Catalysis Communications 125 (2019) 43–47

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Strong Brønsted acid-modified chromium oxide as an efficient catalyst for the selective oxidation of methacrolein to methacrylic acid

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ARTICLE INFO

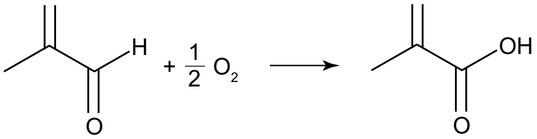
Keywords:
Methacrolein oxidation
Acid modification
Chromium oxide
Keggin-type heteropoly acid
Gas phase oxidation

ABSTRACT

Gas–phase oxidation of methacrolein to methacrylic acid was carried out over an acid-modified Cr_2O_3/SiO_2 catalyst. While only total oxidation occurred over bare Cr_2O_3/SiO_2, the acid-modified Cr_2O_3/SiO_2 showed catalytic activity for the formation of methacrylic acid. In particular, $H_3PW_{12}O_{40}$ strong Brønsted acid was the most effective modifier for improving both activity and selectivity. The interface between Cr_2O_3 and $H_3PW_{12}O_{40}$ particles on SiO_2 appears to be responsible for the formation of active sites for the selective formation of methacrylic acid. The strong Brønsted acid would help the activation of methacrolein through rendering it more electrophilic, which is a key step for the formation of methacrylic acid over the present catalyst.

1. Introduction

Methacrylic acid (MAA) is an important chemical for the production of methyl methacrylate and other derivatives and is commercially produced by gas–phase catalytic oxidation of methacrolein (MAL) (Eq. (1)) [1–3].



(1)

Heteropolyacids with a Keggin structure composed of P, Mo and V have been utilized as industrial catalysts [1–3]. So far, partial substitution of H^+ in $H_3PMo_{12}O_{40}$ with other cations, substitution of some Mo atoms with V and supporting them on carriers have been investigated to improve the catalytic performance [4–17]. However, further improvement is still desired. A new catalyst not consisting of Mo and V must trigger diverse researches, and accordingly open the way for the development of more effective catalysts for the MAL oxidation.

It is well-known that hexavalent chromium compounds including CrO_3 and $Na_2Cr_2O_7$ are useful oxidizing agents in organic synthesis, especially for oxidations of alcohols and aldehydes into corresponding carboxylic acids, known as Jones oxidation. However, considering cost and environmental factors, it would be advantageous to use chromium oxides as a heterogeneous catalyst. While hexavalent chromium oxide (CrO_3) has very strong oxidizing ability, it is unstable at a relatively high temperature and spontaneously releases oxygen to be reduced into Cr_2O_3 (non toxic) at around 473 K or higher even in an oxidizing atmosphere [18]. Thus, Cr_2O_3 and Cr^{3+}-containing materials are more suitable in oxidation catalysts. So far, oxidation catalysis of Cr_2O_3 and Cr^{3+}-containing materials for organic synthesis has been extensively investigated. While some efficient oxidation reactions catalyzed by them with organic peroxides including tert-butyl hydroperoxide have been developed [19–23], utilization of O_2 or air as an oxidizing agent is more advantageous for cost economy and environmental impact. In 1940's, the pioneering work on the oxidation of para-substituted ethylbenzene into corresponding acetophenone with air in the presence of Cr_2O_3 at 403–433 K was reported [24]. Recently, it was found that supported Cr_2O_3 [25,26] and Cr^{3+}-containing mesoporous materials [27–29] and metal-organic framework (Cr-MIL-101, Ref. [30]) effectively promoted oxidation of benzyl alcohol to benzaldehyde [25], cycloalkanes to α,β-unsaturated ketones [28,30], monoterpenic alkenes to epoxide and allylic derivatives [27,30], and autooxidation of cyclohexane into cyclohexanone and cyclohexanol [26,29] in an O_2 or air atmosphere. However, to the best of our knowledge, there is no report on the selective oxidation of aldehyde into carboxylic acid with O_2 over Cr_2O_3-based catalysts.

