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### Short Communication

# Pt nanoparticles entrapped in ordered mesoporous carbons for liquid-phase hydrogenation of unsaturated compounds

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### A R T I C L E I N F O

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### 1. Introduction

Ordered mesoporous carbon materials have attracted much attention due to periodic mesopores, uniform pore size, high surface areas, adequate pore volume and high thermal, chemical and mechanical stabilities [1–3]. Synthesis of ordered mesoporous carbon materials with various structures has achieved great progress [4–7]. Among the ordered mesoporous carbons (OMCs), CMK-3 and CMK-8 have attracted wide interest because of their excellent properties. The CMK-3 OMCs with p6mm symmetry are synthesized using a nanocasting route [8]. Similar to the CMK-3 OMCs, the CMK-8 OMCs are also synthesized through a nano-casting route, whereas the CMK-8 OMCs have three-dimensional cubic structure of Ia3d symmetry with larger pore volume [9,10]. Thus, the CMK-8 OMCs have better adsorption characteristics compared with the CMK-3 analogues [10].

In our previous work, the cinchonidine-modified Pt/CMK-3 catalysts worked better in the chiral hydrogenation of ethyl pyruvate [11]; while the cinchonidine-modified Pt/CMK-8 catalyst ran relatively fast in the enantioselective hydrogenation of ethyl 2-oxo-4-phenylbutyrate [12]. To the best of our knowledge, the results with Pt/OMC catalysts are the best ones among those obtained with Pt catalysts supported on carbon materials. Moreover, the Pt/OMC catalysts also showed comparable or slightly higher activity than the well-known Pt/Al<sub>2</sub>O<sub>3</sub> catalyst towards the chiral hydrogenation of  $\alpha$ -ketoesters [11,12]. Encouraged by these achievements, we expected to broaden the application of novel Pt/OMC catalysts in the clean hydrogenation and to reveal the

### ABSTRACT

Pt nanoparticles entrapped in ordered mesoporous carbons were proved effective for liquid-phase hydrogenation of benzaldehyde and its derivatives in water. Due to higher hydrophobicity, Pt/CMK-3 catalyst was slightly superior to Pt/CMK-8 catalyst towards benzaldehyde hydrogenation. Nevertheless, the larger pore volume of Pt/CMK-8 catalyst is more beneficial for mass transfer of benzaldehyde derivatives. In addition, the surface electronic state of Pt particles deposited on CMK-8 is helpful for the activation of carbonyl compounds. Therefore, the Pt/CMK-8 and Pt/CMK-3 catalysts showed tiny differences in most cases. The Pt catalysts can also catalyze the hydrogenation of olefins and other carbonyl compounds.

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differences between Pt/CMK-3 and Pt/CMK-8 catalysts in the hydrogenation reactions.

Among the hydrogenation reactions, the Pt-based carbon catalysts usually have excellent catalytic activity for the hydrogenation of aldehydes [13,14]. In addition, hydrogenation of arenes represents an important industrial process and Pt-based catalysts are also active in this kind of reaction [15,16].

In this work, the Pt/CMK-3 and Pt/CMK-8 catalysts were investigated in the liquid-phase hydrogenation of benzaldehyde and its derivatives, arenes, olefins and other unsaturated compounds under mild conditions. The differences between Pt/CMK-3 and Pt/CMK-8 catalysts were discussed in combination with the relevant characterizations.

### 2. Experimental

### 2.1. Catalyst preparation and characterization

The 5 wt.% Pt/CMK-3 and Pt/CMK-8 catalysts were prepared according to Refs. [11,12]. The thermogravimetric (TG) analysis of the samples was conducted from r.t. to 423 K under nitrogen atmosphere with Mettler Toledo TGA/SDTA851<sup>e</sup> apparatus. The X-ray photoelectron spectroscopy (XPS) measurements of the sample were taken with a Thermo Fisher Scientific ESCALAB 250 spectrometer with Al K $\alpha$  radiation (1486.6 eV) as incident beam.

