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Preparation of supported core-shell structured Pd@Pd$_x$S$_y$/C catalysts for use in selective reductive alkylation reaction

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Abstract: Supported noble metal sulphides catalysts have received extensive scientific interest for their good selectivity in the selective hydrogenation. However, the application of the noble metal catalysts is limited due to their lower activity leading to harsh reaction conditions and poor conversion in the hydrogenation reactions. In this paper, Pd/C was sulphidized by H$_2$S to prepare a series of core-shell structured Pd@Pd$_x$S$_y$/C catalysts. The catalysts were characterized by BET, EDS, XPS, XRD and CO chemisorption to investigate the influences of sulphidation temperature, sulphidation time and sulphidation atmosphere on the structure of the resulting catalysts. The sulphidation of Pd/C at low temperature resulted in a core-shell structured catalyst —Pd@Pd$_x$S$_y$/C, while raising the sulphidation temperature, the size of Pd^0 as the core decreased, and the thickness of palladium sulphides as the shell increased correspondingly. When the sulphidation temperature is up to 150℃, the resulting catalyst has been transformed to complete palladium sulphides catalyst—Pd$_x$S$_y$/C. The structure of Pd@Pd$_x$S$_y$/C sulphidized at 30℃ was independent of the sulphidation time and sulphidation atmosphere. The sulphidized catalysts were applied to reductive alkylation of PADPA and MIBK to DBPPD. The sulphidized catalysts presented a much higher selectivity of DBPPD comparing with Pd/C, and Pd@Pd$_x$S$_y$/C showed a higher activity than Pd$_x$S$_y$/C, moreover, the more content of Pd$_x$S$_y$ in the resulting catalyst led to a lower activity.

KEYWORDS: core-shell, Pd@Pd$_x$S$_y$/C, reductive alkylation reaction

1. Introduction

Supported noble metal catalysts are among the most industrially applied heterogeneous catalysts in the various reductive reactions and have received extensive scientific interest [1~10].

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However, these catalysts are not qualified to catalyze selective hydrogenation of the organic compounds with multiple reducible functionalities for their too high activity. Therefore, the modifications of noble metal catalysts for selective hydrogenation have been extensively applied in synthetic chemistry [5-10]. It is also an effective way to improve the selectivity for using noble metal sulphide catalysts during the selective hydrogenation [11-17]. The supported noble metal sulphide catalysts have good performance in reductive alkylation reaction of aldehydes / ketone and amine [11-14], and the selective hydrogenation of halogenated nitrobenzene to the corresponding halogenated aniline [15-17]. They are also suitable for hydrogenation of sulfur-containing compounds [18-23]. Moreover, the noble metal sulphide catalysts as famous hydrotreating catalysts are widely used in hydrodesulfurization and hydrodenitrogenation [24-28].

However, the activity of the noble metal sulphide catalysts is much lower than the unmodified noble metal catalysts, so that the noble metal sulphide catalysts are often used under harsh conditions during hydrogenation [13-20]. This severely limits their application. The key to solving the problem is to improve the activity of noble metal sulphide catalysts. Michele Breyssey et al revealed that the activity of RuS_2 catalysts depended on the S/Ru ratio and high S/Ru ratio corresponded to low activity during their research about the catalytic mechanism of RuS_2 catalysts [29,30]. In our previous study, we also have found that catalytic activity of several types of activated carbon supported palladium sulphides in the hydrogenation of 4-nitrothioanisole were ranked as the following order: $Pd_4S/C \approx Pd_{16}S_7/C > Pd_3S/C >> PdS/C$ [21], which indicated the Pd atoms with less number of the coordinated S atoms showed relatively higher activity in the hydrogenation of sulfur-containing compounds. It seems an efficient way to improve the activity of noble metal sulphide catalysts by reducing the number of the coordinated S atoms.

Core-shell catalysts as the core particles coated with a functional material increase the physical properties such as electrical, optical, magnetic and thermal properties of the combined particles, and present special catalytic performance [31-35]. Recently, core-shell catalysts have been attracting more and more attention. Bao's group reported that Pt shell coated at Cu core decorated with FeO patches used much less Pt but exhibited performance similar to that of just Pt nanoparticles covered with surface FeO patches in the catalytic oxidation of CO [34]. Wei and coworkers prepared a polyaniline (PANI)-decorated Pt/C@PANI core-shell catalyst, and they found this novel catalyst presented high activity and stability in the oxygen reduction reaction for

not only the electron delocalization between the Pt d orbitals and the PANI π-conjugated ligand but also electron transfer from Pt to PANI [35].

N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenedianine (DBPPD) as a rubber antioxidant is synthesized by the reductive alkylation of p-aminodiphenylamine (PADPA) and methylisobutyl ketone (MIBK) over copper or noble metal catalysts in industry [36,37]. In this reaction, PADPA and MIBK are underwent a condensation reaction to form an imine compound, which is hydrogenated in the presence of catalyst to DBPPD (Scheme1). PADPA, MIBK, imine and DBPPD are prone to undergo over-hydrogenation to byproducts using ordinary catalysts. Noble metal sulphide catalysts such as palladium sulphide and platinum sulphide show high selectivity in synthesis of DBPPD, and just their activity is not so good [14].
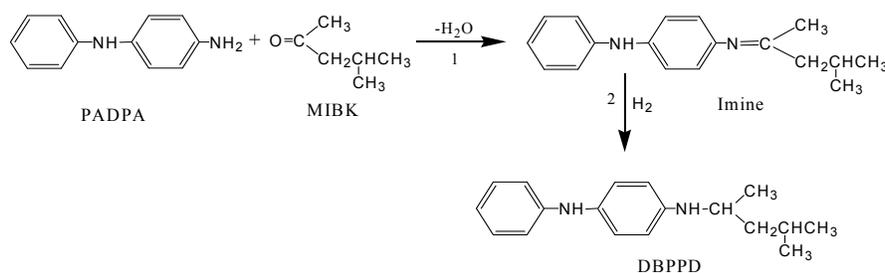
Scheme 1 Reaction pathways

In this paper, a serial of activated carbon supported Pd metal core with Pd_xS_y shell catalysts were prepared by a simple method and characterized by CO chemisorption, BET, EDS, XRD and XPS. Then the catalysts were employed to reductive alkylation of PADPA and MIBK to DBPPD.

