Graphite encapsulated molybdenum carbide core/shell nanocomposite for highly selective conversion of guaiacol to phenolic compounds in methanol

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Abstract

Graphite encapsulated molybdenum carbides ($\text{Mo}_2\text{C}@\text{C}$) were synthesized *via* the hydrothermal carbonization of a solution of glucose and ammonium molybdate followed by temperature programmed reduction. Characterization and structural analyses revealed that the synthesized $\text{Mo}_2\text{C}@\text{C}$ nanoparticles had a molybdenum core/carbon shell structure with a particle size ranging from 50 nm to 100 nm and a core size range of 5-45 nm. The catalytic performance of the graphite encapsulated molybdenum carbides was evaluated on conversion of guaiacol to phenolic compounds in methanol. At 340°C under 2.8 MPa hydrogen pressure, a 76.3% guaiacol conversion was obtained with selectivities of 68.6% for phenol and 93.5% for phenolic compounds. Thus, $\text{Mo}_2\text{C}@\text{C}$ showed high selectivity for phenolic compounds in methanol.

Keywords: Encapsulation; Molybdenum carbides; Nanoparticles; Hydrothermal carbonization; Phenolic compounds

1. Introduction

Bio-oil produced from the pyrolysis of lignocellulosic biomass consists of a significant amount of phenolic compounds that were mainly derived from lignin [1]. The presence of these compounds with high oxygen contents leads to undesired properties for the bio-oil, such as low heating value, thermal instability, high acidity, high viscosity, and incomplete volatility. Therefore, hydrodeoxygenation is often considered as a competitive route for upgrading bio-oil to transportation fuels or desired fine chemicals [2-5]. Guaiacol is one of the major phenolic compounds in pyrolytic bio-oil. Guaiacol has the greater propensity for coking than other phenolic compounds [6], and the complete deoxygenation is challenging due to its oxygenated hydroxyl and methoxy functional groups. Guaiacol was thus chosen as a model compound for the current study on the catalytic conversion of bio-oil components to desired chemicals.

The most widely studied catalysts for guaiacol hydrogenation are noble metal catalysts (such as supported Ru [7], Re [8], Rh [9, 10], Pd [7, 10], and Pt [11-14]) and molybdenum-based sulfide catalysts (such as sulfided CoMo [15-17] and NiMo [9, 18]), and the reaction schemes proposed in literature are summarized in Fig. 1. Noble metals are commonly presented as highly active hydrogenation catalysts. Noble metal catalysts could fully hydrogenate the guaiacol benzene ring, and then demethoxylate and dehydroxylate oxygenates to form saturated deoxygenated hydrocarbons, *e.g.* cyclohexanol and cyclohexane. Hydrogenation of guaiacol over Mo-based sulfide catalysts starts with demethylation and demethoxylation, which is followed by the benzene ring saturation to form major products such as catechol, phenol, benzene, and cyclohexane. Both noble metals and sulfide catalysts have their own shortcomings. For

example, the use of noble metal produces completely saturated hydrocarbons, resulting in undesired H_2 consumption; while sulfide catalysts can be deactivated easily without sulfur addition [19]. Hydrogenation catalysts for phenolic compounds should have high activities towards selected products without causing saturation of the double bonds. Recently, molybdenum carbide catalysts showed promising performances in many reactions involving hydrogen, including isomerization [20], hydrogenation [21-23], hydrodesulfurization [24-26], hydrodenitrogenation [27], and deoxygenation [28, 29]. Simultaneously, they exhibited good activity and selectivity in C–O/C=O bond cleavage [28, 30, 31], leading to dominant products with unsaturated C=C bonds rather than alkanes [32-34]. Therefore, molybdenum carbide was chosen as an efficient catalyst for the selective conversion of guaiacol to phenolic compounds.

Figure 1. Reaction pathways for guaiacol hydrogenation over noble metal catalysts and Mo-based sulfide catalysts (according to ref. 3-14).

