Indian Journal of Chemistry
Vol. 56A, May 2017, pp. 488-492

Notes

Cu-ZSM-5 catalyzed low-temperature hydrogen peroxide-induced methane-to-methanol conversion

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Received 1 February 2017; revised and accepted 21 April 2017

We report herein that Cu-ZSM-5 is an effective catalyst for methane oxidation with hydrogen peroxide, provided Cu-ZSM-5 is synthesized by ion exchange. The reaction conditions for efficient conversion of methane to methanol over Cu-ZSM-5 are also reported.

Keywords: Catalysts, Cu-ZSM-5 catalysts, Methane oxidation by hydrogen peroxide, Methanol formation under moderate conditions, Ion exchange methods, Copper, Hydrogen peroxide

Efforts to reduce dependence on imported oil has stimulated research on a variety of alternative technologies: production of gasoline from coal, biomass, natural gas; mixing alternative fuels in gasoline (ethanol, methanol, biodiesel); and production of H_2 with solar power etc.[1-3] These approaches have challenges and lead to limited displacement of foreign oil. Methanol was explored as a fuel additive in the 80s but limited success of M85 fuel led to its abandonment.[4] In New Zealand, methanol was manufactured from natural gas and was converted to gasoline beginning in 1986 at a rate of about 600,000 tons per year meeting one third of its gasoline demand.[5] Aside from its potential use in transportation, methanol is an industrially important chemical and is ranked eight in production value in the United States.[6] Eighty percent of the world's methanol production uses natural gas as the basic raw material and synthesis is carried out in two steps – conversion to syn gas and subsequent methanol production.[7,8] The ΔH^0 of syn gas production is 49.3 kcal/mol and that of conversion to methanol is −21.7 kcal/mol. Of the total investment, 40% is dedicated to synthesis gas generation, 50% for methanol synthesis and 10% for refining.[9]

Techno-economic analysis in literature[10] suggests that direct conversion of methane to methanol can be economically viable if methanol can be obtained with a selectivity of >95% at a conversion of about 10%. The efforts to produce methanol directly from natural gas employing molecular oxygen or N_2O have had limited success. Periana *et al.*[11] suggest that three distinct types of catalytic systems can convert natural gas to methanol below 250 °C. The electron-poor catalysts in acidic solvents can remove electrons from bonding orbitals of CH bonds where solvent protects CH_3OH by converting it to electron poor $[CH_3OH_2]^+$ species. The electron-rich catalysts with basic solvents can react with net donation of electrons to antibonding orbitals of CH bond with solvent protecting CH_3OH by deprotonating it to $[CH_3O]^-$. The amphiphilic catalyst can react with both HOMO and LUMO of CH bond and will require neutral solvents. Although, Periana *et al.*[11] made some progress in developing concepts along these lines, they have not yet shown a successful process. Starokon *et al.*[12] show that dimethylether yield can be obtained in 6-7% by reaction of methane over Fe-ZSM-5.[12] Schoonheydt *et al.*[13-15] found that copper modified zeolites exhibit high activity in the stoichiometric conversion of methane to methanol with oxygen at low temperatures (*ca.* 125 ºC) and binuclear copper species $[Cu\text{-}\mu\text{-}O_2\text{-}Cu]^{2+}$ resembling the active sites in pMMO enzyme act as the reaction center where methane undertakes a homolytic cleavage of the C–H bond with a low theoretically predicted activation energy (15.7 kcal/mol). Bitter *et al*[13, 16]. correlate $[Cu\text{-}O\text{-}Cu]^{2+}$ or $[Cu\text{-}\mu\text{-}O_2\text{-}Cu]^{2+}$ center in Cu-ZSM-5 to the efficiency of methane conversion to methanol. Theoretical studies suggest that methane activation is only feasible on Cu-O-Cu.[17] Deng *et al.*[18] reported the room temperature activation of methane over Zn-ZSM-5.

