Controlling the complex reaction network of the hydrogenation of CO to higher alcohols using Co-based catalysts derived from prussian blue analogues

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Abstract

Higher alcohol synthesis (HAS) can play an important role in the development towards reducing CO_2 emissions since the obtained product mixtures containing higher alcohols as well as olefins can be applied as climate-neutral fuels and bulk chemicals, provided that the synthesis gas is obtained using renewable electricity to produce H_2 and industrial exhaust gases as carbon source.[1] Recently, a new promising class of catalysts derived from prussian blue analogues (PBAs) was reported for the heterogeneously catalyzed CO hydrogenation to higher alcohols.[2] Pyrolysis of the K-promoted Co- and Mn-containing PBAs resulted in the metal atoms being embedded in a unique functionalized carbon matrix, which enabled a facile carbidization of Co to Co_2C, which is the crucial phase for HAS.[3,4] In contrast to established HAS catalysts,[5,6] a rather unusual product spectrum was obtained including primary and secondary alcohols, aldehydes, acids, and olefins. Consequently, a complex reaction network was proposed for this catalyst including the carbide-based mechanism, carbonylation of primary alcohols, reductive hydroformylation of olefins, and hydration of olefins.[2]

Due to this plethora of occurring reactions, this network offers various opportunities to influence the obtained product spectrum by modification of the catalyst preparation and implementation of suitable promoters. One example is the addition of different amounts of Cu to the PBA-based catalysts aiming at the acceleration of the carbonylation reaction, which was deemed the most important mechanism,[2] by increasing the amount of methanol. Another example is the adjustment of the K content by intensive washing after the synthesis of the PBA precursor. Besides catalytic long-term testing, the different catalysts were thoroughly characterized by XRD, TG-MS, N_2 physisorption, ICP-MS, TEM-EDX, XPS, and N_2O-RFC, thereby providing comprehensive information about the capabilities of PBA-based HAS catalysts and the reaction network. Finally, the relevance of the choice of the reaction conditions will be addressed taking the dependance of the selectivities on conversion and the strong exothermicity of the involved reactions into account.

Acknowledgements

References

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