2 Experimental

2.1 Catalyst preparation

10 % Pd/C was prepared by incipient wetness impregnation method using H_2PdCl_4 as a Pd precursor. The commercial activated carbon (Xinsen Chemical Industry Co. Ltd.) and deionized water were mixed in the weight ratio of 1 to 50. Then a desired volume of 0.05 g/ml H_2PdCl_4 was added into the continuously stirred slurry solution at 80 ℃, and the pH value of the sample was adjusted to 11 by adding 10% NaOH aqueous solution. The precipitated $Pd(OH)_2$ was reduced by hydrazine hydrate, and then washed with deionized water until the pH value reached about 7 and dried in the vacuum at 110 ℃ for 10 h.

A suspension of 1.0 g of 10% Pd/C and 50 ml deionized water was stirred in a three necked

flask, then a stream of gas containing H_2S was passed into the suspension under different condition as listed in Table 1. The resulting catalyst was collected on filter paper, washed with deionized water until the pH is 7, and then dried in the vacuum at 110℃ for 10h.

2.2 Catalyst characterization

The morphology and particle size of the catalysts were detected by a Philips-FEI Tecnai G2 F30 S-Twin transmission electron microscope operated at 300 kV.

X-ray diffraction (XRD) of the catalysts was carried out on a Thermo ARL X′TRA diffractometer using Cu K^{α} radiation. The tube voltage was 40 kV and tube current was 45 mA. The samples were scanned at 4° min^{-1} in 2θ.

X-ray Photoelectron Spectroscopy (XPS) analysis was performed with a Kratos AXIS Ultra DLD system. A monochromatized incident Al X-ray radiation (Al K^{α} = 1486.6 eV) with a fixed analyser pass energy of 80 eV was used for excitation of the sample, and the binding energy values were referenced to the C 1s level (284.6 eV) resulting from surface contaminants.

The elemental content of the catalysts was detected by EDS (Thermo Vantage ESI).

The surface area of the catalysts was determined by nitrogen physical adsorption at 77 K. The samples were heated to 473 K under vacuum condition for 10 h to remove the adsorbed species, and then nitrogen adsorption isotherm was performed using a NOVA 1000e surface area analyzer (Quantachrome Instruments Corp.). The surface area of samples was calculated by the BET equation.

CO chemisorption uptake was measured by a pulse chemisorption with a mass spectrometry (Omnistar TM) at ambient temperature and pressure.

2.3 Reductive alkylation reaction

Liquid phase reductive alkylation was carried out at 200℃ and 3 MPa of hydrogen for 4 hours in a 75 ml stainless steel autoclave (Parr Instruments Company), which contained 3.7g (0.02 mol) PADPA, 10 mL (0.08 mol) MIBK and 0.037g catalyst. The final products were analyzed by a gas chromatography (Agilent-6890) equipped with an HP-5 capillary column and a FID detector. The area normalization method was used for quantitative determination of components.

3 Results and Discussion

3.1 Catalyst preparation and characterization

Supported metal sulphide catalysts are usually sulphidized from metal or metal oxide as the precursor by H_2S or S as sulphidation agent[14, 38]. The sulphidation conditions such as sulphidation temperature, sulphidation time and sulphidation atmosphere, always cause important influence on the structure of the resulting supported metal sulphide catalysts.

Table 1 The sulphidation conditions and properties of the sulphidized catalysts and fresh Pd/C