Recent reports from Hutchings *et al.*[19, 20] show that methane conversion of about 10% is achievable by employing iron substituted silicalites as catalysts operating at 30.5 bar, 50 °C, and using hydrogen peroxide as an oxidant; however methanol selectivity is only 8%. The Cu substituted silicalite was found to be inactive in methane oxidation but could dramatically promote methanol selectivity to 93% when mixed with Fe-silicalite by preventing over-oxidation. The active species in these systems is proposed to be oligomeric Fe^{3+}, whether present as impurity in commercial ZSM-5 samples or introduced via solid state exchange in silicalite samples. Interestingly, the Fe-ZSM-5 sample (2.5% Fe) showed only 0.7% conversion with 12% methanol selectivity which is more effective than commercial ZSM-5 (0.3% conversion and 19% methanol selectivity). Cu-ZSM-5, on the other hand, showed methane conversion comparable to that of commercial H-ZSM-5 although with higher methanol selectivity.

Here, we describe our results on methane oxidation with hydrogen peroxide on Cu-ZSM-5 which clearly show that Cu-ZSM-5 is an effective catalyst for methane oxidation. We find that synthesis via ion-exchange and reaction conditions are important factors for the observed efficiency of Cu-ZSM-5.

Experimental

Diffuse reflectance UV-vis-NIR spectra were collected on Cary 5000 UV-vis-NIR spectrophotometer under reflectance mode. The STEM dark-field images were recorded on a JEOL JEM-2200FS scanning transmission electron microscope outfitted with a CEOS GmbH aberration corrector and a Bruker XFlash-AXS 5030 silicon-drift detector. The imaging was done at an acceleration voltage of 200 kV. Each energy dispersive X-ray spectroscopy (EDS) map was obtained with an acquisition time of 10 min. Powder samples were dispersed on beryllium-grid coated with holey carbon films for STEM imaging. In the EDS spectra, small Co and Fe signals at 6.4 and 6.9 keV are irrelevant to the samples, but originate from inside the bore of the objective lens pole piece due to electron scattering causing X-rays.

H-Sil-1 and H-ZSM-5 were synthesized as per literature procedures.[19,20] The samples of Cu_s-Sil-1, Cu_s-ZSM-5, 1%Fe_s-ZSM-5, and 2.5%Fe_s-ZSM-5 were prepared by solid state impregnation, shown with a subscript "s" on metal. Sample of Cu_i-ZSM-5, with a subscript "i" was prepared with ion exchange.

For preparation of solid-state impregnated Cu_s-ZSM-5 and Cu_s-Sil-1, the solid-state synthesis method was a slightly modified literature method based on the report from Hutchings *et al.* [19,20] A sample of 7.8, 15.7, 23.6 or 39.3 mg of $Cu(OAc)_2.xH_2O$ (Aldrich) was ground with 0.5 g of H-ZSM-5 for 1 h. The resulting solid was calcined in air at 550 ºC for 6 h at a ramp rate of 2 ºC/min to obtain 0.5%, 1%, 1.5% or 2.5% Cu-ZSM-5. The samples of 0.5%, 1%, 1.5% or 2.5% Cu-Sil-1 were prepared identically except H-ZSM-5 was replaced by Silicalite-1.

Cu_i-ZSM-5 was prepared by ion exchange as follows: A 12.5 mL of 0.1 *M* $Cu(NO_3)_2.xH_2O$ (Aldrich) solution was added to 0.5 g of H-ZSM-5 and the mixture was heated under reflux for 5 h at 80 ºC with stirring. The resulting solid was filtered, washed with deionized water to remove residual Cu^{2+}, and dried at 120 ºC for 4 h. The dried powder was calcined in air at 550 ºC for 6 h, at a ramping rate of 2 K/min.

Methane oxidation reactions were carried out as follows: The standard run was carried out by loading the reaction with 0.82 g of catalyst, and 30 mL of 0.5 *M* H_2O_2 aqueous solution, and heated to and kept at 50 ºC. For the scale-up reaction, the reactor was loaded with 1.56 g of catalyst and 270 mL of 0.5 *M* H_2O_2 aqueous solution, and heated to and kept at 50 ºC. After sealing, while stirring the headspace of the reactor was purged first with helium for five times, then with methane for at least five times, and finally charged with methane to 30.5 bar. The reactor was kept at 50 ºC while stirring at the maximum speed of ~600 rpm. Additional impellers were installed to minimize the hindrance of reaction rate due to mass transfer limits.

