The conversion of silicon contained in agriculture waste to alkoxysilanes

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The growth of biomass accumulated certain amount of silicon, especially the growth of rice straw, rice husk etc., in which about 5-15 wt% of silica was usually contained [1], as shown in Table 1. Thus, for the effective utilization of agriculture waste, it is necessary to consider simultaneously the conversion and utilization of both organic and inorganic components. Alkoxysilanes is one of the most imperative precursors of siloxane materials, which play indispensable roles in various applications, including coatings, electronics, precise casting, and organic synthesis, among many others [2,3]. The current industrial production of alkoxysilanes is mainly carried out by using silicon tetrachloride or pure silicon as starting materials, characterized by serious pollution and energy consumption concerns [4]. The conversion of silicon contained in agriculture waste to alkoxysilanes via greener route is of significant importance.

Table 1. Silica content of typical agriculture waste

Biomass	Rice straw	Wheat straw	Corn straw	Rice hask
Silica wt%	9.8	4.7	4.6	15.0

Supercritical ethanol promoted conversion of silicon contained in rice straw to alkoxysilanes. It was found that tetraethyl orthosilicate (TEOS) and diethyl dimethyl orthosilicate (EMOS)could be obtained when treating rice straw with ethanol. Figure 1 provide the formation of TEOS and EMOS under different reaction conditions, where TEOS could be obtained with high yield in supercritical ethanol. The sharp increase of TEOS yield indicates the important role of supercritical state. It was indicated that both organsilicon connected with organic components in rice straw and the inorganic silica deposited in silica cell exists in rice straw can be converted to alkoxysilcanes. Furthermore, exogenous silica could be converted to alkoxysilanes directly when mixed with biomass, indicating a new conversion process.

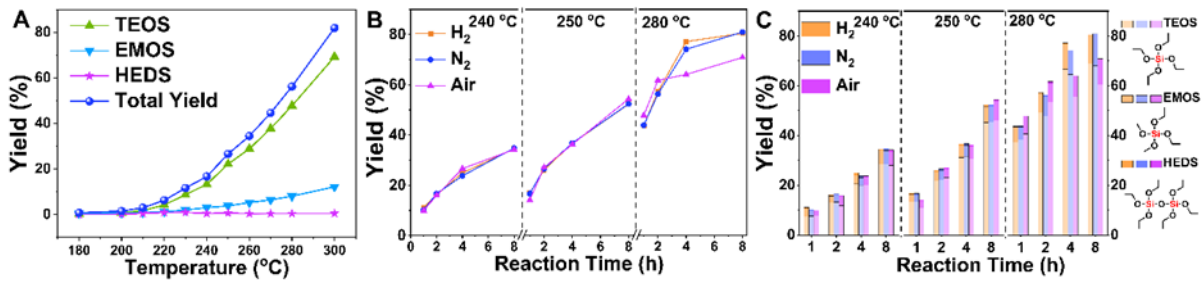

Fig. 1. Effect of reaction conditions on the yield of alkoxysilanes. (A) Temperature effects at 2MPa N_2 for 2 h. (B) Time effects on the total yield of alkoxysilanes under 2 MPa H_2/N_2 or no extra gas pressure at 240 °C, 250 °C and 280 °C. (C) Time effects on the specific yields of TEOS, EMOS, and HEDS under 2 MPa H_2/N_2 or no extra gas pressure at 240 °C, 250 °C and 280 °C.

