

The age of methanol and hydrogen economies. The conversion of green- house gases CO₂ and methane¹. The influence of alcohol reaction kinetics in gas phase and liquid phase on size-controlled Pt nanop

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Abstract:

Need for clean energy is imminent and methanol is considered a promising alternative energy source. Conventional process for the production of methanol has been achieved via syngas, which is derived by the steam reforming of methane or naphtha and the gasification of coal. Methanol can also be prepared by direct oxidation of methane (natural gas) or reduction of carbon dioxide (CO₂) with hydrogen. In this way, carbon-neutral cycling can be achieved and the world's dependence on fossil fuels will be alleviated. In this presentation, we will address, case by case, some recent advancement in the conversion of methane and CO₂ to methanol both homogeneously and heterogeneously with emphasis on the contribution from Professor George A. Olah's and our group. In the end, a short outlook is provided towards existing problems and future opportunities. Alcohol oxidation reaction over platinum nanoparticles with size ranging from 2 to 8 nm deposited on mesoporous silica MCF-17 was studied in the gas and liquid phases. Among methanol, ethanol, 2-propanol, and 2-butanol oxidations, the turnover frequency increased as the nanoparticle size became large in both reaction phases. The activation energy in the gas phase was higher than that in the liquid phase. Water co-adsorption decreased the turnover rate of all the gas and liquid phase oxidations except for the gas-phase 2-butanol case, while certain amount of water promoted 2-propanol oxidation in the liquid phase. Sum

Frequency Generation vibrational spectroscopy (SFG) study and DFT calculation revealed that the alcohol molecules pack horizontally on the metal surface in low concentration and stand up in high concentrations, which affect the dissociation of β -hydrogen of the alcohol as the critical step in alcohol oxidation. Time evolution of catalytic CO₂ hydrogenation to methanol and dimethyl ether (DME) has been investigated in a high temperature high-pressure reaction chamber where products accumulate over time. The employed catalysts are based on a nano-assembly composed of Cu nanoparticles infiltrated into a Zr doped SiO_x mesoporous framework (SBA-15): Cu-Zr-SBA-15. The CO₂ conversion was recorded as a function of time by gas chromatography-mass spectrometry (GC-MS) and the molecular activity on the catalyst's surface was examined by diffuse reflectance in-situ Fourier transform infrared spectroscopy (DRIFTS). The experimental results showed that after 14 days a CO₂ conversion of 25% to methanol and DME was reached when a DME selective catalyst was used which was also illustrated by thermodynamic equilibrium calculations. With higher Zr content in the catalyst, greater selectivity for methanol and a total 9.5 % conversion to methanol and DME was observed, yielding also CO as an additional product. The time evolution profiles indicated that DME is formed directly from methoxy groups in this reaction system. Both DME and methanol selective systems show the thermodynamically highest possible.