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Selective oxidation of methane to methanol with H_2O_2 over Fe-MFI zeolite catalyst using sulfolane solvent

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The effect of reaction conditions for direct oxidation of methane to methanol over Fe-MFI zeolite with H_2O_2 has been investigated. Sulfolane has been proved to be an efficient solvent for liquid-phase methane oxidation. Sulfolane/water mixture with an appropriate proportion led to an extremely high methanol production with a high selectivity.

Methane (CH_4), as the main component of natural gas, is a highly abundant and inexpensive source of fuel and chemicals.[1, 2] The synthetic path for direct conversion of methane to methanol (CH_3OH) is a hot topic since methanol is useful as a fuel and a good building block for the generation of many chemical goods.[3, 4]

The approaches of direct conversion of methane to methanol mainly include gas phase using O_2,[5, 6] N_2O [7, 8] or H_2O [9] as oxidants under high temperature, liquid phase using homogenous catalysts in highly concentrated acids, and liquid phase using H_2O_2 or O_2 as oxidant on heterogeneous catalysts. Direct oxidation of CH_4 in gas phase requires high temperatures (473 to 773 K) to activate the reactants,[2, 9, 10] but the oxidation products are prone to further oxidize to CO_2. Recently, Bokhoven and co-workers developed a direct stepwise method for converting of CH_4 to CH_3OH over Cu-MOR with water under 473 K and 7 bars of CH_4; they achieved the production of 0.2 mol_{MeOH} mol_{Cu}^{-1}.[9] The homogeneous liquid phase system achieves high methane conversion and methanol selectivity, but it usually accompanies by high acid and high pollution, and methanol is not the direct product. [2, 11,12] Periana *et al.* described the oxidation of methane through methyl bisulfate catalyzed by mercuric bisulfate. An unprecedented 85% selectivity of methyl bisulfate at 50% methane conversion was reported.[13] Liquid phase using H_2O_2 or O_2 as environmentally benign oxidants and heterogeneous substances as catalysts is the trend of development. Hutchings and co-workers have made outstanding contributions in aqueous medium with H_2O_2 under low temperature on various kinds of heterogeneous catalysts, including Cu and/or Fe-ZSM-5,[14-17] Au-Pd/TiO_2,[18,19] AuPdCu/TiO_2[20] and Au-Pd colloids[21]. Among of these catalysts, the highest 0.5% of CH_4 conversion with 92% of selectivity to CH_3OH was achieved by using Fe-Cu/ZSM-5 as catalyst in the continuous flow fixed bed reactor, even so the highest total productivity was only 0.08 mol kg_{cat}^{-1} h^{-1}.[15] Chadwick *et al.* found the generation of $CH_2(OH)_2$ in the liquid phase and H_2 in the gas phase for selective oxidation of methane using Fe-ZSM-5 and H_2O_2 in aqueous medium. The productivity was high to 26.7 mol kg_{cat}^{-1} h^{-1}, but the yield and selectivity of MeOH were only 14.9 μmol and 30%.[22] Recently, Shan and co-workers used O_2 and CO as co-oxidants, Rh-ZSM-5 as catalyst to oxidize methane at 423 K in aqueous medium. The highest yield of MeOH and total liquid products were up to 1.2 and 13.9 mol kg_{cat}^{-1} h^{-1}, but the selectivity of methanol was less than 9%.[23] Very recently, Ohkubo' s group successfully produced methanol from methane using perfluorohexane as solvent and $NaClO_2$ as oxidant without catalyst, achieving 99% CH_4 conversion with 14% methanol selectivity.[24]

The inertia C-H bond of CH_4 molecule [4] and the extremely low solubility of CH_4 result in the low CH_4 conversion under the liquid-phase system. CH_4 is a kind of non-polar molecule with very symmetrical tetrahedron structure, and only 1.9 mg CH_4 dissolves in 100 g water at 303 K and 0.1 Mpa.[25] Besides, the solubility of CH_4 is highly dependent on the temperature and pressure of CH_4. It is increased to 87.5 mg at 5 Mpa and 303 K.[25] We have focused on the use of organic solvents to enhance the solubility of CH_4. Among the variety kinds of organic solvents, sulfolane is a very stable aprotic polar solvent. Furthermore, it is water-soluble with strong affinity for CH_4.[26, 27] The solubility of CH_4 reaches 1.4 g/100 g sulfolane at 313 K and 3.7 Mpa, almost 100 times higher than that in water.[28]

