Electronic Supporting Information

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

Peipei Xiao[a], Yong Wang[a], Toshiki Nishitoba[a], Junko N. Kondo[a], Toshiyuki Yokoi[a, b, *]
[a]*Institute of Innovative Research, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.*
[b]*PRESTO, JST, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

*Corresponding author: Phone: +81-45-924-5238, Fax: +81-45-924-5282,
E-mail address: yokoi@cat.res.titech.ac.jp

S.1.1 Materials

Colloid silica (HS-40) and tetrapropylammonium hydroxide (TPAOH) (20-25% in water) were purchased from Tokyo Chemical Industry. $Fe(NO_3)_3{\cdot}9H_2O$, NH_4NO_3, H_2O_2 (30 wt.%), ethanol, acetonitrile, sulfolane, mesitylene, 1,4-dioxane, tetramethylsilane (TMS), 2,2,3,3-d(4)-3-(Trimethylsilyl)propionic acid sodium (TMSP-D4), CD_3CN and D_2O were purchased from Wako. Methane (99.99%) gas was provided by Taiyo Nippon Sanso Co., Ltd.. All of the reagents were used as received, without further purification.

S.1.2. Catalysts preparation

The **MFI**-type Fe-MFI zeolites was directly prepared by hydrothermal method. First, colloid silica was added to the solution containing water, TPAOH and Fe $(NO_3)_3{\cdot}9H_2O$. The gel with the molar composition of 1 Si: 0.067 Fe: 0.25 TPA: 20 H_2O was crystallized at 443 K for 7 days with 40 rpm before aging at 353 K for 24 h. Then, the solid product was collected after filtering, rinsing and drying. The as-synthesized material was calcined at 823 K for 10 h to remove TPA^+ species. The resultant sample was NH_4^+ exchanged and calcined at 823 K for 5 h to obtain the H-type one.

S.1.3. Characterization of catalysts

XRD pattern was collected on a Rint-Ultima III (Rigaku) using a Cu Kα X-ray source (40 kV, 20 mA). Field-emission scanning electron microscopic (FE-SEM) image of the powder sample was obtained on S-5200 (Hitachi) microscope operating at 1 kV. Elemental analyses of the sample were performed on an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Shimadzu ICPE-9000). Nitrogen adsorption and desorption measurements to obtain information on the micro- and meso-porosities were conducted at 77 K on a Belsorp-mini II (MicrotracBEL).

UV-vis diffuse reflectance spectrum was recorded on a V-650DS spectrometer (JASCO). The diffuse reflectance spectrum was converted into the absorption spectra using the Kubelka-Munk function. Fourier Transform Infrared (FT-IR) spectrum was obtained by a JASCO FT-IR 4100 spectrometer equipped with a triglycine sulfate (TGS) detector. For FT-IR observation, the sample was pressed into a self-supporting disk (20 mm diameter, ca. 30 mg) and placed in an IR cell attached to a closed gas-circulation system. After the sample was pretreated by evacuation at 773 K for 2 h, then adsorbed 5-1000 Pa NO at ambient temperature. The IR spectrum resulting from the subtraction of the background spectra from those with NO adsorbed is shown unless otherwise noted.

S.1.4. Catalytic tests

The direct oxidation of methane reaction was carried out in a 100 ml PTFE autoclave. The CH_4 pressure was controlled by the pressure gage ranging from 0.5 to 3 MPa. The reactants were stirred vigorously by an agitator blade. Aqueous hydrogen peroxide (30 wt.%) was used as oxidant. In a typical “standard” CH_4 oxidation experiment, 10 ml sulfolane was exploited as solvent, 50 mg catalyst and 27 mmol H_2O_2 were added to the autoclave and heated to 323 K. The sealed reactor was then purged with CH_4 to achieve the desired pressure, typically 3 Mpa. After the desired reaction time, usually 2 h, the autoclave was cooled rapidly to 278 K in an ice bath to minimize any further chemical reaction and reduce the loss of volatile products.

