

Effects of Heterogeneous Catalyst Preparation Methods on Biomass Conversion

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Abstract:

The molecules extracted from bio-based resources already contain functional groups, so that the synthesis of chemicals generally requires a lower number of steps than from alkanes, while heterogeneous catalysts are still required to convert these molecules to valuable chemicals and/or biofuels. Catalyst preparation method plays an important role in its performance for biomass conversion. In the present work, effects of heterogeneous catalyst preparation methods on biomass conversion are compared and discussed. For certain biomass molecules, specific catalyst preparation method is proposed.

1 Introduction

Biomass is first converted by gasification to synthesis gas, or by pyrolysis to a mixture of small molecules. Synthesis gas may then be converted to hydrocarbons which are subsequently converted to intermediates, using the classical synthesis routes developed for petroleum feedstock. Similarly, small molecules obtained by biomass pyrolysis may, after separation, be converted to valuable chemicals via the existing flow sheets of chemical synthesis. [1, 2, 3, 4, 5, 6, 7] This is not a cost-effective and environmentally sustainable route for chemical production, as highly functionalized molecules from biomass are first degraded to C_1 molecules or hydrocarbons which are then subjected to the traditional chemical synthesis steps in order to be functionalized again. [8, 9, 10, 11, 12, 13]

A biorefinery is a facility that integrates biomass conversion processes to produce fuels and chemicals. According to this scheme, part of the biomass is converted to fuels via pyrolysis and gasification, and the other part is converted by fermentation or chemocatalytic routes to well-identified platform molecules, that can be employed as building blocks in chemical synthesis. The fermentation processes are continuously improved with new, genetically modified bacteria or yeasts. [14, 15, 16, 17]

Vegetables oils, and most of the carbohydrates used to produce chemicals, are issued from grains harvested primarily for food and feed, and their productivity is rather low, for example between 3 and 8 tons of dry matter per hectare of cultivated land. [18, 19, 20, 21, 22, 23] In contrast,

the non-grain portion of biomass - that is, the agricultural wastes (cobs, stalk, stovers) and vegetative biomass (trees, leaves, etc.) - are barely used to produce chemicals, in spite of their much greater availability. Lignocellulosic materials are built on the intimate mixture of cellulose, hemicellulose and lignin that is difficult to separate and to process. Cellulose polymers are glucoside units connected via 1,4-glycosidic linkages instead of β -linkages in the case of starch; they are therefore more stable and difficult to hydrolyze by chemical or enzymatic means. Hemicelluloses are more easily hydrolyzed than celluloses, and yield valuable pentoses such as xylose and arabinose. [24, 4, 25, 26, 27] They are, potentially, a very important and as-yet largely untapped renewable source of chemicals. Lignins have a very complex polymeric structure based on interconnected aromatic derivatives, and they are very recalcitrant materials to process. Nonetheless, chemicals such as vanillin can be obtained via the catalytic oxidation of lignosulfonate.

2 Supported Catalysts

The activity of solid catalysts is usually proportional to the active surface area per unit volume of catalyst, provided that transport limitations are not present. [28, 7, 29, 30] A high activity per unit volume calls for small particles. [31] As most active species sinter rapidly at the temperatures at which the thermal pretreatment and the catalytic reaction proceed, small particles of the active species alone generally do not provide thermostable, highly active catalysts. To arrive at solid catalysts of the desired shape, mechanical strength, porous structure, activity, and thermal stability, two different materials, the support and the active material - provide the different functions that the catalyst must fulfill. [32] The support, which is usually highly thermostable, furnishes the shape, mechanical strength and porous structure, while the catalytic activity and selectivity are due to the active component(s). As indicated in Figure 1, the sintering of small particles alone leads to a low active surface area, whereas application of the active component on a support can stabilize the active surface area.

The most favorable size for supported active particles has only seldom been established, the reason being that it is difficult to vary systematically the size of the active particles deposited onto a support while maintaining a narrow particle size distribution. [33] It is, consequently, desirable to apply the active component(s) uniformly and densely distributed over the surface of the support as particles the size of which can be controlled. This is one of the main goals when preparing supported catalysts by deposition-precipitation.

3 Ion Exchange and Impregnation

The methods most frequently used to achieve the deposition of the active component precursor are impregnation, ion exchange, anchoring, grafting, spreading and wetting, heterogenization of complexes, deposition-precipitation (homogeneous and redox), and adapted methods in the case

of supported bimetallic catalysts. [34, 35] In some cases, the active component (not its precursor form) can be deposited directly onto the support. In the following sections only the case of a single active component will be discussed. When several active components are required, they can be deposited consecutively or simultaneously. Although the problem becomes more complicated because of possible interferences, it can be treated with the same basic concepts presented here. [36, 37, 38]

Ion exchange is an operation which consists of replacing an ion in an electrostatic interaction with the surface of a support by another ion species. The support containing ion A is plunged into an excess volume (much larger than the pore volume) of a solution containing ion B that is to be introduced. Ion B gradually penetrates into the pore space of the support and takes the place of ion A, which passes into the solution, until an equilibrium is established corresponding to a given distribution of the two ions between the solid and the solution. The solid is then washed, and finally separated by filtration or centrifugation. [39, 40]

When the pore space of the support has first been filled up with pure solvent of the impregnation solution prior to being placed in contact with the latter, the characteristics defined above are valid only for the first step of saturation by the solvent. The second step is generally an immersion that consists of plunging the solvent-saturated support into the impregnation solution. This step is no longer exothermic and does not cause the development of high pressure inside the pore space. The driving force of the progressive migration of the salt into the heart of the grains is the concentration gradient between the extragranular solution and the moving front of the soluble precursor in the intergranular solution. [41] The migration time is obviously much longer than for capillary impregnation.

