### COMMUNICATION

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# Heterogeneous Jacobsen's catalyst on alkoxyl-modified zirconium poly (styrene-phenylvinylphosphonate)-phosphate (ZPS-PVPA) for asymmetric epoxidation

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Chiral Jacobsen's catalysts grafted onto alkoxyl-modified ZPS-PVPA exhibit excellent activities (conv%, up to 96; sele%, up to 96; ee%, up to >99) in the asymmetric epoxidations of unfunctionalized olefins. The superior stabilities and the comfortable dispositions in large-scale reactions contribute to the potential applications in industry.

#### **KEYWORDS**

alkoxyl-modified, asymmetric epoxidation, heterogeneous catalyst, Jacobsen's catalyst, unfunctionalized olefins

# **1** | **INTRODUCTION**

Chiral epoxides are versatile building blocks in the synthesis of various pharmaceutical products, so the design and preparation of effective catalysts for asymmetric epoxidations of alkenes have become an important challenge for chemists.<sup>[1]</sup> The discovery of efficient and atom-economic catalyst systems for asymmetric epoxidation is an important objective of catalytic chemistry.<sup>[2–4]</sup> Epoxidations of unfunctionalized olefins catalyzed by chiral manganese (III) salen complexes,

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initially developed by Jacobsen and Katsuki, have emerged as practical methods for the synthesis of optically active epoxides.<sup>[5,6]</sup> Although homogeneous chiral salen Mn (III) catalysts display a broad substrate scope for epoxidations of olefins, the separation and recycling of this catalyst are still problematic issues. The development of heterogeneous catalysts able to promote enantioselective organic reactions is a field of growing interest. A major advantage of the use of a heterogeneous catalyst for reactions is the ease with which it can be recovered and subsequently reused.<sup>[7–9]</sup> Therefore, many efforts have been taken to anchor these catalysts on polymer, organic or inorganic, and ionic liquids.<sup>[10–13]</sup> However, in spite of their excellent properties in easy separation, the heterogenized catalysts are often faced with decreased catalytic performance and the inaccessibility of the reagents to the reactive centers<sup>[14]</sup> as well as poor reusability. Additionally, nearly all the asymmetric epoxidations<sup>[15]</sup> catalvzed by heterogeneous Mn(III) salen complexes indicate superior activities only in the presence of excess and expensive additives as axial bases, which is not conductive to their utilization in industry.

Inorganic-organic hybrid materials have been a topical target of considerable investigations owing to their combining properties of the inorganic and organic components.<sup>[16,17]</sup> Particularly, quite a few hybrid materials with various chemical compositions and organic groups have been well-documented<sup>[18]</sup> and employed as the catalysts or the supports, such as the catalyst support for immobilizing salen Mn(III) complexes. We have devoted ourselves to Jacobsen's catalyst attached on a series of hybrid materials, such as zirconium oligostyrenylphosphonate-phosphate (ZSPP) and zirconium poly (styrene-phenylvinylphosphonate)phosphate (ZPS-PVPA) and zinc poly(styrene-phenylvinylphosphonate)-phosphate (ZnPS-PVPA) as well as calcium poly(styrene-phenylvinylphosphonate)-phosphate (CaPS-PVPA). Moreover, the heterogeneous chiral salen Mn (III) catalysts indicate superior dispositions in asymmetric epoxidations of unfunctionalized olefins.<sup>[19-26]</sup>

In this work, we are intrigued with the idea that chiral Jacobsen's catalysts are immobilized onto alkoxyl-modified ZPS-PVPA for asymmetric epoxidations of unfunctionalized olefins (Scheme 1–3). And we also report the catalytic



SCHEME 1 Synthetic route of the heterogeneous catalysts



**SCHEME 2** The synthesis of homogeneous catalysts

activity and the reusability as well as the performance in large-scale reactions systematically. In addition, the mechanism of epoxidation in *m*-CPBA/NMO system is investigated here.