Liquid-phase products were analyzed by ^1H NMR spectroscopy on JEOL ECA-600 spectrometer (14.1 T) equipped with an additional 1 kW power amplifier. Mesitylene and 1.4-dioxane were used as the internal standard when the solvent was sulfolane and water, respectively. TMS/CD_3CN and TMSP-D4/D_2O were used as a chemical shift calibrator when sulfolane and water were used as solvent, respectively. The detectable products in the liquid-phase were CH_3OH, HCOH and HCOOH. The products in the gas phase were analyzed by GC-TCD. The amount of unconverted H_2O_2 was quantified by standard titration method with 0.1 mol/L $Ce(SO_4)_2$ solution.

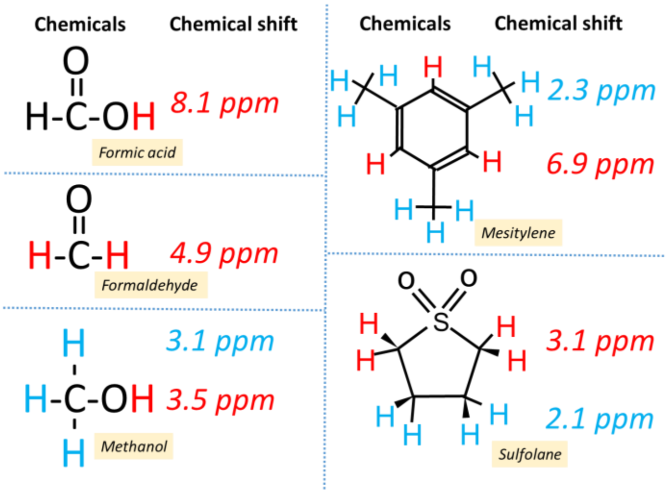


Fig. ^1H chemical shifts of the solvents and the products.

S.2. Characterization results

The characterization results of the catalyst are presented in Fig. S1 and Table S1. The XRD pattern indicates the typical MFI structure, and no features belonging to large iron oxide particles were observed (Fig. S1(a)). The SEM image reveals the small coffin particle with the size of 0.35 μm (Fig. S1(b)). The UV-vis spectrum in Fig. S1(c) shows that the main coordination state of the Fe species in the framework was four-coordination, which located at around 215 nm. The main Fe species on the extra framework was the isolated and oligomeric Fe species ranging from 250 to 350 nm.[1] The NO-adsorbed FT-IR technique was used to estimate the states of Fe species on the extra framework. Fig. S1(d) points out that the main Fe species is oligomer due to the highest band at 1867 cm^{-1}, which was attributed to $Fe^{2+}(NO)$ [2, 3] or $Fe^{3+}(NO)$ [4, 5] complexes located on the oligomeric Fe species [5, 6]. The minor Fe species is isolate with difference unsaturation condition. Because the bands at 1915 and 1810 cm^{-1}, which were attributed to $Fe^{2+}(NO)_3$ complexes, and the bands at 1843 and 1765 cm^{-1}, which were assigned to $Fe^{2+}(NO)_2$ complexes, were observed on the isolated Fe species.[2, 5, 6]

References:

1. C. Hammond, N. Dimitratos, R. L. Jenkins, J. A. Lopez-Sanchez, S. A. Kondrat, M. H. ab Rahim, M. M. Forde, A. Thetford, S.H. Taylor, H.Hagen, E. E. Stangland, J. H. Kang, J. M. Moulijn, D. J. Willock and G. J. Hutchings, *ACS Catal.*, 2013, **3**, 689-699.
2. J. Szanyi, F. Gao, J. H. Kwak, M. Kollar, Y. Wang and C. H. Peden, *Phys. Chem. Chem. Phys.*, 2016, **18**, 10473-10485.
3. R. Q. Long, R. T. Yang, *J. Catal.*, 2000, **194**, 80-90.
4. A. M. Ferretti, C. Oliva, L. Forni, G. Berlier, A. Zecchina and C. Lamberti, *J. Catal.*, 2002, **208**, 83-88.
5. G. Berlier, C. Lamberti, M. Rivallan and G. Mul, *Phys. Chem. Chem. Phys.*, 2010, **12**, 358-364.
6. F. Gao, M. Kollár, R. K. Kukkadapu, N. M. Washton, Y. Wang, J. Szanyi and C. H. F. Peden, *Appl. Catal., B*, 2015, **164**, 407-419.

