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Ultramicroporous niobia-silica membranes are hydrothermally stable and highly permeable to H_2. At the same time they show high CO_2 retention. Thus, they offer great potential as separation units in hydrogen purification and CO_2 capture technologies. Despite that, it is not well understood yet how transition metal ions affect the structure of ultramicroprous silica networks .In the present work we investigate structure and stability of microporous silica and Nb_2O_5-silica membranes. The influence of thermal and hydrothermal exposures on porosity, silanol concentration, and phase transitions of pure silica and niobia-silica membranes is studied by means of gas sorption measurements, simultaneous thermal analyzer, and X-ray diffraction technique. The short and medium-range order structure of the membranes is probed by using the ^{29}Si nuclear magnetic resonance spectroscopy. We show the consequences of the high temperature treatment (up to 1270 °C) to both the microporous structure and the non-crystalline structure of the membrane materials. The results provide information on how Nb(V) ions stabilize microporous silica network.