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Enhanced activity and stability of ALD-immobilized #-Ga_2O_3 ex-situ tailored nanoparticles for propane dehydrogenation: in situ XAS and XRD study	A31-1-33

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Report:

Abstract

Metastable γ-Ga_2O_3 nanocrystals have gained growing interest for a broad range of technological applications. However, a precise description of their atomic structure and changes thereof during thermally induced transformations that is required to understand and fully exploit their physical and chemical properties is still lacking. In this work, we investigate the structure of γ-Ga_2O_3 nanocrystals (2.5 nm in diameter) obtained via a colloidal synthesis route and their evolution with thermal treatment. To this end, we have applied synchrotron X-ray atomic pair distribution function (PDF) analysis, complemented by ^{71}Ga solid-state magic-angle spinning nuclear magnetic resonance (MAS NMR), X-ray absorption spectroscopy (XAS), and electron microscopy. The local structure of the γ-Ga_2O_3 nanocrystals deviates from the average cubic spinel-type structure, revealing a high degree of structural disorder. The average structure of the γ-Ga_2O_3 nanocrystals is described as a defective spinel with gallium sites in tetrahedral and octahedral (Ga_{IV} and Ga_{VI}) coordination with oxygen

atoms. The modeling of the local structure revealed a low-symmetry distortion of the polyhedra, which are disorderly oriented. The surface structure of the γ-Ga_2O_3 nanocrystals is different from their bulk, whereby Ga_{VI} sites at the outermost layers of the nanocrystals are found in a nonperiodical stacking arrangement with a higher occupancy than in the core, as revealed by high-angle annular dark field imaging scanning transmission electron microscopy (HAADF-STEM). The structural evolution of γ-Ga_2O_3 nanocrystals upon thermal treatment in air was probed by in situ time-resolved PDF. A gradual transformation of the γ-Ga_2O_3 nanocrystals toward the thermodynamically stable β-Ga_2O_3 polymorph occurs at different structural domains at different temperatures. At ca. 300 °C, changes in the local structure showed an increased distortion of the polyhedral units and revealed the appearance of small β-Ga_2O_3 domains (ca. <1 nm), while the bulk phase transformation took place between 550 and 750 °C and was associated with an increase in the coherence length of the β-Ga_2O_3 phase. [1]

α-Ga_2O_3, β-Ga_2O_3, and γ-Ga_2O_3 as well as the silica-supported catalysts γ-Ga_2O_3/SiO_2, β-Ga_2O_3/SiO_2, and $Ga(NO_3)_3$-derived Ga/SiO_2 were prepared, characterized, and evaluated for propane dehydrogenation (PDH) at 550 °C. The coordination environment and acidity of surface sites in stand-alone and SiO_2-supported Ga_2O_3 catalysts were studied using FTIR, ^{15}N dynamic nuclear polarization surface-enhanced NMR spectroscopy (^{15}N DNP SENS), and DFT modeling of the adsorbed pyridine probe molecule. The spectroscopic data suggest that the Lewis acidic surface Ga sites in γ-Ga_2O_3 and β-Ga_2O_3 (the latter obtained from colloidal nanocrystals of γ-Ga_2O_3 via thermal treatment at 750 °C) are similar, except that β-Ga_2O_3 contains a larger relative fraction of weak Ga^{3+} Lewis acid sites. In contrast, α-Ga_2O_3 features mostly strong Lewis acid sites. This difference in surface sites parallels their difference in catalytic activities: i.e., weak Lewis acid surface sites are more abundant in β-Ga_2O_3 relative to α-Ga_2O_3 and γ-Ga_2O_3 and the increased relative abundance of weak Lewis acidity correlates with a higher initial catalytic activity in PDH, 0.41 > 0.28 > 0.14 mmol C_3H_6 m^{-2} (Ga_2O_3) h^{-1} at 550 °C, for respectively β-, α-, and γ-Ga_2O_3 with initial propene selectivities of 86, 83, and 88%. Dispersion of γ-Ga_2O_3 or β-Ga_2O_3 on a silica support introduces strong as well as abundant weak Brønsted acidity to the catalysts, lowering the PDH selectivity. The γ-Ga_2O_3/SiO_2 catalyst was slightly more active than β-Ga_2O_3/SiO_2 in PDH (Ga normalized activity) with initial propene formation rates of 11 and 9 mol C_3H_6 mol Ga^{-1} h^{-1} (sel = 76 and 73%, respectively). However, these catalysts deactivated by ca. 55% within 100 min time on stream (TOS) due to coking. In contrast, Ga/SiO_2, with mostly tetracoordinated surface Ga sites and abundant, strong Brønsted acid sites, gave a lower activity and selectivity in PDH (3.5 mol C_3H_6 mol Ga^{-1} h^{-1} and 49%, respectively) but showed no deactivation with

TOS. DFT calculations using a fully dehydroxylated oxygen-deficient model β-Ga_2O_3 surface show that tetra- and pentacoordinated Ga Lewis acid sites bind pyridine more strongly than tricoordinated Ga sites and a higher relative fraction of strong Lewis acid sites correlates with increased coking. Overall, our results indicate that weakly Lewis acidic, tricoordinated Ga^{3+} sites are likely driving the superior PDH activity of β-Ga_2O_3.[2]

1. Castro-Fernández, P.; Blanco, M. V.; Verel, R.; Willinger, E.; Fedorov, A.; Abdala, P. M.; Müller, C. R., Atomic-Scale Insight into the Structure of Metastable γ-Ga_2O_3 Nanocrystals and their Thermally-Driven Transformation to β-Ga_2O_3. *J. Phys. Chem. C* **2020,** *124* (37), 20578-20588.
2. Castro-Fernández, P.; Mance, D.; Liu, C.; Moroz, I. B.; Abdala, P. M.; Pidko, E. A.; Copéret, C.; Fedorov, A.; Müller, C. R., Propane Dehydrogenation on Ga_2O_3-Based Catalysts: Contrasting Performance with Coordination Environment and Acidity of Surface Sites. *ACS Catalysis* **2021,** *11* (2), 907-924.