

## Highly efficient acrylic acid production from formaldehyde and acetic acid over the NASICON-type catalyst

Qiliang Gao,<sup>a,c</sup> Kaiwen Zheng,<sup>a,c</sup> Chao Li,<sup>a,c</sup> Jiahao Wang,<sup>a,c</sup> Guojie Zhang,<sup>b</sup> Qingde Zhang,<sup>a</sup> FaenSong,<sup>a</sup> Tao Zhang,<sup>a</sup> Junfeng Zhang<sup>\*,a</sup> and Yizhuo Han<sup>\*,a</sup>

<sup>a</sup>State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China

<sup>b</sup>State Key Laboratory of Clean and Efficient Coal Utilization, Taiyuan University of Technology, Taiyuan 030024, China

<sup>c</sup>University of Chinese Academy of Sciences, Beijing, 100049, China

### Experimental section

#### 1. Catalyst preparation

NASICON materials were prepared by sol-gel method as described in the literature.<sup>1</sup> The catalysts prepared by  $\text{Ti}(\text{SO}_4)_2$  and  $\text{TiOSO}_4$  were named as x-TS or TOS, respectively, x represents the Ti/P molar ratio in the synthetic mother liquor. Taking 0.85-TS as an example, 18 g of 96%wt  $\text{Ti}(\text{SO}_4)_2$  was dissolved in an appropriate amount of deionized water, and then 15.28 g of 30%  $\text{H}_2\text{O}_2$  was added to obtain a red-brown liquid. After that, the reddish brown liquid was poured into a thick solution containing the 5.04 g PEG, stirring vigorously for 1 h. 9.76 g of 85%  $\text{H}_3\text{PO}_4$  was added to the above solution, continuously stirring for another 2 hours. The resulting slurry was oven-dried at 50 °C for 3 days and calcined in a muffle furnace at 600 °C for 10 hours. Finally the catalysts were obtained. For other catalysts, only the amount of  $\text{Ti}(\text{SO}_4)_2$  or  $\text{TiOSO}_4$  can be changed.

#### 2. Catalyst Characterization

X-ray diffraction (XRD) patterns of all the catalysts obtained on Rigaku MiniFlex II X-ray diffractometer with Cu  $\text{K}\alpha$  radiation. Raman spectra of the catalysts were obtained at room temperature on a LabRAM-HR Raman Evolution spectrometer with laser source at 532 nm. Morphology and microstructure of the catalysts were analysed by 7900F thermal field emission scanning electron microscope (SEM) and JEM-2100F field emission transmission electron microscope (TEM). The  $\text{N}_2$  adsorption isotherm of the catalysts were collected by BELSORP MAX II; and Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) models were used to obtain the surface area and pore size distributions, respectively. X-ray photoelectron spectroscopy (XPS) of the catalysts were collected on a Thermo ESCALAB 250XI spectrometer equipped with an Al  $\text{k}\alpha$  excitation source. Binding energies were calibrated against the  $\text{C}1\text{s}$  signal (284.8 eV) of contaminant carbon. The content of S element in the catalysts was confirmed by the elemental analyzer Vario EL CUBE. The contents of Ti and P elements in the catalysts were detected by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) method on Varian ICP-OES 720 equipment.

The surface acidity and basicity of the catalysts were measured by the temperature programmed desorption of  $\text{NH}_3$  and  $\text{CO}_2$  ( $\text{NH}_3$ -TPD,  $\text{CO}_2$ -TPD), respectively (temperature-programmed desorption TP5080 instrument). 0.1g catalyst was used to remove adsorbed impurities at 300 °C for 30 minutes, and then ammonia was adsorbed at 100 °C for 15 minutes. After that, the temperature was programmed to 600 °C, and the desorption curve was recorded. The measurement process of  $\text{CO}_2$ -TPD is the same as that of  $\text{NH}_3$ -TPD, except that  $\text{NH}_3$  is replaced. Pyridine infrared spectroscopy (Py-IR) was used to distinguish the types of acidic sites (Bruker Tensor 27 spectrometer). Thin sections were made with a small amount of catalyst, and then adsorbed impurities was removed under vacuum at 450 °C for 3 h. Pyridine was adsorbed

for 15 min after cooling to room temperature. Subsequently, the samples were evacuated at 150 °C for 1 hour and the corresponding spectra were recorded. The adsorption and activation of HAc on the catalyst surface were observed by in-situ DRIFTS (Bruker Tensor 27 FT-IR spectrometer). The *in-situ* DRIFTS experiments was done through introducing HAc vapour to NASICON material with Ar and exposed for 30 min at 360 °C. Detail operation are referred to our previous work. <sup>2</sup>

