In the present study the influence of the amount of carbon dioxide on the catalytic performance during the propylene carbonate synthesis from propylene oxide and CO₂ was investigated. The reaction was performed in high-pressure batch autoclaves using immobilized 1-hydroxyethyl-9-propyl-cyclic guanidinium bromide on SBA-15 (HEPCGBr/SBA-15) as catalyst in the absence of any co-catalyst. It was found that the yield was strongly dependent on the amount of CO₂ added to the system and that the phase behavior strongly changes along the reaction pathway. The Cubic-Plus-Association (CPA) equation of state was used to predict the phase behavior during the reaction and the number and composition of coexisting phases in the multicomponent reaction system were determined. In accordance with the experimental data, the maximum conversion was achieved in the transition region between the two- and the one-phase region where a CO₂-expanded reactant/product phase (larger volume due to the dissolution of carbon dioxide in the liquid phase) is present. Optimal conditions for performing the reaction have been derived which requires consideration not only of the phase behavior of the starting phase but also of the mixture during reaction. © 2013 Elsevier B.V. All rights reserved.