

Effective Dispersing and NMR Characterization of Polyoxometalates on Mesoporous Zeolite

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Introduction

Polyoxometalates (POMs) are widely investigated for acid and oxidation catalytic reactions due to their unique structural and electronic properties. [1] To maximize their surface site accessibility and activity, POMs supported on porous materials like mesoporous silica have been studied. [2] The properties and the active phases are typically studied by transmission electron microscopy (TEM), X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) techniques. In particular, ^{31}P MAS NMR technique is used to characterize pure and supported phases, and the different species are commonly identified by the shift of NMR resonance positions. [3, 4] However, achieving good dispersing of POMs while fully understanding the distribution of the active and inactive species is still a challenge.

Zeolites are attractive catalyst or support materials because of the local crystalline and electronic structure, but their small pore sizes can not be accessed by POM clusters. In this paper, we prepare a new mesoporous zeolite material by using carbon nanoparticles as the pore template, and disperse POMs ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) in the mesoporosity. XRD, TEM and nitrogen physisorption studies confirmed that POMs resides inside the mesopores, consistent with the significantly high activity observed supported POMs for 1-butene isomerization. More significantly, we find that the chemical shift in ^{31}P MAS NMR can not be used to unambiguously assign POM species on surfaces of zeolites. This information can be only obtained from spin-lattice relaxation time measurements.

Materials and Methods

Mesoporous silicalite-1 with MFI structure is prepared by using carbon nanoparticles as the pore template. [6] The carbon black nanoparticles are removed by calcinations at 550 °C. $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is loaded by rotary vacuum evaporation of an ethanol solution, followed by drying in oven overnight at 120 °C. ^{31}P Magnetic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) experiments were performed on a Varian-Chemmagetics 300MHz Infinity spectrometer, corresponding to ^1H and ^{31}P Larmor frequencies of 299.982 and 121.43MHz, respectively. The catalytic activity measurements for 1-butene isomerization were carried out with a quartz flow fixed-bed reactor (1cm i.d.) at atmospheric pressure.

Results and Discussion

For catalytic isomerization of 1-butene at 70 °C for HPA/silicalite-1 and HPA/Meso-silicalite-1, the conversions and selectivity towards cis-/trans- products are shown in Figure 1. Much higher catalytic isomerization activity is observed over HPA/meso-silicalite-1 than HPA/silicalite-1. The initial conversion of 1-butene is 72 % on HPA/Meso-silicalite-1 with a trans- to cis- ratio of 2-butene around 1.7, while conversion for HPA/silicalite-1 is less than 1%.

Spin-lattice relaxation measurements suggest that the relaxation time can be fit with two components, as shown in Figure 2. The value of T_1 for the fast relaxing component is 2.7s and this component makes up 46% of the sample. The slow relaxing component has $T_1=64$ s and makes up 54% of the sample. With conventional zeolites only the latter could be found. Therefore, we conclude that the fast relaxing component is the well-dispersed active surface species for isomerization of 1-butene.

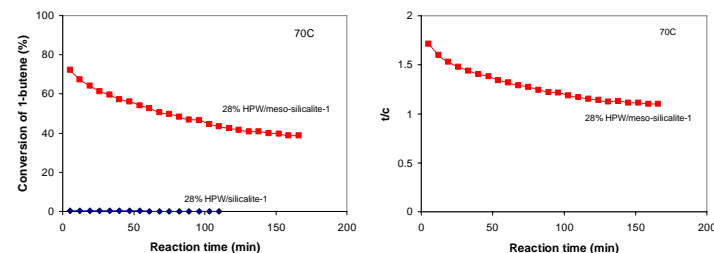


Figure 1. Conversion (left) and selectivity (right) for isomerization of 1-butene over HPA/Meso-silicalite-1 and HPA/Silicalite-1 as a function of time on stream

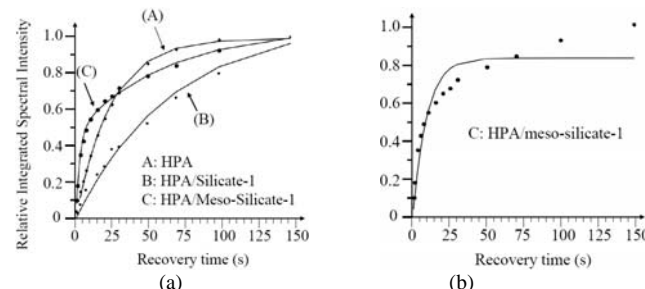


Figure 2. The integrated ^{31}P MAS spectral intensity from -14 to -16 ppm as a function of the saturation-recovery time for HPA. (a) HPA: $T_1=24.4\text{s}$ (100%); Silicate-1: $T_1=67.7\text{s}$ (100%); Meso-Silicate-1 (double exponential fit): $T_{1f}=2.7\text{s}$ (46%) $T_{1s}=63.7\text{s}$ (54%) (b) Meso-Silicate-1 (single exponential fit): $T_1=9.3\text{s}$.

Significance

We report a new method to effectively disperse POM catalysts on mesoporous supports. We also show that while the active species cannot be identified by NMR line shifts, the ^{31}P spin-lattice relaxation time can instead be used to identify and quantify both the active and inactive phases.

References

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