Here, we report that a strong Brønsted acid ($H_3PW_{12}O_{40}$)-modified

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https://doi.org/10.1016/j.catcom.2019.03.020
Received 22 November 2018; Received in revised form 24 March 2019; Accepted 24 March 2019
Available online 25 March 2019
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Cr_2O_3/SiO_2 is a highly active and selective catalyst for the gas-phase oxidation of MAL to MAA. The loading amounts of Cr_2O_3 and $H_3PW_{12}O_{40}$, and the kind of acidic component used were systematically investigated. Based on the structural analysis of the catalyst and results on transient responses of reaction, the active sites formed on the catalyst surface and the reaction mechanism are discussed.

2. Experimental

2.1. Catalysts preparation

Silica-supported chromium oxide (Cr_2O_3/SiO_2) was prepared by using the wet impregnation method. $Cr(NO_3)_3 \cdot 9H_2O$ (9.895 g, 24.7 mmol, Sigma-Aldrich) was dissolved in Milli-Q water (100 mL). To the solution, SiO_2 (3 g, AEROSIL 300, EVONIK) was added and the suspension was vigorously stirred at room temperature for 1 h. The suspension was then evaporated to dryness by using a rotary evaporator at 323 K. The resulting solid was dried in air at 373 K overnight and calcined in air at 823 K for 5 h. The loading amount of Cr_2O_3 on SiO_2 was 38.5 wt%.

Modification of Cr_2O_3/SiO_2 with $H_3PW_{12}O_{40}$ was carried out by also using the incipient wetness impregnation method. 12–Tungstophosphoric acid ($H_3PW_{12}O_{40} \cdot nH_2O$, Nippon Inorganic Colour and Chemical Co., Ltd.) was purified by extraction with diethyl ether and recrystallized from its aqueous solution in advance. Cr_2O_3/SiO_2 (1.8 g) was added to 100 mL Milli-Q water and impregnated with an aqueous solution of $H_3PW_{12}O_{40}$ (0.08 mol L^{-1}, 3.35 mL) at room temperature. Then the resulting wet solid after impregnation was dried in air at 373 K overnight and calcined in air at 523 K for 2 h. The loading amount of $H_3PW_{12}O_{40}$ on Cr_2O_3/SiO_2 was 30 wt%. The resulting supported catalyst is denoted as $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2. As a reference, $H_3PW_{12}O_{40}/SiO_2$ without Cr_2O_3 was prepared by a similar manner to that of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 but using SiO_2 instead of Cr_2O_3/SiO_2.

H_2SO_4-Cr_2O_3/SiO_2 and H_3PO_4-Cr_2O_3/SiO_2 were also prepared by using the wet impregnation procedure similar to that of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 now using dilute sulfuric acid (Wako Pure Chem. Ind., Ltd., 0.08 mol L^{-1}) and aqueous solution of phosphoric acid (Wako Pure Chem. Ind., Ltd., 0.08 mol L^{-1}). The loading amounts of H_2SO_4 and H_3PO_4 were 1.5 and 1.0 wt%, respectively, which correspond to the same number of H^+ (0.31 mmol g^{-1}) as that in $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2. Preparation procedures for other catalysts are described in the Electronic Supporting Information (ESI).

2.2. Catalysts characterization

Powder X-ray diffraction (XRD) patterns of the various solid catalysts were recorded on an X-ray diffractometer (MiniFlex, Rigaku) equipped with a Cu Kα radiation (λ = 0.154 nm). Infrared (IR) spectra of the samples were recorded for self-supporting disks on an IR spectrometer (FT-IR/230, JASCO). X-ray photoelectron (XPS) spectra were taken by using a ULVAC-PHI Quantera II (Al Kα radiation). Binding energy was calibrated with respect to C 1 s peak of a carbon tape at 284.6 eV.

2.3. Catalytic oxidation of MAL

Catalytic oxidation of MAL was performed in a continuous flow reactor under atmospheric pressure. After pretreatment of the catalyst (1 g) at 593 K with a mixture of O_2 (10.7 vol%), H_2O (17.9 vol%) and N_2 (balance) at the total flow rate of 28 mL min^{-1} for 1 h, the temperature was decreased to 573 K and the reaction mixture of MAL (3 vol %), O_2 (6 vol%), H_2O (13 vol%) and N_2 (balance) at the total flow rate of 72 mL min^{-1} was fed into the reactor. The reaction products at the outlet of reactor were analyzed by using on-line gas chromatography. Details of the reaction products analysis is given in the Electronic Supporting Information (ESI).