Calcination of rice husk provide another way to produce TEOS. As show in Figure 2, proper temperature calcined rice hask could also be effectively converted to TEOS. Supercritical ethanol is also found responsible for the conversion. Calcination temperature plays also an important role for the calcined ash from both types of rice hask, that is, below 400 °C and over 700 °C (Fig. 2c and 2d), the alkoxysilanes yield was only about 20 mol% for RHA300 and RHA750, but the alkoxysilanes yield maintained at around 85 mol% from 400 to 625 °C (RHA400-625). It was interesting to note that the introduction of proper amount of rice straw improved the yield of alkoxysilanes, with the highest yield of 94.4 mol% obtained at 10-90 of RSHA-A and 93.5 mol% obtained at 20-80 of RSHA-C, respectively. The control experiment with rice straw ash calcinated at 500 oC as raw material afforded alkoxysilanes yield of 57.3 mol%. The inherent complexity of the ash catalyses the reaction, where

potassium ion catalyses the synthesis of alkoxysilanes in a most pronounced positive effect in alkaline system, and the co-existence of phosphorus species exhibited synergetic effect to promote the selectivity to TEOS.

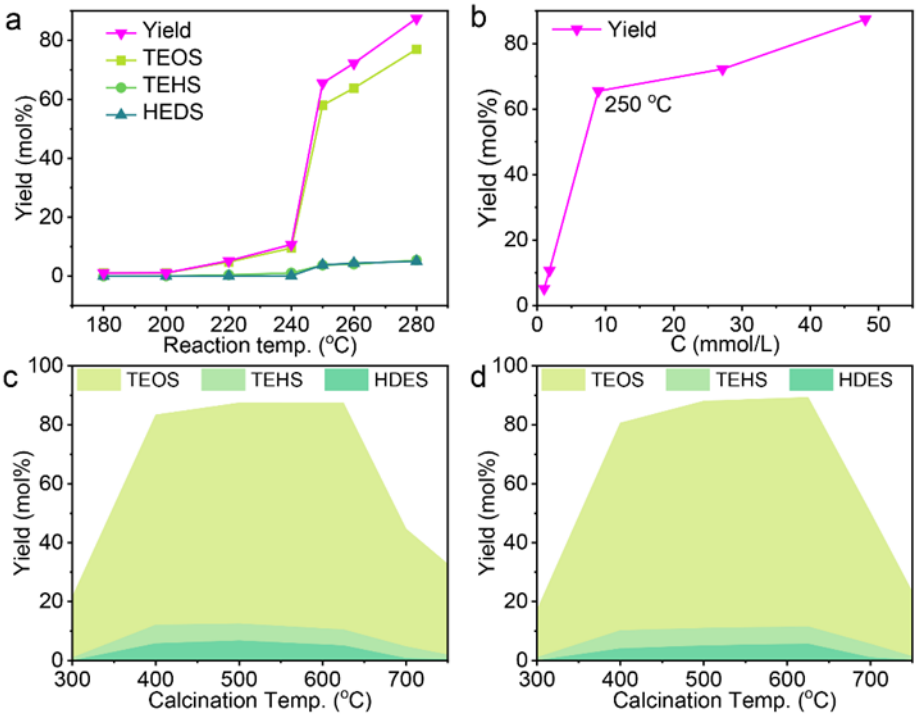

Fig. 2 The effects of reaction variables on the yield of alkoxysilanes. a) The effects of reaction temperature on the yield of alkoxysilanes from RHA-A625 (Rice husk ash Anhui, ash calcined at 625 °C). b) The ethoxy anion concentration dependence of the TEOS yield. c) The effects of calcination temperature of RHA-A on the yield of alkoxysilanes. d) The effects of calcination temperature of RHA-C (the rice husk ash from Chongqing) on the yield of alkoxysilanes. Reaction conditions: rice husk ash (100 mg), ethanol (50 mL), 280 °C, 2 MPa N_2, 1 h.

The production of TEOS from agriculture waste such as rice straw and rice husk shows promise to pave a new way for the synthesis of alkoxysilanes, which not only makes effective use of the waste, but also produces value-added alkoxysilanes with a totally new greener method. Detailed mechanism and correlation of the obtained data need further careful research.

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References

[1]. Vassilev, S. V. et al. (2010)
[2]. B. Yi, et al. (2021)
[3]. S.T. Lazar, et al. (2020).
[4]. J.C. Furgal, et al. (2019)