The conventional method for the synthesis of molybdenum carbides is temperature programmed reduction (TPRe) [35, 36]. The TPRe method involves gas-solid reactions between oxide or nitride precursors and a mixture of hydrogen and carbon-containing gas such as CH₄ [36-38], C₂H₄ [39], C₂H₆ [40], C₃H₈ [41, 42], C₄H₁₀ [43], etc. Unfortunately, high temperature during the TPRe process favors particle agglomeration, which makes it impossible to obtain a catalyst with nanoscale particles capable of potentially higher activities. In order to avoid the agglomeration of catalyst particles, one strategy is to prepare core/shell structure catalysts by using the hydrothermal carbonization (HTC) method. Hydrothermal carbonization has been employed successfully to synthesize carbonaceous spheres with controlled sizes from a solution of saccharides [44] and encapsulate metal nanoparticles in carbon nanospheres [45-49]. Through this method, homogeneously dispersed metal nanoparticles are encapsulated and isolated largely by permeable carbonaceous matrices that are generated in-situ [50].

Lignin is the only relevant renewable feedstock for aromatic compounds [51], but with low selectivity for specific compound [52]. In this study, carbon encapsulated molybdenum carbides were synthesized *via* a one-step hydrothermal carbonization followed by TPRe, and the catalyst activity was tested on conversion of guaiacol to phenolic compounds in methanol. The possible mechanism for the fabrication of this core/shell nanoparticle is proposed. The effects of temperature, pressure of hydrogen, and solvents on phenolic compounds production were investigated to elucidate the reaction pathway.

2. Experimental

2.1 Catalyst synthesis

Carbon encapsulated molybdenum carbides were prepared *via* hydrothermal carbonization of a solution of glucose and ammonium molybdate followed by temperature programmed reduction. A total of 0.0015 mol ammonium molybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O, 99%, Sigma-Aldrich) and 0.132 mol glucose (96%, Sigma-Aldrich) were dissolved in 600 mL deionized water. The solution was then treated hydrothermally in an autoclave at 180°C for 8 h. The resultant precipitate was washed thoroughly with deionized water and ethanol. The solid product was dried at 80°C. This hydrothermal carbonization derived compound was denoted as MoO₂@C, in which MoO₂ represents molybdenum oxide including molybdenum dioxide and molybdenum trioxide. The dried MoO₂@C was further carbonized in 20 vol% CH₄ and 80 vol% H₂ at a flow rate of 50 mL/min. The carburization temperature was raised to 300°C at a heating rate of 5 °C/min and then ramped to 900°C at a heating rate of 1 °C/min and kept at 900°C for 2 h. The resulting material was then cooled down to room temperature in argon and subsequently passivated under 1 vol% O₂ and 99 vol% N₂. The synthesized sample from the carbonization process was denoted as Mo₂C@C.

2.2 Catalyst characterization

X-ray powder diffraction (XRD) patterns were obtained using an Agilent Gemini X-ray Diffraction System (Santa Clara, CA, USA) operated at 40 kV and 40 mA with Cu-K α radiation. The morphology was examined on a JEOL JSM-7600F scanning electron microscope (SEM) (Tokyo, Japan) operated at 2 kV with energy-dispersive

X-ray spectroscopy (EDX). Prior to the imaging, the sample was sputter-coated with 5 nm of gold-palladium. High-resolution transmission electron microscopy (HRTEM) was performed with a JEOL 2010F operated at 200 kV (Tokyo, Japan). Fourier Transform Infrared (FT-IR) spectra were collected on a Varian 670 FT-IR spectrometer (Santa Clara, CA, USA) equipped with a single-bounce diamond attenuated total reflectance accessory. The amount of Mo in catalysts was measured using a Varian 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES) (Santa Clara, CA, USA). The content of carbon and hydrogen were determined using a Perkin-Elmer 2400 CHN/S analyzer (Waltham, MA, USA). Thermogravimetric analyses (TGA) were performed using a TA SDT Q600 thermogravimetric analyzer (New Castle, DE, USA), in which samples were heated to 900°C at a heating rate 10 °C/min in nitrogen. Surface area and porosity were analyzed by measuring physical nitrogen adsorption using a Micromeritics ASAP 2020 (Norcross, GA, USA).