## 2 | RESULTS AND DISCUSSION

# **2.1** | IR spectroscopy and UV–Vis spectroscopy

All the supported catalysts 4a–f and Jacobsen's catalyst have indicated the same bands at 1630 cm<sup>-1</sup> (Figure S1) owing to the azomethene(C = N) stretching band. The bands in the scope of 1340–1456 cm<sup>-1</sup> for the catalysts are ascribed to the stretching vibration of C-H groups. The stretching vibration at 1030 cm<sup>-1</sup> which is assigned to characteristic vibrations of the phosphonate and phosphate in the support ZPS-PVPA, is obviously weakened by virtue of the electronic structure changes for the hostguest interactions.

The spectra of 4b and 4 g have displayed features similar to Jacobsen's catalyst at 252, 430 and 500 nm in view of UV–vis observation (Figure S2). According to the supported catalysts, the bands at 320 nm and the bands at 430, 505 nm are ascribed to  $\pi$ - $\pi$ \* and d-d transition of C = N respectively; and the bands at 253 nm are due to the transition of benzene ring.

#### 2.2 | Thermal gravimetric analysis

According to the catalyst 4f (Figure S3), the initial weight loss is 6.92% below 160 °C, owing to surface-bound or intercalated water in this stage. Subsequently, the organic moieties decompose with 54.43% weight loss in the temperature range of 160–700 °C. Ultimately, the small weight losses in the scope of 700–1000 °C are due to the dehydration changes



SCHEME 3 Asymmetric epoxidaion of alkene

from  $Zr(HPO_4)_2$  to  $ZrP_2O_7$ . Notably, the heterogeneous catalyst 4f could still maintain superior stability lower than 160 °C, which provide the catalyst enough stability to be utilized in the asymmetric epoxidations smoothly.

# **2.3** | Nitrogen adsorption-desorption isotherms

The nitrogen adsorption–desorption isotherms of the catalyst 4f are characteristic type IV, accompanied with a sharp increase in N<sub>2</sub> adsorption at higher  $p/p_0$  values (~0.9) and a distinct hysteresis loop (type H<sub>3</sub>). As for the desorption isotherm (Figure 1), BJH analysis indicates a broad and non-uniform distribution of pore size (in the range 2–20 nm), which demonstrates that the mesoporous structure exists in the catalyst.

The corresponding textural parameters calculated by  $N_2$  adsorption–desorption isotherms are presented in Table 1.

Varying from the chloromethylation to the alkoxylation and further to the immobilization, obvious decreases in BET surface area are observed (1 vs 2 vs 3f vs 4f, 180 vs 120.3 vs 84.8 vs 66.0 m<sup>2</sup>/g), and in the pore volume (1 vs 2 vs 3f vs 4f, 3.5 vs 2.7 vs 1. 9 vs  $1.1 \times 10^{-2}$  cm<sup>3</sup>/g) as well as in average pore diameter (1 vs 2 vs 3f vs 4f, 46.8 vs 38.1 vs 30.8 vs 25.2 nm). The occupation of caves and channels



FIGURE 1 The nitrogen adsorption-desorption isotherm and pore distribution of the catalyst 4f

**TABLE 1** The physical properties of 1, 2, 3f and 4f

Sample	Surface area (m²/g)	Pore volume (×10 <sup>-1</sup> cm <sup>3</sup> /g)	Average pore size (nm)
1	180	3.5	46.8
2	120.3	2.7	38.1
3f	84.8	1.9	30.8
4f	66.0	1.1	25.2

contributes to the phenomenon, which agrees with the most articles reported such as the catalysts anchored onto ZSPP.<sup>[19]</sup> On account of the results, it could be deduced that chiral salen Mn (III) complexes are either immobilized on the external surface of ZPS-PVPA or introduced into the channels and holes.