Catalyst	Sulphidation temperature/$^\circ$C	Sulphidation atmosphere	Sulphidation time /h	Surface area /m^2g^{-1}	Mean diameter of Pd particles /nm	CO chemisorption uptake /ml g^{-1}	Elemental composition /wt%			Mole ratio of S/Pd
							C	Pd	S	
SPC 1	30	$H_2/H_2S=9/1$	3	1508	5.9	0	81.79	9.73	1.45	0.50
SPC 2	60	$H_2/H_2S=9/1$	3	1437	6.2	0	82.06	9.88	1.53	0.51
SPC 3	100	$H_2/H_2S=9/1$	3	1552	6.5	0	82.61	9.82	1.55	0.52
SPC 4	150	$H_2/H_2S=9/1$	3	1539	6.6	0	82.02	10.03	1.67	0.55
SPC 5	200	$H_2/H_2S=9/1$	3	1477	7.0	0	82.31	9.68	1.72	0.59
SPC 6	30	$H_2/H_2S=9/1$	5	1521	6.0	0	82.01	9.94	1.50	0.50
SPC 7	30	$H_2/H_2S=9/1$	10	1570	6.1	0	81.33	9.67	1.49	0.51
SPC 8	30	$N_2/H_2S=9/1$	3	1498	5.8	0	81.94	10.12	1.38	0.45
SPC 9	30	H_2S	3	1463	5.5	0	82.65	9.75	1.48	0.50
SPC 10	30	$H_2/H_2S=4/1$	3	1509	5.8	0	82.58	9.84	1.48	0.50
SPC 11	30	$H_2/H_2S=49/1$	3	1526	5.9	0	82.11	9.88	1.46	0.49
Fresh Pd/C	—	—	—	1517	5.7	3.5	82.53	9.85	0	—
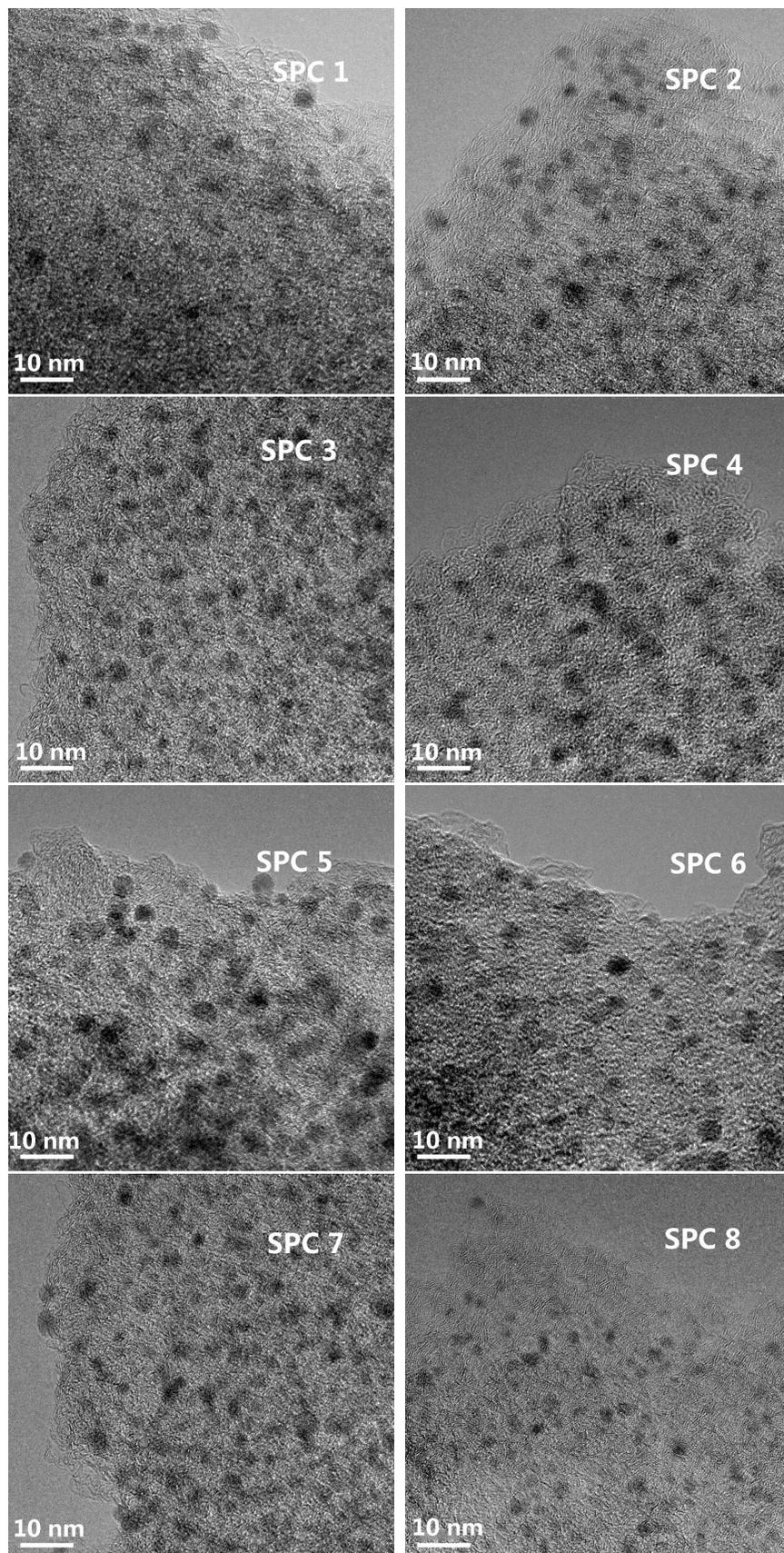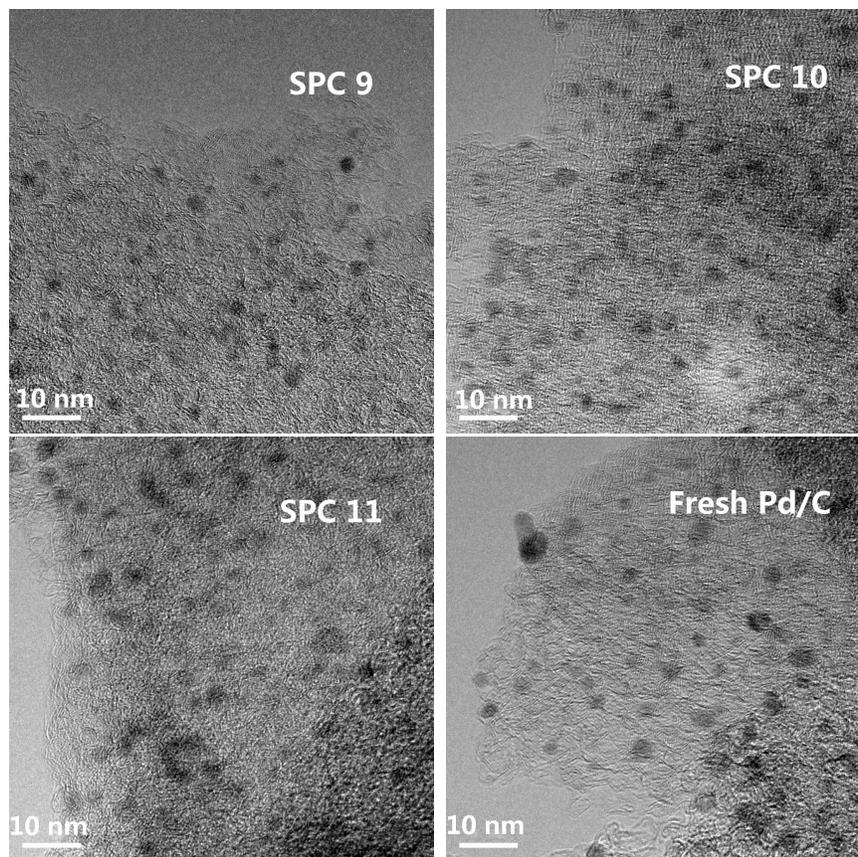
Fig. 1 TEM images of the sulphidized catalysts and fresh Pd/C

We firstly investigated the influence of sulphidation temperature on the structure of the palladium sulphide catalysts. 10 wt% Pd/C was sulphidized under the atmosphere of H_2/H_2S with the volume ratio as 9/1 for 3 hours at the temperature of 30, 60, 100, 150, 200℃, respectively, and the resulting catalysts signed as SPC 1~5 were characterized busing N_2 physisorption for surface area, CO chemisorption, TEM, EDS, XPS, XRD. The surface areas of SPC 1~5 (Table 1) were almost the same as that of fresh Pd/C, suggesting that the influence of the sulphidation temperature on the structure of the activated carbon was slight. The morphology of Pd particles of the fresh Pd/C and SPC 1~5 observed by TEM (Fig. 1) showed the Pd particle size of the six catalysts were all about 4~10 nm. The elemental content of SPC 1~5 catalysts determined by EDS (Table 1) showed all five catalysts after sulphidation contained S, and its content was increased from 1.45 wt% to 1.76 wt% with the sulphidation temperature from 30 ℃ to 200 ℃, While the content of Pd in SPC 1~5 was nearly unchanged. CO chemisorption is used to determine the content of Pd^0 on the surface of the supported palladium catalyst. In our experiment, the CO chemisorption uptakes of five catalysts (Table 1) after sulphidation at different temperature were