2.3 Catalytic tests

The catalytic performance of Mo₂C@C was evaluated in a 75 ml Parr stainless steel batch autoclave (St. Moline, IL, USA). A mixture of 0.2 mL guaiacol (98%, Sigma-Aldrich), 10 mL solvent methanol, 0.05 mL hexadecane (99%, Sigma-Aldrich) as the internal standard, and 0.1 g catalyst was loaded into the reactor vessel. The vessel was evacuated by pressurization-depressurization with nitrogen to purge out any air and then charged with hydrogen to a certain pressure. A higher initial hydrogen pressure of 2.8 MPa was used to ensure excess hydrogen supplement. The hydrotreating process proceeded at a given temperature for 4 h. Table S1 gives the experimental conditions.

After the hydrotreatment, the liquid samples were analyzed by using an Agilent 7890A gas chromatograph (Santa Clara, CA, USA) equipped with a 5975C mass spectrometry (GC-MS), a flame ionization detector (FID), and a DB-1ms capillary column. Helium gas was used as carrier gas with a split ratio of 50:1. The GC oven was held at 35°C for 5 min, then ramped to 200°C at 5 °C/min.

The conversion was determined by averaging the data measured twice. The conversion efficiency and selectivity of guaiacol during hydrotreating were defined as:

$$\text{Guaiacol conversion (\%)} = \frac{N_{\text{guaiacol loaded}} - N_{\text{unconverted guaiacol}}}{N_{\text{guaiacol loaded}}} \times 100 \quad (1)$$

$$\text{Selectivity to specific product (\%)} = \frac{N_{\text{specific product}}}{N_{\text{guaiacol loaded}} - N_{\text{unconverted guaiacol}}} \times 100 \quad (2)$$

where “N” represents the moles of the reactants or products.

3. Results and discussion

3.1 Characterization of carbon encapsulated molybdenum oxide

Carbon encapsulated molybdenum oxide (MoO₂@C) was synthesized *via* hydrothermal carbonization of a solution of glucose and ammonium molybdate followed by drying at 80°C. XRD spectra showed that this synthesis method formed a poorly crystalline phase (Fig. 2a), which was assigned to hexagonal MoO₂ (PDF 50-0739) with 2θ peaks at 36.5° (1 0 0), 53.8° (1 0 2), 65.7° (1 1 0), and 41.4° (1 0 1). The carbonaceous phase in these samples was amorphous as no graphitic carbon peaks were observed. EDX analysis confirmed the exclusive existence of Mo, C, and O in the as-synthesized

MoO₂@C. The Mo element was evenly distributed in MoO₂@C (supplementary information Fig.S1). The elemental analysis shows that the contents of C and Mo were 51.0 and 15.9 wt%, respectively. The BET surface area and total pore volume of the catalyst were 37.6 m²/g and 0.25 cm³/g, respectively. Morphological images of MoO₂@C exhibited a porous structure composed of numerous attached carbonaceous spheres with sizes ranging from 50 to 100 nm (Fig. 3a-3b). In Fig. 4a, the HRTEM shows that the catalyst had a core-shell structure with the molybdenum oxide encapsulated inside carbonaceous spheres during the hydrothermal carbonization treatment. Molybdenum oxide cores had a size distribution between 5 and 56 nm and were dispersed homogeneously in a carbonaceous matrix. The lattice spacing of 0.25 and 0.17 nm (Fig. 4b) could be assigned to the (1 0 0) and (1 0 2) planes of MoO₂. Fig. 5a shows the surface functional groups on the carbonaceous shells identified by FT-IR spectroscopy. The bands around 1615 cm⁻¹ were attributed to in-plane C=C stretching vibration in an aromatic ring, and the band at 767 cm⁻¹ was for aromatic C-H out-of-plane bending vibrations [53]. These characteristic absorptions of aromatic rings confirmed the aromatization of glucose during the hydrothermal treatment. The band at 1698 cm⁻¹ was attributed to C=O vibration of aldehydes, ketones, carboxylic acids, or esters [48]. The broad band centered around 3400 cm⁻¹ corresponded to O-H stretching vibration and 1292 cm⁻¹ was from C-OH bending vibration, which implied the existence of hydroxyl groups. The bands at 2975 and 2934 cm⁻¹ were stretching vibrations of aliphatic C-H, which showed that the carbonaceous shell also possessed an aliphatic structure. In summary, the dehydration and subsequent aromatization of glucose during hydrothermal

treatment resulted in carbonaceous hydrophilic shells with abundant –OH and C=O groups.