### 2.2. Catalytic tests

0.05~g~5~wt.% Pt catalyst was pretreated in a hydrogen flow at 673 K for 2 h before use. The catalyst was then mixed with 20 mL solvent and transferred to a 100 mL autoclave. The hydrogenation reaction began at

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# Table 1 Optimization of reaction conditions for benzaldehyde hydrogenation with Pt/CMK-3 catalyst <sup>a</sup>.

Entry	Solvent	Catalyst (mg)	Time (h)	Conv. (%) <sup>b</sup>	Sele. (%) <sup>b</sup>
1	Ethanol	100	1	98	62
2	Cyclohexane	100	1	99	83
3	Acetic acid	100	1	73	72
4	10 mL water + 10 mL ethanol	100	1	88	91
5	18 mL water + 2 mL ethanol	100	1	99	>99
6	18 mL water + 2 mL ethanol	100	0.5	99	>99
7	18 mL water + 2 mL ethanol	50	0.5	58	>99
8	18 mL water + 2 mL ethanol	50	1	99	>99

<sup>a</sup> Reaction conditions: Pt/CMK-3 catalyst; 21 mmol benzaldehyde; 4.0 MPa H<sub>2</sub>; 1200 rpm; r.t.

<sup>b</sup> Determined by GC.



**Fig. 1.** Kinetic profiles of benzaldehyde hydrogenation (a) with Pt/CMK-3 catalyst and (b) with Pt/CMK-8 catalyst. Reaction conditions are identical to Table 3 except for reaction time.

a designated temperature after 4.0 MPa hydrogen was introduced into the autoclave. The reaction was stopped after an allotted period and the products were analyzed by GC–FID (GC-2014, Shimadzu Co.) equipped with a capillary column (DM-WAX, 30 m×0.32 mm× 0.25  $\mu$ m).

#### 3. Results and discussion

### 3.1. Optimization of reaction conditions for benzaldehyde hydrogenation

In order to optimize the reaction conditions, benzaldehyde was chosen as a model substrate and Pt/CMK-3 catalyst was chosen as a model catalyst.

The solvents were firstly screened for the hydrogenation of benzaldehyde (Table 1). In ethanol, the conversion of benzaldehyde could

Relevant parameters of Pt/CMK-3 and Pt/CMK-8 catalysts.

reach 98% within 1 h, but obtaining the medium selectivity of 62% to benzyl alcohol, due to side-reaction to form 1-(ethoxymethyl)benzene and 2-ethoxy-1,2-diphenylethanone detected by GC–MS (Table 1, entry 1). To avoid the side reaction, the reaction was performed in cyclohexane. Notably, a 99% conversion of benzaldehyde with 83% selectivity within 1 h was achieved (Table 1, entry 2). Nevertheless, there still has room to increase the selectivity. When the hydrogenation of benzaldehyde was carried out in acetic acid, mediocre conversion and selectivity were achieved (Table 1, entry 3).

Considering that water is an environmentally benign solvent, and the solubility of benzaldehyde in water is low but that of benzyl alcohol is relatively high, we anticipate that Pt/CMK-3 catalyst can work well in water for the hydrogenation of benzaldehyde. However, due to high hydrophobicity of CMK-3 OMCs, the Pt/CMK-3 catalyst cannot be soaked at all in neat water, so that the catalyst fine powders were floated on water surface and cannot contact the substrates dispersed in water. Therefore, the mixed solvents containing water and ethanol with different ratios were used in the benzaldehyde hydrogenation.

To our delight, the selectivity was increased to 91% in a mixed solvent containing water and ethanol with an equal volume, although the conversion of benzaldehyde was not complete, obtaining 88% conversion within 1 h (Table 1, entry 4). If the volume ratio of water was further increased in the mixed solvent, nearly full conversion with >99% selectivity was obtained within 1 h (Table 1, entry 5), which is consistent with our previous observations for benzaldehyde hydrogenation on Pt/FDU-14 catalyst [17]. Hence, we chose the mixed solvent containing 18 mL water and 2 mL ethanol as an optimal solvent in the following researches.

