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Catalyzed Oxidation of Methanol on Acid/Base Modified $\text{VO}_x/\text{Al}_2\text{O}_3$ Studied by Solid-state NMR

ZENG Dan-lin, YANG Jun, ZHENG An-min, CHEN Lei, XU Jun,
YE Chao-hui, DENG Feng*

(State Key Laboratory of Magnetic Resonance and Atomic and Molecular Physics
(Wuhan Institute of Physics and Mathematics, the Chinese Academy of Sciences), Wuhan 430071, China)

Abstract : Oxidation of methanol catalyzed by NaOH or HNO_3 modified $\text{VO}_x/\text{Al}_2\text{O}_3$ was studied by solid-state nuclear magnetic resonance (NMR) spectroscopy. The acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst showed stronger Brønsted acid sites compared to the unmodified $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst, while the base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst had no Brønsted acid sites. As a result, the former exhibited higher selectivity in producing dimethoxymethane from oxidation of methanol whereas the oxidation reaction catalyzed by the later yielded mainly formate. These results indicate that the Brønsted acid sites in $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts play a key role in the oxidation reaction converting methanol to dimethoxymethane.

Key words: solid-state NMR, catalysis, methanol oxidation, vanadium oxide

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Introduction

Alumina-supported vanadium oxide exhibits high activity for the catalytic oxidation of methanol to more valuable compounds such as dimethoxymethane (DMM), formaldehyde, and formic acid or formate^[1-8]. The redox property of vanadium species on the alumina surface has been extensively studied by various techniques such as solid-state nuclear magnetic resonance (NMR)^[4], Raman^[5], and X-ray near edge absorption spectroscopies (XANES)^[7]. However, the acidity of this catalyst is also very important for

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Biography: Zeng Dan-lin(1977-), Male, Shiyan, Hubei, China, PhD Student, Radiophysics.

* **Corresponding author**: Deng Feng, Tel: +86 27 8719 8820, E-mail:dengf@wipm.ac.cn.

the catalytic selective oxidation reaction^[9], but the effect of the acidic property on the catalytic performance and the role of the acid sites in this reaction are still poorly understood.

Solid-state NMR has been proved to be a powerful technique for characterizing structures of heterogeneous catalysts and elucidating reaction mechanisms^[10–15]. It is also a very successful tool for characterization of the acidity of solid catalysts with the application of probe molecules such as 2-¹³C-acetone and trimethylphosphine oxide (TMPO)^[16–22]. In the present work, three kinds of VO_x/Al₂O₃ catalysts with different acid properties were prepared. The catalytic oxidation reaction of methanol and the acidity of the catalysts were investigated in detail by solid-state NMR spectroscopy. The relationships between product distribution and acid strength of the catalysts as well as the role of the acid sites in the reaction have been discussed on the basis of our experimental results.

1 Experimental

1.1 Sample preparation

Vanadium was introduced onto γ -Al₂O₃ (Merk) by wetness impregnation with an aqueous NH₄VO₃ solution. After impregnation, the materials were dried at 393 K for 5 h and then calcined at 773 K for 12 h in air. For the preparation of acid-treated sample, the calcined sample was impregnated with 1×10^{-4} mmol/L HNO₃ solution (pH = 4) with the solid to liquid ratio of 1 : 4 for 5 h at room temperature and then the sample was filtered, washed thoroughly with deionized water, dried at 393 K overnight, placed into a glass ampoule and then activated at 673 K under vacuum (10^{-3} Pa) for 5 h. For the preparation of base-treated sample, the procedure is the same as above except that the calcined sample was impregnated with 1×10^{-4} mmol/L NaOH solution (pH = 10). 1 mmol methanol (¹³C, 99%, Cambridge Isotope Inc.) and 0.5 mmol O₂ per gram catalyst were adsorbed in the ampoule under vacuum at the temperature of liquid nitrogen and then the ampoule was flame sealed. Prior to NMR measurements, the sealed ampoule was warmed to room temperature, heated at the desired temperature for 15 min and then the reaction was quickly quenched by liquid nitrogen. For the adsorption of probe molecules, samples were kept at 673 K under a vacuum less than 1×10^{-3} Pa for at least 8 h. To minimize the possible chemical exchange and polymerization, the adsorption of 2-¹³C-acetone was done at room temperature with a loading of ca. 0.1 mmol per gram catalyst. The trimethylphosphine oxide (TMPO) adsorption procedure was different from that of 2-¹³C-acetone. About 0.5 g dehydrated sample was mixed with 3 mL CH₂Cl₂ solution containing 0.1 mmol/L TMPO in a glovebox before the mixture was stirred for 3 h by an ultrasonic shaker, allowed to equilibrate for 5 h, and then evacuated under vacuum to remove CH₂Cl₂ completely before NMR measurements.

