

## Supercritical Ion Exchange: A New Method to Prepare Cu-Exchanged Mordenite for Direct Conversion of Methane to Methanol

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The discovery of new sources and increased production rate of methane are driving the development of new technologies for conversion of methane into methanol (MTM) since the conventional method of conversion of MTM requires syngas production from methane at high temperatures (>800 °C) which is expensive. On the other hand, the direct selective oxidation of MTM is challenging due to difficulty in activation of methane and its oxidation to highly reactive products which easily convert to CO<sub>2</sub>. The stepwise direct methane to methanol (sDMTM) process at low temperatures over copper exchanged mordenite (Cu-MOR) catalyst is one of the alternative methods in which the intermediates are protected by Cu-oxo species resulting in a very high methanol selectivity. This process consists of activation of O<sub>2</sub> over active Cu-oxo sites in the presence of oxygen stream followed by the reaction with methane to form stable intermediates which can then be converted to methanol via hydration. The sDMTM steps could be carried out non-isothermally at atmospheric pressure or isothermally at a higher pressure during methane reaction step. Incorporation of Cu sites on the zeolite backbone using the conventional aqueous ion exchange (AIE) route leads to the formation of a variety of active and inactive Cu species including monomers, dimers and/or clusters. Thus, there is considerable interest to introduce new synthesis routes to increase the concentration of the desirable Cu-oxo species on the surface to increase methanol productivities. Here, we report, for the first time in the literature, a new technique which we termed supercritical ion exchange (SCIE) to synthesize Cu-MOR catalysts. The technique consists of the dissolution of a Cu complex (Copper(II) trifluoroacetylacetonate) in supercritical CO<sub>2</sub> followed by ion-exchange of Cu<sup>2+</sup> with the extra-framework H<sup>+</sup> sites of mordenite (Si/Al=10) in the absence of an aqueous phase. The occurrence of the ion exchange reaction was confirmed by visual observation and analysis of the high-pressure fluid phase samples using Nuclear Magnetic Resonance (NMR) during the SCIE. The change in the fluid phase color from blue to yellow and the presence of the peaks for trifluoroacetylacetone in NMR spectra demonstrated the formation of trifluoroacetylacetone as the product of the ion exchange reaction. Further evidence were provided by characterization of the solid catalysts using X-Ray Fluorescence (XRF) and Fourier Transform Infrared (FTIR) spectroscopy before and after supercritical extraction. Only certain sites were exchanged using SCIE at thermodynamic equilibrium as inferred from the ion-exchange isotherm. The effects of Cu loading, O<sub>2</sub> activation temperature (200-450 °C), O<sub>2</sub> activation time (1-10 h), methane reaction time (0.5-10 h) and methane pressure (0.1-3 MPa) on methanol productivity and selectivity were investigated and the results of the catalysts prepared using SCIE (Cu-MOR<sub>S</sub>) and AIE (Cu-MOR<sub>A</sub>) were compared. For both SCIE and AIE, methanol productivity increased linearly with increasing the Cu content up to a certain Cu loading (365 μmol/g<sub>catalyst</sub> for Cu-MOR<sub>S</sub>, 371 μmol/g<sub>catalyst</sub> for Cu-MOR<sub>A</sub>) indicating that the type of the active copper species remained unchanged up to a certain Cu loading. For the non-isothermal sDMTM over Cu-MOR<sub>S</sub> catalyst, maximum methanol productivity was 73 μmol/g<sub>catalyst</sub> after 10 h reaction of methane and methanol selectivity values were higher than 90%. For the isothermal DMTM, the methanol productivity increased from 2.8 to 46.5 μmol/g<sub>catalyst</sub> with increasing methane pressure from 1 to 16 MPa at 200 °C for the catalyst prepared by SCIE. After O<sub>2</sub> activation, FTIR spectra of the catalyst showed significant changes in the Brønsted site region (3800-3500 cm<sup>-1</sup>), an indication of Cu exchange with Brønsted acid sites. The presence of methoxy peaks in FTIR spectra of the Cu-MOR<sub>S</sub> after methane reaction demonstrated the successful activation of methane and intermediate protection during the process. H<sub>2</sub>-TPR experiments and Raman spectroscopy demonstrated that more controllable synthesis of copper active sites could be achieved via SCIE route in which mostly dicopper active sites were formed upon O<sub>2</sub> activation and used towards CH<sub>4</sub> to methanol reaction while a more heterogeneous mixture of mono, di, and tricoppers were formed by AIE. The results indicate that SCIE may lead to development of a wide variety of catalysts with enhanced reactivities or selectivities than catalysts prepared by conventional ion-exchange.