# NJC



Check for updates

Cite this: New J. Chem., 2021, 45, 696

Received 11th October 2020, Accepted 29th November 2020

DOI: 10.1039/d0nj04994h

rsc.li/njc

### 1. Introduction

Today, much attention is paid towards the exploration of alternative feedstock for fossil fuel resources, as we have become more aware of the impact of the energetic dependence on oil. Ethanol, as a high-quality liquid fuel, is considered for use as a fuel additive. Coal (syngas) to ethanol is the most promising new ethanol production route.<sup>1,2</sup> Rh-based catalysts have become the hotspot and core of this catalytic process due to their superior selectivity to ethanol-based  $C_2$  oxygenates (*e.g.*, ethanol, acetaldehyde and acetic acid).<sup>3-6</sup> The Rh catalysts promoted by Mn have been found to provide increasing activity and selectivity towards  $C_2$  oxygenates, which revealed that the auxiliary of Mn plays an important role in this behavior.<sup>7-10</sup> Therefore, continuous efforts focus on improving the efficiency of Rh–Mn active sites by modulating the carrier.

Metal–organic frameworks (MOFs) are a series of periodic multi-dimensional crystal materials which are self-assembled by metal ions and organic ligands. Owing to the intrinsic nature of the topologies, functionality, and ultrasmall metal sites of MOFs, they can effectively interact with the loading metals and restrict their size distribution. MOFs, in particular Zr-based MOFs with outstanding structural stability,<sup>11–13</sup> have been



View Article Online View Journal | View Issue

# Synthesis of C<sub>2</sub> oxygenates from syngas over UiO-66 supported Rh–Mn catalysts: the effect of functional groups

Ying Han, Jun Yu, 🕩 \* Qiangsheng Guo, Xiuzhen Xiao, Xiaoming Guo, ២ Haifang Mao and Dongsen Mao 🕩 \*

UiO-66 and its modified forms (UiO-66-NH<sub>2</sub> and UiO-66-OH) were used as supports to prepare Rh–Mn catalysts by using a co-impregnation method, and their catalytic activities were investigated for the direct synthesis of ethanol-based  $C_2^+$  oxygenates from CO hydrogenation. The catalysts were comprehensively characterized using N<sub>2</sub> sorption, XRD, XPS, DRIFT, and TPSR analyses. The structural and textural properties of the catalysts clearly show that Rh and Mn are highly dispersed in the pores of MOFs, but the order of the original structure is partially sacrificed due to the loading of metals and the synergistic effect of Rh, Mn, and Zr would be influenced by various functional groups present in UiO-66. On combining both *in situ* FT-IR and TPSR analyses, it is confirmed that the higher number of active sites of Rh<sup>0</sup> on RM/UiO-66 promotes the CO dissociation ability and hydrogenation rate, which result in its best catalytic activity with the highest yield of  $C_2^+$  oxygenates, 197.3 g (kg h)<sup>-1</sup>.

extensively investigated for catalytic reactions such as esterification,<sup>14</sup> cross-aldol condensation,<sup>15</sup> citronellal cyclization,<sup>16</sup> and hydrogenation.<sup>17</sup> In our previous studies, compared with the traditional carriers such as  $SiO_2$ ,<sup>18</sup>  $TiO_2^{19,20}$  and  $ZrO_2$ ,<sup>21</sup> the promoted catalytic performance of the Rh–Mn catalyst supported on UiO-66 for the synthesis of C<sub>2</sub> oxygenates from CO hydrogenation has been found.<sup>22</sup>

On the other hand, it is widely accepted that the promoter/ Rh boundary plays a key role in generating the required active sites for the selective synthesis of C<sub>2</sub> oxygenates.<sup>23,24</sup> Furthermore, previous studies have shown that UiO-66 modified by various functional groups or metal ions can play a key role in generating the required active sites. For example, Vermoortele *et al.*<sup>25</sup> used UiO-66 and UiO-66-NH<sub>2</sub> as acid catalysts to study the reaction of benzaldehyde with heptaldehyde aldol to form  $\alpha$ -*n*-pentyl citronellol. As a result, it was found that UiO-66-NH<sub>2</sub> showed higher catalytic activity. Hu *et al.*<sup>26</sup> reported that mixed matrix membranes containing UiO-66(Hf)-(OH)<sub>2</sub> nanoparticles have both increased H<sub>2</sub> permeability and H<sub>2</sub>/CO<sub>2</sub> for efficient H<sub>2</sub>/CO<sub>2</sub> separation.

Therefore, in this work, we tried to use UiO-66 and its modified forms (UiO-66-NH<sub>2</sub> and UiO-66-OH) as supports to prepare Rh–Mn catalysts, and the effects on CO hydrogenation on the selective synthesis of  $C_2$  oxygenates were investigated. The structure and surface properties of the supports and the corresponding catalysts were analyzed by means of various characterization studies, to gain a better understanding of the relationships between the catalytic performance and physicochemical properties of the catalysts.

