PdCu alloy membranes have been widely studied as they show better resistance to sulphurous components than the Pd membranes (Shamsi 2009). In this work a 1.7 µm thickness PdCu membrane (80 wt% Pd) was tested with H₂S ppm in pure hydrogen and in a mixture containing hydrogen that is obtained from methane catalytic partial oxidation (CPO).

To analyse the effect of H₂S addition on membrane permeance, tests with different amounts (100, 60 and 40 ppm) of H₂S were performed. Alternatively, hydrogen flow across the membrane was measured in pure hydrogen to analyse the recovery of the permeance. Membrane behaviour was also analysed when operating under real hydrogen containing mixtures with 32 ppm of H₂S during 6 hours.

In the Figure 1, the results obtained in the tests with 100 and 40 ppm of H₂S are shown. The hydrogen flow across the membrane when adding 100 ppm of H₂S was a 20 % of the value under pure hydrogen. When removing the H₂S, pure hydrogen atmosphere, the hydrogen flow value measured across the membrane was the one before the sulphur test. Doing the same test but with 40 ppm of H₂S, membrane behaviour was similar to the observed in the test with 100 ppm. The hydrogen flow measured with 40 ppm of H₂S was slightly higher, 25 % of the value measured in pure hydrogen, and when taking out the H₂S the initial hydrogen flow value was measured. The selectivity of the membrane was not affected by H₂S addition, as the inert flow across the membrane was kept in negligible values compared to the measured hydrogen flows. Similar results were obtained in a second test where the effect of 100 and 60 ppm of H₂S was analysed. In this second test, hydrogen flow across the membrane decreased significantly with the presence of H₂S, but values were recovered under pure hydrogen operation. Membrane selectivity was not affected by the H₂S.

When H₂S was added to a real mixture obtained from methane CPO (containing CO, CO₂, H₂, CH₄ and Ar) hydrogen recovery in the membrane (percentage of the hydrogen flow fed to the membrane module that is separated by the membrane) decreased from 80 % (without H₂S) to 45 % (with 32 ppm of H₂S). In this case, the selectivity was affected by the mixture components and H₂S as the inert gas flow across the membrane measured after the test was around 150 mL/min.

After the tests performed in this work, it can be concluded that the prepared PdCu membrane can operate with temporary addition of 100, or lower, ppm of H₂S without damaging the membrane, as the hydrogen permeance was restored when removing the H₂S. The negative effect of gases as CO and CO₂, together with H₂S has a significant irreversible effect on the membrane, as its selectivity decreased a lot.
Figure 1. H₂S addition effect on hydrogen flow across the PdCu membrane.

References:


Keywords: PdCu membrane, Hydrogen purification, Sulphur