3.2 Characterization of graphite encapsulated molybdenum carbide

Graphite encapsulated molybdenum carbide ($\text{Mo}_2\text{C}@\text{C}$) was synthesized through the process of the temperature programmed reduction at 900°C under 20% $\text{CH}_4/80\% \text{H}_2$. TPre treatment resulted in the formation of hexagonal $\beta\text{-Mo}_2\text{C}$ (PDF 35-0787) with 2 θ peaks at $\sim 39.4^\circ$ (1 0 1), 38.0° (0 0 2), 52.1° (1 0 2), 34.4° (1 0 0), 61.7° (1 1 0), 69.6° (1 0 3), and 74.7° (1 1 2) (Fig. 2b). Besides the peaks of $\beta\text{-Mo}_2\text{C}$, the diffraction peaks at 26.1° (0 0 2), 42.7° (1 0 0), and 44.4° (1 0 1) confirmed the formation of graphite (PDF 41-1487). Clair et al. [54] and Hanif et al. [40] also observed a similar phenomenon that graphite was formed from methane at a temperature higher than 700°C . The TPre treatment did not significantly change the morphology of $\text{Mo}_2\text{C}@\text{C}$ and the size of carbonaceous shells for $\text{Mo}_2\text{C}@\text{C}$ that was still in the range of 50-100 nm as shown in Fig. 3d. EDX analysis showed that Mo and C were evenly distributed in the sample (supplementary information Fig.S2). The HRTEM images indicated that the size of the molybdenum carbide cores was between 32 and 45 nm in Fig. 4c and between 5-15 nm in Fig. 4d, and the carbonaceous matrix effectively inhibited the agglomeration of the molybdenum nanoparticles. The lattice spacings of 0.23, 0.24, and 0.26 nm could be assigned to the (1 0 1), (0 0 2), and (1 0 0) planes of Mo_2C , respectively, while the lattice spacing of 0.34 nm could be assigned to the (0 0 2) plane of graphite. A multilayer graphite was found to be formed on the surface of molybdenum carbide particles in Fig. 4d. The BET surface area and the total pore volume of the synthesized material increased

significantly from 37.6 m²/g to 177.0 m²/g and 0.25 cm³/g to 0.34 cm³/g, respectively, while the carbon content increased from 51.0 wt% to 55.7 wt% and the oxygen content decreased from 28.3 wt% to 12.7 wt% in Table 1. This core-shell structured porous material with large pore sizes acts as a physical barrier, but still allow reactants reach reactive sites and products flow freely through the pores, which is in agreement with the results reported in the literature [50]. FT-IR spectra of Mo₂C@C indicated that most of functional groups on the carbon surface of MoO₂@C were removed during the heat treatment. The hydroxyl bands at 3400 cm⁻¹ and 1292 cm⁻¹ were not observed, indicating that dehydration occurred during carbonization. The disappearance of C=O at 1698 cm⁻¹ was associated with the decomposition of carboxylic acids. The disappearance of the peak at 767 cm⁻¹ and 1615 cm⁻¹ was due to internal structural reorganizations of aromatic structures and the further carbonization of the shell during the heat treatment. Therefore, almost all the oxygen-containing functional groups on the surface were removed at 900°C. This process may also have resulted in the development of mesopores in the carbonaceous matrix of Mo₂C@C as evidenced by the significant increase in BET surface area. Newly developed pores would increase not only the surface area but also the penetration of reactive species for catalytic reactions.

188

189 **Figure 2.** XRD patterns of (a) $\text{MoO}_2@\text{C}$, and (b) $\text{Mo}_2\text{C}@\text{C}$.

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191 **Figure 3.** SEM images of (a, b) MoO₂@C, and (c, d) Mo₂C@C.

Figure 4. HRTEM images of (a, b) MoO₂@C, and (c, d) Mo₂C@C.

Figure 5. FT-IR spectra of (a) MoO₂@C, and (b) Mo₂C@C.