Research Institute of Applied Catalysis, School of Chemical and Environmental Engineering, Shanghai Institute of Technology, Shanghai 201418, China. E-mail: yujun@sit.edu.cn, dsmao@sit.edu.cn; Fax: +86-21-6087-7231; Tel: +86-21-6087-7223

Table 1 Conversion and selectivity for various products from CO hydrogenation over catalysts

		Selecti	electivity (%)						
Catalyst	CO conv. (C%)	$\rm CO_2$	$CH_4$	МеОН	ACH	EtOH	${\rm C_2}^+{ m HC}^a$	${\rm C_2}^+ {\rm Oxy}^b$	STY $(C_2^+ \text{ Oxy}) \text{ g } (\text{kg } h)^{-1}$
RM/UiO-66	14.7	2.4	29.5	1.7	8.1	29.2	20.7	45.7	197.3
RM/UiO-66-NH <sub>2</sub>	8.3	5.2	49.7	2.5	4.5	20.7	14.1	28.5	66.1
RM/UiO-66-OH	6.3	2.8	34.9	2.9	9.0	29.4	15.1	44.3	77.6

Reaction conditions: T = 300 °C, P = 3 MPa, catalyst: 0.3 g, and flow rate = 50 ml min<sup>-1</sup> (H<sub>2</sub>/CO = 2). Data taken 13 h after the steady state was reached. Experimental error:  $\pm 5\%$ . <sup>*a*</sup> C<sub>2</sub><sup>+</sup> HC denotes hydrocarbons containing two and more carbon atoms. <sup>*b*</sup> C<sub>2</sub><sup>+</sup> Oxy denotes oxygenates containing two and more carbon atoms.

Table 2	Comparison	of the	catalytic	properties	of Rh-Mn	catalysts i	n the literatu	ire
---------	------------	--------	-----------	------------	----------	-------------	----------------	-----

Catalyst	$T(^{\circ}C)$	P (MPa)	$\mathrm{SV}^{ab}$	$X_{\rm CO}$ (%)	$S_{\mathrm{CH}_{4}}\left(\% ight)$	$S_{ m EtOH}$ (%)	Ref.
Rh-Mn/Al <sub>2</sub> O <sub>3</sub> (Rh 3.0 wt%, Mn 1.6 wt%)	250	2.0	6000 <sup>a</sup>	5.9	20.0	29.0	24
Rh-Mn/SiO <sub>2</sub> (Rh 2.5 wt%, Mn 1.5 wt%)	260	5.4	$5833^{b}$	9.4	41.0	21.0	29
Rh-Mn/ZrO <sub>2</sub> (Rh 3.0 wt%, Mn 3.0 wt%)	300	3.0	$10000^{a}$	3.6	15.6	24.4	22
Rh-Mn/TiO <sub>2</sub> -Ar (Rh 2.0 wt%, Mn 2.0 wt%)	280	3.0	$10000^{a}$	6.8	10.1	20.0	20
Rh-Mn/UiO-66 (Rh 3.0 wt%, Mn 3.0 wt%)	300	3.0	$10000^a$	14.7	29.5	29.2	This work
<sup><i>a</i></sup> Space velocity in mL $(g_{cat} h)^{-1}$ . <sup><i>b</i></sup> Space velocity	city in $h^{-1}$ .						

### 2. Experimental

#### 2.1. Catalyst preparation

UiO-66 can be prepared by referring to the literature.<sup>27</sup> Briefly, 250 mg of ZrCl<sub>4</sub> (99.95 + %, J&K) and 246 mg of benzenedicarboxylic acid (H2BDC, 99%, Damas-Beta) were dissolved in 30 mL of N,N-dimethylformamide (DMF, 99%, General-Reagent) premixed with 2 mL of concentrated HCl (37%, General-Reagent) by using ultrasonic treatment for 15 min until the solution turned pellucid. Then, the solution was transferred to a glass bottle, and placed in an oven at 80 °C under static conditions for 10 h. Afterwards, the obtained precipitates were cooled down to room temperature and separated by centrifugation. The solids were washed several times with DMF and methanol by centrifugation, and dried under vacuum at room temperature. UiO-66-NH<sub>2</sub> and UiO-66-OH were prepared using the same method as UiO-66, while H<sub>2</sub>BDC was changed to 2-aminoterephthalic acid and 2-dihydroxyterephthalic acid, respectively. Noteworthy, this synthetic reaction can be performed as a 10-fold scale up.

RhCl<sub>3</sub> hydrate (Rh ~ 39 wt%, Fluka), Mn (NO<sub>3</sub>)<sub>2</sub>6H<sub>2</sub>O (99.99%, SCRC) and the supports synthesized above were used in the preparation of catalysts. 2 g of support was weighed and immersed in a mixed solution of RhCl<sub>3</sub> and Mn(NO<sub>3</sub>)<sub>2</sub> hydrate, the weight percent of Rh and Mn were respectively 3 wt% and 3 wt%. After drying at room temperature, the catalyst was shifted to an oven at 80 °C for 12 h, and then calcined at 300 °C for 4 h. The obtained samples were denoted as RM/UiO-66, RM/UiO-66-NH<sub>2</sub>, and RM/UiO-66-OH.

#### 2.2. Reaction

CO hydrogenation was performed in a fixed-bed microreactor of length ~350 mm and internal diameter ~5 mm. The Fig. 1 The catalytic performance vs. time-on-stream for RM/UiO-66.

catalyst (0.3 g) diluted with inert  $\alpha$ -alumina (0.6 g) to avoid channeling and hot spots was loaded between quartz wool and axially centered in the reactor tube; the temperature was monitored using a thermocouple close to the catalyst bed. Prior to the reaction, the catalyst was heated to 400 °C (heating rate ~3 °C min<sup>-1</sup>) and reduced with  $H_2/N_2$  (molar ratio of  $H_2/N_2 = 1/9$ , total flow rate = 50 mL min<sup>-1</sup>) for 2 h at atmospheric pressure. The catalyst was then cooled down to 300 °C and the reaction started as the gas flow was switched to a H<sub>2</sub>/CO mixture (molar ratio of  $H_2/CO = 2$ , total flow rate = 50 mL min<sup>-1</sup> (STP)) at 3 MPa. All post-reactor lines and valves were heated to 150 °C to prevent product condensation. The products were analyzed for both hydrocarbons and oxygenates on-line (FL GC 9720) using a HP-PLOT/Q column (30 m, 0.32 mm ID) with a flame ionization detector (FID) and a TDX-01 column with a thermal conductivity detector (TCD). The CO conversion was calculated based on the fraction of CO that formed carbon-containing products and





