DIRECT CATALYTIC CONVERSION OF METHANE TO METHANOL AND ACETIC ACID USING MOLECULAR OXYGEN IN AN AQUEOUS MEDIUM OVER RH/ZSM-5 AND IR/ZSM-5

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Abstract

The direct oxidative conversion of methane to liquid oxygenates has long been considered as a great challenge due to the difficulty of activating the first C-H bond and the over-oxidation of the liquid oxygenates produced. Here we demonstrate that isolated Rh cations supported on ZSM-5 catalyze this reaction using O₂ as the oxidant and CO as promoter at mild conditions. The reaction is heterogeneous and the preferred product is acetic acid. Ir/ZSM-5 was also found to be active for this reaction, but of inferior activity to the rhodium catalyst. Adding a second metal (Cu, Pd) cation to Ir/ZSM-5 drastically increases the activity of the latter, with Cu selectively promoting the formation of methanol.

Keywords

Methane to oxygenates, Rh/ZSM-5, Ir/ZSM-5, Methanol, Acetic acid

Introduction

Methane has long been an important source of fuel and chemicals. The recent breakthrough in hydraulic fracturing for harnessing shale gas makes methane even more affordable; hence converting methane to value-added liquid oxygenates has gained renewed interest. Being a liquid, methanol is the most desirable among the C₁ oxygenates since it has the highest energy density. Also methanol itself is an important chemical feedstock in large demand (Tullo, 2014) as the starting material for making dimethyl ether, formaldehyde, acetic acid, and olefins. Acetic acid, on the other hand, has even higher market value than methanol. Commercially, both of these two materials are synthesized through highly energy-demanding multi-step processes from methane (Hammond, et al., 2012a), while a simple direct conversion method is not commercially available yet.

Catalytic systems developed for the direct oxidative conversion of methane date back to the early 70s and there has been continued research dedicated to achieve a reaction system with high product yields. Periana et al. (1998) reported a homogeneous platinum-based catalyst in concentrated sulfuric acid that can convert methane selectively to a methanol derivative. Also by using palladium cations in the same system, methane can be converted to acetic acid directly (Periana, et al., 2003). However, the use of highly corrosive and expensive sulfuric acid as both the solvent and the oxidant along with the difficulty of the separation of products limits the application of this process. An environmentally benign aqueous process was reported by Hammond, et al. (2012b) catalyzed by copper-promoted Fe-ZSM-5 but the use of H₂O₂ which is more expensive than the product limits...
application. An aqueous phase conversion of methane using O₂ as a cheap oxidant is much more attractive. Here we report that single-site Rh cation supported on ZSM-5 and single-site Ir cation supported on ZSM-5 are active catalysts for the conversion of methane to methanol and acetic acid using O₂ as the oxidant and CO as a promoter at mild conditions.

Results and Discussions

The catalysts were synthesized by incipient wetness impregnation followed by a reduction step to form isolated Rh and Ir cations anchored on the internal pores of the zeolite. The presence of isolated metal atoms and their oxidation state in the pores of zeolite was probed by STEM, XPS, XANES/EXAFS and UV-Vis spectroscopies. A 0.5wt% Rh/ZSM-5 catalyst with Si/Al=15 can convert methane to methanol and acetic acid with high yields. The C-H bond of methane can be activated in the presence of oxygen and carbon monoxide at mild temperatures (<200 °C) to form M-CH₃ species. Subsequent hydroxy-functionalization or carbonylation can produce methanol or acetic acid using CO as the promoter. Under some conditions, acetic acid can be formed with selectivity of 65% and with an amount of 5482 µmol/g-cat, as shown in Figure 1.

Conclusions

Isolated Rh cation supported on ZSM-5 is an active catalyst that catalyzes conversion of methane to methanol and acetic acid with high yields. On Ir/ZSM-5, adding second metal cations can further improve the activity and selectivity. This bimetallic system offers new possibilities for the design of new catalysts for the direct conversion of methane to select liquid oxygenates.

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References