1.2 Sample characterization

All the NMR experiments were carried out at 9.4 T on a Varian Infinityplus-400 spectrometer using a Chemagnetic 7.5 mm probe, with resonance frequencies of 400.12, 100.41, and 161.91 MHz for ¹H, ¹³C, and ³¹P, respectively. The 90° pulse widths for ¹H, ¹³C, and ³¹P were measured to be 3.7, 4.4, and 3.6 μs, respectively. The chemical shifts were referenced to tetramethylsilane (TMS) for ¹H, to hexamethylbenzene (HMB) for ¹³C, and to 85% H₃PO₄ solution for ³¹P, respectively. Repetition times of 6 s for ¹H, 60 s for ³¹P single-pulse experiments were used. The magic angle spinning rate was 5 kHz. For the cross-polarization (CP)/MAS NMR experiments, the Hartmann-Hahn condition was achieved by using hexamethylbenzene (HMB), with a contact time of 2.0 ms and a repetition time of 2.0 s. Single-pulse ¹³C magic-angle spinning (MAS) NMR spectra in all experiments were recorded with a 10 s recycle delay, ensuring a quantitative measurement of the ¹³C signals.

2 Results and discussion

Figure 1 shows the ¹³C MAS spectra of methanol oxidation on the acid-treated VO_x/Al₂O₃ at various temperatures. The resonance at 113 ppm in all the spectra is due to the background of the probe. There are four peaks (at δ 49, 53, 69, and 97) in the spectrum of the sample heated at 373 K for 15 min. The relatively intense signal at δ 49 is assigned to methoxyl group^[23]. This species can not be easily removed by vacuum pumping (Fig. 2), indicating that it should correspond to surface-bound species. The peak at δ 53 is due to the physisorbed methanol. The resonance at δ 69 likely arises from the methylene group of ethylene glycol (HOCH₂CH₂OH)^[24], and the signal at δ 97 is due to the methylene group of dimethoxymethane (DMM)^[25]. When the reaction temperature increases to 423 K, a trace of formic acid (δ 162)^[26] and paraformaldehyde (δ 90)^[23] appear in the spectrum. As the temperature further increasing to 473 K, the two signals of formic acid and paraformaldehyde grow up, along with the decrease in the intensity of ethylene glycol (δ 69) and dimethoxymethane (δ 97) signals. When the reaction temperature is higher than 523 K, most of the valuable hydrocarbons such as dimethoxymethane, paraformaldehyde and formic acid disappear, they have been further oxidized into CO₂ (δ 126). The resonance at δ 58 (due to dimethyl ether)^[27] becomes predominant as the reaction temperature increases to 573 K. By careful integration of the various ¹³C NMR signals (Table 1), we can find that the acid-treated VO_x/Al₂O₃ displays a higher selectivity for DMM (52.5%) at 423 K.

¹³C MAS NMR spectra of methanol oxidation on VO_x/Al₂O₃ at various temperatures are shown in figure 3. The overall results are almost analogous to the reaction on the acid-treated VO_x/Al₂O₃ with the exception that the relative content of some hydrocarbon species is different at the various reaction temperatures. Compared the products selectivity of these two catalysts (Table 1), we can find that the selectivity of DMM on

the $\text{VO}_x/\text{Al}_2\text{O}_3$ (27.9%) is much lower than that of the acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ (52.5%) at the reaction temperatures of 423 K. The different selectivity for DMM is probably due to the different acidic property of the two catalysts.

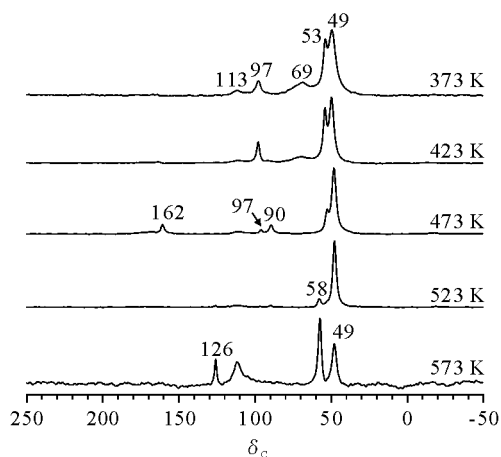


Fig. 1 ^{13}C MAS single-pulse NMR spectra (with proton decoupling) of methanol oxidation on acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ at various temperatures.