 Table 3
 BET surface area and pore volume of different carriers

	Surface	e area (m <sup>2</sup> g	$^{-1})$	Pore v	volume (cm <sup>3</sup>	<sup>3</sup> g <sup>-1</sup> )
Sample	Total	Micropore	External	Total	Micropore	Mesopore
UiO-66 UiO-66-NH <sub>2</sub> UiO-66-OH	1320.8 1105.8 282.8	1115.8 924.8 228.4	205.0 181.0 54.1	0.79 0.68 0.19	0.57 0.48 0.12	0.22 0.20 0.07

the selectivity of a certain product was calculated based on carbon efficiency, as reported previously.<sup>28</sup>

#### 2.3. Catalyst characterization

The specific surface area ( $S_{\text{BET}}$ ), pore volume ( $V_{\text{p}}$ ), and pore diameter ( $D_{\text{p}}$ ) were measured by N<sub>2</sub> sorption at -196 °C using Micromeritics ASAP 2020 HD88 adsorption apparatus. All samples were degassed at 150 °C for 10 h prior to sorption testing.

The X-ray powder diffraction (XRD) patterns of samples were recorded using a PANalytical X'Pert diffractometer operated at

(n.e) (n.e) (1.e) (1

Fig. 3 XPS spectra (region Zr 3d) for three supports.

40 kV and 40 mA using Ni  $\beta$ -filtered Cu K $\alpha$  radiation. Two theta angles (2 $\theta$ ) ranged from 5° to 75° with a speed of 6° min<sup>-1</sup>.

X-ray photoelectron spectra (XPS) experiments were performed using a Kratos Axis Ultra DLD spectrometer equipped with an Al K $\alpha$  (1486.6 eV) X-ray source. The background pressure in the analysis chamber was kept below 7  $\times$  10<sup>-9</sup> mbar during data acquisition. The powder of samples was pressed into copper holders and then mounted on a support rod placed in the pretreatment chamber. For the reduced samples, they were pretreated *in situ* at 400 °C for 1 h under 200 mbar H<sub>2</sub> flow in the pretreatment chamber. The binding energies were calibrated relative to the C 1s peak from carbon contamination of the samples at 284.9 eV to correct for contact potential differences between the sample and the spectrometer.

CO adsorption was investigated using a Nicolet 6700 FTIR spectrometer equipped with a diffuse reflectance infrared Fourier transform (DRIFT) cell with CaF<sub>2</sub> windows. The powder of samples pressed in the cell was pretreated using a mixed H<sub>2</sub>/N<sub>2</sub> flow (molar ratio of H<sub>2</sub>/N<sub>2</sub> = 1/9, total flow rate = 50 mL min<sup>-1</sup>) at 400 °C for 2 h, followed by He flow (50 mL min<sup>-1</sup>) flushing at 400 °C for 0.5 h. During cooling down to room temperature, a series of background spectra were captured at required temperatures. Followed by introducing 0.5% CO/He (50 mL min<sup>-1</sup>)



Fig. 4 XRD patterns of different supports.



Fig. 5 N<sub>2</sub> sorption isotherms (A) and the pore size distributions (B) of RM/UiO-66 (red), RM/UiO-66-NH<sub>2</sub> (magenta) and RM/UiO-66-OH (blue).

into the IR cell, the IR spectra at the specified temperatures were recorded. Moreover, after treating with the CO/N<sub>2</sub> mixture at 300 °C for 60 min, an additional H<sub>2</sub> flow (1 mL min<sup>-1</sup>) was added to the flow, and the IR spectra were recorded as a function of time. The spectral resolution was 4 cm<sup>-1</sup> and the scan times were 64.

The temperature-programmed surface reaction (TPSR) experiments were carried out as follows: The sample (0.1 g) was reduced in H<sub>2</sub>/He (molar ratio of H<sub>2</sub>/He = 1/9) at 400 °C for 1 h, followed by He flow (50 mL min<sup>-1</sup>) flushing at this temperature for 0.5 h. After cooling down to room temperature, diluted CO (1% CO in Ar, 50 mL min<sup>-1</sup>) was introduced for adsorption for 0.5 h. Afterwards, the H<sub>2</sub>/He mixture was swept again, and the temperature was increased at the rate of 10 °C min<sup>-1</sup>. The exhaust gas was detected using a quadrupole mass spectrometer (QMS, Balzers OmniStar 200) as the detector to monitor the signal of CH<sub>4</sub> (*m*/*z* = 15).

### 3. Results and discussions

#### 3.1. Catalytic performance

Table 1 shows the effect of the Rh–Mn catalysts supported on UiO-66, UiO-66-NH<sub>2</sub>, and UiO-66-OH for the catalytic hydrogenation performance at 300 °C. As observed, the CO conversion of the catalysts follows the order: RM/UiO-66 > RM/UiO-66-NH<sub>2</sub> > RM/UiO-66-OH. With respect to selectivity, the selectivity of CH<sub>4</sub> for RM/UiO-66-NH<sub>2</sub> is the highest and that of C<sub>2</sub><sup>+</sup> oxygenates is the lowest. Further calculations show that the space–time yield (STY) of the C<sub>2</sub><sup>+</sup> oxygenates is from large to small in the following order: RM/UiO-66 > RM/UiO-66-OH > RM/UiO-66-NH<sub>2</sub>.