Here, the Fe-MFI zeolite catalyst, which was synthesized by direct hydrothermal method, was applied as catalyst for methane oxidation in liquid phase. The details of the synthesis and characterization are described in ESI (Fig. S1 and Table S1).

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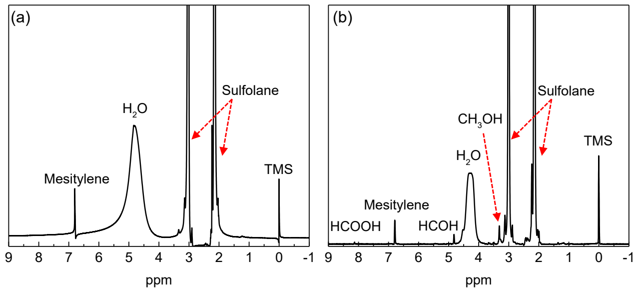

Fig. 1 ^{1}H-NMR spectra of the liquid phase after (a) blank test (without CH_4 as reactant) and (b) with CH_4 as reactant, using mesitylene as internal standard and CD_3CN/ TMS as chemical shift calibrator. Reaction conditions: (a) 323 K, 10 ml sulfolane, 50 mg Fe-MFI, 27 mmol H_2O_2, 2 h. (a) 323 K, 10 ml sulfolane, 50 mg Fe-MFI, 27 mmol H_2O_2, P_{CH4}=3 Mpa, 2 h.

Prior to the effects of various reaction parameters, the stability of different organic solvents under the typical reaction conditions was investigated. Figs. S2 and S3 show the ^{1}H-NMR spectra of the liquid phase after blank test (without CH_4 as reactant) of acetonitrile and ethanol, respectively. The peaks at around 4.9 and 8.1 ppm are assigned to the hydrogen of formaldehyde (HCOH) and formic acid (HCOOH), respectively, which could be produced from the reaction of the solvents with H_2O_2. As a result, acetonitrile and ethanol were not stable in the reaction conditions. When sulfolane was employed as solvent, the peaks ascribed to the products were not observed after the blank test in the ^{1}H-NMR spectrum (Fig. 1(a)), indicating that sulfolane was stable under this reaction condition. Actually, sulfolane is a widely used polar aprotic, stable and water-soluble industrial solvent.[27] However, to the best of our knowledge, it has not been applied as solvent in direct oxidation of methane with H_2O_2. Thus, the direct oxidation of methane in sulfolane/H_2O_2 aqueous solution over Fe-MFI was carried out at 323 K. The ^{1}H-NMR spectrum of the liquid-phase after the reaction is presented in Fig. 1(b), showing the hydrogens of CH_3OH (3.4 ppm), HCOH (4.9 ppm) and HCOOH (8.9 ppm). These products resulted from the reaction between CH_4 and H_2O_2 in sulfolane.