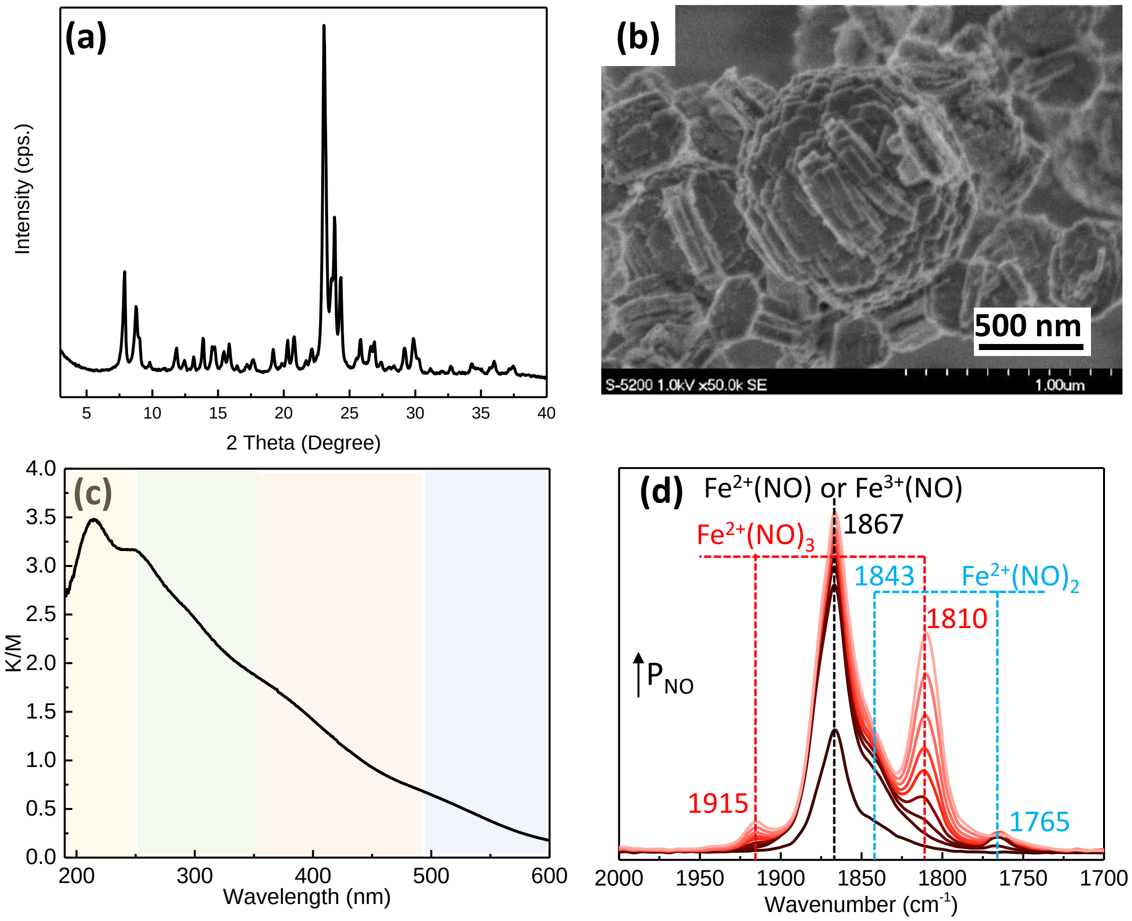


Fig. S1 (a) XRD pattern, (b) SEM image, (c) UV-vis spectrum and (d) NO-adsorbed FT-IR spectrum of the Fe-FI zeolite.

Table S1 Physicochemical characteristics of the Fe-MFI zeolite catalyst.

Sample	**Si/Fe**	**Si/Fe**	**Fe (wt.%)**	**S_{BET}**	**S_{EXT}**	**V_{Total}**	**V_{Micro}**
	In gel	**In product** [a]		**(m^2g^{-1})** [b]	**(m^2g^{-1})** [c]	**(cm^3g^{-1})** [b]	**(cm^3g^{-1})** [c]
Fe-MFI	15	19	4.7	474	183	0.46	0.18

[a] Determined by ICP-AES analysis.

[b] Calculated using the Brunauer-Emmett-Teller (BET) equation on the N_2 adsorption isotherms.

