

2D Silica and Aluminosilicate Bilayers on Pd(111): From Incommensurate to Commensurate Crystalline

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Zeolite silicate frameworks are essential in facilitating numerous catalytic reactions. Although zeolites have been used for decades, it is still a long-term challenge to understand how surface properties of zeolites promote catalytic reactions. Recently, two-dimensional (2D) van der Waals silica and aluminosilicate bilayers have been successfully prepared on metal substrates, e.g. Pd(100) [1], Pt(111) [2], and Ru(0001) [3,4]. This achievement creates a new pathway for investigating zeolites using surface science approaches.

Both silica and aluminosilicate bilayers can grow in crystalline and amorphous forms. On Pt(111) only amorphous silica bilayer can be formed likely due to the relatively large lattice mismatch with the crystalline form, whereas on Ru(0001) both crystalline and amorphous bilayers are seen due to a low lattice strain. However, the structural information of the bilayer-growth transition between crystalline and amorphous phases is still lacking. Pd(111) thus becomes a suitable substrate to gain the information because of the degree of the lattice mismatch: Pt(111) = 4.6% > Pd(111) = 3.7% > Ru(0001) = 2%. We report structural studies of silica and aluminosilicate bilayers on Pd(111) via low energy electron diffraction and scanning tunneling microscopy, complemented by density functional theory (DFT) calculations. Our results reveal that silica bilayers grow in an incommensurate crystalline form on Pd(111) which is found neither on Pt(111) nor Ru(0001) and is in contrast to Pd(100) where a commensurate form is observed. It puts the maximum biaxial tensile strain that can be imparted on the bilayer to less than 3.7%. The aluminosilicate bilayer was successfully prepared by replacing 25% of the Si with Al, and importantly, it grows commensurately on Pd(111). The DFT calculations reveal that the longer Al-O bonds reduce the strain energy by decreasing the mismatch to 1.9% as well as by softening it; thereby explaining the transition from incommensurate to commensurate forms. Overall, this work clearly provides an insight into the possibility of manipulating the structure of a 2D material.

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