all 0 ml g^{-1}, while the CO chemisorption uptakes of the fresh Pd/C was 3.5 ml g^{-1}. This result indicates that there was no Pd^0 on the surface of the catalysts after sulphidation at different temperature. Considering the content of Pd in SPC 1~5 did not decrease after sulphidation, we conjecture Pd metal on the surface of these catalysts had been transferred to palladium sulphide.
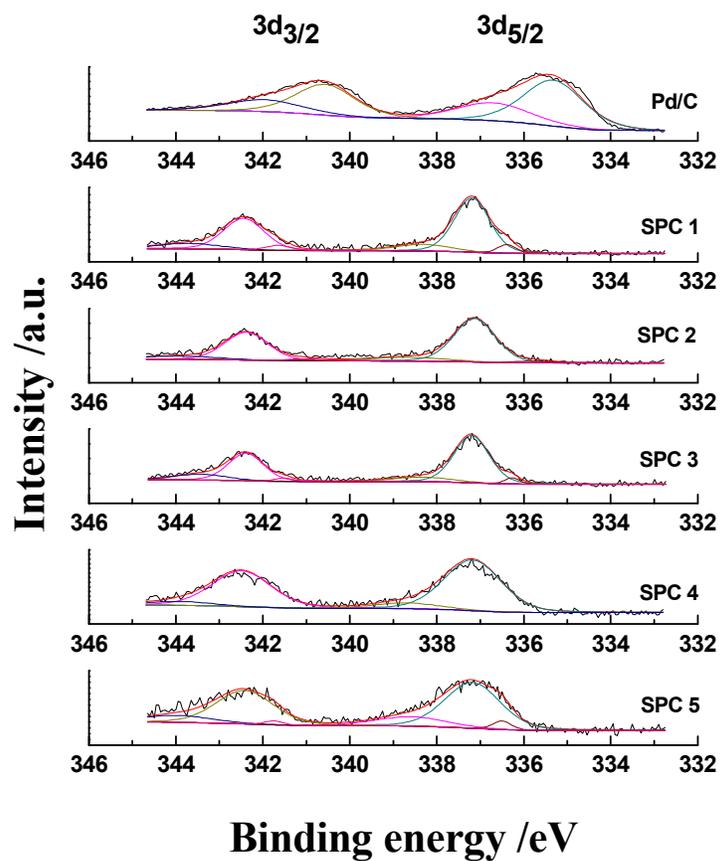
Fig. 2 Pd 3d XPS spectra of Pd/C and SPC 1~5
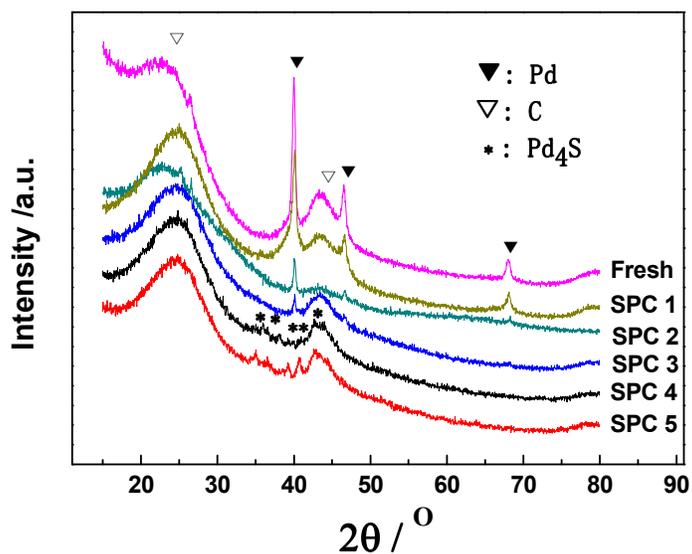
Fig. 3 XRD patterns of Pd/C and SPC 1~5

The fresh Pd/C and SPC 1~5 catalysts were also detected by XPS (Fig. 2 and Table 2). The fitted XPS spectra of Pd $3d_{5/2}$ of the fresh Pd/C contain the peak at 335.3 eV as indicative of Pd^0 and the peak at 336.7 eV as indicative of Pd^{2+} for a part of palladium atoms on the surface of the Pd/C catalyst were oxidized by air. However, there is no peak at about 335.3 eV for the catalysts SPC 1~5, suggesting that there was no Pd^0 on the surface of the catalysts SPC 1~5. The fitted XPS spectra of Pd $3d_{5/2}$ of SPC 1~5 contain the peaks at 336.4, 337.1 and 338.2 eV, meaning that Pd atoms on the surface of these catalysts had been all changed to high-valence palladium ions as palladium sulphides. This is consistent with the result of CO chemisorption examinations. There are several types of palladium sulphide crystalline phases such as Pd_4S, Pd_3S, $Pd_{16}S_7$, PdS and PdS_2 with their different valence of Pd element. It is also found that the areas of the peaks at 337.1 and 338.2 eV increase with the increasing of the sulphidation temperature, which indicates that there were more high-valence palladium ions in the catalyst sulphidized at higher temperature. The XRD patterns of the fresh Pd/C and sulphidized catalysts are shown in Fig. 3. The broad diffraction peaks at about 25° and 44° of 2θ are ascribed to the activated carbon. The sharp diffraction peaks of Pd of the fresh Pd/C are at 40.1°, 46.6° and 68.1° of 2θ. The XRD pattern of the catalyst SPC 1 sulphidized at 30℃ is similar to that of the fresh Pd/C, and no peaks of palladium sulphides are observed, indicating that the catalyst sulphidized at 30℃ did not form a