### 3. Catalytic test

Aldol condensation of FA with HAc was carried out at 360°C with 2 g catalyst (20–40 mesh) in a fixed-bed glass tube reactor. The catalyst was firstly heated up to the reaction temperature in an empty atmosphere, and then the mixed solution of formaldehyde and acetic acid was put into the reaction system with a syringe pump, and the reaction pressure was normal pressure. The raw material is preheated and vaporized by quartz sand, and condensation reaction occurs on the surface of the catalytic bed. The products were cooled and separated by gas-liquid separator, and the gas products were detected online. According to the previous work, the selectivity of AA+MA was calculated based on the HAc of the input, and the activity of the catalyst was measured by the space–time–yield (STY). It is important to note that when the selectivity of AA+MA is calculated, the molar amount of MAC produced is treated as the equivalent of the unreacted HAc.

**Table S1 Efficient catalysts for AA/MA synthesis by condensation of aldol.**

Catalysts	Reaction temperature	Reactant	Catalytic performance		Reference
			$S_{AA+MA}/Y_{AA+MA}/X$	$STY_{AA+MA}$ $\mu\text{mol}\cdot\text{g}_{\text{cat}}^{-1}\cdot\text{min}^{-1}$	
Bulk VPO	360°C	MAc & FA	$X_{\text{MAc}}= 85.0\%$	19.8	3
VPO-Zr	380°C	MAc & FA	$X_{\text{FA}}= 45.7\%$	18.6	4
Bulk VPO	360°C	HAc & FA	$Y_{AA+MA}= 41.8\%$	70.8	5
Cs/SBA-15	390°C	MAc & FA	$Y_{AA+MA}= 31.0\%$	43.4	6
H-ZSM-35	400°C	MAc & FA	$S_{AA+MA}= 86.2\%$ $Y_{AA+MA}= 61.1\%$	unspecified	7
NASICON (TiOSO <sub>4</sub> )	360°C	HAc & FA	$S_{AA+MA}= 50.7\%$	37.2	2
NASICON (Ti(SO <sub>4</sub> ) <sub>2</sub> )	360°C	HAc & FA	$S_{AA+MA}= 78.4\%$	123.9	this study

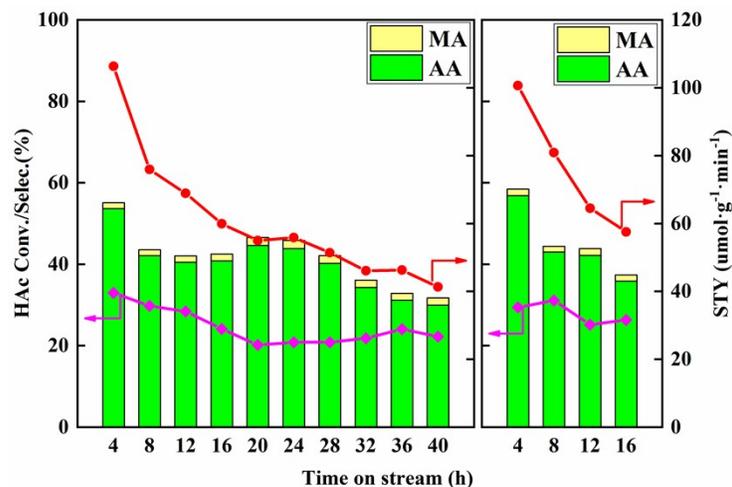


Figure S1 Test of catalyst stability over 0.94-TS: (a) fresh catalyst subject to a period of 40-h reaction, and (b) reactivated catalyst subject to a period of 16-h reaction. Reaction conditions: atmospheric pressure,  $T=360\text{ }^{\circ}\text{C}$ , Air:  $30\text{ mL}\cdot\text{min}^{-1}$ ,  $t=4\text{ h}$ .