The reaction was then stopped by releasing the headspace gases which were collected for GC-TCD analysis. The suspension was rapidly cooled with ice to minimize the loss of volatile liquids. Ethanol was added to the suspension as an internal standard. This suspension was filtered through an Aldrich Millex syringe filter (pore size: 0.22 μm), and the clear colorless solution was used for GC-MS analysis. Agilent GC 6890 equipped with HP PLOT-Q capillary column and thermal conductivity detector (TCD) was used for headspace gases analysis. Agilent 6850-5975C GC-MS system equipped with a DB-624UI capillary column was used for liquid phase separation and analysis.

Results & discussion

The samples of H-ZSM-5, H-Sil-1, Cu_s-Sil-1, Cu_s-ZSM-5 were prepared by slightly modified literature procedure.[19] The Si:Al ratio and metal concentration is shown in Table S1 (Supplementary data). The iron impurity in commercial H-ZSM-5 was 0.014% while that synthesized in our lab was 0.002%. The Si:Al ratio in commercial H-ZSM-5 was 11.5 while that in synthesized sample was 15.

The silicalite-1 and Cu$_s$-Sil-1 samples show a sharp peak at ~210 nm due to zeolitic structure (Supplementary data, Fig. S1).[22] A broad band in 300-800 nm, indicative of CuO, is seen for 2.5%Cu$_s$-Sil-1.[23] X-ray powder diffraction pattern for both H-Sil-1 and Cu-Sil-1 are identical suggesting that Cu substitution does not impact zeolitic structure and copper oxide particles are too small to be seen by XRD. The UV-vis spectra of Cu$_s$-ZSM-5 samples (Fig. 1) show a sharp peak at ~210 nm due to zeolitic structure, a broad peak in 300-600 nm which merges with a broad band centered at ~830 nm is observed due to Cu(II) cations in hexagonal coordination.[24-27] The UV-vis spectrum of Cu$_i$-ZSM-5 is similar to that of Cu$_s$-ZSM-5 except the band in 300-600 nm is not observed. We have previously reported the UV-vis spectrum of ion exchanged Cu$_i$-ZSM-5 which does not exhibit any peak in 300-600 nm region and shows a very weak band centered at ~830 nm.[28] The XRD of H-ZSM-5, Cu$_s$-ZSM-5, and Cu$_i$-ZSM-5 are identical and show diffraction peaks due to zeolitic structure with no peaks for copper containing species. The high-angle annular dark-field (HAADF) scanning transmission electron micrographs (HAADF-STEM) of 1%Cu$_i$-ZSM-5 exhibit a fine dispersion of copper oxide with no discrete nanoparticles or aggregates (Supplementary data, Fig. S2, left). The energy dispersive spectrum (EDS) of 1%Cu$_i$-ZSM-5 (Supplementary data, Fig. S2, right] exhibits expected peaks due to Si, Al, and O. In addition, both Cu K and L peaks of almost equal intensity are observed. This feature is typical of well-dispersed Cu.

For methane oxidation, 0.81 g of catalyst, 30 mL of 0.5 *M* H_2O_2, and 520 mmol (30 bar) of methane were employed. It was found that methane oxidation over H-ZSM-5, H-Sil-1, Cu$_s$-ZSM-5, or Cu$_s$-Sil-1, prepared by solid-state impregnation, was comparable to that previously reported by Hutchings *et al.*[19, 20] (Table 1). The methane conversion over 2.5%Fe$_s$-ZSM-5, under these conditions, showed 0.12% conversion with 2.9% methanol selectivity. Decreasing iron loading to 1% (i.e. 1%Fe$_s$-ZSM-5) and increasing the catalyst loading to 1.56 g and 0.5 *M* H_2O_2 to 270 mL resulted in improved methane conversion and methanol selectivity.

