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In-situ ^{13}C MAS NMR investigation of solvent effect on the formation of phenylacetaldehyde over TS-1 zeolite

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ABSTRACT

In-situ ^{13}C MAS NMR techniques were used to investigate the effects of different solvent systems on the formation of phenylacetaldehyde (PADH) over TS-1 zeolite. Protic solvents such as water and methanol provide acidic centers during the reaction. These acidic species catalyzed the transformation of the intermediates to PADH. Whereas in the presence of aprotic solvents such as acetone, the precursor of PADH remains stable on the framework of TS-1 and accordingly there is no PADH formation.

1. Introduction

A titanium-containing molecular sieve, such as TS-1, is an active and highly selective industrial catalyst for oxidizing many organic compounds using aqueous H_2O_2 as an oxidizing agent under ambient conditions [1–4]. During the oxidation, different solvents have major influences on the reaction kinetics and product selectivity [5,6]. Numerous experimental and computational researchers have focused more on the solvent effect on alkene oxidation over TS-1 zeolite [5–8]. Protic solvents, such as water and methanol, have been proposed to be coordinated with catalyst. They can form five-membered-ring intermediate to stabilize the active sites and enhance the catalytic activity of TS-1 for alkene oxidation [3,6,9,10]. Several reports have also claimed that the five-membered-ring intermediate can provide acidity during the reaction, which is a key to isomerizing the pre-product (styrene epoxide) to phenylacetaldehyde (PADH) in styrene oxidation reaction catalyzed by TS-1 zeolite [11].

In our previous investigation, a mechanism involving a radical formation in styrene oxidation over TS-1 zeolite was verified by *in-situ* magnetic resonance technologies and theoretical calculations [12]. PADH does not result from further reaction of styrene epoxide [12]. In that study, we used urea-hydroperoxide (UHP) as a solid oxidizing agent without any solvent. While in the real catalytic reaction, aqueous H_2O_2 is usually used as an oxidizing agent. Protic and aprotic solvents can also have a marked influence on the distribution of products in styrene oxidation reactions [13]. Therefore, the objective of the current study is to monitor the reaction under realistic conditions as well as to investigate the influence of the solvent nature on the formation of PADH over TS-1 zeolite. Here, we still utilized UHP as an oxidizing agent to avoid introducing protic molecule through an oxidant. Similar to aqueous H_2O_2 solution, UHP can also produce different Ti-superoxo complexes by mechanical mixing with TS-1 zeolite, which was considered to be the active centers of oxidation [13,14]. Furthermore, the TS-1 zeolite without Brϕnsted acid sites was used in order to avoid the acidic influence from the catalyst itself.

2. Experimental

2.1. Materials and characterization

The TS-1 zeolite used in this investigation was synthesized according to a BASF Aktiengesellschaft patent (WO 01/14251). The structure of the obtained zeolite was checked with a D/max-γb type X-ray diffractometer (Rigaku) using monochromatic Cu Kα radiation (40 kV and 100 mA), with a scan speed of 5°/min in 2θ. The XRD measurements confirmed that the synthesized material had a typical MFI structure. Chemical analysis was performed with

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a SRS 3400 X-ray fluorescence spectrometer. The overall SiO_2/TiO_2 ratio of the sample was 50:1. The characterization of acidity in the sample was carried out by ^{31}P MAS NMR spectroscopy of trimethylphosphine (TMP) adsorbed on TS-1 zeolite.

2.2. Sample preparation for NMR

In-situ ^{13}C MAS NMR measurements were performed by adsorbing β-^{13}C-rich styrene (99%, Cambridge Co.) on the sample with a homemade device. Before adsorption, the sample was dehydrated at 673 K under vacuum (below 10^{-2} Pa) for 20 h and then uniformly mixed with urea-hydroperoxide (Acros Organics) under N_2 protection. The mixture was evacuated at room temperature for 5 min and β-^{13}C-rich styrene was then loaded at 77 K (liquid nitrogen) for 30 min. The sample was evacuated for 20 min to remove physisorbed styrene at room temperature. The adsorption of solvent (water, methanol, and acetone) was performed by exposing the treated sample to their vapor pressure at room temperature for 30 min and then the sample was packed into the rotor and sealed. In a typical *in-situ* NMR experiment, the sealed sample was rapidly heated to 313 K and maintained for a precisely controlled period of time.