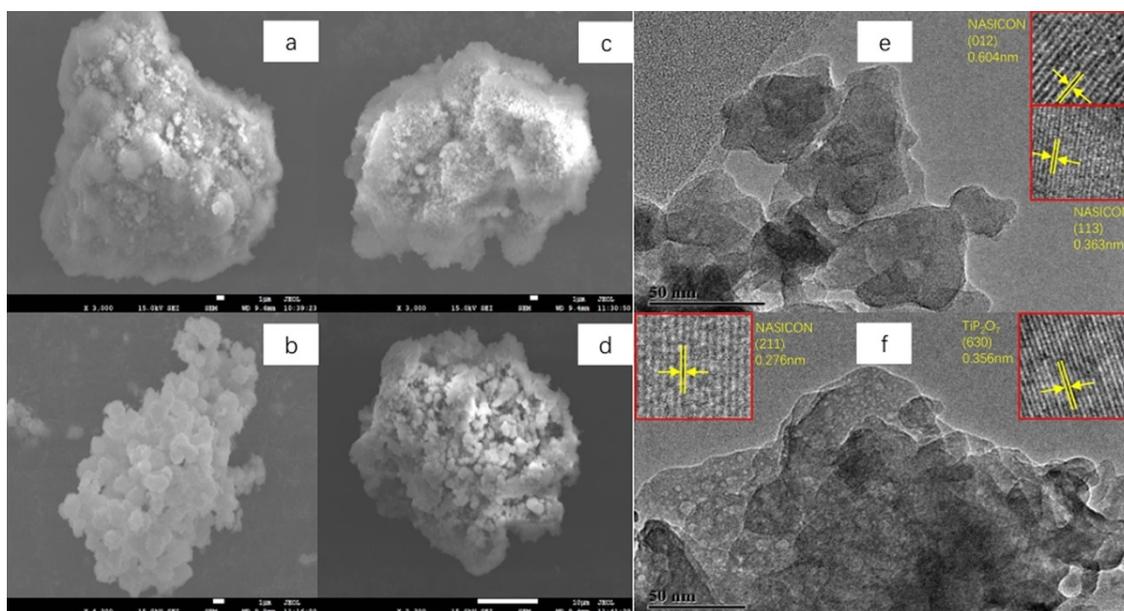


Figure S2 SEM images of catalysts with different titanium sources: 0.76-TS (a), 0.94-TS (b), 0.76-TOS (c), 0.94-TOS (d). TEM images of catalysts with different titanium sources: 0.94-TOS (e), 0.94-TS (f).

**Table S2 Texture properties of the prepared catalysts.**

catalyst	surface area ( $\text{m}^2\cdot\text{g}^{-1}$ )	total pore volume ( $\text{cm}^3\cdot\text{g}^{-1}$ )	average pore diameter (nm)
0.76-TOS	30.8	0.20	26.0
0.94-TOS	34.7	0.20	22.9
0.66-TS	37.4	0.22	23.9
0.76-TS	17.9	0.17	40.0
0.85-TS	13.4	0.13	38.9
0.94-TS	16.3	0.13	31.8

1.01-TS	14.9	0.10	27.9
1.07-TS	21.4	0.18	34.0

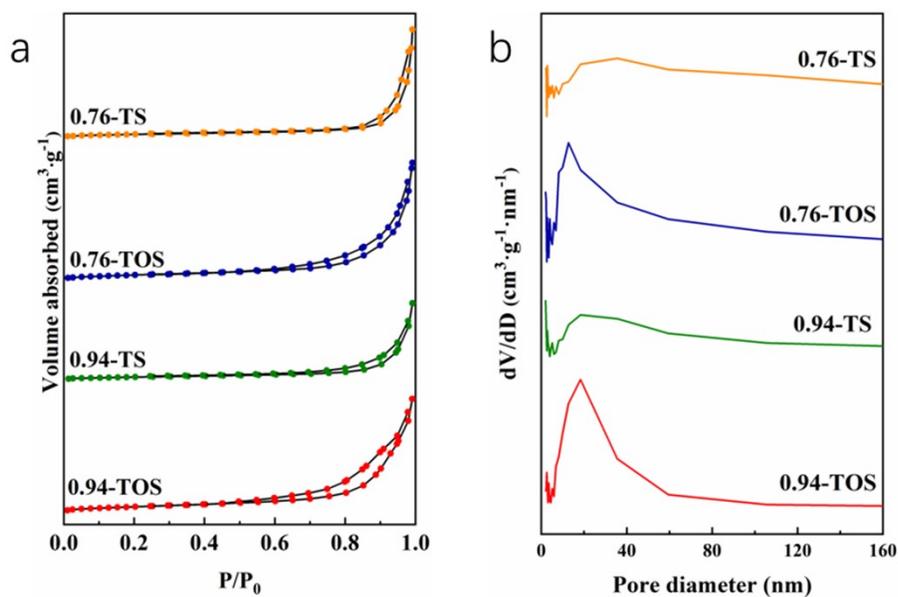


Figure S3 N<sub>2</sub> adsorption-desorption isotherms (a) and pore size distributions (b) of catalysts with different titanium sources.