4 Deposition-Precipitation

Precipitation of an active precursor onto a support suspended in a solution of the precursor can provide high loadings, as the compound(s) dissolved in a liquid volume that is large compared to the support pore-volume, are concentrated onto the support. [42, 43] Besides coprecipitation of the precursors of the support and the active material and subsequent selective removal of some components, precipitation in the presence of a suspended support is also often carried out to achieve high loadings of the support. The apparatus and procedures do not differ significantly, but the precipitation usually proceeds where the precipitating liquid enters the suspension, and the precipitant necessarily does not enter the liquid present in the porous conglomerates of the support. When nucleation and growth of the precipitate of the precursor are rapid, large crystallites of the precursor result. With a rapid nucleation and slow growth (which is usually encountered with poorly soluble compounds), clusters of small particles of the active precursor outside the pore system of the support are often obtained. [44, 45] At high concentrations, at a point where the precipitant enters the suspension, the small particles rapidly and irreversibly flocculate, which leads to the clustering of small particles. Catalysts prepared in this way are liable to rapid deacti-

vation during pretreatment or use at elevated temperatures, as the small elementary particles of the precursor are intimately connected and therefore sinter readily.

The chemical interaction of metal ions precipitating from a homogeneous solution with silica at higher temperatures has been widely confirmed. With finely divided silica, reaction to synthetic clay minerals has been established. Consequently, the reaction is not confined to the surface of silica, but also involves the bulk of small silica particles. Reaction to another solid phase was already concluded from the maximum through which the pH curve often passes during the deposition-precipitation of nickel at a temperature of about 350 K, or higher. The complete reaction of the silica particles is also evident from electronmicrographs, which show a complete disappearance of the silica particles initially present. When the amount of bivalent metal ions is insufficient to convert the silica completely, the growth of platelets of clay minerals from the silica particles can easily be seen. [15, 46]

5 Concluding Remarks

In the present work, effects of heterogeneous catalyst preparation methods on biomass conversion are compared and discussed. It is concluded that for certain biomass molecules, specific catalyst preparation method is proposed.

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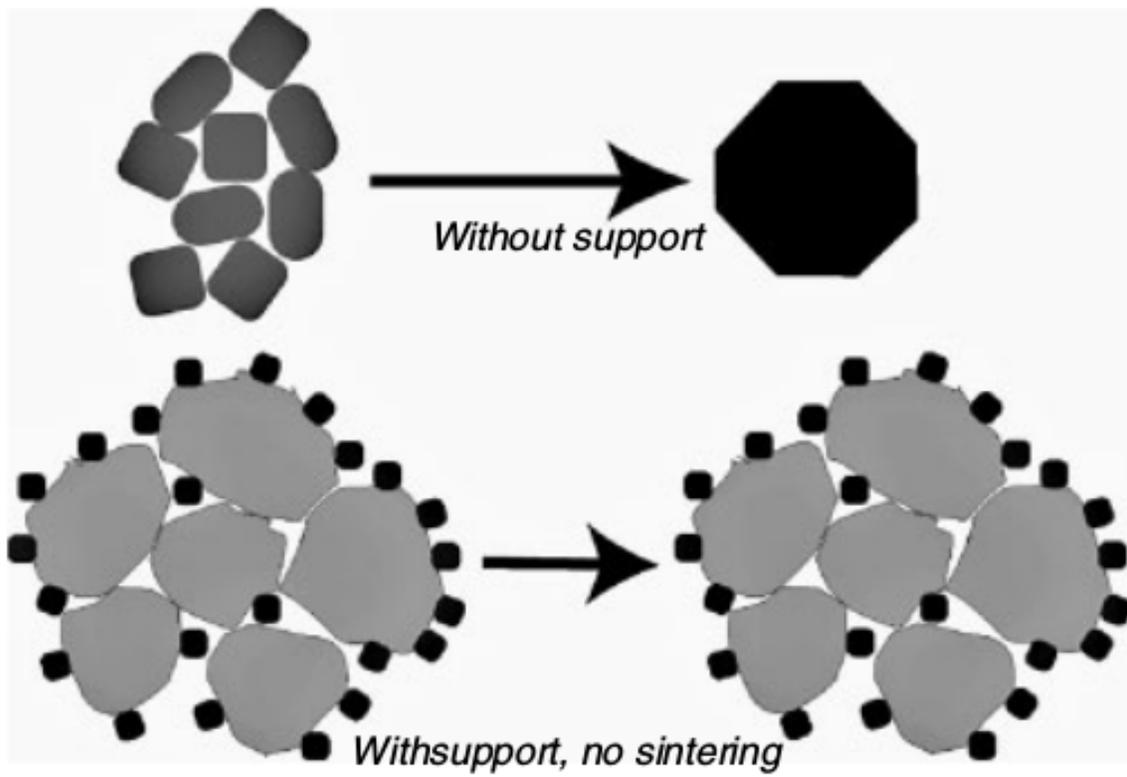


Figure 1: Rapid Sintering of Unsupported Active Particles and Supported Thermostable Active Material

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