[c] Calculated by the *t*-plot method based on the adsorption isotherms.

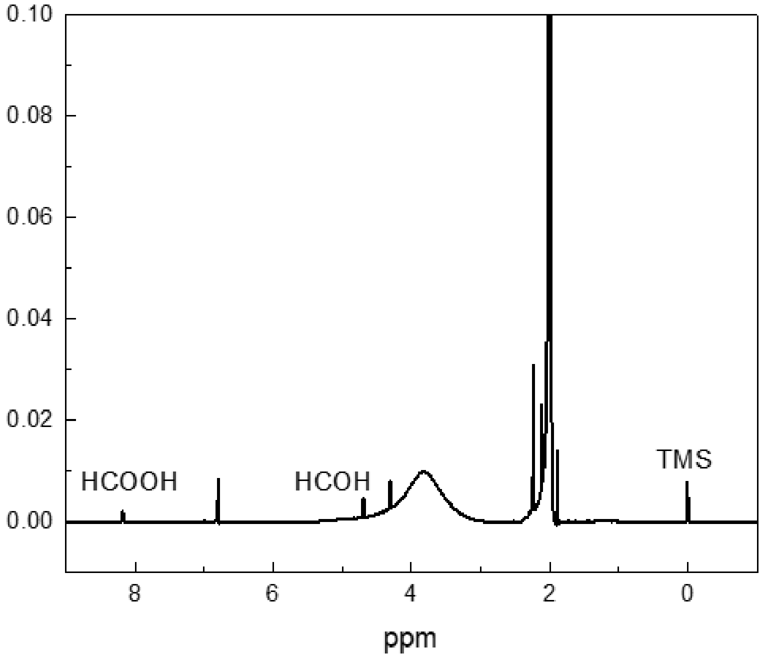


Fig. S2 ^{1}H-NMR spectrum of blank test (no CH_4 as reactant) over Fe-MFI zeolite catalyst using acetonitrile as solvent. Mesitylene was used as internal standard and CD_3CN/ TMS was used as a chemical shift calibrator.

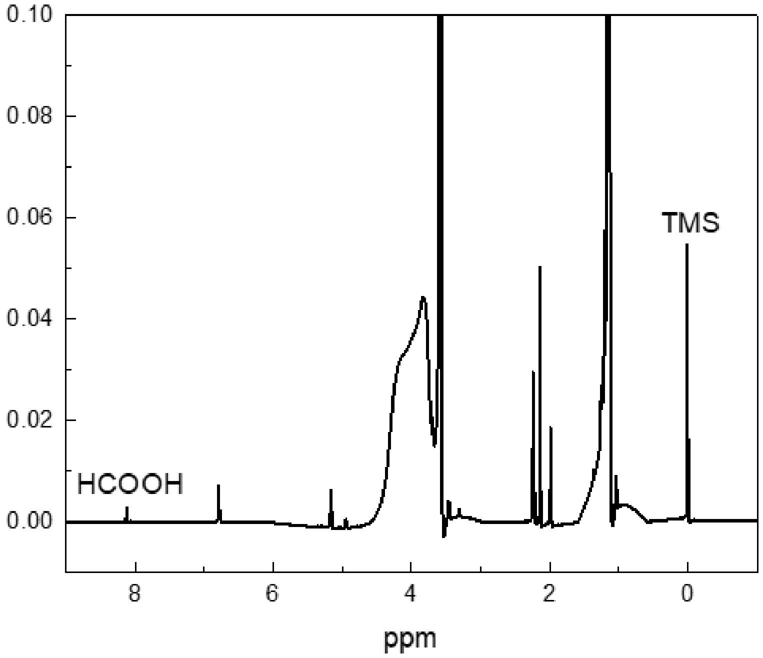


Fig. S3 ^{1}H-NMR spectrum of blank test (no CH_4 as reactant) over Fe-MFI zeolite catalyst using ethanol as solvent. Mesitylene was used as internal standard and CD_3CN/ TMS was used as a chemical shift calibrator.