For comparison, the available results of Rh–Mn catalysts supported on various carriers for CO hydrogenation are collated in Table 2. Compared to the UiO-66 supported Rh–Mn catalyst, the Rh–Mn catalysts supported on traditional oxides exhibit relatively low CO conversion and ethanol selectivity. This shows that our catalyst is very promising.

Typical time dependent changes of CO conversion and  $C_2^+$  oxygenate selectivity over the representative RM/UiO-66 catalyst are shown in Fig. 1. It can be seen that both the CO conversion and  $C_2^+$  oxygenate selectivity decrease distinctly during the first 15 h on stream. However, the catalyst keeps good stability after 15 h, and the catalytic activity is hardly reduced until 150 h.

#### 3.2 Structural and textural properties of supports

Fig. 2 shows the N<sub>2</sub> sorption curves and corresponding pore size distribution of the supports. As seen from Fig. 2A, all N2 sorption curves are I-type isotherms, which is typical for the MOFs.<sup>11</sup> UiO-66 has the maximum amount of N<sub>2</sub> adsorption. In contrast, the smallest N2 adsorption capacity is obtained on the UiO-66-OH support. Correspondingly, the specific surface area and pore volume of UiO-66-OH are far lower than those of the other two carriers. It is suggested that because of the strong interaction between the polar hydroxyl group with metal ion and solvent, the movement of the organic substance and the formation of the 3D pores are restrained, resulting in a large decrease in the specific surface area and pore volume.30 The pore size distribution of UiO-66 is similar to that of UiO-66-NH2, which is concentrated in the ranges of 0.52-1.0 nm and 1.5-2.0 nm. The pores in the range of 0.5-1.0 nm should consist of the regular octahedral and tetrahedral cages. And the partial micropores in the range of 1.5-2.0 nm might be likely caused by the missing-linker defects in

M.	
19 /	
30:	
1 6:	
02	
15/2	
12/	
l on	
lanc	
dIS	
varo	
Edv	
JCe	
Prir	
of	
sity	
ver	
Uni	
by	
led	
load	
wn	
Õ	
20.	
r 20	
lbei	
cen	
De	
1 08	
l or	
shec	
bli⊱	
Ъ	

 Table 4
 BET surface area and pore volume of different catalysts

Surface area	$a (m^2 g^{-1})$		Pore volume (cm <sup><math>3</math></sup> g <sup><math>-1</math></sup> )				
Total	Micropore	External	Total	Micropore	Mesopore		
129.4	83.5	45.9	0.15	0.04	0.11		
47.2 45.6	21.3 18.5	25.9 27.1	0.10 0.06	0.01 0.01	0.09 0.05		
	Surface area Total 129.4 47.2 45.6	Surface area (m² g <sup>-1</sup> )           Total         Micropore           129.4         83.5           47.2         21.3           45.6         18.5	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		



Fig. 6 (A) XPS spectra (region Rh 3d) of fresh catalysts; (B) XPS spectra (region Rh 3d) of the reduced catalysts; (C) XPS spectra (region Mn 2p) of catalysts before and after reduction; and (D) XPS spectra (region Zr 3d) of catalysts before and after reduction.

the structure.<sup>11</sup> Compared with UiO-66 and UiO-66-NH<sub>2</sub>, the lower intensity of the micropores in the range of 0.5-1.0 nm is obtained on UiO-66-OH, which is consistent with the results of N<sub>2</sub> adsorption capacity and pore volume (Table 3).

X-ray photoelectron spectroscopy was performed to provide information about the oxidation state of Zr present on the surface of the supports. The Zr  $3d_{5/2}$  peaks of UiO-66 and its modified forms are all centered at about 183 eV as seen in

Table 5         Surface status and content of Rh for the different catalysts							
Catalyst	$\operatorname{Rh}^{\delta^+ a}$	Rh <sup>0 a</sup>	$Rh^{\delta^+}/Rh^0$	$CO(dgc)^b$	$CO(l)^b$	$CO(b)^b$	CO(dgc)/CO(l)
RM/UiO-66	1532.5	2812.1	0.54	7.6	1.9	9.1	4.1
RM/UiO-66-NH <sub>2</sub>	1749.7	2783.7	0.63	8.6	1.7	2.3	5.1
RM/UiO-66-OH	2296.6	3047.9	0.75	7.8	1.2	2.3	6.7

<sup>a</sup> Peak areas of Rh<sup>+</sup> and Rh<sup>0</sup> are derived from XPS peak data. <sup>b</sup> Peak areas of CO (dgc), CO (l) and CO (b) are derived from IR spectra.

Paper



Fig. 7 XRD patterns of different catalysts

Fig. 3, which is consistent with the coordination structure of UiO-66 series materials.<sup>31</sup>

Fig. 4 shows the XRD patterns of the supports. The three different carriers have characteristic diffraction peaks unique to the UiO-66 series materials at  $2\theta = 7.3^{\circ}$ ,  $8.5^{\circ}$ ,  $25.7^{\circ}$ ,  $43.3^{\circ}$ , *etc.*<sup>11,32</sup> Nevertheless, the peak intensity of UiO-66 is much stronger than those of the others, which is the result of the change in the unique connection state of the original structure of UiO-66 due to the insertion of the relevant functional groups.

#### 3.3. Properties of catalysts

Fig. 5 shows the N<sub>2</sub> sorption curves of different catalysts and their corresponding pore size distribution. After loading of Rh and Mn, the amount of N<sub>2</sub> adsorption of catalysts decreases, while the law of N<sub>2</sub> adsorption is satisfied with the rule: RM/UiO-66 > RM/UiO-66-NH<sub>2</sub>  $\approx$  RM/UiO-66-OH. Compared with pore size distribution of the supports, the micropores of catalysts with the pore size bigger than 0.6 nm almost disappear due to the filling of metals, which can be further supported by the data in Table 4.

