KINETICS AND MECHANISM OF THE SULFUR OXIDATIVE COUPLING OF METHANE (SOCM) REACTION OVER SULFIDED IRON OXIDE CATALYST

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Abstract

Detailed kinetic and mechanistic studies were carried out to decipher the reaction mechanism involved in the sulfur oxidative coupling of methane reaction (SOCM) over a sulfided iron oxide catalyst. Furthermore, insights into the active sites and the site-dependent reaction pathway are gained via density functional theory (DFT) studies. The kinetic studies done show a first order dependence with respect to both methane as well as sulfur with a low apparent activation barrier of 66 kJ/mol. Theoretical studies predict the activation to occur predominantly over the adsorbed sulfur sites (S_{dim}/S_{mono}) with the low activation barrier resulting because of the high adsorption energies of sulfur on the surface. The dominant product over these adsorbed sulfur sites (S_{dim}/S_{mono}) is shown to be carbon-di-sulfide (CS_2) which likely forms via subsequent C-H activation steps occurring over these sites. The selective ethylene (C_2H_4) formation on the other hand is shown to directly form from methane via CH_2 coupling over the Fe-S_{brid} site pairs present on the sulfided iron oxide surface.

Introduction

Recently, significant efforts have been dedicated towards identifying efficient methane conversion technologies to produce useful chemical feedstocks since the discovery of shale gas reserves during the past decade. Ethylene is one such useful feedstock which is widely used for the production of polyethylene. Oxidative coupling of methane (OCM) over metal oxide catalysts provides an attractive route for direct conversion of methane to ethylene feedstock [Lunsford, 1995]. Studies over the past three decades which examine using oxygen as the oxidant for this process however have till now been unsuccessful to realize high ethylene yields due to the high thermodynamic driving force for over-oxidation to carbon-di-oxide which makes this process still economically unviable for commercialization. We recently reported a new strategic approach to increase ethylene selectivity by using a softer oxidant such as sulfur (SOCM) which lowers the thermodynamic driving force for overoxidation [Zhu et al., 2012].

We subsequently examined various metal oxides for their SOCM activity and selectivity [Peter and Marks, 2015], from which ethylene selectivities as high as 33% were obtained for iron oxide catalyst (Fe_3O_4). Thus, in this study, we focus our attention on studying the kinetics and reaction mechanism of SOCM over iron oxide (Fe_3O_4) catalyst, which afforded the highest ethylene selectivities. XRD and XPS studies done post reaction indicate the iron oxide catalyst to be fully sulfided. Thus, under reaction conditions, Fe_3O_4 likely gets converted to a sulfide thus forming FeS_2. Mechanistic and DFT studies were used to explore the reaction pathway and active sites responsible for the formation of observed reaction products over this highly selective sulfided iron oxide (FeS_2) catalyst. Additionally, kinetic studies were also done to
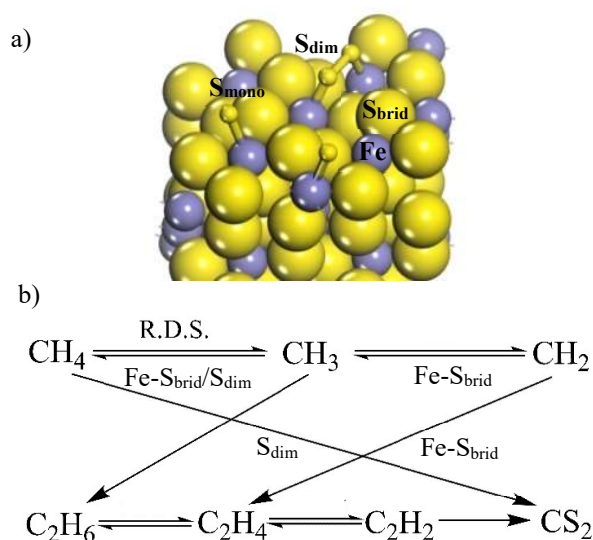

Figure 1: a) FeS_2 surface model used for the DFT investigation depicting the active sites involved in the SOCM mechanism over sulfided Fe_3O_4 b) Summary of the site dependent mechanistic reaction pathway for SOCM over sulfided Fe_3O_4

determine the rate orders and activation barriers of the reaction which were further validated by DFT studies.

Results and Discussion

Delplot analysis was initially done to gain insights into the origins of the products formed during the SOCM process. A non-zero intercept was obtained for CS_2 and C_2H_4 in a first

order delplot which indicates the formation of CS_2 and C_2H_4 to occur directly from CH_4. Furthermore, DFT studies were then done to further probe the active sites and their involvement in the formation of the different observed products. The studies show that there are 3 possible active sites that can possibly participate in the SOCM mechanism as shown in Figure 1a: Adsorbed sulfur sites which can exist either as a monomeric pair (S_{mono}) or as a dimer (S_{dim}), or metal-sulfur sites (Fe-S_{brid}). Figure 1b summarizes the results of the quantum chemical and mechanistic studies done which show the site dependent distribution of the reaction products wherein the adsorbed sulfur sites predominantly form CS_2 via sequential C-H activation of CH_4 whereas the Fe-S_{brid} sites give rise to ethylene via CH_2 coupling.

Further, kinetic studies done show a first order dependence with respect to both sulfur and methane unlike OCM which shows a half order dependence with respect to oxygen [Lunsford, 1985]. This unique rate law for SOCM is consistent with methane activation occurring mostly over the adsorbed dimeric sulfur sites (S_{dim}) or over two monomeric sulfur sites (S_{mono}), thus predominantly leading to CS_2 formation. Also, low apparent barriers of activation of 66 kJ/mol were reported which is shown to occur due to the strong adsorption of the active sulfur to these sites, which in turn lowers the apparent barrier.

Conclusion

Sulfur can be used as a soft oxidant to selectively activate methane to form ethylene with selectivities as high as 33%. The ethylene is shown to form directly from methane over Fe-S_{brid} sites via CH_2 coupling. The ethylene yields are limited by the direct formation of CS_2 from CH_4 which occur over the adsorbed sulfur sites via subsequent C-H activation steps. The rate determining step (RDS) of methane activation predominantly proceeds over the adsorbed sulfur sites, thus giving a first order dependence with respect to methane as well as sulfur. The high adsorption energies of sulfur on the surface likely leads to the observed low apparent activation barrier of 66 kJ/mol.

Acknowledgements

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