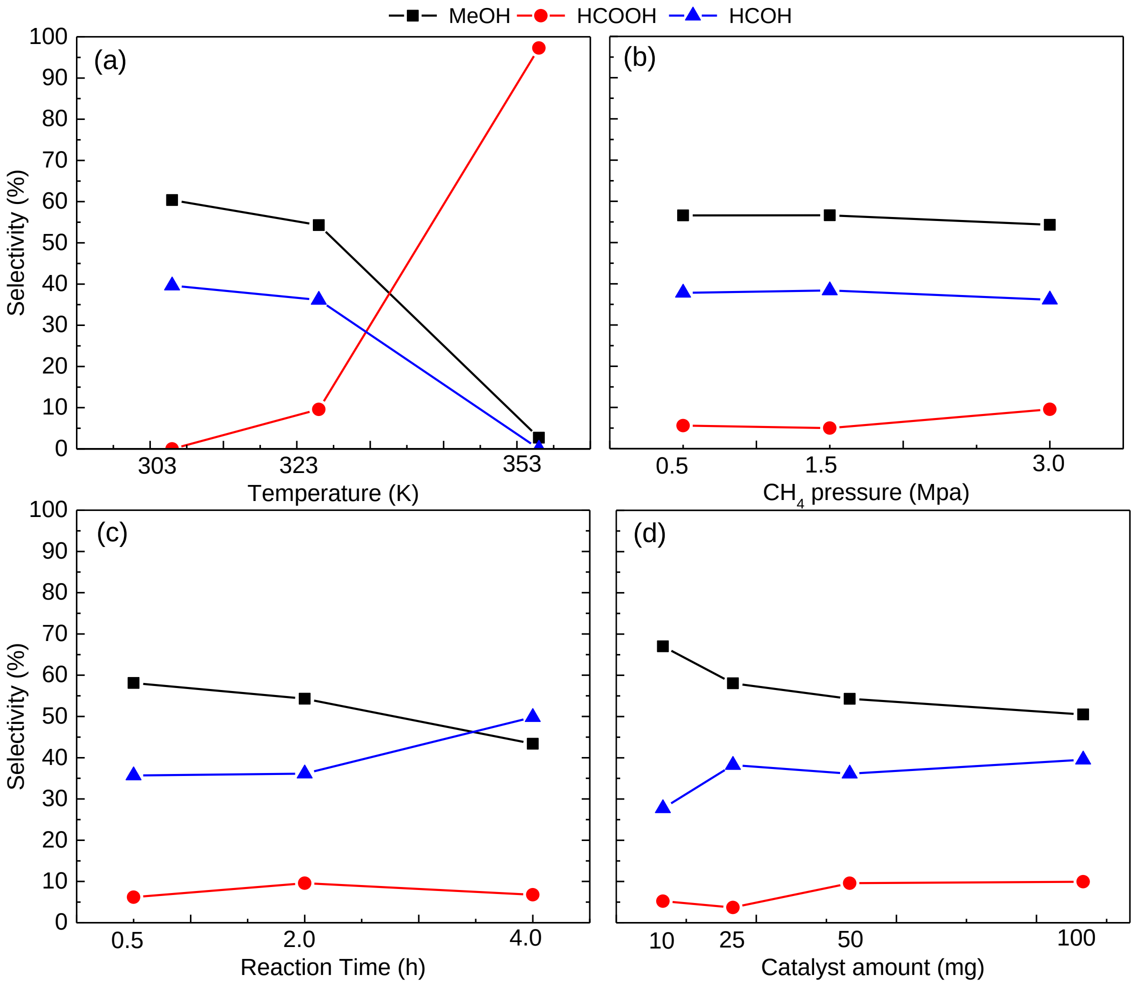


Fig. S4 Products' selectivities over Fe-MFI catalyst under different (a) temperature, (b) CH_4 pressure, (c) reaction time and (d) catalyst amount. Reaction conditions: (a) 10 ml sulfolane, 50 mg catalyst, 27 mmol H_2O_2, 2 h, P_{CH4}=3 Mpa. (b) 323 K, 10 ml sulfolane, 50 mg catalyst, 27 mmol H_2O_2, 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.