The surface chemistry of the catalysts before and after reduction at 400 °C was obtained by XPS characterization. As shown in Fig. 6A, the Rh species in all the fresh catalysts exist in the form of Rh<sub>2</sub>O<sub>3</sub> (310.0 eV). After reduction, the peak shifts to the lower binding energy and can be deconvoluted into two components,  $Rh^0$  (306.8-307.4 eV) and  $Rh^{\delta+}$ (307.7–308.5 eV).<sup>33,34</sup> The proportion of Rh<sup>0</sup> is relatively higher on the catalyst surface, and the ratios of  $Rh^{\delta+}/Rh^0$  for the catalysts are listed in Table 5. The binding energy of the Mn  $2p_{3/2}$  peaks are centered at about 642 eV on fresh catalysts. Generally, the XPS spectra around the Mn  $2p_{3/2}$  peak between 645 eV and 641 eV cannot be deconvoluted into various Mn components of the signal, suggesting that Mn exists in the form of Mn<sup>2+</sup> or higher valence states (Mn<sup>3+</sup> and Mn<sup>4+</sup>).<sup>20</sup> After reduction, the binding energy of Mn 2p<sub>3/2</sub> shifts towards lower values, indicating that the electronic density on Mn particles increases caused by the interaction between Mn and Rh (or Zr). Fig. 6D shows the chemical states of Zr for the catalysts. After loading Rh-Mn, the peaks of Zr<sup>4+</sup> in the three samples have hardly changed compared with those of the state of Zr for carriers (Fig. 3). However, the peaks of Zr4+ after reduction shift to the lower binding energy to some extent. It is further revealed that the interaction among Zr node, Rh, and Mn may occur during the reduction process, which, in turn, is reflected by the presence of  $Rh^{\delta+}$  and shift of Mn  $2p_{3/2}$  and Zr  $3d_{5/2}$  peaks after reduction.

Fig. 7 shows the XRD patterns of the different catalysts. Compared with the supports, the diffraction peaks of the overall framework structure almost disappear after loading of metals and the diffraction peaks attributed to  $ZrO_2$  appear at  $2\theta$  of about 30.5°, 50.6° and 60.3° (PDF 17-0923). This indicates that the linkers of MOFs would be partially distorted or missing because of the introduction of Rh and Mn particles, and partial Zr nodes would be agglomerated, which destroyed the order of the original structure. In addition, no characteristic diffraction peaks of Rh and Mn are found in all XRD patterns, indicating that the Rh and Mn are highly dispersed in the pores of MOFs.



Fig. 8 The infrared spectra of chemisorbed CO in CO/N<sub>2</sub> flow over different catalysts at 30 °C (A) and 300 °C (B).

NJC

Paper



Fig. 8 shows the infrared spectra of the in situ reduced catalysts after CO adsorption at 30 °C and 300 °C in a flowing CO/N<sub>2</sub> atmosphere. The change of the active component Rh in different catalysts can be inferred based on the change of the CO adsorption peak in the infrared spectra. As observed in Fig. 8A, the IR spectra of the adsorbed CO at 30 °C all exhibit two main peaks at  $\sim$  2100 cm<sup>-1</sup> and  $\sim$  2036 cm<sup>-1</sup>, which can be attributed to the symmetric and asymmetric carbonyl stretching of the gem-dicarbonyl Rh<sup>+</sup>(CO)<sub>2</sub> [CO(gdc)].<sup>35</sup> Besides, two weak bands at  $\sim$  2060 cm<sup>-1</sup> and  $\sim$  1860 cm<sup>-1</sup> correspond to the linear CO [CO(1)] and bridge CO bonded to Rh(111) [CO(b)], respectively.36,37 The total CO adsorption amounts of different catalysts is in the order of RM/UiO-66 > RM/UiO-66-NH<sub>2</sub> > RM/UiO-66-OH, which can be confirmed by the data found in Table 5. Under a reaction temperature of 300 °C, the CO(gdc) species disappears, and the adsorbed CO of catalysts exist as the species of CO(l) and CO(b) (Fig. 8B). It is clear that the adsorption of CO is dominated by linear adsorption at the reaction temperature. In addition, the CO adsorption amount of RM/UiO-66 is smaller than the other two catalysts. On the other hand, the position of CO (l) under the reaction temperature decreases in the following order: RM/UiO-66-OH > RM/UiO-66-NH<sub>2</sub> > RM/UiO-66, which can be interpreted by the decrease in surface coverage.39

Because the CO(gdc) is considered to be formed on the Rh<sup>+</sup> sites and CO(l) is on the Rh<sup>0</sup> sites,<sup>38,39</sup> it is obvious in Fig. 8A that the ratio of CO(gdc)/CO(1) (Rh<sup>+</sup>/Rh<sup>0</sup>) in RM/UiO-66 is much smaller than that of the other two catalysts, which is consistent with the ratio of chemical state distribution of Rh using XPS (Table 5). Between the active sites of Rh<sup>+</sup> and Rh<sup>0</sup>, H<sub>2</sub> is more easily adsorbed on Rh<sup>0.40</sup> Therefore, the coverage of H\* species ( $\theta_{\rm H}$ ) on RM/UiO-66 should be higher during the reaction process. In the whole process of CO hydrogenation on Rh-based catalysts, the rate of CO hydrogenation to formyl species (HCO\*) is the slowest, that is to say, it controls the whole rate of the entire reaction.<sup>41</sup> Thus, it is inferred that high  $\theta_{\rm H}$  on RM/UiO-66 is likely to promote the formation of formyl species, resulting in the higher CO conversion.