palladium sulphide crystal and most of the palladium on the sulphidized catalyst still existrf as Pd^0. The results of CO chemisorption and XPS as described above have confirmed that Pd atoms on the surface of the sulphidized catalyst had been all changed to palladium sulphides, and then these palladium sulphides should just located on the surface of the palladium particles and the core of palladium particles should be still Pd^0. Therefore, the catalyst SPC 1 has such a structure with Pd^0 as the core and a membrane of palladium sulphides as the shell ($Pd@Pd_xS_y/C$). With increasing the sulphidation temperature, the peaks of Pd^0 of the sulphidized catalysts become weak and broad. Considering the palladium particle size observed from TEM didn't change much after the sulphidation, this result meant the particle size of Pd^0 on the resulting catalysts was decreased with increasing the sulphidation temperature. When the sulphidation temperature is raised to 150℃, the diffraction peaks of Pd^0 has been disappeared, which suggests that Pd^0 particle on this catalyst has been reduced to a range that can not be detected by XRD. We also observe that the diffraction peaks of Pd_4S appear on the XRD pattern of the catalyst sulphidized at 150℃, and the intensity of the peaks of Pd_4S is further enhanced when the sulphidation temperature is raised to 200℃, which indicates the content of Pd_4S was increased and the particle of Pd_4S grew larger with raising the sulphidation temperature. Therefore, the sulphidation temperature has a significant influence on the structure of the resulting catalysts. When Pd/C was sulphidized at low temperature, the sulphidized catalyst was a core-shell structure —$Pd@Pd_xS_y/C$. With raising the sulphidation temperature, the size of Pd^0 as the core decreased, and the thickness of palladium sulphides as the shell increased correspondingly. Moreover, if the sulphidation temperature was up to 150℃, the resulting catalyst had been transformed to a complete palladium sulphides catalyst—Pd_xS_y/C.
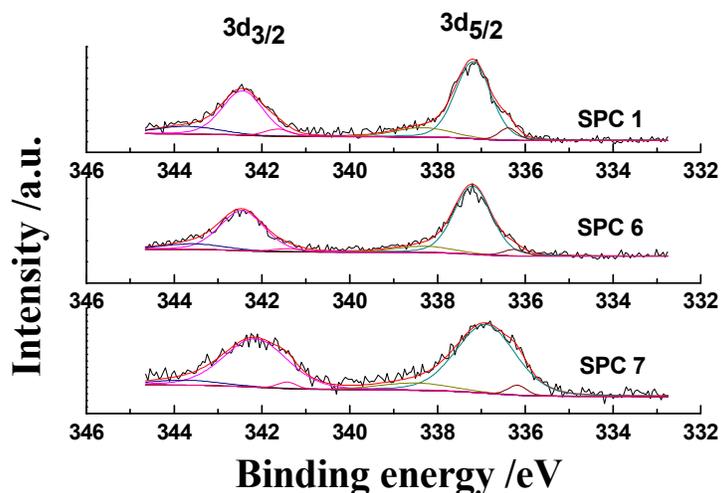
Fig. 4 Pd 3d XPS spectra of SPC 1, 6, 7
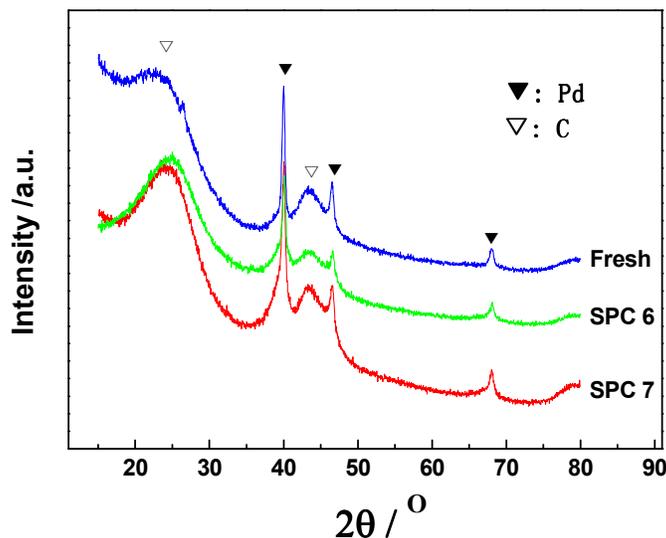
Fig. 5 XRD patterns of Pd/C and SPC 6, 7

The influence of the sulphidation time on $Pd@Pd_xS_y/C$ catalysts was also investigated. 10 wt% Pd/C was sulphidized under the atmosphere of H_2/H_2S with the volume ratio as 9/1 at 30℃ for 5, 10 hours respectively, and the resulting catalysts signed as SPC 6, 7. The surface areas of this series of sulphidized catalysts were all ranged between 1508 to 1570 m^2g^{-1} as similar to that of the fresh Pd/C, meaning there was also little impact of the sulphidation time on the structure of the activated carbon. The TEM images (Fig. 1) also showed that the Pd particle size did not changed significantly after the sulphidation treatment for different time. The content of S of SPC 1, 6, 7 detected by EDS was all maintained at 1.45～1.50 wt%, and also, the content of Pd of these catalysts was at 9.67～9.94 wt%. The CO chemisorption uptakes of all three catalysts were all 0 ml g^{-1}. SPC6, 7 were also detected by XPS and XRD. The XPS spectra of Pd $3d_{5/2}$ of these catalysts (Fig. 4 and Table 2) contain the peaks at 336.4, 337.1 and 338.2 eV, and there is no peak at 335.3 eV. The results of CO chemisorption and XPS show that the Pd atoms on the surface of the catalysts had been all transformed to palladium sulphides. XRD patterns of SPC 6, 7 (Fig. 5)contain only the diffraction peaks of Pd^0 and activated carbon, and no peaks of palladium sulphides were detected. Furthermore, the intensity of the peaks Pd^0 of is similar to that of the fresh Pd/C. Therefore, after the sulphidation for 3, 5 and 10 hours, the resulting catalysts still kept Pd^0 as the core. In addition, the particle size of the Pd^0 core did not decreased unambiguously. The