3. Results and discussion

Table 1 summarizes the catalytic performance results for the oxidation of MAL. While the unmodified Cr_2O_3/SiO_2 showed no MAA formation (Entry 1), the modification with acid components dramatically increased the selectivity to MAA and simultaneously decreased that to CO_x. It should be noted that $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 showed the highest activity and highest selectivity to MAA (Entry 2) among the catalysts tested. Since $H_3PW_{12}O_{40}/SiO_2$ (Entry 3) as well as Cr_2O_3/SiO_2 did not form MAA at all, combination of Cr_2O_3 with $H_3PW_{12}O_{40}$ was indispensable to form MAA. However, the physical mixture of Cr_2O_3/SiO_2 and $H_3PW_{12}O_{40}/SiO_2$ were less active and less selective (Entry 4) than $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2, indicating that adjacency of the two solid components was important for the selective formation of MAA.

Next, we optimized the loading amount of $H_3PW_{12}O_{40}$ and Cr_2O_3 to improve the catalytic performance of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 (Figs. S1 and S2, ESI). The loading amount of both Cr_2O_3 and $H_3PW_{12}O_{40}$ had great impact on the catalytic performance. It was found that the loading amount of 38.5 and 30 wt% for Cr_2O_3 and $H_3PW_{12}O_{40}$, respectively,

Table 1
Catalytic performance results for gas–phase oxidation of MAL over various catalytic systems.[a]

Entry	Catalyst	Reaction rate/mmol h^{-1} g^{-1}		Selectivity/ %		
		MAL consumption	MAA formation	MAA[b]	AcOH[b]	CO_x
1	Cr_2O_3/SiO_2	0.42	0.00	0	3	97
2	$H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2	0.60	0.44	72	4	24
3	$H_3PW_{12}O_{40}/SiO_2$	0.54	0.00	0	0	100
4	Cr_2O_3/SiO_2 + $H_3PW_{12}O_{40}/SiO_2$[c]	0.30	0.12	39	7	54
5	$H_3PW_{12}O_{40}/Cr_2O_3$	0.06	0.04	74	5	21
6	H_2SO_4-Cr_2O_3/SiO_2	0.36	0.19	52	6	41
7	H_2SO_4-Cr_2O_3/SiO_2[d]	0.30	0.17	55	6	39
8	H_3PO_4-Cr_2O_3/SiO_2	0.24	0.09	36	7	56
9	H_3PO_4-Cr_2O_3/SiO_2[d]	0.36	0.16	45	7	48
10	$Na_3PW_{12}O_{40}$-Cr_2O_3/SiO_2	0.12	0.08	68	4	28
11	$H_3PW_{12}O_{40}$-Mn_2O_3/SiO_2	0.12	0.01	9	12	79
12	$H_3PW_{12}O_{40}$-CuO/SiO_2	2.52	< 0.01	< 1	2	98

[a] Reaction conditions: MAL: O_2: H_2O: N_2 = 3: 6: 13: 78; temperature, 573 K; catalyst weight, 1.0 g; total flow rate, 72 mL min^{-1}; total pressure = 0.1 MPa. The data in the table were taken after 3 h or more from the beginning of the reaction. Activity and selectivity were estimated from the data with conversion less than 16 %.

[b] MAA and AcOH represent methacrylic acid and acetic acid, respectively.

[c] Physical mixture of Cr_2O_3/SiO_2 (1.0 g) and $H_3PW_{12}O_{40}/SiO_2$ (1.0 g). Two catalysts were mixed well in a mortar and afforded to the reaction.

[d] The loading amounts of H_2SO_4 and H_3PO_4 were twice as much as those for the catalysts in entries 6 and 8.

