

A highly efficient Nafion-H catalyst for vapour phase

carbonylation of dimethoxymethane

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Experimental Section

Preparation of catalysts

Nafion-H catalyst: Nafion-H resin powder (<200 mesh, commercially available from Aldrich) was mixed with silica powder by mechanical mixture. The Nafion-H resins loading in the catalyst were 60 wt.%. The obtained mixture was pressed to pellets, then, crushed, sieved to 40–60 mesh particles.

Polystyrenesulfonic acid resins catalysts: Polystyrenesulfonic acid resins, which were purchased from Dandong Mingzhu Special Type Resin Co., Ltd., were used without further treatment.

H-faujasite catalysts: Zeolite samples were obtained commercially with different Si/Al ratios in H⁺ form (Si/Al=4.3, Nankai University catalyst Co., Ltd.; Si/Al=15, Si/Al=40, Zeolyst). The zeolite samples were calcined in static air at 723 K for 4 h, and then, pelletized, crushed, sieved to 40–60 mesh size for activity test.

Sample Preparation for ¹H MAS NMR

Prior to the pyridine-*d*₅ adsorption and NMR experiments, all the samples were dehydrated at 120 °C for 12 h under vacuum condition (<1×10⁻² Pa). When the samples were cooled to ambient temperature, the pyridine-*d*₅ was introduced from a vacuum line at room temperature. Then, the overloaded pyridine-*d*₅ was removed at 313 K for 10 min in vacuum. After adsorption of pyridine-*d*₅, the sealed samples were transferred into a NMR rotor under a dry nitrogen atmosphere in a glovebox.

Solid-State NMR Experiments

¹H MAS NMR spectra were recorded on a Bruker AvanceIII 600 spectrometer equipped with a 14.1 T wide-bore magnet using a 4 mm MAS probe with resonance frequencies of 600.13 MHz. The pulse width was 2.2 μs for a π/4 pulse, and 32 scans were accumulated with a 10 s recycle delay. Samples were spun at 12 kHz, and chemical shifts were referenced to adamantane at 1.74 ppm.

Catalytic test

DMM (commercially available from Aldrich) carbonylation reactions were performed in a continuous-flow fixed-bed stainless steel reactor. Typically, 0.1 g of catalyst was loaded into a reactor tube (8 mm internal diameter). The sample was then heated to 120 °C for an hour under nitrogen atmosphere (30 ml min⁻¹) to remove residual water and then cooled to the reaction temperature. DMM was carried into reactor by carbon monoxide, which was bubbled through a stainless steel saturator containing liquid DMM isothermally held at 20 °C. The chemical inert nitrogen was introduced to the reaction system to adjust the partial pressure of CO. The reaction effluent was analyzed by gas chromatography (Agilent 7890) equipped with a flame ionization detector. The DMM conversion and MMAc selectivity were calculated with the followed equations.

$$\text{DMM Conversion} = [1 - 3C_{\text{DMM}} / (3C_{\text{DMM}} + 2C_{\text{DME}} + 2C_{\text{MF}} + C_{\text{methanol}} + 3C_{\text{MMAc}})] \times 100\% \quad (1)$$

$$\text{MMAc selectivity} = [3C_{\text{MMAc}} / (2C_{\text{DME}} + 2C_{\text{MF}} + C_{\text{methanol}} + 3C_{\text{MMAc}})] \times 100\% \quad (2)$$

where C_i was the molar concentration of compound i in the reaction effluent and n was the number of carbon derived from DMM.

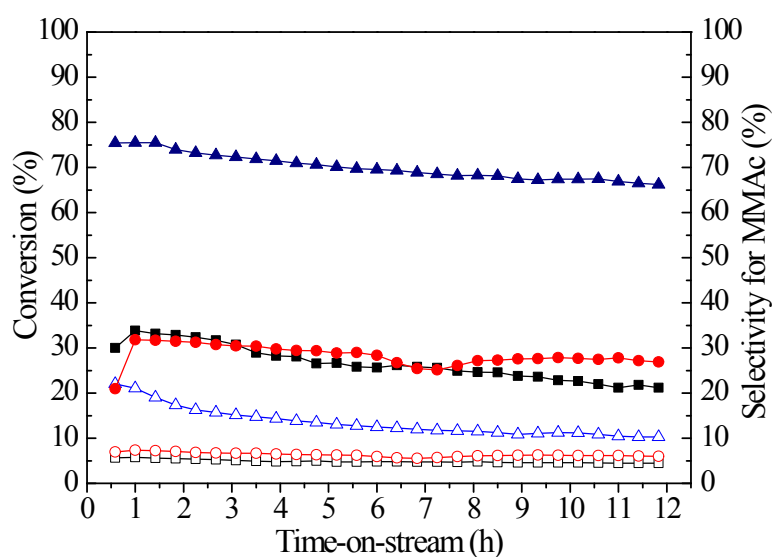


Figure SI 1 the effect of Si/Al ratio on the DMM conversion(▲ Si/Al=40; ○Si/Al=15;

□Si/Al=4.3) and selectivity to MMAc (▲Si/Al=40; ●Si/Al=15; ■Si/Al=4.3) at the same reaction condition (catalyst weight = 0.1 g, reaction pressure = 30.0 atm, reaction temperature = 110°C, DMM partial pressure = 0.42 atm, CO stream = 85 ml min⁻¹).

Table SI 1 the catalytic performance over various sulfonic acids with different acid strength

Sulfonic Acids	H ₀ ^a	Selectivity / %	Conversion /%	Rate of MMAc Synthesis/ mol (mol H ⁺) ⁻¹ h ⁻¹
CF ₃ SO ₃ H	-14.1 ^{b1}	92.8	27.0	12.6
C ₄ F ₉ SO ₃ H	-13.2 ^{b1}	91.7	20.2	10.6
H ₂ SO ₄	-12.0 ^{b1}	90.0	10.5	4.4
CH ₃ SO ₃ H	-7.8 ^{b2}	88.9	<5.0	<2.0
CH ₃ CH ₂ SO ₃ H	>-7.8	72.9	<5.0	<2.0
p-CH ₃ C ₆ H ₄ SO ₃ H	+0.55 ^{b3}	79.2	<5.0	<2.0
p-CH ₃ CH ₂ C ₆ H ₄ SO ₃ H	>0.55	76.1	<5.0	<2.0

a: H₀, value of Hammett acidity function

b1: G. A. Olah, G. K. S. Prakash, J. Sommer, *superacids* Wiley, 1985 and G.A. Olah, G.K.S. Prakash, A. Molnar, J. Sommer, *Superacid Chemistry*. Wiley, 2009; b2: D. Fărcașiu and A. Ghenciu, *Progress in Nuclear Magnetic Resonance Spectroscopy*, 1996, **29**, 129-168. b3: L. K. Doraiswamy, *Organic Synthesis Engineering*, Oxford University Press, 2001.