The effects of various reaction parameters were investigated. First the temperature was changed from 303 to 353 K to study the influence on the reaction performance, as shown in Fig. 2(a). The amount of total liquid products and HCOOH increased with temperature. The yields of MeOH and HCOH were increased with temperature raising from 303 to 323 K. Further increase in the temperature to 353 K led to the decrease in the productions. This is probably caused by the successive oxidation of MeOH and HCOH to HCOOH. The H_2O_2 conversion increased from 3 to 100% along with temperature. Because the liquid phase boiled at 3 Mpa and 353 K, leading to the dissociation of H_2O_2. The solubility of CH_4 in sulfolane is decreased by increasing the temperature. Based on the literature, the solubility of CH_4 in sulfolane was decreased from 1229 mg/ 100 g sulfolane at 298 K and 3.36 Mpa to 1137 mg/ 100 g sulfolane at 343 K and 3.04 Mpa.[29] However, high temperature could improve the reaction activity for both catalysts and reactants.[30] Thus, temperature is a “double-edged sword”. The reaction performance was investigated over a range of CH_4 pressure from 0.5 to 3 Mpa. As expected, the yields in the liquid-phase were enhanced along with CH_4 pressure, as shown in Fig. 2(b). MeOH gave the highest selectivity and the selectivity of every liquid product was relatively stable under different CH_4 pressures (Fig. S4(b)). In addition, H_2O_2 conversion enlarged from 4 to 14 % with CH_4 pressure growing from 0.5 to 3 Mpa. It is clear that the CH_4 pressure mainly influences the solubility of methane, *i.e.* the reactant amount. The solubility of CH_4 in sulfolane was enhanced from 917 mg/ 100 g sulfolane at 2.37 Mpa and 313 K to 2460 mg/ 100 g sulfolane at 7.44 Mpa and 313 K.[29] Obviously, high CH_4 pressure under the maximum pressure of the instrument is beneficial to the reaction. The effect of reaction time was depicted in Fig. 2(c). The yields of the products in liquid phase were increased over time, especially the production of HCOH, which was improved from 314.4 to 864.4 μmol by extending reaction time from 2 to 4 h. The H_2O_2 conversion was relatively stable at around 12% against reaction time. HCOOH as the oxidation production of HCOH presented lower selectivity than the results of Hutchings[14, 16] and Chadwick[22], probably due to the solvent effect (Fig. S4(c)). Fig. 2(d) shows the relationship between the amount of the products in the liquid-phase and the catalyst mass. When the catalyst mass was increased from 10 to 100 mg, the yields of the products and the H_2O_2 conversion were increased but the selectivity to MeOH was decreased.

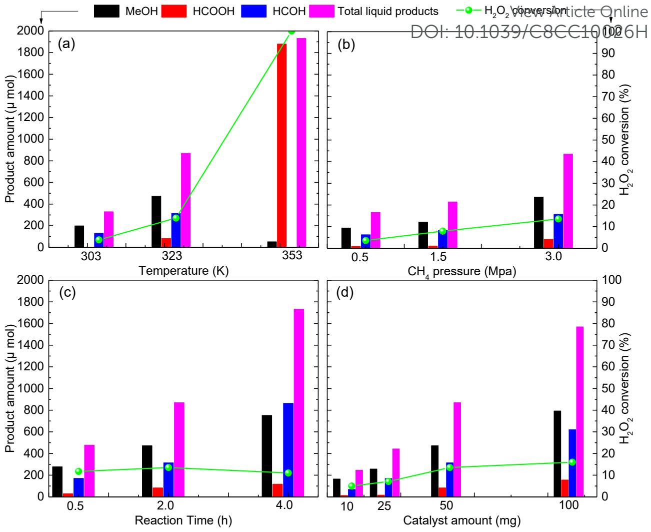

Fig. 2 Liquid product amount and H_2O_2 conversion over Fe-MFI catalyst under different (a) temperatures, (b) CH_4 pressures, (c) reaction times and (d) catalyst amounts. Reaction conditions: (a) 10 ml sulfolane, 50 mg catalyst, 27 mmol H_2O_2, 2 h, P_{CH4}=3 Mpa. (b) 323 K, 10 ml sulfolane, 50 mg catalyst, 27 mmol H_2O_2, 2 h. (c) 323 K, 10 ml sulfolane, 50 mg catalyst, 27 mmol H_2O_2, P_{CH4}=3 Mpa. (d) 323 K, 10 ml sulfolane, 27 mmol H_2O_2, 2 h, P_{CH4}=3 Mpa.