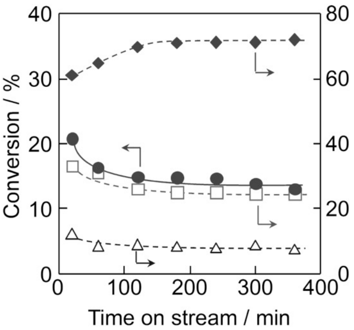


Fig. 1. Time courses for the oxidation of MAL over $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2. (●) MAL conversion and selectivities to (◆) MAA, (△) acetic acid, and (□) CO_x. Reaction conditions: MAL: O_2: H_2O: N_2 = 3: 6: 13: balance; catalyst weight = 1.0 g; $W F^{-1}$ = 230 g_{cat} h^{-1} mol^{-1}; and total pressure = 0.1 MPa.

were the best for both the activity and selectivity to MAA. Subsequently, we further examined the stability of catalyst for the selective oxidation of MAL (Fig. 1). While the activity was slightly decreased for the initial 100 min of reaction, the catalyst showed stable activity and selectivity for at least 360 min (6 h).

$H_3PW_{12}O_{40}$-modified unsupported Cr_2O_3 showed high selectivity to MAA comparable to $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2, but the activity was very low (Entry 5). This was due to the low surface area of Cr_2O_3 (2 m^2 g^{-1}). In other words, utilization of SiO_2 support was effective to give small-sized Cr_2O_3 particles deposited on it. By the modification of Cr_2O_3/SiO_2 with H_2SO_4 (Entry 6) and H_3PO_4 (Entry 8), the activities of catalysts for MAA formation were brought about, but the catalysts were less active and less selective than $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2, while H_2SO_4 was better than H_3PO_4 for the modification. We investigated the modification of Cr_2O_3/SiO_2 with twice amounts of H_2SO_4 and H_3PO_4, but improvements in the activity and selectivity were not so significant (Entries 7 and 9). Hammett acidity functions (H_0) of H_3PO_4, H_2SO_4 and $H_3PW_{12}O_{40}$ are −5, −12 and −13, respectively, meaning that the acid strength increases in this order. The order of the MAA formation rate as well as the selectivity to MAA was correlated well with that of the acid strength. This fact suggests that the strong Brønsted acid is required for the MAA formation. In fact, Cr_2O_3/SiO_2 modified with neutral sodium salt of $H_3PW_{12}O_{40}$ ($Na_3PW_{12}O_{40}$) showed only little activity for the MAA formation (Entry 10).

Manganese oxides are well-known oxidizing agents commonly used in organic synthesis as the chromium oxides ones. However, $H_3PW_{12}O_{40}$-Mn_2O_3/SiO_2 gave mainly CO_x and the selectivity to MAA was only 9% (Entry 11). In addition, there was no MAA formation over $H_3PW_{12}O_{40}$-CuO/SiO_2 (Entry 12). These results demonstrate that the combination of Cr_2O_3 with strong Brønsted acid like $H_3PW_{12}O_{40}$ is absolutely necessary for the selective and effective formation of MAA.

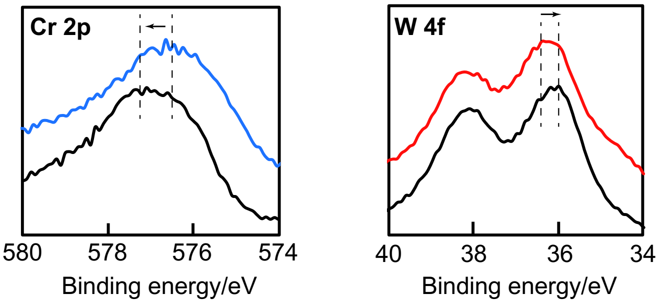


Fig. 3. XPS spectra of Cr 2p and W 4f for (—) $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2, (—) Cr_2O_3/SiO_2 and (—) $H_3PW_{12}O_{40}/SiO_2$ catalysts.