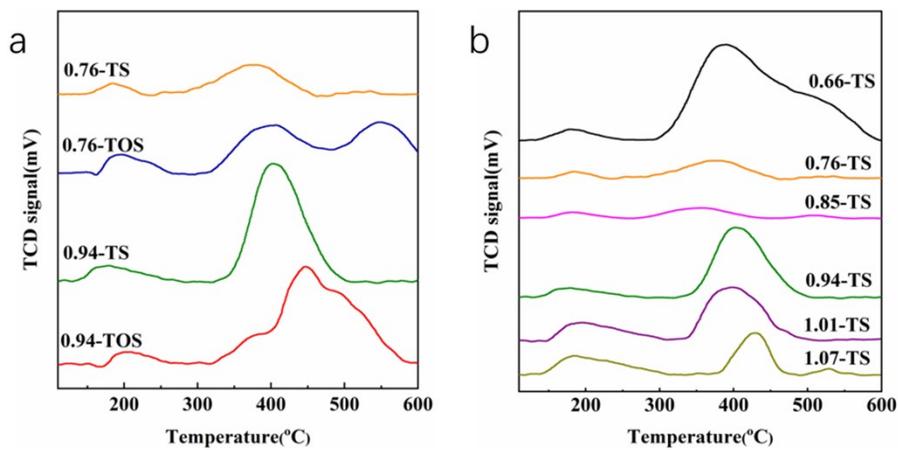


Figure S4. CO<sub>2</sub>-TPD profiles of catalysts with different titanium sources (a) and x-TS (b).