#### 2.4 | X-ray photoelectron spectroscopy

The binding energy of the immobilized salen Mn(III) complex 4f at 641.2 eV (Figure S4) is slightly higher than Mn  $2p_{3/2}$  core level peak of neat chiral salen Mn(III) complex (642.1 eV), which is in compliance with the earlier articles reported.<sup>[27]</sup> The deflection of chemical shift is attributed to the decrease of Mn atomic electron cloud density which is originated in the impacts of Zr atoms in the interlayer of ZPS-PVPA.

### 2.5 | Analysis of surface morphology

On account of SEM photograph (Figure 2). the morphology of the catalyst 4f is transformed tremendously according to ZPS-PVPA whose structure is loose and amorphous. Compared with the morphology of ZPS-PVPA (Figure 2A), the smooth anomalous structure resides in the catalyst 4f (Figure 2B) owing to the immobilization of chiral salen Mn (III). Meanwhile, many small caves and channels with irregular shapes also are present. Amorphous morphology and porous structure of the catalysts together could endure the substrates with the further opportunity to approach the catalytic active sites.

Shown in Figure 3, TEM images of the catalyst 4d (Figure 3A) and 4f (Figure 3B) indicate loose configuration which contain the channels, holes and cavums. The similar morphologies confirm that the disposition of the linkers hardly put effects on the morphology. Moreover, the special configurations of the catalysts could be propitious to the substrates approaching the internal catalytic active sites easily and provide enough space for asymmetric epoxidation of unfunctionalized olefins.

# **2.6** | Catalytic epoxidation of unfunctionalized olefins

In the asymmetric epoxidation of indene in Table 2, ee values increase from 65% to 85% or 90% (Jacobsen's vs 6a vs 6b, entry 1 vs 10 vs 12) owing to the modification of alkoxy and further increase even up to >99% (6a vs 3a, 85% vs 93%, entry 10 vs 2; 6b vs 4d, 90% vs 95%, entry 12 vs 6) upon the immobilizing on ZPS-PVPA. In a word, the congenerous effect of ZPS-PVPA and the linker alkoxy as well as the chiral ligand contribute to the superior activities. Additionally, the catalysts indicate superior catalytic disposition only when the asymmetric epoxidation of indene are carried out for 1 hour. However, in the reported articles according to the alkoxyl-modified salen Mn (III) catalysts with MCM-41, ITQ-2 and IT-6 as the supports, merely 56% ee values are gained even after the asymmetric epoxidation of indene proceeds for 70 hours with NaCIO as the oxidant.<sup>[28]</sup>

Notably, the catalytic activities are increasing with the carbon number of linkage, which agree with the results reported by C.  $\text{Li}^{[29]}$  and our group.<sup>[21]</sup> As described in Table 2, ee values increase from 93% to 99% according to indene (entry 2–4, 6–8) and vary from 56% to 82% for  $\alpha$ -methylstyrene (entry 15–17, 19–21). At the same time, the similar tendency happens to the homogeneous catalysts 6a–b with the increase of the chain length (ee%: 6a vs 6b,



FIGURE 2 SEM photograph of (a) ZPS-PVPA and (b) the catalyst 4f



FIGURE 3 TEM photograph of (a) the catalyst 4d; (b) the catalyst 4f

85 vs 90; entry 10 vs 12). The phenomenon might be interpreted that the augmentation of the linkage is in favor of the heterogeneous salen Mn(III) complexes approaching the active intermediates of salen Mn(V) or their transition states more easily.