Besides the solvent, the catalyst dosage and reaction time were also optimized. When the reaction time was reduced to 0.5 h, to our surprise, the benzaldehyde conversion still reached 99% (Table 1, entry 6). To further explore the catalytic property, the catalyst amount was decreased to half amount. Within 0.5 h, the conversion of benzaldehyde was 58% with 50 mg catalyst (Table 1, entry 7). When prolonged to 1 h, a 99% conversion was furnished with 50 mg catalyst (Table 1, entry 8). Therefore, 50 mg Pt catalyst, 1 h, 18 mL water and 2 mL ethanol were determined as the standard parameters in the following studies.

## 3.2. Hydrogenation of benzaldehyde on Pt/CMK-3 and Pt/CMK-8 catalysts

The Pt/CMK-8 catalyst was more active for the chiral hydrogenation of ethyl pyruvate and ethyl 2-oxo-4-phenylbutyrate due to the large pore volume compared with Pt/CMK-3 catalyst [12]. Consequently, we firstly compared the kinetic profiles of benzaldehyde hydrogenation with Pt/CMK-3 and Pt/CMK-8 catalysts, respectively.

As displayed in Fig. 1, the conversion of benzaldehyde with Pt/CMK-3 catalyst was about 7-13% higher than that obtained with Pt/CMK-8 catalyst within the same time. This can be interpreted mainly in terms of the chemical and physical properties of CMK-3 and CMK-8 OMCs.

As summarized in Table 2, the Pt/CMK-3 and Pt/CMK-8 catalysts had similar structural properties, including the specific surface area, pore diameters and Pt particle sizes, except that Pt/CMK-8 catalyst had relatively larger pore volume. The similar Raman spectra of CMK-3 and CMK-8 OMCs also indicate that both CMK-8 and CMK-3 OMCs had

Sample	$S_{\rm BET} ({\rm m}^2~{\rm g}^{-1})^{\rm a}$	$D_{\rm P} (\rm nm)^{a}$	$V_{\rm P} ({\rm cm^3 \ g^{-1}})^{\rm a}$	Pt size (nm) <sup>a</sup>	Pt disp. (%) <sup>a</sup>	Surface comp. (%) <sup>b</sup>		
						С	0	Pt
Pt/CMK-3	1290	3.5	1.18	2.6	43.7	94.1	5.56	0.34
Pt/CMK-8	1318	3.7	1.43	2.3	48.8	91.7	7.91	0.35

<sup>a</sup> Quoted from Refs. [11,12].

Table 2

<sup>b</sup> Calculated by XPS analysis.



Fig. 2. TG curves of Pt/CMK-3 and Pt/CMK-8 catalysts under a nitrogen atmosphere.

plenty of  $\pi$  electrons [11,12]. Nevertheless, Pt/CMK-8 catalyst has more surface oxygen amount according to XPS analysis than Pt/CMK-3 catalyst (also see Table 2).

Although Pt/CMK-3 and Pt/CMK-8 catalysts had similar structural features, the hydrophobicity of these two catalysts is different and it possibly plays an important role in the catalytic performance in mixed solvent containing water. As the TG curves of Pt/CMK-8 and Pt/CMK-3 catalysts under nitrogen atmosphere shown in Fig. 2, in the temperature

range to remove the physisorbed water, a 14.0% weight was lost for the Pt/CMK-8 catalyst, about twice of that for the Pt/CMK-3 catalyst. This indicates that Pt/CMK-3 catalyst is more hydrophobic than Pt/CMK-8 catalyst. As a result, benzaldehyde is more easily to be adsorbed on Pt/CMK-3 than on Pt/CMK-8 catalyst. The photographs in Fig. 3 also confirm the different soakage properties of CMK-3 and CMK-8 OMCs in different media. In addition, the higher oxygen-containing carbon amount on Pt/CMK-8 catalyst surface deconvoluted from C1s XPS spectra (Fig. 4A) also indicates that CMK-8 is less hydrophobic than CMK-3.

