same (about 20 nm), but larger than that of $\text{C}_{\text{RH-623}}$ (16 nm), indicating that the atmosphere of RH pyrolysis is the key point to result in the formation of smaller Cu crystalline size and amorphous ZnO phase.

The TG-DTA curves of RH in argon and air, as well as the precursor of C_{RH} were displayed in Fig. S2(ESI). It is deduced that during this pyrolysis process, CO and H_2 are released and act as the reducing agent, that can reduce Cu^{2+} to metallic Cu^0 at relatively low temperature.

H_2 -TPR of the burnt catalysts is compared in Fig. 3. For $\text{C}_{\text{RH-623}}$, only a small broad peak, which is assigned to the reduction of small quantities of CuO or Cu_2O oxidized by 1% oxygen, is observed at about 470 K in Fig. 3a. As displayed in Fig. 3b, the TPR profiles of $\text{C}_{\text{RH-623-Reduction}}$, which is after 10 h reduction at 623 K by a flow of 5% hydrogen and passivated by 1% oxygen, are nearly the same as those in Fig. 3a. But, the amount of the hydrogen consumption in Figs. 3a and 3b is much lower than that in Figs. 3c and 3d, which are corresponded to the TPR profiles of $\text{C}_{\text{RHA-623}}$ and $\text{C}_{\text{SC-623}}$. Above

mentioned phenomena evidently prove that Cu phase in C_{RH-623} is almost reduced to metallic Cu^0 , which is in good accordance with XRD analysis in Fig. 2a. As shown in Figs. 3c-3d, the hydrogen consumption is observed in the range from 440 to 550 K, and the shapes of the TPR profiles are asymmetric with a shoulder, suggesting that the reduction processes are complicated with an overlapping of different copper species. The broad peak at about 470 K is attributed to the reduction of Cu_2O [14], indicating that part of Cu^{2+} can be reduced to Cu^{1+} species in the presence of amorphous carbon during the calcination process. The main peaks at about 523 K are derived from the reduction of well dispersed CuO [14] on the support. This finding is also proved by XRD analysis that CuO and Cu_2O species are left in $C_{RHA-623}$ and C_{SC-623} .

The activities of C_{RH-623} without further reduction, as well as $C_{RH-623-Reduction}$, $C_{RHA-623-Reduction}$ and $C_{SC-623-Reduction}$ after 10 h reduction were conducted at 453 K and 5.0 MPa for 6 h in low-temperature methanol synthesis from syngas containing CO_2 using the ethanol as a co-catalyst and solvent. Characterization results of the catalysts and batch reaction records are compared in Table 1. It is obvious that the BET and the copper (Cu^0) surface areas of the as-burnt catalysts increase with the increased calcination temperatures when RH is used as the support and the reductant, because at lower calcination temperature, more organic residues are left, which obviously decrease the BET and the copper (Cu^0) surface areas. The BET and Cu^0 surface areas of C_{RH-623} (67.2 and $4.3\text{ m}^2\text{g}^{-1}$) are much larger than $C_{RHA-623-Reduction}$ (54.9 and $3.4\text{ m}^2\text{g}^{-1}$), although the compositions of C_{RH-623} and $C_{RHA-623-Reduction}$ are nearly the same. The BET and Cu^0 surface areas of $C_{RHA-623}$ before reduction are about 56.3 and $0.1\text{ m}^2/\text{g}$ respectively, indicating that almost no metallic Cu can be available if RHA is applied as the reductant. We consider that this novel catalyst preparation method can highly disperse Cu and ZnO,

because both Cu and ZnO crystalline sizes of C_{RH-623} are smaller than those of $C_{RHA-623-Reduction}$, as displayed in Fig. 1. The BET surface areas of $C_{SC-623-Reduction}$ is the largest, because the activated carbon support has larger BET surface areas ($943\text{ m}^2\text{g}^{-1}$).

As displayed in Table 1, with increasing the calcination temperature from 523 to 623 K in argon, the total carbon conversion of the as-burnt catalyst remarkably increases from 28.9 to 52.2% because of the enhanced metallic copper (Cu^0) and BET surface areas. Meanwhile, the selectivity of methanol also significantly increases from 12.3 to 37.4%. As stated, if the precursor were burnt at lower temperature, more organic residues are left in C_{RH} , which will remarkably affect the final valence states of Cu in the as-burnt catalyst. The proposed mechanism [12] for low-temperature methanol synthesis has already proved that Cu^+ and ZnO are the active sites for the formation of formate and ethyl formate, but only Cu^0 is active for the hydrogenation of ethyl formate. So the methanol selectivities of the as-burnt catalysts C_{RH} increase with the increased calcination temperature from 523 to 623 K.