As it is known to all, the additives N-methylmorpholine N-oxide (NMO), which are usually used to improve epoxidation yields and enantioselections, bind to the Mn (III) center prior to the epoxidation reaction, as evidenced by the alteration of the Mn (III) parallel mode EPR signal.<sup>[30]</sup> However, superior catalytic performances are generated for the heterogeneous catalyst 4c and 4f as well as the alkoxyl-modified catalyst 6a-b without the addition of NMO. For instance, ee values increase from 25% to 97% and conversions from 43% to 96% (entry 5 vs 4) in the asymmetric epoxidation of indene. And for the epoxidation of  $\alpha$ -methylstyrene, the similar results have also been obtained (ee%, 15 vs 75; conv.%, 43 vs >99; entry 17 vs 18). Our group has reported the similar phenomenon<sup>[24,31]</sup> that happen to the immobilized chiral salen Mn (III) onto phenoxy-modified ZPS-PVPA and Jacobsen's catalyst anchored onto ZnPS-PVPA, respectively. According to chiral salen Mn (III) immobilized on phenoxy-modified ZPS-PVPA, the special phenomenon is correlated to the support ZPS-PVPA and the phenoxide axial coordinating group. On account of Jacobsen's catalyst anchored onto ZnPS-PVPA, structure direction of the rigid linker aryldiamines could contribute to this unusual Applied WILEY-Organometallic 5 of 8 Chemistry

phenomenon. Whereas, as described in Table 2, the supported catalysts 4a–f with flexible alkoxy as the linkers and the alkoxyl-modified catalyst 6a (conv%, 85 vs 76; ee%, 95 vs 24; entry 10 vs 11) and 6b (conv%, 90 vs 70; ee%, 84 vs 52; entry 12 vs 13) also take on similar phenomenon. Based on these facts, it could be deduced that the special phenomenon has no concern with the support ZPS-PVPA, which agree with the results from List's group.<sup>[32]</sup>

On account of the articles reported<sup>[31,32]</sup> and the results in Table 2, we conclude that the coordination complexes such as Mn(salen)OPh and Mn(salen)OP as well as alkoxy-Mn (salen) could afford superior properties in the absence of NMO, which is not fit for N-Mn (salen) complexes. The following three factors may contribute to this particular phenomenon in this context. Firstly, when hexamethylene diamine and NMO approach Mn center simultaneously, the spatial repellant and the formative Mn-O ionic bond may put effect on the bond length of Mn(V) = O and induce the axial ligand NMO deviating to the plane of salicylaldehyde. And then the stability of reactive intermediate or transition state may step down, accompanying with the lower ee value.<sup>[33]</sup> Secondly, the alkoxy linker group as the axial coordinating group for the supported catalysts 4a-f has similar properties in electronic structure and coordination performance with O-coordinating axial base NMO. When N-oxide ligand (NMO) is added to the catalytic system, the welldefined molecular geometry and conformation of the immobilized chiral salen Mn (III) catalysts may be interfered with. Then the optimal geometric configuration of the reactive intermediate salen Mn(V) = O would be altered and further lead to the decrease of the conversion and chirality recognization. Thirdly, a balance transformation (Figure 4) between Mn (V) = O and Mn (III) coordination complex lies in the asymmetric epoxidation of unfunctional olefins.<sup>[34]</sup> Meanwhile, NMO binds to unsaturated Mn (III) coordination compound by means of coordination bond. When NMO is added, this type of coordination would be destroyed owing to Mn (III) bonded to alkoxyl-modified ZPS-PVPA, accompanying with the increase of the concentration of Mn (III) and the decrease of Mn(V) = O. The lower ee value would be obtained spontaneously.

#### 2.7 | The reusability of the catalysts

To investigate the reusability of the immobilized catalyst and the leaching of chiral salen Mn(III) complex from the heterogeneous catalyst, the catalyst 4f is employed in recycling epoxidation with indene as a model substrate. As described in Figure 5, the catalytic disposition merely decreases slightly for the first seven runs (conv.%: from 96 to 88; ee%: from >99 to 98) and is still superior to that of the homogeneous counterpart even after recycling for twelve (ee%: 82 vs 65; 4f vs Jacobsen's).