### 3.3. Hydrogenation of benzaldehyde derivatives with Pt/OMC catalysts

Besides the simplest benzaldehyde, we also extended the hydrogenation with Pt/CMK-3 and Pt/CMK-8 catalysts to a series of benzaldehyde derivatives with substituents at the phenyl ring.

For the hydrogenation of benzaldehydes substituted with methoxy, the conversions obtained with the Pt/CMK-8 catalyst were a little higher than those with Pt/CMK-3 catalyst (Table 3, entries 1–8). For the hydrogenation of benzaldehydes substituted with chlorine, the conversions were nearly the same with the two Pt/OMC catalysts (Table 3, entries 9–14). The GC yields obtained with Pt/CMK-3 and Pt/CMK-8 catalysts for the hydrogenation of benzaldehydes substituted with MeO — and Cl — were nearly identical, with an exception encountered for 2-methoxybenzaldehyde (Table 3, entries 3–4).

This can be interpreted by support hydrophobicity and the surface electronic state of Pt particles. On the one hand, Pt/CMK-3 has relatively high hydrophobicity, which is beneficial for the adsorption of



Fig. 3. The soakage properties of CMK-3 and CMK-8 OMCs in different media.



Fig. 4. XPS spectra of C1s region (A) and Pt4f region (B) of Pt/CMK-3 and Pt/CMK-8 catalysts.

substrates in an aqueous medium. On the other hand, according to the Pt4f XPS spectra of Pt/CMK-8 catalyst (Fig. 4B), there are three Pt species on the surface, metallic platinum (the peak of  $4f_{7/2}$ =

### Table 3

Hydrogenation of benzaldehyde derivatives with Pt/CMK-3 and Pt/CMK-8 catalysts<sup>a</sup>.

CH	10	логион
R — —	Pt Catalyst	R R

Entry	R group	Catalyst	Conversion (%)	TOF $(h^{-1})$	Yield (%)
1	2-MeO	Pt/CMK-3	100	-	98.0
2		Pt/CMK-8	100	_	92.0
3	2-MeO <sup>b</sup>	Pt/CMK-3	65	4881	56.5
4		Pt/CMK-8	79	5311	68.7
5	3-MeO	Pt/CMK-3	37	1389	30.3
6		Pt/CMK-8	42	1412	31.5
7	4-MeO	Pt/CMK-3	93	3491	92.1
8		Pt/CMK-8	96	3227	92.2
9	2-Cl	Pt/CMK-3	81	3040	70.5
10		Pt/CMK-8	80	2690	70.4
11	3-Cl	Pt/CMK-3	70	2628	65.1
12		Pt/CMK-8	74	2488	65.9
13	4-Cl	Pt/CMK-3	34	1276	30.9
14		Pt/CMK-8	33	1109	30.3
15	2-F	Pt/CMK-3	80	3003	74.4
16		Pt/CMK-8	96	3227	86.4
17	3-F	Pt/CMK-3	73	2741	72.3
18		Pt/CMK-8	96	3227	91.2
19	4-F	Pt/CMK-3	48	1802	47.5
20		Pt/CMK-8	61	2051	60.4

 <sup>&</sup>lt;sup>a</sup> Reaction conditions: 0.05 g Pt catalyst; 21 mmol substrate; 18 mL water and 2 mL ethanol; 4.0 MPa H<sub>2</sub>; 1 h; 1200 rpm; r.t.
 <sup>b</sup> 0.5 h