As compared with those of $C_{RH-623-Reduction}$ after reduction, the characterization results and the batch reaction records of C_{RH-623} are nearly the same, fully proving that the CuO phase is almost reduced to metallic Cu^0 during the pyrolysis of RH in argon. The total carbon conversion and the selectivity of C_{RH-623} are a little higher than those of $C_{RHA-623-Reduction}$, because C_{RH-623} has larger copper (Cu^0) surface areas and smaller Cu crystalline size. Cu^0 is the active site for the rate-determining step in this low-temperature methanol synthesis. It is considered that the methanol selectivity is associated with the crystalline size of Cu. Smaller crystallite size of Cu is in favor of methanol formation, exhibiting higher hydrogenation ability.

As compared with $C_{SC-623-Reduction}$ (33.8%), the total carbon conversion of $C_{RHA-623}$

(45.5%) is much higher, although $C_{SC-623-Reduction}$ has larger copper (Cu^0) surface areas. It was reported [15] that K promoter had promotional effect in the formation of the thermodynamically stable carbonate, and K promoted copper catalyst by stabilizing the Cu^+ species. K is just the main impurity left in the burnt catalysts when using RHA [1-3] as the support. As reported [12-14], Cu^+ is the active site in this low-temperature methanol synthesis, so K-contained support can significantly improve the activity of Cu-based catalysts. However, the methanol selectivity of C_{RH-623} is 37.4%, about 8.7% lower than that of $C_{SC-623-Reduction}$, because some organic residues, which are derived from pyrolysis of rice husk, are left in C_{RH-623} and may affect the valence state of Cu during the reaction. Only Cu^0 is active for hydrogenation of the ethyl formate. Considering the fact that no organic reagents were used in the preparation of $C_{SC-623-Reduction}$, the methanol selectivity of C_{RH-623} is slightly lower than that of $C_{SC-623-Reduction}$.

4. Conclusion

A novel method is developed to prepare metallic catalyst (Cu-ZnO/RHA) directly without further reduction. Here, rice husk is not only used as the catalyst support, but also as the reductant and fuel. During the calcination process in argon, CO and H_2 , which are released from the degradation of hemi-cellulose or cellulose, act as the reducing agent, that can reduce Cu^{2+} to metallic Cu^0 at relatively low temperature (523 K). The XRD and TPR analysis prove that Cu phase in C_{RH-623} is almost reduced to metallic Cu^0 . The activity and the methanol selectivity of C_{RH-623} are much higher than those of $C_{RHA-623-Reduction}$ prepared by a conventional impregnation method and reduced by 5% hydrogen for 10 h. As compared with $C_{SC-623-Reduction}$, the total carbon convention

of $C_{\text{RHA-623}}$ is much higher, because K promoter from RH can stabilize the Cu^+ species, which is the active site for the formation of ethyl formate.

The whole catalyst-preparation process is very easy and the extra cost for reduction energy and engineering is saved with low-valued by-product RH as the reductant, the fuel and the catalyst support. The activity of as-burnt nano-structured Cu-ZnO/RHA (about 15 nm Cu^0) without further reduction is much higher than that prepared by a conventional impregnation method. Some catalytic reactions promoted by K, Ca, Mg and Mn are especially suitable for this novel method to prepare the corresponding metallic catalysts, as biomass-derived traces of K, Ca, Mg and Mn are left from RHA.