In order to further investigate the state and change of adsorbed CO in the reaction condition, the IR spectra taken

after CO reaction with H<sub>2</sub> as a function of time at 300 °C are shown in Fig. 9. It is found that the CO(l) band decreases significantly due to the reaction between H<sub>2</sub> and CO and remains basically unchanged after 30 min. It is further observed that the reaction rate of adsorbed CO on RM/UiO-66 is faster than that of the others, indicating that although the CO adsorption amount of RM/UiO-66 is smaller than that of the others, the higher  $\theta_{\rm H}$  on RM/UiO-66 promotes the hydrogenation rate, resulting in a higher CO conversion.

Fig. 10 shows the patterns of  $CH_4$  formation for different catalysts measured using a quadrupole mass spectrometer in the TPSR test. Since the hydrogenation of dissociated CO into  $CH_4$  is rapid, the desorption of  $CH_4$  in TPSR can be used as a tool for measuring the CO dissociation and hydrogenation ability over the Rh-based catalyst.<sup>24</sup> It can be seen that the temperature of the  $CH_4$  peak is in the following order: RM/UiO-66 < RM/UiO-66-OH < RM/UiO-66-NH<sub>2</sub>, suggesting that RM/ UiO-66 has better CO dissociation ability. However, the CO dissociation of all the catalysts can be accomplished within the reaction temperature. On the other hand, the areas of the  $CH_4$  peak produced by the catalysts are summarized in Table 6, following the order: RM/UiO-66  $\approx$  RM/UiO-66-OH < RM/UiO-66-NH<sub>2</sub>. This result reveals that there are more active sites for



Fig. 10 CH<sub>4</sub> desorption profiles from TPSR of three catalysts.

Table 6 Relative quantities of  $\mathsf{CH}_4$  formed in TPSR experiments on catalysts

Catalyst	Area of $CH_4^a$
RM/UiO-66	202.5
RM/UiO-66-NH <sub>2</sub>	247.8
RM/UiO-66-OH	203.4

<sup>*a*</sup> The CH<sub>4</sub> peak area is obtained by integration.

 $\rm CH_4$  formation on RM/UiO-66-NH\_2, which is consistent with the results of catalytic performance.

## 4. Conclusion

A series of Zr-based metal-organic framework (UiO-66, UiO-66-NH<sub>2</sub>, UiO-66-OH) supported Rh–Mn catalysts were prepared using the incipient wetness impregnation method, and their catalytic performance was investigated for the direct synthesis of ethanol-based  $C_2^+$  oxygenates from CO hydrogenation. The catalyst supported on UiO-66 is more active than those supported on UiO-66-NH<sub>2</sub> and UiO-66-OH, and the maximum STY of  $C_2^+$  oxygenates is obtained with the RM/UiO-66 catalyst.

The structural results show that Rh and Mn are highly dispersed in the pores of MOFs, but the order of the original structure is partially sacrificed by the loading of metals. The XPS result indicates that interaction among Zr node, Rh, and Mn occurs during the reduction process, and the degree can be regulated by the different functional groups in UiO-66. On combining both *in situ* FT-IR and TPSR analyses, it is further confirmed that the higher number of active sites of Rh<sup>0</sup> on RM/UiO-66 promotes the CO dissociation ability and hydrogenation rate, resulting in a higher CO conversion. Furthermore, the greater number of active sites for CH<sub>4</sub> formation on RM/UiO-66 NH<sub>2</sub> can be responsible for its higher CH<sub>4</sub> selectivity.

## Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

This project was financially supported by the National Natural Science Foundation of China (21808142), Shanghai Institute of Technology (ZQ2018-3, CHJJ-7).

## References

- 1 M. Al-Zareer, I. Dincer and M. A. Rosen, Production of hydrogen-rich syngas from novel processes for gasification of petroleum cokes and coals, *Int. J. Hydrogen Energy*, 2020, **45**, 11577–11592.
- 2 Y. Fan, N. Tippayawong, G. Wei, Z. Huang, K. Zhao, L. Jiang, A. Zheng, Z. Zhao and H. Li, Minimizing tar formation whilst enhancing syngas production by integrating biomass

torrefaction pretreatment with chemical looping gasification, *Appl. Energy*, 2020, **260**, 114315.