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TABLE 2 Asymmetric epoxidation of alkenes catalyzed by catalysts 4a–f and 6a–b <sup>[a]</sup>									
Entry	Subs-trate <sup>[b]</sup>	Catalyst	Oxidant	Conv (%) <sup>[c]</sup>	sele (%) <sup>[d]</sup>	ee (%)	$TOF^{[g]} \times 10^{-3} (s^{-1})$		
1	А	Jacob-sen's	m-CPBA /NMO	>99	>99	65 <sup>e</sup>	5.50		
2	А	4a	<i>m</i> -CPBA	93	94	93 <sup>e</sup>	5.17		
3	А	4b	<i>m</i> -CPBA	95	93	96 <sup>e</sup>	5.27		
4	А	4c	<i>m</i> -CPBA	96	96	97 <sup>e</sup>	5.33		
5	А	4c	<i>m</i> -CPBA/NMO	43	99	25 <sup>e</sup>	2.39		
6	А	4d	<i>m</i> -CPBA	94	93	95 <sup>e</sup>	5.22		
7	А	4e	<i>m</i> -CPBA	93	95	98 <sup>e</sup>	5.17		
8	А	4f	<i>m</i> -CPBA	96	96	>99 <sup>e</sup>	5.33		
9	А	4f	<i>m</i> -CPBA/NMO	46	>99	33 <sup>e</sup>	2.56		
10	А	6a	<i>m</i> -CPBA	95	73	85 <sup>e</sup>	5.27		
11	А	6a	m-CPBA /NMO	24	90	76 <sup>e</sup>	1.33		
12	А	6b	<i>m</i> -CPBA	84	26	90 <sup>e</sup>	4.67		
13	А	6b	m-CPBA /NMO	52	97	70 <sup>e</sup>	2.89		
14	В	Jacobsen's	m-CPBA /NMO	>99	99	52 <sup>f</sup>	5.50		
15	В	4a	<i>m</i> -CPBA	>99	63	56 <sup>f</sup>	5.50		
16	В	4b	<i>m</i> -CPBA	>99	61	67 <sup>f</sup>	5.50		
17	В	4c	<i>m</i> -CPBA	>99	63	75 <sup>f</sup>	5.50		
18	В	4c	m-CPBA /NMO	43	60	15 <sup>f</sup>	2.39		
19	В	4d	<i>m</i> -CPBA	>99	56	66 <sup>f</sup>	5.50		
20	В	4e	<i>m</i> -CPBA	>99	61	78 <sup>f</sup>	5.50		
21	В	4f	<i>m</i> -CPBA	>99	62	82 <sup>f</sup>	5.50		
22	В	4f	m-CPBA /NMO	51	52	$28^{\mathrm{f}}$	2.83		
23	В	6a	<i>m</i> -CPBA	89	22	91 <sup>f</sup>	4.94		
24	В	6a	m-CPBA /NMO	37	31	25 <sup>f</sup>	2.05		
25	В	6b	<i>m</i> -CPBA	98	25	96 <sup>f</sup>	5.44		
26	В	6b	m-CPBA /NMO	44	58	37 <sup>f</sup>	2.43		

<sup>a[]</sup> Reactions were carried out at 0 °C in CH<sub>2</sub>Cl<sub>2</sub> (3.0 ml) with alkene (0.5 mmol), *m*-CPBA (1.0 mmol), NMO (340.0 mg, 2.50 mmol), *n*-nonane (internal standard, 90.0 µl, 0.5 mmol) and salen Mn(III) catalysts (0.0250 mmol, 5.0 mol%).

<sup>b[]</sup> A = indene, B =  $\alpha$ -methylstyrene.

<sup>c[]</sup> Conversions were determined by GC with a chiral capillary column (HP19091G-B233, 30 m  $\times$  0.32 mm  $\times$  0.25  $\mu$ m).

<sup>d[]</sup> Selectivities were determined by GC, by integration of product peaks against an internal quantitative standard (nonane), correcting for response factors.

e[] Epoxide configuration 1S, 2R.

f]] Epoxide configuration S.

