The structure of □–Al2O3, a crucial catalyst support, remains debated, particularly the Al3□ cation and vacancy locations. While models propose spinel and non–spinel structures, NMR and DFT data support a predominantly spinel structure (62.5–65% octahedral Al3□), contradicting non–spinel models. TEM reveals significant □–Al2O3 surface reconstruction, with (111) facets favored over atomically flat (110) surfaces. The non–spinel model requires reevaluation.