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References

- [1] S. Chandrasekhar, K.G. Satyanarayana, P.N. Pramada, P. Raghavan, J. Mater. Sci. 38 (2003) 3159-3168.
- [2] R. Pode, Renew. Sust. Energ. Rev. 53 (2016) 1468-1485.
- [3] N. Soltani, A. Bahrami, M.I. Pech-Canul, L.A. González, Chem. Eng. J. 264 (2015) 899-935.
- [4] T. Madhiyanon, P. Sathitruangsak, S. Soponronnarit, Appl. Therm. Eng. 30 (2010) 347-353.
- [5] D. Sud, G. Mahajan, M.P. Kaur, Bioresour. Technol. 99 (2008) 6017-6027.
- [6] M. Rafatullaha, O. Sulaimana, R. Hashima, A. Ahmadb, J. Hazard. Mater. 177 (2010) 70-80.
- [7] S. Gu, J.S. Zhou, C.J. Yu, Z.Y. Luo, Q.H. Wang, Z.L. Shi, Ind. Crop. Prod. 65 (2015) 1-6.
- [8] O. Ioannidou, A. Zabaniotou, Renew. Sust. Energ. Rev. 11 (2007) 1966-2005.
- [9] S. Chiarakorn, T. Areerob, N. Grisdanurak, Sci. Technol. Adv. Mater. 8 (2007) 110-115.
- [10] L. Shi, K. Tao, R.Q. Yang, F.Z. Meng, C. Xing, N. Tsubaki, Appl. Catal. A-Gen. 401 (2011) 46-55.
- [11] L. Shi, Y.S. Tan, N. Tsubaki, ChemCatChem 4 (2012) 863-871.
- [12] L. Shi, G.H. Yang, K. Tao, Y. Yoneyama, Y.S. Tan, N. Tsubaki, Accounts Chem. Res. 46 (2013) 1838-1847.
- [13] L. Shi, W.Z. Shen, G.H. Yang, X.J. Fan, Y.Z. Jin, C.Y. Zeng, K. Matsuda, N. Tsubaki, J. Catal. 302 (2013) 83-90.
- [14] L. Shi, D. Sun, Y.X. Wang, Y.S. Tan, J. Li, S.R. Yan, R.G. Fan, N. Tsubaki, Catal.

Sci. & Technol., 2016, DOI: 10.1039/C5CY02010G.

[15] G.R. Sheffer, T.S. King, J. Catal. 115 (1989) 376-387.

Figure caption

Fig. 1. XRD patterns of the as-burnt catalysts (a) C_{RH-623} , (b) $C_{RHA-623}$ and (c) C_{SC-623} without further reduction ($\blacktriangledown$, SiO_2 ; $\star$, Cu; $\bullet$, Cu_2O ; $\circ$, CuO ; $\blacksquare$, ZnO).

Fig. 2. XRD patterns of the catalysts (a) $C_{RH-623-Reduction}$, (b) $C_{RHA-623-Reduction}$ and (c) $C_{SC-623-Reduction}$ after reduction ($\blacktriangledown$, SiO_2 ; $\star$, Cu; $\blacksquare$, ZnO).

Fig. 3. TPR profiles of the as-burnt catalysts (a) C_{RH-623} , (b) $C_{RH-623-Reduction}$, (c) $C_{RHA-623}$ and (d) C_{SC-623} .

Fig. 1. Shi et al

Fig. 2. Shi et al

Fig. 3. Shi et al

Table 1 Characterization results and batch reactions for low-temperature methanol synthesis.

Catalysts	S_{BET}^b (m ² /g)	S_{Cu}^c (m ² /g)	Cu ^d Dia. (nm)	Conversion (%)			Selectivity (%)		Yield (%)	
				CO	CO ₂	C_{Total}^e	CH ₃ OH	HCOOC ₂ H ₅	CH ₃ OH	HCOOC ₂ H ₅
C _{RH-523}	28.4	1.9	13	25.5	50.3	28.9	12.3	87.7	3.5	25.3
C _{RH-573}	52.7	3.2	14	39.6	69.2	43.7	20.3	79.7	8.9	34.8
C _{RH-623}	67.2	4.3	16	48.6	74.9	52.2	37.4	62.6	19.5	32.7
C _{RH-623-Reduction}	72.4	4.4	16	47.9	74.1	51.5	35.2	64.8	18.1	33.4
C _{RHA-623-Reduction}	54.9	3.4	20	42.3	65.7	45.5	28.3	71.7	12.9	32.6
C _{SC-623-Reduction}	245.3	7.1	20	29.4	61.2	33.8	46.1	43.9	15.6	14.8

^a Reaction conditions: T = 453 K, P = 5.0 MPa, catalyst weight: 1 g, ethanol solvent: 40 mL, stirring speed: 2000 rpm, reaction time: 6 h, syngas: Ar/CO/CO₂/H₂ = 3.13/33/5.23/58.64.

^b Determined by N₂ physical adsorption-desorption at 77 K.

^c Determined from N₂O pulse chemisorption.

^d Calculated by Scherrer formula.

^e $C_{\text{Total}} = \text{CO conv.} \times a/(a + b) + \text{CO}_2\text{conv.} \times b/(a + b)$, (a, b were the contents of CO, CO₂ in the feed gas).