 $^{g[]}$  Turnover frequency (TOF) is calculated by the expression of [product]/ [catalyst] × time (s<sup>-1</sup>).

The nature of the recovered catalyst 4f is followed by SEM (Figure S5B). The morphology of the reused catalyst varies from amorphous loose structure (Figure S5A) to

compact surfacing structure, which indicates that the configuration of the catalyst is partly destroyed in the process of circulation. At the same time, Mn content of the catalyst 4f



FIGURE 4 The scheme of concentration equilibria



FIGURE 5 The recycles of the catalyst 4f in the asymmetric epoxidation of indene

drops from 0.72 to 40 mmol/g after recycling for twelve times. As for the decrease of the disposition, it is mainly ascribed to the physical leaching of active salen Mn (III) and the blockage of some pore channels and the micropores, which may give rise to the substrates approaching the active sites difficultly and further could result in the decrease of the catalytic performances.

# **2.8** | Large-scale asymmetric epoxidation reaction

We further carry out different proportions of large-scale asymmetric epoxidation reactions with indene as substrate and *m*-CPBA as oxidant. The same catalyst loading of 5 mol% as that in the experimental scale is utilized. The large-scale experiments could be facilely performed according to the same procedure of the experimental scale reactions. The catalytic activities are shown in Figure S6. Delightfully, superior catalytic performance could still be obtained for the large-scale reactions even when the large scale is 200 times (Figure S6) as much as the experimental scale.

### **3 | CONCLUSIONS**

In summary, chiral homogeneous Jacobsen's catalysts attached on alkoxyl-modified zirconium poly (styrenephenylvinyl- phosphonate)-phosphate (ZPS-PVPA) have been synthesized and utilized in the asymmetric epoxidation of olefins. The as-synthesized heterogeneous catalysts could effectively participate in the reaction, which is due to congenerous effect of ZPS-PVPA and the linker alkoxy as well as the chiral ligand. Moreover, the supported catalysts could still keep their activity even after recycling for ten times and could be performed on a large-scale with the enantioselectivity -WILEY-Organometallic 7 of 8 Chemistry

being maintained at the same level. Notably, the heterogeneous catalysts could furnish distinguished increases of activities without the addition of expensive NMO for asymmetric epoxidation of olefins, which paves the way for the potential applications in industry.

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#### REFERENCES

- [1] S. L. Wei, Y. H. Tang, X. Q. Xu, G. J. Xu, Y. Yu, Y. Sun, Y. S. Zheng, *Appl. Organometal. Chem* **2011**, 25,146.
- [2] R. V. Ottenbacher, K. P. Bryliakov, E. P. Talsi, Adv. Synth. Catal 2011, 353, 885.
- [3] D. Q. Xu, S. F. Wang, Z. Q. Shen, C. G. Xia, W. Sun, Org. Biomol. Chem. 2012, 10, 2730.
- [4] S. H. Cho, B. Q. Ma, S. T. Nguyen, J. T. Hupp, T. E. A. Schmitt, *Chem. Commun* **2006**, 2563.
- [5] E. M. McGarrigle, D. G. Gilheany, Chem. Rev. 2005, 105, 1563.
- [6] W. Zhang, J. L. Loebach, S. R. Wilson, E. N. Jacobsen, J. Am. Chem. Soc. 1990, 112, 2801.
- [7] R. Chico, C. Domínguez, B. Donnio, S. Coco, P. Espinet, *Dalton Trans* **2011**, 40, 5977.
- [8] P. Goodrich, C. Hardacre, C. Paun, A. Ribeiro, S. Kennedy, M. J. V. Lourenço, H. Manyar, C. A. Nieto de Castro, M. Besnea, V. I. Pârvulescuc, *Adv. Synth. Catal* **2011**, *353*, 995.
- [9] L. Alaerts, J. Wahlen, P. A. Jacobs, D. E. D. Vos, Chem. Commun 2008, 1727.
- [10] J. Cubillos, M. Vargas, J. Reyes, A. Villa, C. M. D. Correa, *Chiral-ity* **2010**, *22*, 403.
- [11] Q. H. Zhang, S. G. Zhang, Y. Q. Deng, Green Chem. 2011, 13, 2619.
- [12] C. V. Doorslaer, J. Wahlen, P. Mertens, K. Binnemans, D. D. Vos, *Dalton Trans* 2010, 39, 8377.
- [13] W. M. Xuan, C. F. Zhu, Y. Liu, Y. Cui, Chem. Soc. Rev. 2012, 41, 1677.
- [14] H. Zhang, S. Xiang, C. Li, Chem. Commun 2005, 1209.
- [15] D. P. Wang, M. Wang, X. N. Wang, Y. G. Chen, A. P. Gao, L. C. Sun, J. Catal. 2006, 237, 248.
- [16] T. Y. Ma, X. J. Zhang, G. S. Shao, J. L. Cao, Z. Y. Yuan, J. Phys. Chem. C 2008, 112, 3090.