Table 1. Textural parameters of materials (on dry basis).

Sample	C ^a (wt%)	H ^a (wt%)	Mo ^b (wt%)	BET ^c (m ² g ⁻¹)	Pore Diameter ^d (nm)	Pore Volume ^e (cm ³ g ⁻¹)
MoO ₂ @C	51.0	4.8	15.9	37.6	40.1	0.25
Mo ₂ C@C	55.7	4.7	26.9	177.0	31.4	0.34

^a Measured with the Perkin-Elmer 2400 CHN/S analyzer.

^b Measured with ICP

^c Brunauer-Emmet-Teller (BET) surface area.

^d Pore diameter calculated by the Barrett-Joyner-Halenda (BJH) method using adsorption branches.

^e Total pore volume calculated from the amount of nitrogen adsorbed at a relative pressure of 0.995.

3.3 Mechanism for the formation of carbon encapsulated molybdenum nanoparticle

The mechanism of formation of carbon nanospheres prepared under hydrothermal conditions in the temperature range of 160-200 °C has been well summarized in studies [55-58]. However, the mechanism for the formation of metal oxide within carbonaceous spheres by one pot method is still under investigation. The interplay between the metal oxide and carbonaceous spheres and the precipitation kinetics of both phases are crucial to carbon encapsulated metal oxide formation [47]. Fig. 6 is a schematic illustration explaining the possible formation process of molybdenum nanoparticles encapsulated in carbon by in situ hydrothermal reduction of molybdenum ions with glucose based on our characterization results. At the initial stage, glucose is hydrolyzed to small carbonaceous colloids. Meanwhile, molybdenum is reduced from the oxidation state Mo^{6+} in $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ to Mo^{4+} in MoO_2 due to the ability of glucose degradation products to act as reductants [59]. The molybdenum nanoparticles combine with carbonaceous colloids through Coulombic interactions until condensing from water [45]. The further growth of carbon spheres *via* intermolecular dehydration of the surface functional groups follows the LaMer model [60]. Because homogeneous nucleation requires higher activation energy than heterogeneous nucleation [61], pure carbon nanospheres form at much lower rate than carbon encapsulated molybdenum oxide nanoparticles. All carbon encapsulated molybdenum oxide nanoparticles and pure carbon nanospheres interconnect randomly in three dimensions to form a hydrophilic microcomposite. During TPRE, molybdenum oxide reacts with methane and hydrogen to form hexagonal molybdenum carbide with a preserved structure, while graphite is formed on the surface of molybdenum carbide particles from methane.

Figure 6. Schematic illustration for possible formation process for carbon encapsulated molybdenum particles.

(a) An aqueous solution of glucose and ammonium molybdate. (b) Molybdenum oxide (green dots) particles nucleate during HTC. (c) Molybdenum oxides (green core) are encapsulated in carbon shell (black shell) and carbonaceous colloids (black dots) formed. (d and e) The carbon encapsulated molybdenum oxides and carbon nanospheres randomly interconnect together to form a microcomposite. (f) Molybdenum carbides were synthesized by TPre.

3.4 Catalytic performance of carbon encapsulated molybdenum carbide

The product profiles can be found in Table S2 of the supporting information. For comparison, the guaiacol conversion efficiencies in the absence of the catalyst at 340°C were 28.4% and 13.6% for the experiments with and without 2.8 MPa H₂, respectively. Fig. 7 shows the product yields obtained at reaction temperatures of 300°C, 320°C, and 340°C under a H₂ pressure of 2.8 MPa for 4 h. The increase of temperature from 300°C to 340°C increased the conversion efficiency of guaiacol from 32.5% to 76.3%, and the selectivities of phenol and phenolic compounds from 66.1% to 68.6% and 81.2% to 93.5%, respectively. The selectivity of catechol that is a reaction intermediate decreased

245 with increasing temperature, which means that more catechol was converted to phenol at
 246 a higher temperature. After the reaction, H₂, CH₄, and CO₂ were detected in the gas
 247 phase.

248
 249 **Figure 7.** Conversion of guaiacol, and the selectivity to phenol, cresols, xylenols,
 250 veratrole, and catechol over Mo₂C@C at temperatures of 300°C, 320°C, and 340°C.