On the other hand, Cu$_i$-ZSM-5, prepared by ion-exchange, exhibited dramatically higher methane conversion and methanol selectivity under our reaction conditions as compared with previous reports.[19,20] In comparison to previously reported catalytic activity of Fe$_s$-ZSM-5, the reaction on Cu$_i$-ZSM-5 proceeds slowly but its methanol selectivity is high, resulting in a much higher methanol yield. The difference in reactivity of

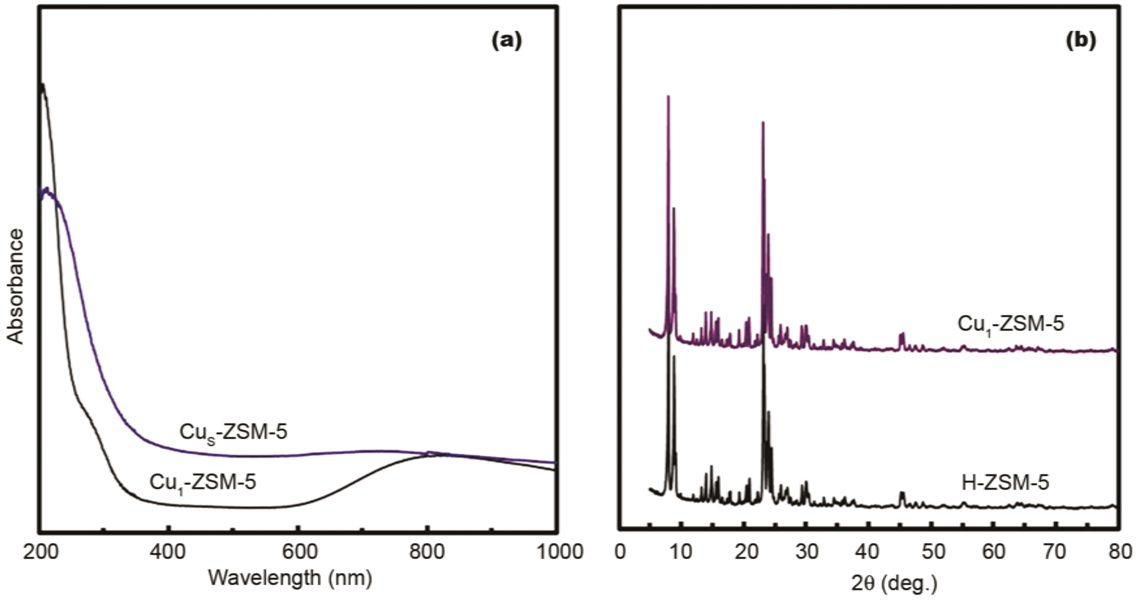

Fig. 1—(a) Diffuse-reflectance UV-vis-NIR spectra of Cu$_s$-ZSM-5, and, (b) X-ray powder diffraction of H-ZSM-5 and Cu$_i$-ZSM-5.

Table 1—Methane conversion and methanol yield

Catalyst	Prep. method	Initial methane (mmol)	Catalyst (g)	H_2O_2 (mL)[a]	MeOH (mmol)[b]	Conv. (%)
H-Sil-1	Hydro	520	0.81	30	0	0
Cu_s-Sil-1	SS	520	0.81	30	0.0066	0.0013
H-ZSM-5	Hydro	520	0.81	30	0.0081	0.0016
H-ZSM-5	Comm.	520	0.81	30	0.016	0.0031
2.5%Fe_s-ZSM-5	SS	520	0.81	30	0.23	0.12
1%Fe_s-ZSM-5	SS	240	1.56	270	0.89	5.5
1%Cu_s-ZSM-5	SS	520	0.81	30	0.16	0.030
1%Cu_i-ZSM-5	IE	240	1.56	270	7.1	4.9

[a] H_2O_2: 0.5 *M*; [b] yield of liquid MeOH.

