Abstract

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Title: Catalytic Conversion of Light Hydrocarbons to Chemicals and Fuels
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The recent surge in shale gas production throughout the United States has led to increased interest in hydrocarbon upgrading such as C—H bond activation and light hydrocarbons conversion to fuels. Methane and other light alkanes in natural gas can be potentially converted into light olefins, which can be further utilized as basic building block for valuable chemicals or upgraded to long-chain hydrocarbons used as fuels.

In the first work, kinetic study on $Mn/Na_2WO_4/SiO_2$ catalyst for oxidative coupling of methane (OCM) into ethane and ethylene were performed with varying Mn (0-2 wt%) and W (0-3.1 wt%) loadings. When the W loading was varied from 0 to 3.1 wt% (Mn kept at 2 wt%), C_2 formation rate increased from 0.2×10^{-6} to 0.9×10^{-6} mol $m^{-2}s^{-1}$ at 730 °C. When the Mn loading was increased from 0 to 2 wt% (W kept at 3.1 wt%), C_2 formation rate increased from 0.2×10^{-6} to 1.2×10^{-6} mol $m^{-2}s^{-1}$ at 0.2 wt% Mn, and decreased slightly when Mn loading was further increased at 730 °C. Apparent activation energy also increased from 140 to 210 kJ mol^{-1} after adding W into $2\%Mn/0.78\%Na/SiO_2$. These results indicated that new active sites are generated when both Mn and W are present on the catalyst surface. Co-feeding water changed both apparent activation energy and orders of methane and oxygen, indicating that measured kinetics of OCM can be affected by water, one of the products from OCM reaction. Both $2\%Mn/0.78\%Na/SiO_2$ and $3.1\%W/0.78\%Na/SiO_2$ catalysts showed rates of 0.2×10^{-6} mol m^{-2} s^{-1} for C_2 formation when tested separately. After they were physically mixed and tested for OCM reaction, the C_2 formation rate was 4 times higher. Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX) elemental mapping were performed on the physical mixture after reaction, and they revealed that W migrated from $3.1\%W/0.78\%Na/SiO_2$ particles onto $2\%Mn/0.78\%Na/SiO_2$ particles, but Mn did not. These results showed the catalytic activity of the physical mixture should come from the particles that have both Mn and W after migration of W. It is therefore concluded that both Mn and W are required to form the active sites on $Mn/Na_2WO_4/SiO_2$ for oxidative coupling of methane.

The second study focused on how higher turnover rate (TOR) and selectivity to olefins can be achieved by alloying Pd or Pt with other inactive metals during light alkane dehydrogenation. These changes in catalytic performance have been attributed to geometric and electronic effects from alloy formation. In this work, during ethane dehydrogenation at 600 °C, $PdIn/SiO_2$, $PtIn/SiO_2$, and $PtZn/SiO_2$ showed ~100% C_2H_4 selectivity at 15% conversion and five to ten times higher

steady-state TOR enhancement compared to monometallic Pd/SiO_2 and Pt/SiO_2 with only 53% to 74% C_2H_4 selectivity at 15% conversion. Apparent activation energy was determined to be ~75 kJ mol^{-1} for Pt/SiO_2, while Pd/SiO_2 exhibited more than 90% deactivation and apparent activation energy was not able to be measured. However, bimetallic $PdIn/SiO_2$, $PtIn/SiO_2$ and $PtZn/SiO_2$ catalysts showed apparent activation energy from 95 to 137 kJ mol^{-1}, higher than those of monometallic catalysts. Synchrotron X-ray Diffraction (XRD) and X-ray Absorption Spectroscopy (XAS) were used to identify Pd_1In_1, Pt_3In, $PtIn_2$, and Pt_1Zn_1 intermetallic alloys in these bimetallic catalysts, causing geometric modification to form isolated Pd and Pt catalysts, and increase ethylene selectivity by suppressing hydrogenolysis pathway as shown in the experiments. Potential electronic effects of the inactive metal on the Pt atoms within intermetallic structure were probed by X-ray Absorption Near Edge Structure (XANES) and Resonant Inelastic X-ray Scattering (RIXS), and were supported kinetically by the higher apparent activation energies and TORs for intermetallic Pt_1Zn_1, Pt_3In, and $PtIn_2$ compared to monometallic Pt during ethane dehydrogenation.

In the third study, the effect of proton density on propylene oligomerization kinetics and product distribution was investigated over H-ZSM-5. Propylene oligomerization product selectivity was measured at 1 bar total pressure under steady state or by extrapolating to zero time on stream to compare among H-ZSM-5 with Si/Al ratio varying from 12 to 140. Oligomer product (C_6, C_9, C_{12}) selectivity was found to decrease with increasing Si/Al ratio when compared under similar reaction conditions and conversions. Propylene oligomerization rate per proton site was shown to increase with increasing Si/Al ratio under steady-state 0.6% conversion. Apparent activation energy was shown to increase from 71 to 183 kJ mol^{-1}, while apparent propylene order decreased from 0.82 to –0.37 as Si/Al ratio increased from 12 to 140 between 25 and 75 kPa propylene partial pressure. Apparent propylene order was also determined with propylene partial pressure from 50 to 310 kPa, and a similar trend was observed. Our current interpretation is that a higher proton density favors oligomer product formation relative to cracking products, while lower propylene oligomerization rate per proton site may be due to limited space to accommodate the products within the H-ZSM-5 open pore volume with a lower Si/Al ratio.