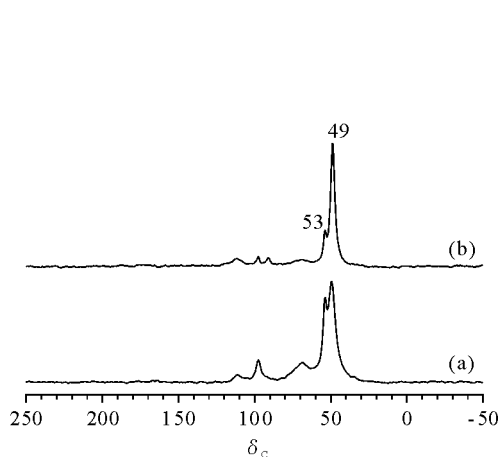


Fig. 2 ^{13}C single-pulse MAS spectra (with proton decoupling) obtained (a) after the methanol oxidation on acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ at 373 K; (b) the same as above except with pumping to remove physisorbed methanol.

Table 1 Methanol oxidation selectivity on the three types of catalysts in sealed ampoule at the same reactant ratio $\text{CH}_3\text{OH} : \text{O}_2 = 2 : 1$ and reaction time (15 min).

catalysts reaction temperature(K)	acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$		$\text{VO}_x/\text{Al}_2\text{O}_3$		base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$	
	423	473	423	473	523	573
selectivity (in C %)						
formic acid/formate	9.9	37.7	55.4	29.2	100	100
DMM	52.5	29.9	27.9	23.3	0	0
Paraformaldehyde	8.9	32.2	12.6	30.2	0	0

Figure 4 illustrates ^{13}C MAS NMR spectra of methanol oxidation on base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ from 373 K to 673 K. One dominating resonance at 49 ppm characteristic of methoxyl group is observed at 373 K. A signal at 168 ppm due to formate begins to appear at 523 K^[28]. As the reaction temperature is elevated from 523 to 673 K, the intensity of formate signal increases remarkably and a small amount of formic acid (at 162 ppm) is present at 623 K. It is noteworthy that the signal of dimethoxymethane (DMM) does not appear in the spectra in the whole reaction temperature range. In comparison with the former two catalysts, the acid sites in the base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ are likely killed by NaOH solution during the sample preparation. Consequently, we can infer that the acid sites play a crucial role in the formation of dimethoxymethane.

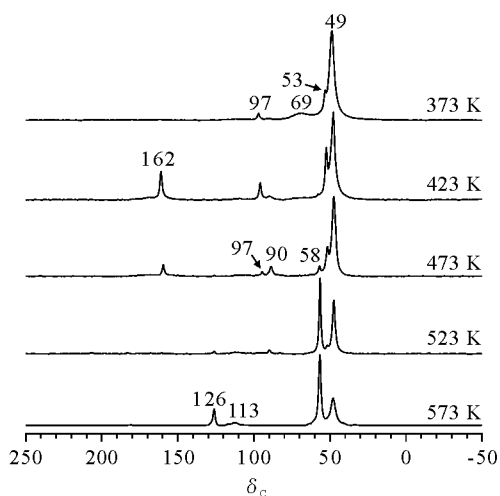


Fig. 3 ^{13}C single-pulse MAS NMR spectra (with proton decoupling) of methanol oxidation on VO_x/Al₂O₃ at various temperatures.

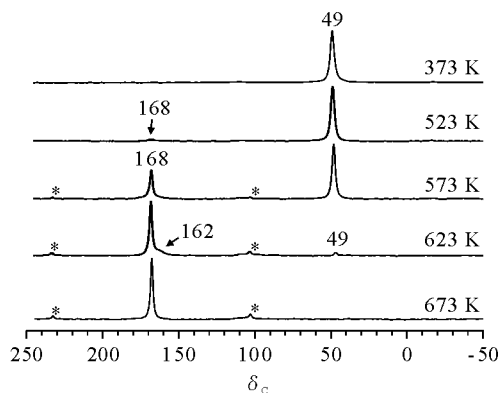


Fig. 4 ^{13}C single-pulse MAS NMR spectra (with proton decoupling) of methanol oxidation on base-treated VO_x/Al₂O₃ at various temperatures.