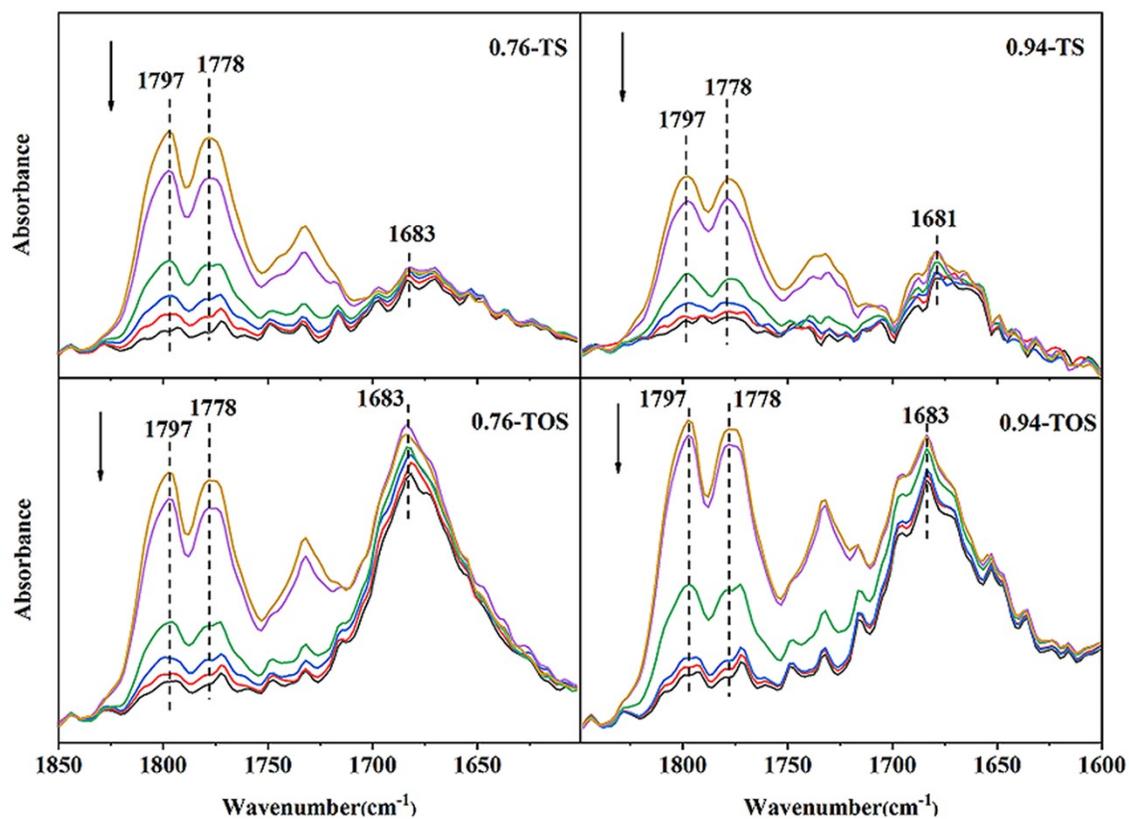


Figure S5 *In-situ* DRIFTS spectra of adsorbed species swept under Ar flow after the adsorption of HAC on catalysts with different titanium sources. The direction of the arrow indicates an increase in purge time.

**Table S3 Bulk and surface elemental compositions of catalysts with different titanium sources.**

catalyst	Ti/S	Ti/S	Ti/P	Ti/P	$\text{Ti}^{4+}/(\text{Ti}^{4+} + \text{Ti}^{3+})^b$
	bulk	surface	bulk	surface	
	a, c	b	c	b	
0.76-TS	2.3551	3.3956	0.5927	0.4987	0.5990
0.94-TS	1.6863	1.7847	0.7295	0.6404	0.5471
0.76-TOS	2.3855	2.5227	0.7515	0.6421	0.5845
0.94-TOS	1.8649	1.8218	0.9303	0.7995	0.5833

<sup>a</sup> Calculated from EA.

<sup>b</sup> Calculated from XPS.

<sup>c</sup> Calculated from ICP-OES.

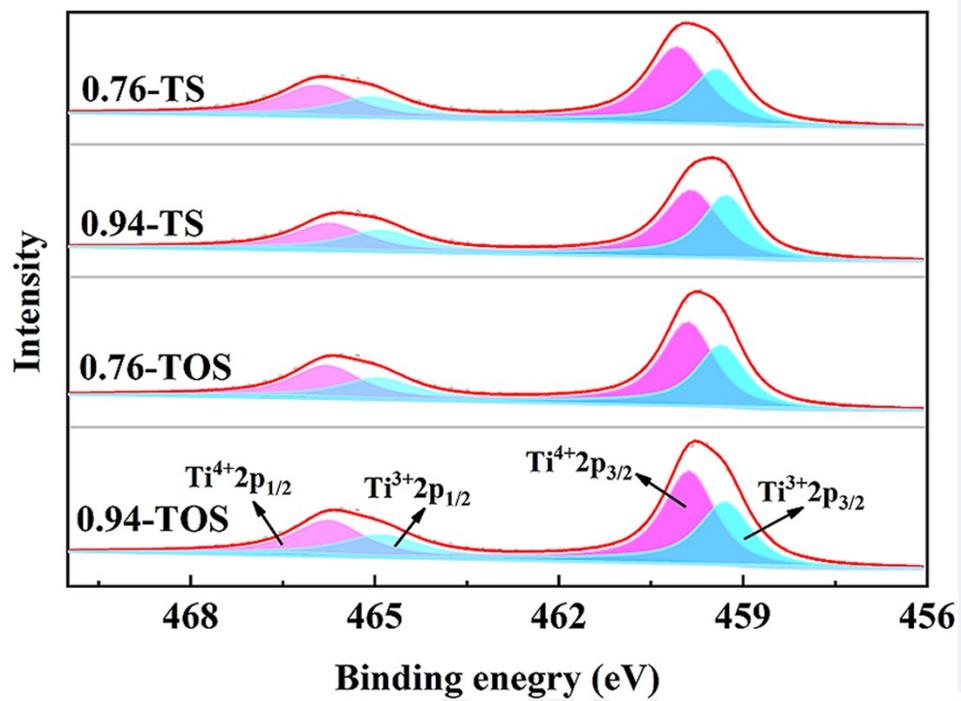


Figure S6 Curve fitting analysis of the Ti 2p peak of catalysts with different titanium sources.

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