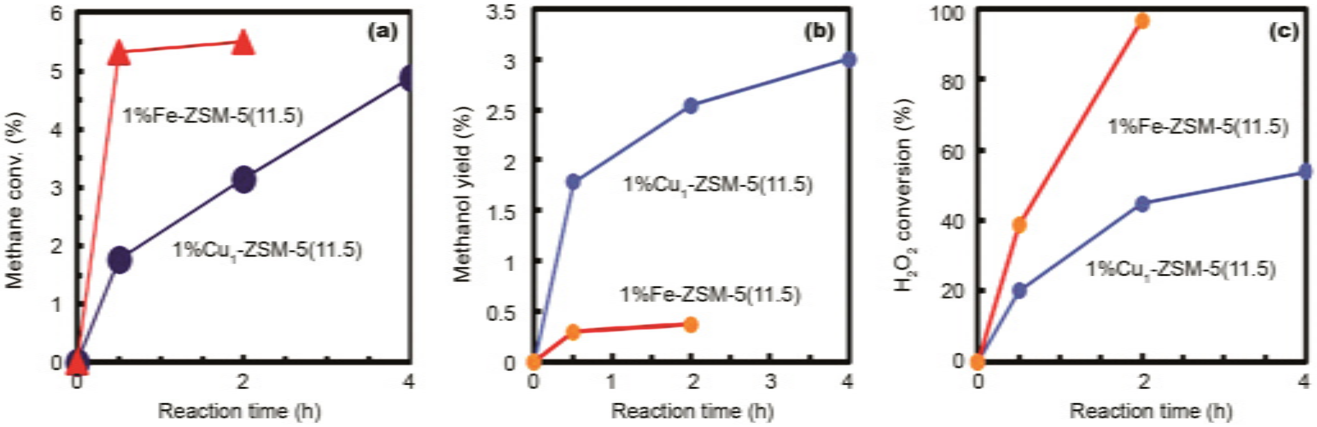

Fig. 2—(a) Methane oxidation over 1%Cu_i-ZSM-5(11.5) and 1%Fe_s-ZSM-5(11.5) as a function of time, (b) methanol yield vs time, and, (c) hydrogen consumption over time.

Cu_i-ZSM-5 prepared by ion exchanged, or solid-state ion exchange for NO_x reduction by hydrocarbons has been previously noted.[21] Ion exchanged copper becomes dispersed in zeolite channels in the form of both isolated, 5-fold coordinate ions and small clusters containing extra-lattice oxygen. The NO_x reduction activity of these catalysts was found to correlate with copper dispersion.

The methane conversion reactions over 1%Cu_i-ZSM-5 and 1%Fe_s-ZSM-5 are shown Fig. 2a. In 30 min, 1%Fe_s-ZSM-5 showed a conversion of ~5.5% with 0.37% methanol yield and balance being formic acid and CO_2 as reported by Hutchings *et al.*[19] The methane conversion over Cu_i-ZSM-5 was 1.8% after 1 h but reached ~4.9% over 4 h (Fig. 2a). Methanol yield over Cu_iZSM-5 reached 3.0%, while it is only 0.4% on 1%Fe_s-ZSM-5 (Fig. 2b). The balance being methyl peroxide and CO_2 which could not be quantified due to low concentrations. The hydrogen peroxide consumption over Fe_s-ZSM-5 is quite rapid and almost 40% is consumed within 30 min which limits the methane conversion (Fig. 2c). The hydrogen peroxide consumption over 1%Cu_i-ZSM-5, on the other hand, slowly reaches 54% over 4 h. Methanol selectivity remains over 60% even though it is being slowly oxidized to formic acid. At 4 h, the formic acid selectivity is 39%. The H_2O_2 selectivity for methanol conversion will be identical to methanol since it is an equimolar reaction if we exclude H_2O_2 decomposition.

In conclusion, we have shown that Cu_i-ZSM-5 is an effective methane oxidation catalyst that can function under mild oxidation condition with high selectivity towards methanol. This high activity, in comparison to solid state synthesized Cu_s-ZSM-5, is due to the nature of copper species and the slow decomposition of hydrogen peroxide allows methane conversion reaction to proceed over longer period. The oxidation of methanol to formic acid over 4 h decreases the methanol selectivity to 61%.

Supplementary data

Supplementary data associated with this article, Table S1 and Figs S1 & S2, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_56A(05)488-492_SupplData.pdf.

Acknowledgement

This research is sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US Department of Energy, USA.

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