It is well known that TMPO is a very sensitive probe molecule for measuring the acid strength of Brønsted acid sites^[17, 29]. Generally, the larger the ^{31}P chemical shift, the stronger the acid strength. In the ^{31}P MAS NMR spectrum (Fig. 5a) of TMPO adsorbed on the base-treated VO_x/Al₂O₃, only one peak at δ 43 is observed. After exposing the sample to air for hydration, this peak did not decrease in intensity, therefore, we assign the signal at δ 43 to physisorbed TMPO on the catalyst^[17]. The ^{31}P MAS NMR spectrum of TMPO adsorbed on the VO_x/Al₂O₃ (Fig. 5b) shows three major peaks at δ 43 (due to physisorbed TMPO), δ 55 (due to TMPO adsorbed on the weakly acidic ALOH groups) and δ 69 (due to TMPO adsorbed on the Brønsted acid sites). The ^{31}P MAS NMR spectrum of TMPO adsorbed on the acid-treated VO_x/Al₂O₃ (Fig. 5c) shows almost similar features as that on the VO_x/Al₂O₃ except for the signal at δ 72. The δ 72 signal can be ascribed to TMPO adsorbed on a much stronger Brønsted acid site. According to the TMPO experimental results, we can conclude that acid strength of the acid-treated VO_x/Al₂O₃ catalyst is slightly stronger than that of VO_x/Al₂O₃ and the base-treated VO_x/Al₂O₃ has no Brønsted acid site.

As a reliable NMR probe molecule, the ^{13}C isotropic chemical shift of carbonyl carbon of 2- ^{13}C -acetone has been used as a mark to evaluate the relative acid strength of various solid acids^[19, 30]. Similarly, the stronger the Brønsted acidity, the stronger the hydrogen bonding between the carbonyl carbon and the acidic proton, and consequently the more downfield of the ^{13}C isotropic chemical shift. Figure 6 shows the ^{13}C MAS NMR spectra of 2- ^{13}C -acetone loaded on the surface of three types of VO_x/Al₂O₃ catalysts. The signals at δ 208, 198, 155, 83, 72, and δ 28 can be assigned to bimolecular, trimolecular and mesityl oxide reaction products of acetone^[30], respectively. In figure 6a, no

signal associated with the acetone adsorbed on the Brønsted acid sites can be observed, indicative of no Brønsted acid site in the base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst. For $2\text{-}^{13}\text{C}$ -acetone loaded on the $\text{VO}_x/\text{Al}_2\text{O}_3$ (Fig. 6b), two signals at δ 217.5 and 225 can be resolved in the deconvoluted spectra. The former is probably due to acetone adsorbed on the weakly acidic AlOH groups and the latter is originated from acetone adsorbed on the Brønsted acid sites. The larger chemical shift at δ 225 indicates that acid strength of the $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst is stronger than that of the bridging OH group in zeolite HZSM-5, where adsorbed $2\text{-}^{13}\text{C}$ -acetone gives rise to a ^{13}C resonance at δ 223. For the acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst (Fig. 6c), three resonances at δ 217 (due to acetone adsorbed on the AlOH groups), 220 and 228 are observed in the ^{13}C MAS NMR spectra. The signal at δ 220 corresponds to the weaker acid sites, while the δ 228 results from the Brønsted acid site with acid strength stronger than that of the bridging OH group in zeolite HZSM-5 but still weaker than that of 100% H_2SO_4 , in which the ^{13}C isotropic chemical shift of $2\text{-}^{13}\text{C}$ -acetone is δ 245. From our $2\text{-}^{13}\text{C}$ -acetone experiment we can infer that acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst has Brønsted acid sites with acid strength stronger than that of $\text{VO}_x/\text{Al}_2\text{O}_3$ and the base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ has no Brønsted acid site, which is in agreement with our TMPO experimental results.

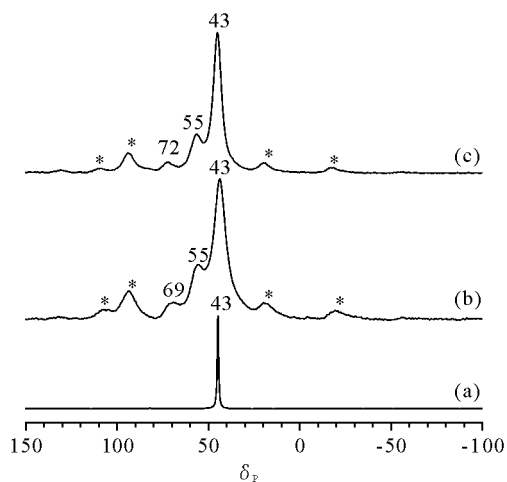


Fig. 5 ^{31}P single-pulse MAS NMR spectra (with proton decoupling) of TMPO adsorbed on (a) base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$, (b) $\text{VO}_x/\text{Al}_2\text{O}_3$ and (c) acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$. The asterisk denotes spinning sidebands.