catalysts sulphidized for different time were all core-shell catalysts —Pd@Pd$_x$S$_y$/C, moreover, the structure of the Pd@Pd$_x$S$_y$/C catalysts is almost independent of the sulphidation time.
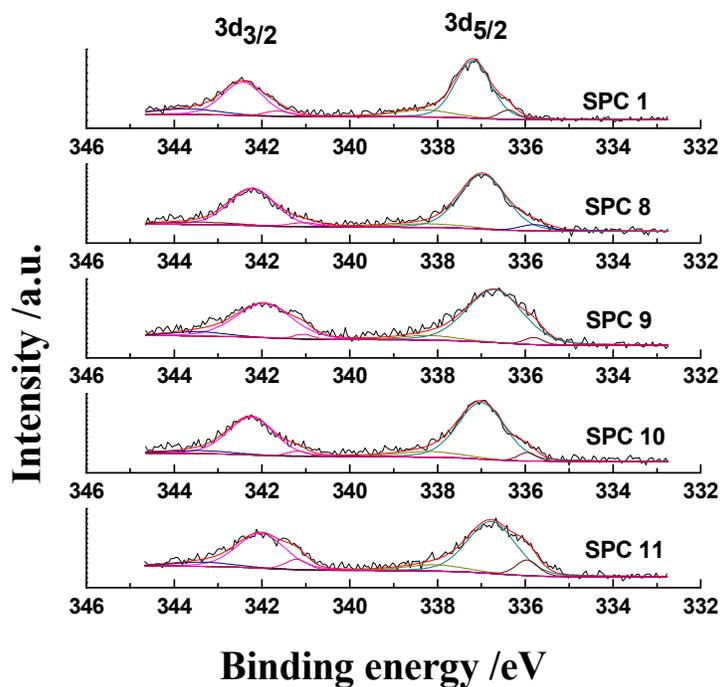
Fig. 6 Pd 3d XPS spectra of SPC 1, 8~11
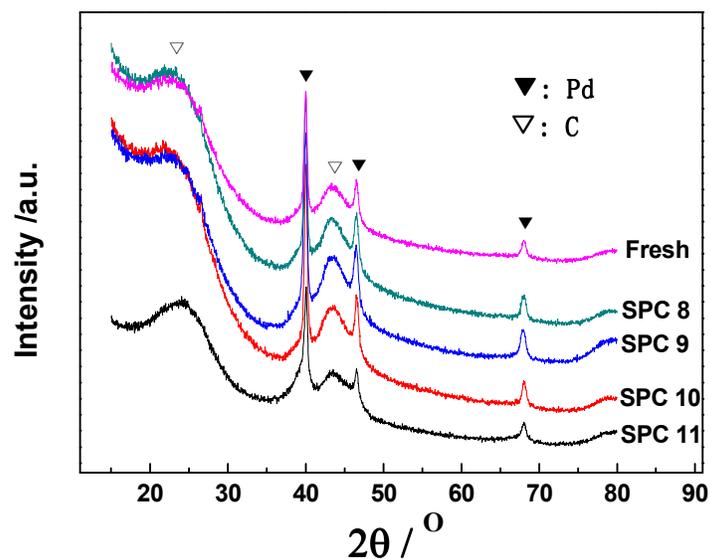
Fig. 7 XRD patterns of Pd/C and SPC 8~11

Recently, we have reported that the formation of palladium sulphides supported on the activated carbon was highly dependent on the composition of the sulphidation atmosphere[14].

Then we investigated the influence of the sulphidation atmosphere on the structure of the $Pd_xS_y@Pd/C$ catalysts. 10 wt% Pd/C was sulphidized at 30℃ for 3 hours under N_2/H_2S with the volume ratio as 9/1, and pure H_2S, and the atmosphere of H_2/H_2S with the volume ratio as 4/1, 49/1 respectively, and the resulting catalysts signed as SPC 8~11. The surface areas of these catalysts were similar to that of the fresh Pd/C. The content of S of SPC 11 sulphidized under the atmosphere of H_2/H_2S with the volume ratio as 49/1 was only 1.38 wt%, which was much lower than that of other sulphidized catalyst. This should be caused by the low content of H_2S in the atmosphere with the sulphidation time just for 3 hours to incomplete sulphidation. When the content of H_2S in the atmosphere was increased to 4/1, and even being used the pure H_2S, the content of S of the resulting catalyst increased negligible. The same result was also found during the sulphidation of Pd/C with N_2/H_2S with the volume ratio as 9/1. The CO chemisorption uptakes of SPC 8~11 were all 0 ml g^{-1}, which indicated all five catalysts including the incompletely sulphidized SPC 11 had no Pd^0 on their surface. This result was also confirmed by XPS spectra (Fig. 6 and Table 2) of theses catalysts for their fitted Pd $3d_{5/2}$ peaks only at 336.4, 337.1 and 338.2 eV meaning there were only high-valence palladium ions on the surface. Moreover, the area of peak at 336.4 eV of SPC 11 is much larger than that of other catalysts, which should be due to the incomplete sulphidation. The XRD patterns of SPC 8~11 (Fig. 7) are similar to that of the fresh Pd/C, and no peak of palladium sulphides is observed, suggesting there was only Pd metal crystal as the core. Therefore, Pd/C sulphidized under different atmospheres also caused to a core-shell catalyst —$Pd@Pd_xS_y/C$, and the influence of the sulphidation atmosphere was also not significant.

Table 2 The XPS data of Pd $3d_{5/2}$ of the sulphidized catalysts and fresh Pd/C

Catalyst	Peak 1		Peak 2		Peak 3	
	Binding energy / eV	Peak area / %	Binding energy / eV	Peak area / %	Binding energy / eV	Peak area / %
SPC 1	336.4	6.6	337.2	78.1	338.3	15.3
SPC 2	335.8	3.4	337.1	83.6	338.7	13.0
SPC 3	336.3	4.4	337.2	81.9	338.3	13.7
SPC 4	—	—	337.2	88.4	338.7	11.6

SPC 5	336.5	4.8	337.2	75.5	338.6	19.7
SPC 6	336.3	4.7	337.2	83.6	338.3	11.7
SPC 7	336.2	3.9	336.9	85.2	338.5	10.9
SPC 8	335.8	6.3	337.0	84.8	338.3	8.9
SPC 9	335.8	4.1	336.7	88.1	338.2	7.8
SPC 10	335.8	5.0	337.0	83.8	338.2	11.2
SPC 11	336.0	10.8	336.8	77.5	338.1	11.7
Fresh Pd/C	—	—	335.3	71.7	336.7	28.3
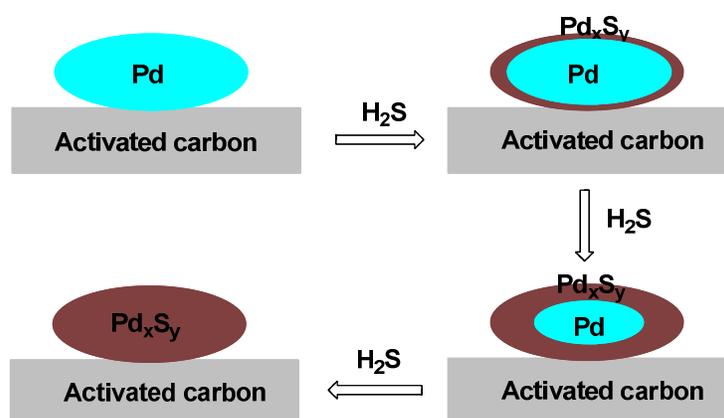
Fig. 8 The sulphidation process of Pd/C with H_2S

