Forschungszentren

Dokumenttyp: Journal Article

Autor(en) des Beitrags: Zhao, Z. J.; Moskaleva, L. V.; Rosch, N.

Titel des Beitrags: Tuning the selectivity for ring-opening reactions of methylcyclopentane over Pt catalysts: A mechanistic study from first-principles calculations

Abstract: Using density functional calculations, we studied the conversion of methylcyclopentane to its ring-opening products: branched hexanes [2-methylpentane (2MP), 3-methylpentane (3MP)], as well as unbranched n-hexane (nHx). We employed flat Pt(1 1 1) and stepped Pt(2 1 1) to describe terrace-rich large and defect-rich small Pt particles, respectively. On Pt(1 1 1), the barriers of all elementary steps for the paths leading to branched hexanes lie below 90 kJ mol(-1), while the formation of nHx features a barrier of 116 kJ mol(-1) in its C-C bond scission step. This higher barrier impedes the formation of nHx on Pt(1 1 1) and thus rationalizes the experimental observations that terrace-rich large Pt particles selectively produce branched hexanes. However, on Pt(211), the barrier of C-C scission for the formation of nHx decreases to 94 kJ mol(-1), thus implying enhanced formation of nHx over the defects, in agreement with the essentially statistical product distribution observed with defect-rich small Pt particles. (C) 2011 Elsevier Inc. All rights reserved.

Excellence; Deutsche Forschungsgemeinschaft; Fonds der Chemischen Industrie (Germany) We thank Prof. J.A. Lercher for stimulating discussions. We thank D. Basaran and H.A. Aleksandrov for assistance during the early stage of this study. Z.J.Z. gratefully acknowledges financial support by the International Doctorate Program NanoCat within the Bavarian Network of Excellence, an associated member of the TUM Graduate School at Technische Universität München. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie (Germany). We also acknowledge generous computing resources at Leibniz Rechenzentrum München. 7 Academic press inc elsevier science San diego