Selective Oxidation of Methane over Iron Oxide Subnanocluster Supported Catalysts Using a Diiron-introduced Polyoxometalate as a Precursor

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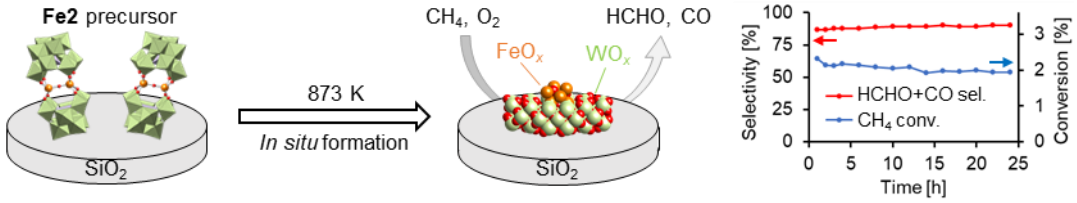
Selective oxidation of methane into value-added C1 products such as HCHO and CO remains challenging due to high stability of methane and facile overoxidation of C1 products into CO_2.[1] Iron oxide cluster catalysts are promising since they selectively convert methane into HCHO and CO with low activation energy.[2] However, our preliminary test revealed that SiO_2-supported iron oxide clusters were agglomerated and deactivated under methane oxidation conditions at 873 K. In this study, we used a diiron-introduced polyoxometalate (**Fe2**) as a precursor to form thermally stable iron oxide subnanoclusters. **Fe2** has the structure that iron dinuclear core is encapsulated in lacunary polyoxometalate ~~(POM)~~ frameworks composed of WO_6 units. Although the lacunary polyoxometalate frameworks are supposed to be decomposed into tungsten oxide at 873 K, the *in situ* formed tungsten oxide is expected to have a protecting effect on iron oxide cluster active sites.

Firstly, **Fe2** was synthesized by stoichiometric reaction of a divacant lacunary silicotungstate~~,~~ and iron(III) acetylacetonate. Then, **Fe2** was dispersed on SiO_2 using an incipient wetness method to prepare **Fe2**/SiO_2. **Fe2**/SiO_2 exhibited high selectivity to HCHO and CO (41% and 46%, respectively) at 2.3% methane conversion at 873 K (CH_4:O_2:Ar = 2:1:7, total flow rate: 50 mL min^{-1})~~,~~ and maintained its catalytic activity even after 24 h. Moreover, several control experiments elucidated that iron species introduction into the lacunary polyoxometalate in advance plays a key role to maintain the catalytic activity. Fe K-edge and W L_3-edge XAFS analyses revealed that, in **Fe2**/SiO_2, **Fe2** precursor was decomposed into iron oxide subnanoclusters and tungsten oxide nanoclusters. Furthermore, STEM-EDS analysis indicated that iron oxide subnanoclusters were dispersed in tungsten oxide nanoclusters. Thus, we concluded that the *in situ* formed tungsten oxide protected iron oxide subnanoclusters from agglomeration by using **Fe2** as a precursor.



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