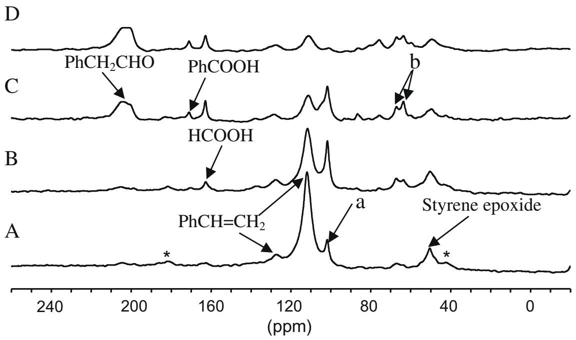

Fig. 1. The *in-situ* ^{13}C MAS NMR spectra of styrene upon reaction with a mixture of UHP and TS-1 zeolite at room temperature after (A) 0 min, (B) 30 min, (C) spectrum for the treated sample adsorbed H_2O for 30 min at room temperature, and (D) heated at 313 K for 40 min after adsorption. $*$ represents the sideband, the structure of a and b shown in Fig. 2.

2.3. NMR experiments

NMR spectra were obtained at room temperature on a Bruker DRX-400 spectrometer with a BBO MAS probe using 4 mm ZrO_2 rotor. The ^{13}C MAS NMR measurements were made at 100.6 MHz with high-power proton decoupling by using a 2 μs pulse and 2 s repetition time ($1 \sim 5T_1$). For each ^{13}C spectrum, 1600 free induction decays were accumulated with a sample spinning rate of 7 kHz. Adamantane was used as a chemical shift reference in ^{13}C MAS solid state NMR. The spectra were not normalized.

3. Results and discussion

As previously demonstrated [12], β-^{13}C-enriched styrene adsorbed on a mixture of TS-1 and UHP generated intense signals. In Fig. 1A, several signals can be identified which are characteristics of β-^{13}C-enriched styrene adsorption on TS-1 zeolite. The peak centered at 113.2 ppm is assigned to β carbon atom of styrene. The weak peaks with chemical shifts ranging from 128.0 to 140.0 ppm are related to the aromatic carbons and α-carbon from the styrene side-chain. In addition to the signals from the reactant, there were two isolated peaks centered at 50.2 ppm and 102.2 ppm in the ^{13}C MAS NMR spectrum, indicating the conversion of styrene during adsorption. The former peak is a typical signal for the β carbon atom of styrene epoxide, which is formed by the epoxidation of styrene with UHP. The latter signal is within the range for O–C–O species, and has been successfully assigned to a hemiacetal species bound to Ti species in the framework of zeolite produced through a radical mechanism [12]. The structure is shown in Fig. 2a. The intensity of the signal for the hemiacetal species increased at the expense of styrene after 30 min at room temperature as shown in Fig. 1B. At the same time, several new signals were identified at 163.2, 172.4, and 64.0–68.0 ppm. These peaks are related to formic acid and phenyl acetic acid, arising from the deep oxidation of styrene, as well as glycol bound to Ti species in the framework of zeolite (shown in Fig. 2b) [12]. It is important to note that no signal at 202 ppm corresponding to PADH, the dominant product for styrene oxidation with aqueous H_2O_2 over TS-1 zeolite, was detected.

When the treated sample adsorbed H_2O at room temperature for 30 min, there was a resonance peak centered at 202.0 ppm, a

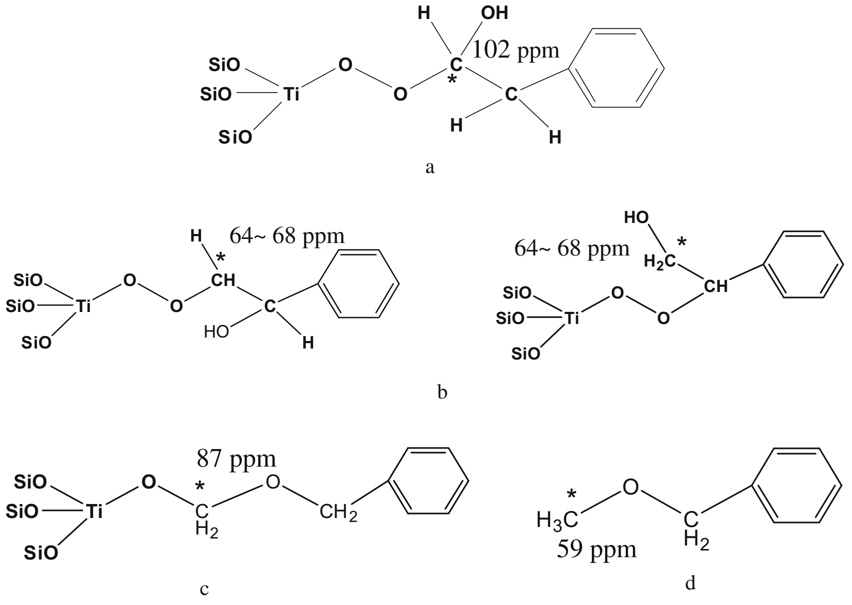

Fig. 2. The structures of the major peaks in ^{13}C MAS NMR spectra.