Selective oxidation of dimethyl ether to methyl formate over trifunctional MoO_3-SnO_2 catalyst under mild conditions

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Experimental

Catalyst Preparation

The MoO_3-SnO_2 catalysts were prepared as follows: the obtained catalysts were referred to their Sn salt precursors: MoO_3-SnO_2 ($SnCl_4$), MoO_3-SnO_2 (Na_2SnO_3) and MoO_3-SnO_2 ($SnCl_2$).

The MoO_3-SnO_2 ($SnCl_4$) catalyst was prepared as follows: co-precipitating Tin chloride ($SnCl_4 \cdot 5H_2O$) aqueous solution and aqueous ammonia in drops at pH=8 at 333K. The obtained suspension was filtered and washed with deionized water until pH=7. Then the cake-like hydroxide was added to the required ammonium molybdate solution. After evaporation of the solvent in a rotary evaporator at 353K, the solid obtained was dried at 393K for 10h and annealed at 573K for 5h and then at 773K for 8h.

The MoO_3-SnO_2 ($SnCl_2$) catalyst was also prepared as above, but using $SnCl_2$ instead of $SnCl_4$.

The MoO_3-SnO_2 (Na_2SnO_3) catalysts were prepared as follows: co-precipitating sodium stannate aqueous solution ($Na_2SnO_3 \cdot 3H_2O$) and hydrochloric acid (HCl) in drops at pH=8. The obtained suspension was filtered and washed with deionized water until pH=7, and there was no precipitation when the $AgNO_3$ was added into the mother liquid. Then the cake-like hydroxide was added to the required ammonium molybdate solution. After evaporation of the solvent in a rotary evaporator at 353K, the solid obtained was dried at 393K for 10h and annealed at 573K for 5h and then at 773K for 8h.

Catalytic Activity Tests

The reactions were carried out in a continuous flow type fixed-bed reactor containing catalyst (5ml, 20-40mesh) diluted with ground quartz. The catalyst was treated in a flow of O_2 (25ml/min) for 2h at 523K before reaction. The reactant mixture consisted of DME and O_2 with molar ratio of 1:1. The outlet stream line from the reactor to the gas chromatograph was heated at 423K. The hydrocarbon of reaction products were analyzed by gas chromatograph GC-9A (Shimadzu Co.) equipped with flame ionization detector (30m x 0.32mm, PEG-20M), and GC-4000A (Beijing Dongxi Co.) with thermal conductivity detector (Porapak T column). The GC-4000 (Beijing Dongxi Co.) equipped with thermal conductivity detector (TDX-01 column) was used to analyze H_2, CO, CO_2 and CH_4.

Surface texture

The surface area and the particle size of the samples were measured by BET nitrogen adsorption isotherms at 77K using a Tristar 3000 machine.

Temperature Programmed Desorption (TPD)

The NH_3-TPD spectra were recorded in a fixed-bed reactor system equipped with a thermal

conductivity detector (TCD). The catalyst (100mg) was pretreated at 873K under Ar flow (40ml/min) for 2h and then cooled down to 373K under Ar flow. Then NH_3 was introduced into the flow system. After purging the residual NH_3 for 4h, the TPD spectra were recorded at a temperature rising rate of 5K/min from 373K to 873K.

The CO_2-TPD spectra were recorded using the same instrument as the NH_3-TPD. The catalyst (100mg) was pretreated at 873K under Ar flow (40ml/min) for 2h and then cooled down to 303K under Ar flow. Then CO_2 was introduced into the flow system. After purging the residual CO_2 for 4h, the TPD spectra were recorded at a temperature rising rate of 5K/min from 303K to 873K.

NH_3 adsorption IR spectra

Diffuse reflectance infrared spectra were measured by a Bruker Tensor 27 with a MCT detector (64 scans, 4 cm^{-1}). The catalyst was placed in an in-situ IR cell equipped with KBr windows (Harrick). After heating at 673 K for 2 h and evacuating at 10^{-4} bar, the cell was cooled down to room temperature and the spectrum was recorded. Next, the NH_3 gas was introduced into the cell, and after the equilibrium the sample was degassed. Finally, the spectra were recorded at 373K and the pressure of the cell was evacuated at 10^{-3} bar.

Temperature Programmed Reduction (TPR)

H_2-TPR was conducted in a fixed-bed reactor system equipped with a thermal conductivity detector. The sample (100mg) was pretreated in Ar at 973K for 2h and then cooled down to 303K. After that, a 10%H_2/Ar mixture gas was switched on and the temperature was increased linearly at a rate of 5K/min from 303K to 973K.

Raman Spectra

Raman spectra were recorded on a Jobin-Yvon Labram-HR Confocal Laser Micro Raman spectrometer with an argon-ion laser at the excitation wavelength of 514.5nm and the resolution of 1cm^{-1}. The Raman spectra were obtained in the range of 100-1100cm^{-1} under ambient conditions.