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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 $2\theta$. 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.

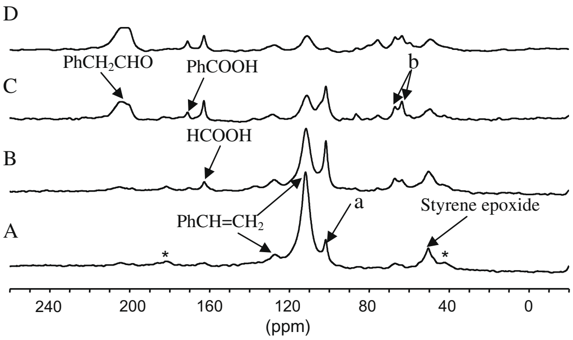

**Fig. 1.** The *in-situ* $^{13}$C MAS NMR spectra of styrene upon reaction with a mixture of UHP and TS-1 zeolite at room temperature after (A) 0 min, (B) 30 min, (C) spectrum for the treated sample adsorbed $H_2O$ for 30 min at room temperature, and (D) heated at 313 K for 40 min after adsorption.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

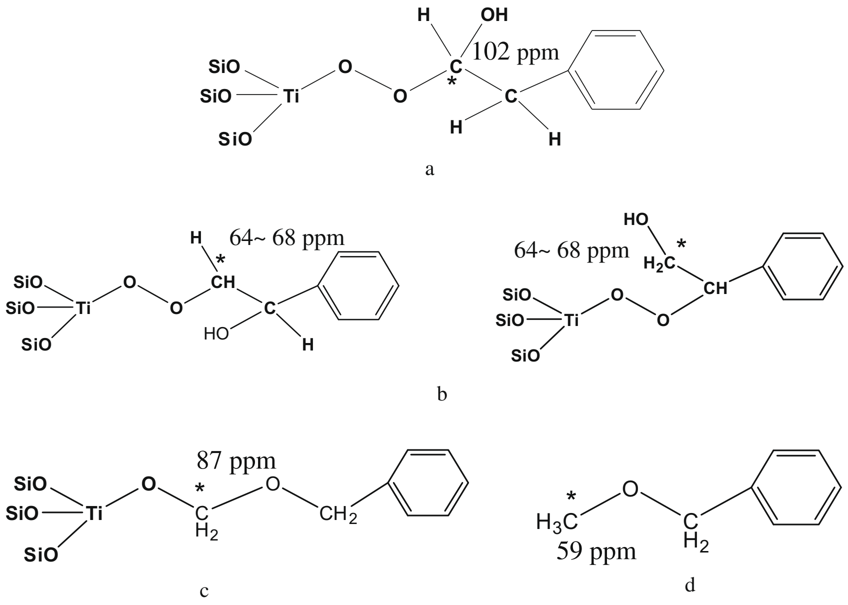

**Fig. 2.** The structures of the major peaks in $^{13}$C MAS NMR spectra.

typical signal of carbonyl group in PADH in the $^{13}$C MAS NMR spectrum (shown in Fig. 1C). At the same time, the intensity of the signals from styrene and hemiacetal species decreased. When the sample was heated at 313 K after adsorption, the intensity of the signal from the aldehyde increased at the expense of the hemiacetal species. Meanwhile, the intensity of the signal from the styrene epoxide decreased slightly. It is clear that hemiacetal species is the intermediate for the formation of PADH. This result is in good correlation with what we have observed before [12]. We also observed the same phenomena when the treated sample adsorbed methanol. The spectra are shown in Fig. 3. After the adsorption of methanol for 30 min at room temperature, styrene was rapidly converted to the hemiacetal species. There are also small amounts of PADH, styrene epoxide, formic acid, phenyl acetic acid, and glycol species appearing as shown in Fig. 3A. The signal at 50.2 ppm also could arise from the methyl group in methanol. After the sample was heated at 313 K for 5 min, the signal of styrene has almost disappeared in the $^{13}$C MAS NMR spectrum (shown in Fig. 3B). Correspondingly, the intensity of the signal for the hemiacetal species was enhanced. It is obvious that methanol promotes the formation of hemiacetal species. In addition, another new peak centered at 87.0 ppm appeared. It is related to an alkoxy group, whose structure is shown in Fig. 3C. As the reaction proceeded, the intensity of the signals for PADH and alkoxy species increased. On the other hand, the intensity of the signal from the hemiacetal species decreased until they disappeared. These experiments suggested that the hemiacetal species are intermediates for PADH production. The existence of water and methanol is conducive for the conversion of hemiacetal species to PADH.

Acetone, one of the solvents usually used in oxidation reaction, was also investigated. The spectrum displayed in Fig. 4 shows the effect of acetone on styrene oxidation over the mixture of TS-1 and UHP. Similar to methanol, when the mixed sample was exposed to acetone vapor at room temperature for 30 min, styrene reacted to form hemiacetal species rapidly. The new signal at 32.0 ppm shown in Fig. 4A arises from the methyl group of adsorbed acetone in the system. After the sample was heated at 313 K for 5 min, styrene was completely depleted. Correspondingly, the amount of hemiacetal species increased. As the reaction proceeded, part of the hemiacetal species were converted to the alkoxy species. It is worth pointing out that no signal at 202.0 ppm was detected, which indicated clearly that no PADH was formed under this condition.

