Binary titania–silica metal oxides (TiO2–SiO2) have preferentially been used as photocatalysts for the degradation of organic contaminants under UV irradiation. Herein we synthesized TiO2–SiO2 aerogel powders with different Si-to-Ti ratios suitable for decolorization of organic pollutants using less expensive silica source (sodium silicate) and titanium oxychloride as a titania precursor. Consequently, the surfaces of the alcogels were hydrophobized using trimethylchlorosilane (TMCS) as a silylating agent to yield hydrophobic aerogel powders at ambient pressure drying. The as-prepared samples were calcined at different temperatures ranging from 200 to 1000 ℃ to evaluate the effect of the heat treatment in the microstructure of the aerogels. The physico-chemical properties of the aerogels were examined by XRD, FTIR, XRF, TEM, SEM, N2 gas physisorption studies, TGA/DTA and diffusive reflectance spectrometry analyses. It was found that calcination temperature is an important factor in improving the porosity and crystallinity of the aerogels however; it has a detrimental effect on the hydrophobicity and photochemical performance of the aerogels. The as-synthesized aerogels were hydrophobic and exhibited the highest activity toward decolorization of methylene blue. The hydrophilic aerogels were obtained after calcination at temperature 500℃ however; the formed samples possessed lower activities. Hydroxyl radicals ($^{\cdot}OH$) detection experiment performed in the presence of the photocatalysts indicated that the generation of radicals during irradiation increases with increasing illumination time.