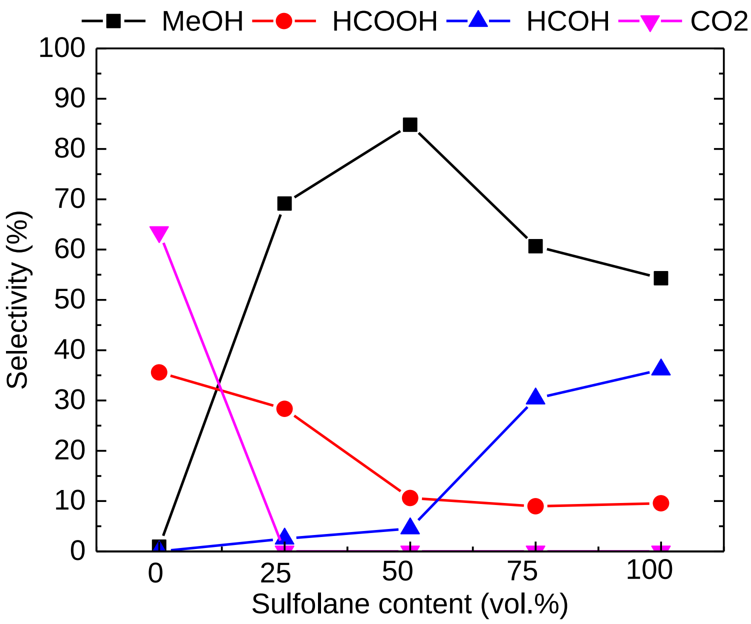
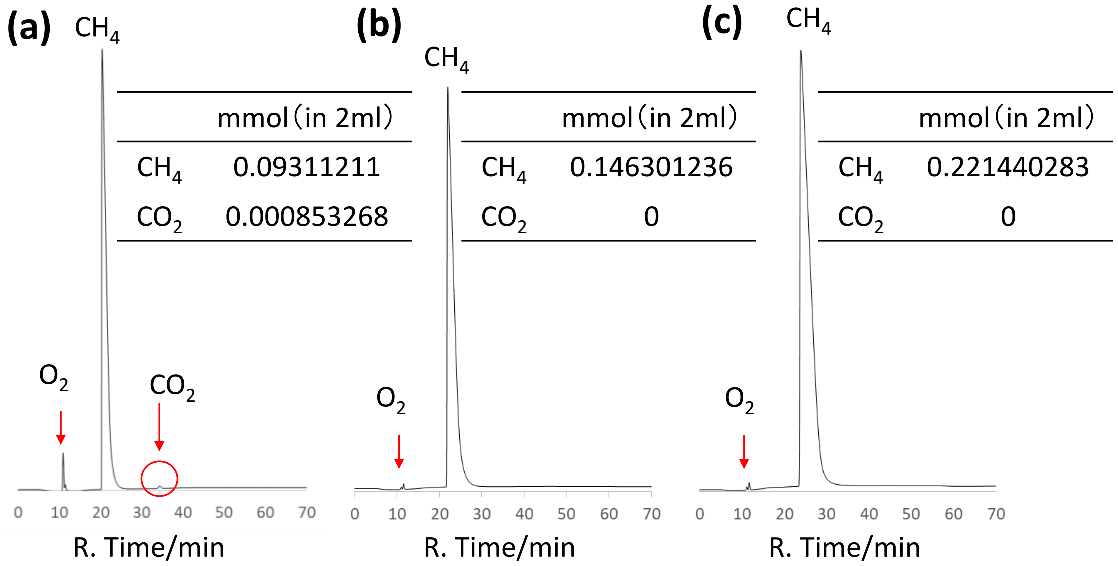


Fig. S5 Products' selectivities over Fe-MFI catalyst under different proportions of sulfolane content. Reaction conditions: 323 K, 10 ml solvent, 50 mg catalyst, 27 mmol H_2O_2, P_{CH4}=3 Mpa, 2 h.



(a)

	mmol (in 2ml)
CH_4	0.09311211
CO_2	0.000853268

(b)

	mmol (in 2ml)
CH_4	0.146301236
CO_2	0

(c)

	mmol (in 2ml)
CH_4	0.221440283
CO_2	0

Fig. S6 GC-TCD spectra of the gas phase after the reaction using (a) water, (b) 50 vol.% sulfolane solution and (c) sulfolane as solvent over Fe-MFI zeolite catalyst with H_2O_2.