- 3 M. Haider, M. Gogate and R. Davis, Fe-promotion of supported Rh catalysts for direct conversion of syngas to ethanol, *J. Catal.*, 2009, **261**, 9–16.
- 4 J. Gong, H. Yue, Y. Zhao, S. Zhao, L. Zhao, J. Lv, S. Wang and X. Ma, Synthesis of ethanol via syngas on Cu/SiO<sub>2</sub> catalysts with balanced Cu<sup>0</sup>-Cu<sup>+</sup> sites, *J. Am. Chem. Soc.*, 2012, 134, 13922–13925.
- 5 J. Liu, Z. Guo, D. Childers, N. Schweitzer, C. L. Marshall, R. F. Klie, J. T. Miller and R. J. Meyer, Correlating the degree of metal-promoter interaction to ethanol selectivity over MnRh/CNTs CO hydrogenation catalysts, *J. Catal.*, 2014, **313**, 149–158.
- 6 W. Liu, S. Wang and S. Wang, Effect of impregnation sequence of Ce promoter on the microstructure and performance of Ce-promoted Rh-Fe/SiO<sub>2</sub> for the ethanol synthesis, *Appl. Catal.*, *A*, 2016, **510**, 227–232.
- P. Lin, D. Liang, H. Luo, C. Xu, H. Zhou, S. Huang and L. Lin, Synthesis of C<sub>2+</sub> -oxygenated compounds directly from syngas, *Appl. Catal.*, A, 1995, 131, 207–214.
- 8 Y. Wang, H. Luo, D. Liang and X. Bao, Different Mechanisms for the Formation of Acetaldehyde and Ethanol on the Rh-Based Catalysts, *J. Catal.*, 2000, **196**, 46–55.
- 9 H. Yin, Y. Ding, H. Luo, H. Zhu, D. He, J. Xiong and L. Lin, Influence of iron promoter on catalytic properties of Rh-Mn-Li/ SiO<sub>2</sub> for CO hydrogenation, *Appl. Catal.*, A, 2003, 243, 155–164.
- 10 W. Mao, J. Su, Z. Zhang, X. Xu, D. Fu, W. Dai, J. Xu, X. Zhou and Y. Han, A mechanistic basis for the effects of Mn loading on C<sub>2+</sub> oxygenates synthesis directly from syngas over Rh-MnO/SiO<sub>2</sub> catalysts, *Chem. Eng. Sci.*, 2015, 135, 301–311.
- 11 J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, A New Zirconium Inorganic Building Brick Forming Metal Organic Frameworks with Exceptional Stability, *J. Am. Chem. Soc.*, 2008, 130, 13850–13851.
- 12 H. Wu, Y. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, Unusual and highly tunable missing-linker defects in zirconium metal-organic framework UiO-66 and their important effects on gas adsorption, *J. Am. Chem. Soc.*, 2013, **135**, 10525–10532.
- 13 Y. Bai, Y. Dou, L. Xie, W. Rutledge, J. Li and H. Zhou, Zr-based metal-organic frameworks: design, synthesis, structure, and applications, *Chem. Soc. Rev.*, 2016, **45**, 2327–2367.
- 14 F. G. Cirujano, A. Corma and F. X. Llabrés i Xamena, Zirconium-containing metal organic frameworks as solid acid catalysts for the esterification of free fatty acids: Synthesis of biodiesel and other compounds of interest, *Catal. Today*, 2015, 257, 213–220.
- 15 J. L. Hajek, M. Vandichel, B. V. Voorde, B. Bueken, D. De Vos, M. Waroquier and V. V. Speybroeck, Mechanistic studies of aldol condensations in UiO-66 and UiO-66-NH<sub>2</sub> metal organic frameworks, *J. Catal.*, 2015, **331**, 1–12.
- 16 F. Vermoortele, M. Vandichel, B. V. Voorde, R. Ameloot, M. Waroquier, V. V. Speybroeck and D. E. De, Vos,

Electronic effects of linker substitution on Lewis acid catalysis with metal-organic frameworks, *Angew. Chem., Int. Ed.*, 2012, **51**, 4887–4890.

- 17 A. H. Valekar, K. Cho, S. K. Chitale, D. Hong, G. Cha, U. Lee, D. W. Hwang, C. Serre, J. Chang and Y. K. Hwang, Catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone over zirconium-based metal-organic frameworks, *Green Chem.*, 2016, **18**, 4542–4552.
- 18 J. Yu, D. Mao, G. Lu, Q. Guo and L. Han, Enhanced C<sub>2</sub> oxygenate synthesis by CO hydrogenation over Rh-based catalyst supported on a novel SiO<sub>2</sub>, *Catal. Commun.*, 2012, 24, 25–29.
- 19 L. Han, D. Mao, J. Yu, Q. Guo and G. Lu, Synthesis of C<sub>2</sub>-oxygenates from syngas over Rh-based catalyst supported on SiO<sub>2</sub>, TiO<sub>2</sub> and SiO<sub>2</sub>-TiO<sub>2</sub> mixed oxide, *Catal. Commun.*, 2012, 23, 20–24.
- 20 J. Yu, J. Yu, Z. Shi, Q. Guo, X. Xiao, H. Mao and D. Mao, The effects of the nature of TiO<sub>2</sub> supports on the catalytic performance of Rh-Mn/TiO<sub>2</sub> catalysts in the synthesis of C<sub>2</sub> oxygenates from syngas, *Catal. Sci. Technol.*, 2019, **9**, 3675–3685.
- 21 L. Han, D. Mao, J. Yu, Q. Guo and G. Lu, C<sub>2</sub>-oxygenates synthesis through CO hydrogenation on SiO<sub>2</sub>-ZrO<sub>2</sub> supported Rh-based catalyst: The effect of support, *Appl. Catal.*, *A*, 2013, **454**, 81–87.
- 22 X. Xue, J. Yu, Y. Han, X. Xiao, Z. Shi, H. Mao and D. Mao, Zr-based metal-organic frameworks drived Rh-Mn catalysts for highly selective CO hydrogenation to C<sub>2</sub> oxygenates, *J. Ind. Eng. Chem.*, 2020, **86**, 220–231.
- 23 R. Burch and M. J. Hayes, The Preparation and Characterisation of Fe-Promoted Al<sub>2</sub>O<sub>3</sub>-Supported Rh Catalysts for the Selective Production of Ethanol from Syngas, *J. Catal.*, 1997, 165, 249–261.
- 24 M. Ojeda, M. L. Granados, S. Rojas, P. Terreros, F. J. García-García and J. L. G. Fierro, Manganese-promoted Rh/Al<sub>2</sub>O<sub>3</sub> for C<sub>2</sub>-oxygenates synthesis from syngas, *Appl. Catal., A*, 2004, **261**, 47–55.
- 25 F. Vermoortele, R. Ameloot, A. Vimont, C. Serrec and D. De Vos, An amino-modified Zr-terephthalate metal-organic framework as an acid-base catalyst for cross-aldol condensation, *Chem. Commun.*, 2011, 47, 1521–1523.
- 26 Z. Hu, Z. Kang, Y. Qian, Y. Peng, X. Wang, C. Chi and D. Zhao, Mixed Matrix Membranes Containing UiO-66(Hf)-(OH)<sub>2</sub> Metal-Organic Framework Nanoparticles for Efficient H<sub>2</sub>/CO<sub>2</sub> Separation, *Ind. Eng. Chem. Res.*, 2016, 55, 7933–7940.
- 27 M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. M. Farha, A facile synthesis of UiO-66, UiO-67 and their derivatives, *Chem. Commun.*, 2013, 49, 9449–9451.
- 28 J. Yu, D. Mao, D. Ding, X. Guo and G. Lu, New insights into the effects of Mn and Li on the mechanistic pathway for CO hydrogenation on Rh-Mn-Li/SiO<sub>2</sub> catalysts, *J. Mol. Catal. A: Chem.*, 2016, 423, 151–159.