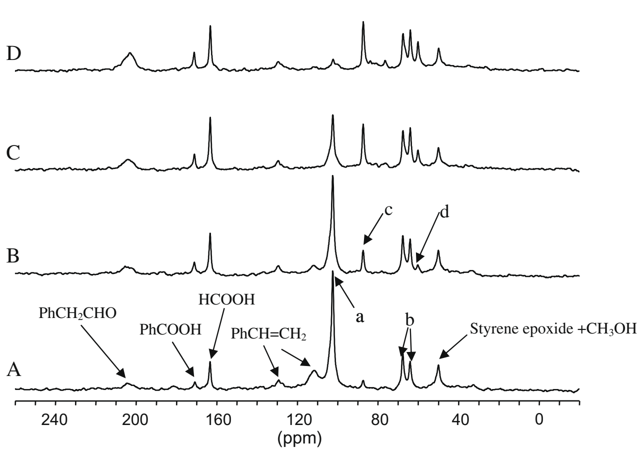

**Fig. 3.** The *in-situ* $^{13}$C MAS NMR spectra of styrene upon reaction with a mixture of UHP and TS-1 zeolite (A) adsorbed methanol at room temperature for 30 min, (B) heated at 313 K for 5 min, (C) 18 min, and (D) 38 min, the structures of a, b, c, and d are shown in Fig. 2.

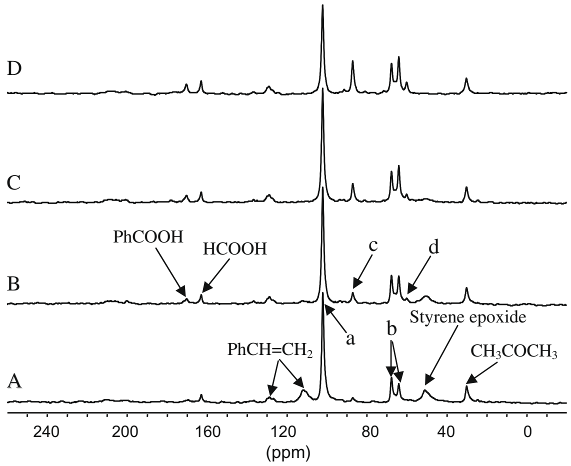

**Fig. 4.** The *in-situ* $^{13}$C MAS NMR spectra of styrene upon reaction with a mixture of UHP and TS-1 zeolite (A) adsorbed acetone at room temperature for 30 min, (B) heated at 313 K for 5 min, (C) 15 min, and (D) 45 min, the structures of a, b, c, and d are shown in Fig. 2.

In our previous investigation [12], the Brϕnsted acidity was a unique factor to catalyze the conversion of hemiacetal into PADH. Despite the absence of Brϕnsted acid sites within the catalyst, we still observe the formation of PADH in the presence of water and methanol as evidence in the appearance of a signal at 202.2 ppm. It is possible that acidic derivatives were generated due to the presence of protic molecules in the system. Several researchers reported that the protic molecule interacted with titanium hydroperoxo moiety to form a five-membered-ring hydrogen bonded structure, which could dissociate Brϕnsted acidic centers [6,9,10,15]. These acidic species catalyzed the transformation of the hemiacetal species to PADH [12]. Meanwhile, in our experiments, we did not observe the conversion of styrene epoxide to PADH, even with the existence of protic molecules. The strength of these acidic species produced by five-membered-ring intermediate is probably too weak to break the ring of the epoxide to form PADH. Therefore, as previously suggested, PADH does result from the hemiacetal species, while not from further reaction of styrene epoxide.

Since aprotic molecule such as acetone cannot be coordinated with TS-1 zeolite to form five-membered cyclic structure, no acidic species was dissociated in the system. Consequently, the hemiacetal species either remain bound to the zeolite framework or through different mechanism produces other by-products instead of PADH. This further confirms that protic conditions are required for the formation of PADH over TS-1 zeolite.

In addition, when the organic solvents (methanol and acetone) were added to the system, almost all of the styrene was converted to hemiacetal species within 10 min. In the absence of the organic solvents, the styrene was not depleted even after 30 min. The plausible explanation could be that organic solvents promoted UHP to release more anhydrous $H_2O_2$ to form active centers. On the other hand, the existence of organic solvents could also stabilize the radicals originating from the solid–solid interaction of TS-1 zeolite and UHP, which was related to the formation of hemiacetal species [12].

## 4. Conclusions

As previously shown, PADH is the dominant product of styrene oxidation over TS-1 zeolite, and results from the conversion of hemiacetal species under acidic condition, not from further reaction of styrene epoxide. The selection of solvent types plays a key role in the formation of PADH. Protic solvents such as water and methanol are coordinated with Ti–peroxo complex and provide acidic centers through hydrogen bonding. These acidic species catalyze the transformation of hemiacetal species to PADH. With aprotic solvent, the hemiacetal species remain stable on the framework of TS-1, and accordingly no PADH is formed. Organic solvents such as methanol and acetone can conduce to producing and stabilizing hemiacetal species, the precursor of PADH.

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