In situ characterization of Pd2Ga catalysts during particle formation and methanol synthesis

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Environmental transmission electron microscopy (ETEM) provides a window to catalyst formation as well as catalytic reactions. In conjunction with complementary techniques such as in situ XRD, new insight into the various steps of reactions can be obtained. In this study, Pd2Ga/SiO2 is characterized during nanoparticle formation and methanol synthesis. In situ XRD is used to investigate the phase at four stages along the catalyst life cycle, i.e. drying, calcination, reduction, and CO2 hydrogenation to methanol. TEM images of identical locations (IL TEM) are acquired after each stage of the life cycle to monitor Pd2Ga nanoparticle formation and evolution ex situ, whereas ETEM is used to monitor the development of the catalyst in situ. Pd2Ga/SiO2 (23 wt.%) catalysts are prepared by impregnation of Pd and Ga nitrates in nitric acid into high surface area SiO2. The catalyst life cycle is carried out at the XRD setup at 105 Pa, using an Anton Paar XRK-900 furnace cell connected to a gas handling system. Drying and calcination are carried out in air at 120°C and 260°C, respectively. Reduction is performed in a flow of 25% H2 in Ar at 550°C. Methanol synthesis is carried out between 175°C and 250°C in a mixture of CO2 (25%) and H2 (75%). In situ XRD measurements are acquired along the life cycle and TEM images of identical locations are recorded at the end of each step of the cycle. In order to follow the evolution of the catalyst in situ and in real time, the catalyst life cycle is reproduced at the ETEM (Titan, FEI) at 400 Pa, where the silica supported Pd and Ga nitrides precursors are deposited on a SiN membrane of MEMS heaters. XRD patterns reveal the PdO crystallographic phase of catalyst during drying and calcination. No distinct peaks are observed in the XRD patterns for Ga and Ga2O3, indicating amorphous gallium compounds. The Pd2Ga phase is formed upon reduction and the in situ XRD pattern of the reduced catalyst is shown in Fig. 1 (a). IL TEM images show particle formation upon calcination, which determine the distribution of the Pd2Ga nanoparticles formed during reduction. A TEM image of the reduced catalyst is shown in Fig. 1 (b). ETEM images acquired along the catalyst life cycle are consistent with the ex situ images. In Fig. 2 (a) an image of the catalyst acquired at the ETEM under reduction conditions is shown together with a high resolution image of a single Pd2Ga nanoparticle (b) and the corresponding FFT (c). The combination of in situ techniques such as XRD and ETEM together with IL TEM imaging proves a valuable route for studying the life cycle of heterogeneous catalysts.

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Fig. 1: (a) In situ XRD pattern of the reduced Pd$_2$Ga/SiO$_2$ catalyst and (b) TEM image acquired after reduction.

Fig. 2: ETEM image of the Pd$_2$Ga/SiO$_2$ catalyst acquired under reduction conditions (400 Pa H$_2$, 550°C). (b) High resolution image of a in situ reduced Pd$_2$Ga nanoparticle and (c) corresponding FFT.