The sulphidation process of Pd/C with H_2S to $Pd@Pd_xS_y/C$ and Pd_xS_y/C is shown in Fig. 8. Firstly, H_2S was adsorbed on the surface of Pd atoms, and then H_2S was cracked and reacted with Pd to yield palladium sulphides, at the same time, H_2 was released. Therefore, the Pd atoms on the surface of Pd/C were firstly sulphidized to palladium sulphides during the sulphidation process. Considering the results as discussed above, we conjecture that it needed certain conditions such as high sulphidation temperature to sulphidize the Pd metal in the core of Pd particle to palladium sulphides. If the temperature was too low (for example, room temperature), using a simple method of increasing the sulphidation time or changing the sulphidation atmosphere was not able to transformed all of Pd atoms to palladium sulphides, and just sulphidized the Pd atoms on the surface to form a core-shell catalyst —$Pd@Pd_xS_y/C$. The reason should be that it became more difficult for H_2S to be adsorbed and cracked on palladium sulphides than on Pd metal, then the palladium atoms in the core of $Pd@Pd_xS_y$ were very difficult to obtain enough sulfur to generate

palladium sulphide. The thickness of Pd_xS_y on $Pd@Pd_xS_y/C$ was dependent on the sulphidation temperature. After raising the sulphidation temperature, H_2S was promoted to be cracked on the surface of catalyst, and then the shell of Pd_xS_y was thickened. When the sulphidation temperature was up to 150℃, it was enough to completely sulphidize the whole Pd particle to palladium sulphides. Therefore, SPC 4 and SPC 5 had been completely sulphidized to Pd_xS_y/C, and the other sulphidized catalysts should be formed a core-shell structure —$Pd@Pd_xS_y/C$.

3.2 Catalytic performances

The catalytic performances of $Pd@Pd_xS_y/C$, Pd_xS_y/C and Pd/C were tested in the reductive alkylation of MIBK and PADPD to DBPPD under the reaction conditions of 200℃ and 3 MPa for 4 hours (Scheme1), and the results are listed in Table 3. 100 % conversion of PADPD was obtained over Pd/C catalyst, but most of PADPD was converted to byproducts such as N-(1,3-dimethylbutyl)-N'-cyclohexane-p-phenylenediamine and aniline, and the selectivity of DBPPD was just only 39.5%. In contrast, with the exception of SPC 11, each of the sulphidized catalysts presented a much higher selectivity of DBPPD up to 96.7%. The low selectivity for SPC 11 in the reductive alkylation should be caused by its incomplete sulphidation under the atmosphere of H_2/H_2S with the volume ratio as 49/1 leading to its content of Pd_xS_y on the surface lower than that of other sulphidized catalysts. The sulphidized catalysts presented a lower activity than Pd/C in the reductive alkylation. However, $Pd@Pd_xS_y/C$ showed a higher activity than Pd_xS_y/C for the conversions of PADPD for SPC 4 and SPC 5 were just 93.2 % and 90.3 %, while the conversions of PADDP for the other sulphidized catalysts were all more than 98.3 %. In addition, we also observed such a phenomenon: the activity of the sulphidized catalyst was decreased with the raising of sulphidation temperature, meaning the more content of Pd_xS_y in the resulting catalyst led to a lower activity.

Table 3 Reductive alkylation over $Pd@Pd_xS_y/C$, Pd_xS_y/C and Pd/C catalysts

Catalyst	Conversion /%	Selectivity /%		
		DBPPD	Imine	Others
SPC 1	100	98.2	0.2	1.6
SPC 2	99.4	97.5	0.4	2.1
SPC 3	98.3	97.4	1.1	1.5

SPC 4	93.2	97.0	1.5	1.5
SPC 5	90.3	96.7	1.9	1.4
SPC 6	99.9	97.9	0.1	2.0
SPC 7	99.8	97.9	0.2	1.9
SPC 8	100	97.9	0.1	2.0
SPC 9	99.8	97.6	0.3	2.1
SPC 10	99.8	97.5	0.2	2.3
SPC 11	100	90.1	0	9.9
Pd/C	100	39.5	0	60.5

Researchers[29,30] had investigated catalytic hydrogenation mechanism of RuS_2 catalyst, they found H_2 adsorbed on the surface of RuS_2 as homolytic adsorption of dihydrogen and heterolytic dissociation on an Ru-S site leading to Ru-H and SH groups. And the activity was directly proportional to the amount of homolytic adsorption of dihydrogen which adsorbed on Ru centers in a low sulfur coordination. The mechanism of palladium sulphide catalyst should be similar to RuS_2 catalyst. $Pd@Pd_xS_y/C$ is a catalyst with a membrane of palladium sulphides as the shell, so it has high selectivity as common Pd_xS_y/C catalyst during the selective hydrogenation. And its core of palladium metal causes the Pd ions on the surface in a lower sulfur coordination than common Pd_xS_y/C catalyst, which improves the activity. Thereby, $Pd@Pd_xS_y/C$ is a hydrogenation catalyst with combination of high selectivity and good activity.

4 Conclusion

A simple and effective method to prepare a core-shell $Pd@Pd_xS_y/C$ catalyst by the sulphidation with H_2S is proposed. The sulphidation temperature played an important role in the structure of the sulphidized catalyst. The low sulphidation temperature caused a core-shell structured catalyst —$Pd@Pd_xS_y/C$. With raising the sulphidation temperature, the size of Pd^0 as the core decreased, and the thickness of palladium sulphides as the shell increased correspondingly. Moreover, when the sulphidation temperature is up to 150℃, the resulting catalyst has been transformed to complete palladium sulphides catalyst—Pd_xS_y/C. The structure of $Pd@Pd_xS_y/C$ sulphidized at 30℃ was independent of the sulphidation time and sulphidation

atmosphere. The sulphidized catalysts presented a much higher selectivity of DBPPD comparing with Pd/C during the reductive alkylation of PADPA and MIBK to DBPPD, and Pd@Pd$_x$S$_y$/C showed a little higher activity than Pd$_x$S$_y$/C. Pd@Pd$_x$S$_y$/C is a promising catalyst with combination of high selectivity and good activity in the selective hydrogenation reactions.