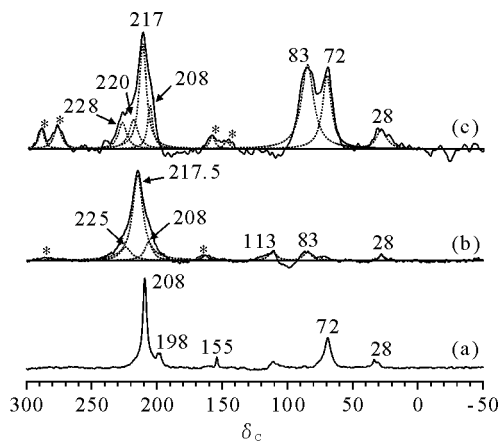


Fig. 6 ^{13}C MAS NMR spectra of $2\text{-}^{13}\text{C}$ -acetone loaded on (a) base-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ (single-pulse with proton decoupling), (b) $\text{VO}_x/\text{Al}_2\text{O}_3$ (single-pulse with proton decoupling) and (c) acid-treated $\text{VO}_x/\text{Al}_2\text{O}_3$ (CP). The asterisk denotes spinning sidebands.

It is known that the VO_x active content is very important to the oxidation performance of VO_x supported catalyst^[31]. In the present case, Brønsted acid sites in the catalysts actually show the significant effect on the product distribution of the methanol oxidation reaction. Comparing to the $\text{VO}_x/\text{Al}_2\text{O}_3$ catalyst, the stronger acid sites on the

acid-treated VO_x/Al₂O₃ catalyst surfaces lead to a higher selectivity for DMM. Furthermore, the base-treated VO_x/Al₂O₃ catalyst with no Brønsted acid site results in no yield of DMM. Iglesia^[32] concluded that CH₃OH converts to DMM via primary CH₃OH reactions to form formaldehyde (HCHO) and subsequent secondary reactions of HCHO with CH₃OH in steps requiring both redox and Brønsted acid sites. Brønsted acid sites are mainly involved in the formation of DMM from HCHO and CH₃OH. Our experimental results reveal that the stronger the acid strength of the catalysts, the higher selectivity for DMM product, which is consistent with Iglesia's conclusions. Therefore, the different acidic nature of the catalysts leads to their different catalytic performances.

3 Conclusions

In summary, methanol selective oxidation over NaOH and HNO₃ modified VO_x/Al₂O₃ was studied by solid-state NMR spectroscopy. Our results indicate that acid sites play a key role in the formation of dimethoxymethane during the reaction. Stronger Brønsted acid site on the catalyst favors higher selectivity for dimethoxymethane, while the base-treated VO_x/Al₂O₃ catalyst without Brønsted acid site mainly gives rise to formate instead of DMM. The detailed information about the role of Brønsted acid sites in the catalyst will help us to understand the mechanism of this reaction and to generate new types of catalyst for selectively producing more valuable compounds.

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改性 $\text{VO}_x/\text{Al}_2\text{O}_3$ 催化剂催化氧化甲醇的固体核磁共振研究

曾丹林, 杨 俊, 郑安民, 陈 雷, 徐 君, 叶朝辉, 邓 风*

(波谱与原子分子物理国家重点实验室(中国科学院 武汉物理与数学研究所), 湖北 武汉 430071)

摘 要: 采用固体核磁共振研究了 NaOH 和 HNO_3 改性的 $\text{VO}_x/\text{Al}_2\text{O}_3$ 上甲醇选择性催化氧化反应. 实验结果表明: 在甲醇的氧化反应中, 酸位对二甲氧基甲烷的生成起了重要作用. 与 $\text{VO}_x/\text{Al}_2\text{O}_3$ 催化剂相比, 酸改性的 $\text{VO}_x/\text{Al}_2\text{O}_3$ 上的强的 Brønsted 酸位对二甲氧基甲烷的选择性较高, 没有 Brønsted 酸位的碱改性的 $\text{VO}_x/\text{Al}_2\text{O}_3$ 上生成的不是二甲氧基甲烷而是甲酸盐.

关键词: 固体核磁共振; 催化; 甲醇氧化; 钒氧化物