The powder XRD pattern of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 (Fig. 2) clearly demonstrates that well-crystallized Cr_2O_3 and $H_3PW_{12}O_{40}$ were present and the mean crystallite size of Cr_2O_3 and $H_3PW_{12}O_{40}$ estimated from Scherrer's equation were 22 and 14 nm, respectively. There was no evidence to prove the formation of a mixed metal oxide from $H_3PW_{12}O_{40}$ and Cr_2O_3 based on the powder XRD pattern and IR spectrum recorded on $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 (Fig. 1). The structure of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 after the oxidation of MAL was basically the same as that before the reaction (Fig. S3). The XPS spectra indicated that Cr^{3+} and W^{6+} were predominantly present on the surface of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 (Fig. 3), as expected from their crystalline phases. The peak due to Cr^{3+} was shifted toward high binding energies and conversely that of W^{6+} moved toward low BEs compared with those of the unmodified Cr_2O_3/SiO_2 and $H_3PW_{12}O_{40}/SiO_2$ solids, respectively. These peak shifts suggest that Cr_2O_3 partly interacts with $H_3PW_{12}O_{40}$ with the charge transfer from Cr^{3+} to W^{6+}. Based on these results, we could conclude that the interface formed between particles of Cr_2O_3 and $H_3PW_{12}O_{40}$ provided active sites for the MAA formation. Further evidence about the interaction between Cr_2O_3 and $H_3PW_{12}O_{40}$ was derived by TPD measurements of benzonitrile (basic probe molecule), where the alteration of the acid strength of $H_3PW_{12}O_{40}$ was probed (Fig. S4, ESI).

For $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2, the change in the electronic states of Cr and W may lead to the decrease in the activity of the unmodified Cr_2O_3/SiO_2, as well as of $H_3PW_{12}O_{40}/SiO_2$ for the total oxidation of MAL, resulting in low selectivity to CO_x over the $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 catalytic system.

To investigate some important issues of the reaction mechanism, the

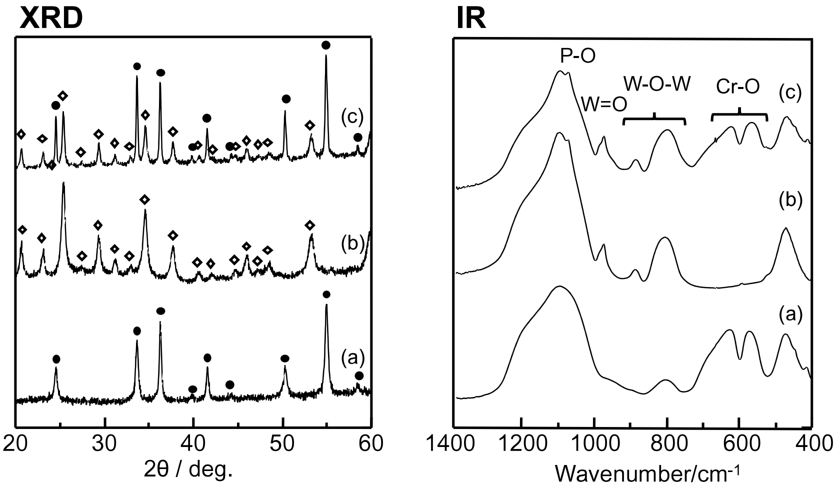
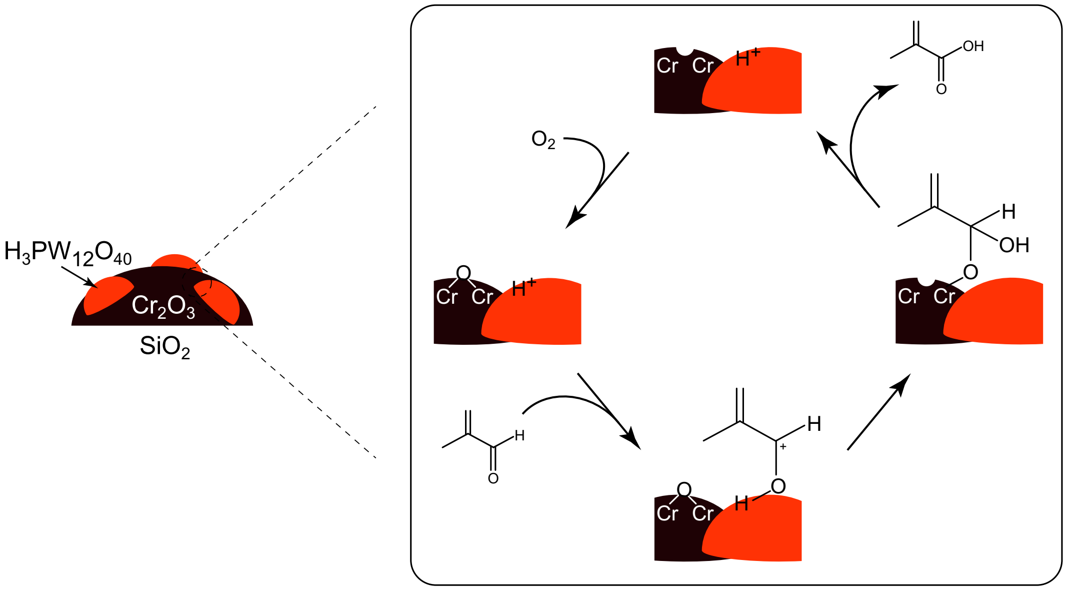