### 8 of 8 WILEY-Organometallic Chemistry

- [17] G. Rogez, C. Massobrio, P. Rabu, M. Drillon, *Chem. Soc. Rev.* 2011, 40, 1031.
- [18] L. N. Rosi, J. Eckert, M. Eddaoudi, T. D. Vodak, J. Kim, M. O. Yaghi, *Science* **2003**, *300*, 1127.
- [19] W. S. Ren, X. K. Fu, H. B. Bao, R. F. Bai, P. P. Ding, B. L. Sui, *Catal. Commun.* **2009**, *10*, 788.
- [20] X. B. Tu, X. K. Fu, Hu, X. Y. Hu, Y. D. Li, *Inorg. Chem. Commun.* 2010, 13, 404.
- [21] B. W. Gong, X. K. Fu, J. X. Chen, Y. D. Li, X. C. Zou, X. B. Tu, P. P. Ding, L. P. Ma, J. Catal. 2009, 262, 9.
- [22] J. Huang, X. K. Fu, G. Wang, C. Li, X. Y. Hu, *Dalton. Trans* 2011, 40, 3631.
- [23] J. Huang, X. K. Fu, G. Wang, Q. Miao, *Dalton Trans* 2012, 41, 10661.
- [24] J. Huang, X. K. Fu, Q. Miao, Appl. Catal., A 2011, 407, 163.
- [25] J. Huang, X. K. Fu, Q. Miao, Catal. Sci. Technol. 2011, 1, 1472.
- [26] J. Huang, M. Tang, X. Li, G. Z. Zhong, C. M. Li, *Dalton Trans* 2014, 43, 17500.
- [27] A. R. Silva, J. L. Figueiredo, C. Freire, B. D. Castro, *Microporous Mesoporous Mater.* 2004, 68, 83.
- [28] Domínguez, V. Fornés, M. J. Sabater, J. Catal. 2004, 228, 92.
- [29] H. Zhang, Y. Zhang, C. Li, J. Catal. 2006, 238, 369.

- [30] A. Campbell, M. R. Lashley, J. K. Wyatt, M. H. Nantz, R. D. Britt, J. Am. Chem. Soc. 2001, 123, 5710.
- [31] X. C. Zou, X. K. Fu, Y. D. Li, X. B. Tu, S. D. Fu, Y. F. Luo, X. J. Wu, Adv. Synth. Catal **2010**, 352, 163.
- [32] S. Liao, B. List, Angew. Chem. Int. Ed 2010, 49, 628.
- [33] T. Kurahashi, M. Hada, H. Fujii, J. Am. Chem. Soc. 2009, 131, 12394.
- [34] E. N. Jacobsen, L. Deng, Y. Furukawa, L. E. Martinez, *Tetrahedron* 1994, 50, 4323.

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