Solid-state NMR spectroscopy is a unique technique in the study of catalytic reaction mechanisms with its advantage of quantitative information. We successfully used the controlled atmosphere MAS NMR technique with $^{13}$C labeled reactant to study the reaction mechanism of n-butane isomerisation over a number of solid acid catalysts, including sulfated zirconia and tungstophosphoric acid-based catalysts. The results show that the increase of the Brönsted acid strength rather than acid density is important to enhance the catalytic activity, which provides useful information on the design of relevant catalysts. Also, we explored a new way to study the acidity and basicity of metal oxide catalysts using basic and acidic probe molecules simultaneously with the NMR technique. Compared to the normal single probe molecule method, the acidity obtained with our new method is more fitting for the catalytic performance of acetone self-condensation reaction over metal oxide catalysts.