**DFT Studies.** We used the Vienna Ab Initio Simulation Package (VASP) to perform all the spin polarized periodic density functional theory based calculations.31–33 The projector augmented wave (PAW) method was used and a cut-off energy of 550 eV was employed for the expansion of the plane-wave basis sets, which gave bulk energies converged to within 10-5 eV.34 For the structural optimization we chose a convergence criterion of 0.01 eV Å-1 and a k-point grid of 3×3×1 was employed for all slab calculations. The Perdew-Burke-Ernzerhof (PBE) version of generalized gradient approximation (GGA) was used to carry out geometry optimizations and the total energy calculations.35 As the dispersive effects may be significant for the systems under consideration we also used Grimme’s dispersion correction (DFT+D3).40 The ideal surfaces of Pd(111) and NiO(110) and rutile TiO2(111) were modelled by a 4x4 cell with 5 atomic layers. Of the five atomic layers, the bottom three layers were fixed to mimic the bulk of the material and in the direction perpendicular to the surface we used a vacuum gap of ~15 Å, which is sufficient to eliminate slab-slab interactions. The slabs were cut from bulk Pd, NiO and rutile TiO2 with a calculated energy minimized lattice constant of 3.904 Å (Exp. 3.891 Å), 4.192 Å (Exp. 4.168 Å) and 4.695 Å (Exp. 4.594 Å), respectively. In all the calculations, the adsorption of furfural was allowed on only one of the two exposed surfaces. The spurious dipole moment due to the adsorbed species, was taken into account by using the methods implemented in VASP according to the procedures of Markov et al. and Neugebauer et al.38,39 For the calculations on the interaction of furfural on the NiO(110) and TiO2(111) surfaces DFT+U was used. Previous studies have shown that an U value of 5.77 eV, obtained by using linear response methods, for the d-orbital of Ni is suitable.36 It has been also reported that an U value of 4.20 eV is suitable for the d-orbitals of Ti.37 To determine the minimum energy paths for the dissociation of H2 we employed the climbing-image nudged elastic band (CI-NEB) method.a,b The transition state of the optimized reaction coordinate was confirmed by calculations of the vibrational frequencies.

a. Henkelman, G.; Uberuaga, B. P.; Jónsson, H. Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, *113*, 9901–9904.

b. Henkelman, G.; Jónsson, H. Improved Tangent Estimate in the Nudged Elastic Band Method for Finding Minimum Energy Paths and Saddle Points. *J. Chem. Phys.* **2000**, *113*, 9901–9904.