Acknowledgments

参考文献

[1] J. Lu, B. Fu, M. C. Kung, G. Xiao, J. W. Elam, H. H. Kung and P. C. Stair, *Sci.*, 2012, 335, 1205-1208.

[2] J. Zhao, T. Zhang, X. Di, J. Xu, J. Xu, F. Feng, J. Ni and X. Li, *RSC Adv.*, 2015, 5, 6925-6931.

[3] J.A. Anderson, A. Athawale, F.E. Imrie, F.-M. McKenna, A. McCue, D. Molyneux, K. Power, M. Shand and R.P.K. Wells, *J. Catal.*, 2010, 270, 9-15.

[4] T. Xu, Q. Zhang, D. Jiang, Q. Liang, C. Lu, J. Cen and X. Li, *RSC Adv.*, 2014, 4, 33347-33354.

[5] Y. Chen, X. Zhang and S. Mitra, *Chem. Commun.*, 2010, 46, 1652-1654.

[6] Q. Zhang, L. Ma, C. Lu, X. Xu, J. Lyu and X. Li, *React. Kinet. Mech. Catal.*, 2015, 114, 629-638.

[7] Y. Wang, X. Cui, Y. Deng and F. Shi, *RSC Adv*., 2014, 4, 2729-2732.

[8] C. Lian, H. Liu, C. Xiao, W. Yang, K. Zhang, Y. Liu and Y. Wang, *Chem. Commun.*, 2012, 48, 3124-3126.

[9] Q. Zhang, C. Su, J. Cen, F. Feng, L. Ma, C. Lu and X. Li, *Chin. J. Chem. Eng.*, 2014, 22, 1111-1116.

[10] A. J. McCue and J. A. Anderson, *Catal. Sci. Technol.*, 2014, 4, 272-294.

[11] F. S. Dovell and H. Greenfield, *J. Org. Chem.*, 1964, 29, 1265-1267.

[12] H. Greenfield and F. S. Dovell, *J. Org. Chem.*, 1966, 31, 3053-3053.

[13] Q. Zhang, J. Wu, C. Su, F. Feng, Q. Ding, Z. Yuan, H. Wang, L. Ma, C. Lu and X. Li, *Chin. Chem. Lett.*, 2012, 23, 1111-1114.

[14] W. Xu, J. Ni, Q. Zhang, F. Feng, Y. Xiang and X. Li, *J. Mater. Chem. A*, 2013, 1: 12811-12817.

[15] H. Greenfield and F. S. Dovell, *J. Org. Chem.*, 1967, 32: 3670-3671.

[16] F. S. Dovell and H. Greenfield, *J. Am. Chem. Soc.*, 1965, 87, 2767-2768.

[17] J. Frimmel and M. Zdrazil, *J. Catal.*, 1997, 167, 286-295.

[18] A. V. Mashkina and L. G. Sakhaltueva, *Kinet. Catal.*, 2002, 43, 107-114.

[19] A. V. Mashkina and A. A. Zirka, *Kinet. Catal.*, 2000, 41, 521-526.

[20] A.V. Mashkina and T.S. Sukhareva, *React. Kinet. Catal. Lett.*, 1999, 67, 103-110.

[21] Q. Zhang, W. Xu, X. Li, D. Jiang, Y. Xiang, J. Wang, J. Cen, S. Romano and J. Ni, *Appl. Catal., A: Gen.*, 2015, 497, 17-21.

[22] C. Sun, M.-J. Peltre, M. Briend, J. Blanchard, K. Fajerwerg, J.-M. Krafft, M. Breysse, M. Cattenot and M. Lacroix, *Appl. Catal., A: Gen.*, 2003, 245, 245-255.

[23] M. Breysse, M. Cattenot, V. Kougionas, J. C. Lavalley, F. Mauge, J. L. Portefaix and J. L. Zotin, *J. Catal.*, 1997, 168, 143-153.

[24] N. Hermann, M. Brorson and H. Topsøe, *Catal. Lett.*, 2000, 65, 169-174.

[25] J. A. D. L. Reyes, *Appl. Catal., A: Gen.*, 2007, 322, 106-112.

[26] Y. Aray and J. Rodríguez, *ChemPhysChem*, 2001, 2, 599-604.

[27] S. Eijsbouts, V. H. J. D Beer and R. Prins, *J. Catal.*, 1988, 109, 217-220.

[28] M. Lacroix, N. Boutarfa, C. Guillard, M. Vrinat and M. Breysse, *J. Catal.*, 1989, 120, 473-477.

[29] C. Dumonteil, M. Lacroix, C. Geantet, H. Jobic and M. Breyssey, *J. Catal.*, 1999, 187, 464-473.

[30] B. Moraweck, G. Bergeret, M. Cattenot, V. Kougionas, C. Geantet, J.-L. Portefaix, J. L. Zotin and M. Breysse, *J. Catal.*, 1997, 165, 45-56.

[31] R. G. Chaudhuri and S. Paria, *Chem. Rev.*, 2012, 112, 2373-2433.

[32] L. Lin, T. Zhang, X. Zhang, H. Liu, K. L. Yeung and J. Qiu, *Ind. Eng. Chem. Res.*, 2014, 53,

10906-10913.

[33] Y. Wei, Z. Zhao, J. Liu, S. Liu, C. Xu, A. Duan and G. Jiang, *J. Catal.*, 2014, 317, 62-74.

[34] X. Guo, Q. Fu, Y. Ning, M. Wei, M. Li, S. Zhang, Z. Jiang and X. Bao, *J. Am. Chem. Soc.*, 2012, 134, 12350-12353.

[35] S. Chen, Z. Wei, X. Qi, L. Dong, Y. Guo, L. Wan, Z. Shao and L Li, *J. Am. Chem. Soc.*, 2012, 134, 13252-13255.

[36] H. L. Merten and L. M. Baclawski, US Patent, 4900868, 1990.

[37] R. M. D'Sidocky and D. K. Parker, US Patent, 4463191, 1984.

[38] A. Zubkov, T. Fujino, N. Sato and K. Yamada, *J. Chem. Thermodyn.*, 1998, 30, 571-581.