Sulfolane is rarely used alone but in admixture with another solutions.[28] The use of mixed solvents is an attractive alternative to either the solvent effect or the economic benefit and environment protection. Sulfolane-water mixed solvent is extensively applied in the lithium batteries [31] and as extraction agent in the petrochemical industry.[32] Thus, the reaction performance in aqueous sulfolane with the volume content ranging from 0 to 100 vol.% were investigated, the results are presented in Figs. 3 and S5. When distilled water (0 vol.% of sulfoalne) was used as solvent, the minimum amount of MeOH (12.2 μmol) and HCOH (0 μmol), but the maximum amount of HCOOH (462.5 μmol) were obtained in the liquid phase. Meanwhile

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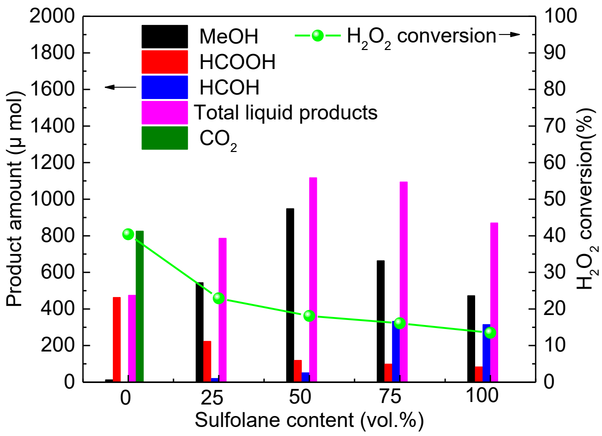

Fig. 3 The amount of products and H_2O_2 conversion under different proportions of sulfolane content. Reaction conditions: 323 K, 10 ml solvent, 50 mg catalyst, 27 mmol H_2O_2, P_{CH4}=3 Mpa, 2 h.

it was worth pointing out that large amount of CO_2 (825.5 μmol) was detected in the gas phase (Fig. S6(a)). The H_2O_2 conversion in water reached the highest to 40%. The consequence of HCOOH as the main liquid product in aqueous medium with Fe-containing zeolite catalyst was consistent with the results of Hutchings[14, 15] and Chadwick[22]. When the proportion of sulfolane was continuously increased from 0 to 50 vol.%, the yields of the products, MeOH and HCOH, were increased, but the HCOOH yield and the H_2O_2 conversion were decreased. When 50 vol.% sulfolane was used as solvent, the yield and selectivity of MeOH reached maximum to 949.8 μmol and 85%, respectively. Compared to those at the use of only water as solvent, the yield of HCOH was also increased to 51.0 μmol, while that of HCOOH was decreased to 118.6 μmol and the H_2O_2 conversion was decreased to 18%. The productivity of the total liquid products based on the catalyst was reached up to 11.2 mol kg_{cat}^{-1} h^{-1}. It was necessary to mention that no CO_2 was detected in the gas-phase (Fig. S6(b)). Continuing to increase the proportion of sulfolane to 100 vol.%, the yields of the total liquid products and the H_2O_2 conversion were decreased, but the HCOH yield was increased. When sulfolane was used as solvent, the yield and selectivity of MeOH were 472.3 μmol and 54%, respectively. The yield of HCOH and HCOOH were increased to 314.4 μmol and decreased to 83.3 μmol, respectively. CO_2 was not discovered in the gas phase (Fig. S6(c)). The H_2O_2 conversion was decreased to 14%.

Thus observed interesting phenomenon could be explained with the solvent effect. On one hand, sulfolane possesses the feature of temporary combination with hydroxyl, which has been reported in other systems.[26] In Balducci's research about the oxidation of benzene to phenol, the selectivity of phenol in sulfolane is twice than in other solvents, because the temporary formation of phenol-sulfolane complex prevents the production of by-products.[33] Murata *et al.* also has reported that sulfolane is effective for improving phenol selectivity in the oxidation of benzene with oxygen and acetic acid using palladium catalyst.[34] On the other hand, water is a protic solvent, which could provide proton, while sulfolane is an aprotic solvent. It is the possible reason that H_2O_2 showed the highest conversion in water but the lowest conversion in sulfolane.

In conclusion, we have successfully found that sulfolane was a stable and effective organic solvent in the direct oxidation of methane with H_2O_2. The dramatic improvement for the yield of MeOH reported herein could have a significant impact on the methane conversion.

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