Fig. 2. Powder XRD patterns and IR spectra of (a) Cr_2O_3/SiO_2 (b) $H_3PW_{12}O_{40}/SiO_2$ and (c) $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2. (●) Cr_2O_3 and (◇) $H_3PW_{12}O_{40}\cdot 14H_2O$.



Scheme 1. Plausible reaction mechanism for the selective oxidation of methacrolein over $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 catalyst.

influence of steam and O_2 in the reaction feed gas stream on the catalytic performance of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 was studied. After the reaction over $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 reached near steady-state, the supply of O_2 to the reactor was stopped while the supply of MAL continued (Fig. S5). The obtained results showed that MAA formation continued up to 3 h after the stop of O_2 supply, suggesting that reaction proceeds with Mars–Van Krevelen mechanism, in which lattice oxygen of the catalyst can oxidize MAL. In addition, there was only little change in the catalytic performance of $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 without steam in the reaction feed gas stream (Fig. S6, ESI). The non-necessity of steam suggests that MAA formation is not passing through 1,1-diol formed by hydration of MAL, unlike conventional oxidation of aldehydes with hexavalent chromium compounds, including CrO_3 and $Na_2Cr_2O_7$, in which aldehyde is hydrated in the first step and the formed 1,1-diol reacts with chromium compounds to give chromium ester as a reaction intermediate. Based on these results, we propose that the reaction mechanism for the MAL oxidation over $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 proceeds as follows (Scheme 1). The reaction occurs on the interface between Cr_2O_3 and $H_3PW_{12}O_{40}$ particles. Firstly, MAL is activated through protonation and the activated MAL is then oxidized with lattice oxygen of Cr_2O_3 to form MAA. Finally, the reduced chromium is re-oxidized with gas-phase O_2 along with the regeneration of lattice oxygen. Since strong acid was preferable, the activation of MAL on H^+ would increase the electrophilicity of carbonyl carbon in MAL, facilitating nucleophilic addition of a lattice oxygen to it. However, there are several unclear points in the reaction mechanism, that is, how chromium species forms a redox cycle, what active oxygen species is, and why the activity of Cr_2O_3 and $H_3PW_{12}O_{40}$ for total oxidation is suppressed by their combination. Therefore, further investigations are absolutely necessary to clarify the reaction mechanism. In addition, successive oxidation of MAA to CO_x might be another problem for $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 (Fig. S7) and this should be suppressed by the addition of additives, choice of support and the control of reaction conditions, subject of a future work.

4. Conclusions

While Cr_2O_3/SiO_2 gave no MAA formation in the gas-phase oxidation of MAL, the modification of it with strong Brønsted acids such as $H_3PW_{12}O_{40}$ dramatically altered the catalytic performance and the resulting $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 catalytic system promoted the formation of MAA. Among the acids, $H_3PW_{12}O_{40}$ was the best modifier for Cr_2O_3/SiO_2, and $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 showed the highest activity (0.44 mmol h^{-1} g^{-1} of MAA formation rate at 573 K) and selectivity to MAA (72%). In addition, $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2 exhibited stable activity and selectivity at least for 6 h. The reaction proceeds through the Mars–Van Krevelen mechanism over $H_3PW_{12}O_{40}$-Cr_2O_3/SiO_2. The presence of steam in the feed gas stream was not necessary, unlike conventional oxidation of aldehydes with hexavalent chromium compounds. The interface formed between Cr_2O_3 and $H_3PW_{12}O_{40}$ particles on SiO_2 provides active sites for the MAA formation and the strong Brønsted acids would increase the electrophilicity of carbonyl carbon in MAL, thus promoting MAA formation.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.catcom.2019.03.020.

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