71.90 eV), PtO species (the peak of  $4f_{7/2} = 73.05$  eV) and PtO<sub>2</sub> species (the peak of  $4f_{7/2} = 74.53$  eV) originated from re-oxidation when exposed to air [18]. The XPS spectra of the Pt/CMK-3 catalyst were similar to those of Pt/CMK-8 except for 0.11 eV shift for the metallic platinum to lower energy. This suggests that the Pt/CMK-8 catalyst is relatively electron-deficient and is more easily to activate the carbonyl compounds. Thus, in combination with above discussion, the Pt/CMK-3 and Pt/CMK-8 catalysts show tiny differences in most cases.

As for F-substituted benzaldehydes, the conversions, TOF and GC yields were higher on the Pt/CMK-8 catalyst (Table 3, entries 15–20). In addition to the higher pore volume of CMK-8, the F-substituted benzaldehydes with strong electronegativity would be easily adsorbed on Pt/CMK-8 catalyst, which has relatively high hydrophilicity with much oxygen containing groups on the surface.

There is distinct electronic effect on the catalytic performance. The *ortho-* and *para-*methoxy substituted isomers were more active than the *meta-*substituted one; while the *para-*Cl or *para-*F substituted benzaldehydes were less active. However, whenever the hydrogenation occurred on Pt/CMK-8 or on Pt/CMK-3 catalyst, the *ortho-*substituted benzaldehydes were more active than the *meta-* and *para-*substituted isomers, probably because the substituent at the *ortho-*position participates in the interaction with Pt particles [17].

#### 3.4. Hydrogenation of other unsaturated compounds

As there is only little difference between the catalytic performances of the two Pt catalysts, Pt/CMK-3 catalyst was further investigated in the hydrogenation of arenes, olefins and other carbonyl compounds. The Pt/CMK-3 catalyst showed high activity in the hydrogenation of other unsaturated compounds, the only exception encountered in the hydrogenation of arenes.

Table 4	
Hydrogenation of other unsaturate	d compounds on Pt/CMK-3 catalyst <sup>a</sup> .

Entry	Substrate	Time (min)	Conversion (%)	TOF $(h^{-1})^{b}$	Selectivity (	%)
1	$\bigcirc$	15	100	14993		100
2	° (	40	100	5622		100
3		100	100	2249	OH C	82
					OH C	14
4		100	18	405	$\bigcirc$	16
	Ť				$\bigcup_{i=1}^{n}$	84

 $<sup>^{\</sup>rm a}$  Reaction conditions: 0.05 g catalyst; 21 mmol substrates; 18 mL water and 2 mL ethanol; 4.0 MPa H\_2; 1200 rpm; 333 K.

<sup>b</sup> Defined as the number of moles of hydrogenation of substrates per mole of Pt per hour.

The cyclohexene was completely converted to cyclohexane within 15 min, the corresponding TOF reaching 14993  $h^{-1}$  (Table 4, entry 1). This result was much higher than that obtained with Ru-based catalyst [16]. The hydrogenation of cyclohexanone was also completely converted to cyclohexanol within 40 min (Table 4, entry 2). For acetophenone hydrogenation, the preferential hydrogenation of carbonyl group occurred. Consequently, the selectivities of 82% to 1-phenylethanol and 14% to 1-cyclohexylethanol were achieved. Only 18% conversion was achieved in the hydrogenation of toluene (Table 4, entry 4). The Pt/CMK-3 catalyst was less active than Ru-based catalyst for the hydrogenation of phenyl ring [16].

### 4. Conclusions

The Pt nanoparticles entrapped in OMCs worked well for the liquid-phase hydrogenation of benzaldehyde and its derivatives, olefins

and other carbonyl compounds under the mild conditions. The minor differences between the catalytic performances of Pt/CMK-3 and Pt/CMK-8 catalysts are mainly ascribed to the different hydrophobicities, different surface electronic states and different pore volumes of these two Pt catalysts.

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