- 29 X. Huang, D. Teschner, M. Dimitrakopoulou, A. Fedorov, B. Frank, R. Kraehnert, F. Rosowski, H. Kaiser, S. Schunk, C. Kuretschka, R. Schlögl, M. Willinger and A. Trunschke, Atomic-Scale Observation of the Metal-Promoter Interaction in Rh-Based Syngas Upgrading Catalysts, *Angew. Chem., Int. Ed.*, 2019, **58**, 8709–8713.
- 30 Z. H. Rada, H. R. Abid, J. Shang, H. Sun, Y. He, P. Webley, S. Liu and S. Wang, Functionalized UiO-66 by Single and Binary (OH)<sub>2</sub> and NO<sub>2</sub> Groups for Uptake of CO<sub>2</sub> and CH<sub>4</sub>, *Ind. Eng. Chem. Res.*, 2016, 55, 7924–7932.
- 31 G. Bakradze, L. P. H. Jeurgens and E. J. Mittemeijer, Valence-Band and Chemical-State Analyses of Zr and O in Thermally Grown Thin Zirconium-Oxide Films: An XPS Study, *J. Phys. Chem. C*, 2011, **115**, 19841–19848.
- 32 Z. Hu, Y. Peng, Z. Kang, Y. Qian and D. Zhao, A Modulated Hydrothermal (MHT) Approach for the Facile Synthesis of UiO-66-Type MOFs, *Inorg. Chem.*, 2015, **54**, 4862–4868.
- 33 A. Bueno-López, I. Such-Basáñez and C. Salinas-Martínez de Lecea, Stabilization of active Rh<sub>2</sub>O<sub>3</sub> species for catalytic decomposition of N<sub>2</sub>O on La-, Pr-doped CeO<sub>2</sub>, *J. Catal.*, 2006, 244, 102–112.
- 34 S. Parres-Esclapez, I. Such-Basañez, M. J. Illán-Gómez, C. Salinas-Martínez de Lecea and A. Bueno-López, Study by isotopic gases and in situ spectroscopies (DRIFTS, XPS and Raman) of the N<sub>2</sub>O decomposition mechanism on Rh/ CeO<sub>2</sub> and Rh/γ-Al<sub>2</sub>O<sub>3</sub> catalysts, *J. Catal.*, 2010, 276, 390–401.
- 35 R. Lang, T. Li, D. Matsumura, S. Miao, Y. Ren, Y. Cui, Y. Tan, B. Qiao, L. Lin, A. Wang, X. Wang and T. Zhang, Hydroformylation of Olefins by a Rhodium Single-Atom Catalyst with Activity Comparable to RhCl(PPh<sub>3</sub>)<sub>3</sub>, *Angew. Chem., Int. Ed.*, 2016, 55, 1–6.
- 36 N. Yang and S. F. Bent, Investigation of inherent differences between oxide supports in heterogeneous catalysis in the absence of structural variations, *J. Catal.*, 2017, **351**, 49–58.
- 37 Y. Liu, L. Zhang, F. Göltl, M. R. Ball, I. Hermans, T. K. Kuech, M. Mavrikakis and J. A. Dumesic, Synthesis Gas Conversion over Rh-Mn-W<sub>x</sub>C/SiO<sub>2</sub> Catalysts Prepared by Atomic Layer Deposition, *ACS Catal.*, 2018, 8, 10707–10720.
- 38 F. Solymosi and M. Pásztor, Infrared Study of the Effect of H<sub>2</sub> on CO-induced Structural Changes In Supported Rh, *J. Phys. Chem.*, 1986, **90**, 5312–5317.
- 39 D. Jiang, Y. Ding, Z. Pan, W. Chen and H. Luo, CO Hydrogenation to C<sub>2</sub>-oxygenates over Rh-Mn-Li/SiO<sub>2</sub> Catalyst: Effects of Support Pretreatment with nC<sub>1</sub>-C<sub>5</sub> Alcohols, *Catal. Lett.*, 2008, **121**, 241–246.
- 40 R. R. Cavanagh and J. T. Yates Jr, Site distribution studies of Rh supported on Al<sub>2</sub>O<sub>3</sub>-An infrared study of chemisorbed CO, *J. Chem. Phys.*, 1981, 74, 4150–4155.
- 41 Y. M. Choi and P. Liu, Mechanism of Ethanol Synthesis from Syngas on Rh(111), *J. Am. Chem. Soc.*, 2009, 131, 13054–13061.