251 As shown in Fig. 8, when the initial H₂ pressure was increased from 0.0 to 2.8 MPa,
 252 the conversion efficiency of guaiacol increased from 50.9% to 76.3% and the phenolic
 253 selectivity increased from 67.0 to 93.5%. In the absence of initial H₂, methanol also
 254 served as a hydrogen donor. However, the selectivity towards phenol without H₂ was
 255 only half of that of the process with H₂. High hydrogen pressures increased the selectivity
 256 for phenolic compounds. Compared with the similar research [34], under the same
 257 reaction condition (in methanol, at 340°C, under 0 MPa H₂, for 4 h), the main products

from guaiacol conversion between two studies were the same. But the selectivity in this study is higher than that in the previous study.

Figure 8. Conversion of guaiacol, and the selectivity to phenol, cresols, xylenols, veratrole, and catechol over Mo₂C@C at an initial H₂ pressure of 0, 1.4, and 2.8 MPa.

The reusability of the catalyst was evaluated at 340°C for 4 h in the methanol solvent for three cycles. A standard reaction was first performed on a freshly prepared Mo₂C@C catalyst. After each cycle, the spent catalyst was retrieved, dried at 105°C overnight, and reused directly in the next run without reactivation. As shown in Fig. 9, the conversion of guaiacol decreased slightly from 76.3% for the first cycle to 62.9% for the third cycle, while the selectivity towards phenol decreased from 68.6% to 64.1% and phenolic compounds decreased from 93.5% to 90.8%.

Figure 9. Conversion of guaiacol, and the selectivity to phenol, cresols, xylenols, veratrole, and catechol over recycled $\text{Mo}_2\text{C}@\text{C}$.

3.5 Reaction pathway for phenolic compounds production over $\text{Mo}_2\text{C}@\text{C}$

The product profiles showed that the selectivities towards phenol, cresols (o-Cresol, and m-Cresol), and xylenols (2, 3-dimethylphenol and 2, 6-dimethylphenol) were high. Trace amounts of veratrole, catechol, and anisole were also measured, but other transalkylation products were not present due to their selectivities less than 1%. Less than 6% selectivity of veratrole suggested that transalkylation was insignificant, which is in agreement with the results reported in the literature [11, 62]. Neither completely deoxygenated products (such as benzene and toluene) nor ring hydrogenation products

(such as cyclohexane, cyclohexene, cyclohexanone, etc.) were detected. High selectivity for phenol formation implied that the removal of the methoxy group was more favorable than the removal of the hydroxyl group of guaiacol in the alcohol solution. As no benzene was observed, the removal of the hydroxyl group to form benzene is more difficult and is not favorable when guaiacol is still present [33]. Based on the experimental results, possible reaction pathways for phenolic compounds production over Mo₂C@C are summarized in Fig. 10. Methyl substituents of cresols and xylenols were mainly formed through methyl-substitution from solvent rather than through transalkylation of guaiacol [63]. The comparative test was carried under the same condition in ethanol, and the main products were phenol, ethylphenols, and diethylphenols. This test proved that alkyl groups on cresols and xylenols were mainly from solvent *via* alky-substitution reactions. It is widely accepted that the selectivity of carbon supported catalysts is high, though their hydrogenation activities are lower than that of catalysts on acidic supports [15, 64]. Therefore, both the active metal Mo and the nature of the carbon support affected catalytic activities and determined the reaction pathway.

Figure 10. Proposed reaction pathway for guaiacol conversion over Mo₂C@C catalyst in methanol.

4. Conclusions

The fabrication of highly dispersed molybdenum oxide nanoparticles embedded in carbon nanospheres was achieved by one-pot hydrothermal carbonization of an inexpensive precursor solution at a mild temperature. After TPre, graphite encapsulated molybdenum carbide Mo₂C@C was formed, which was composed of aggregates of

molybdenum core and carbon shell nanoparticles. The sizes of Mo₂C@C particles and molybdenum cores were 50-100 nm and 5-45 nm, respectively.

Mo₂C@C catalyst showed high selectivity to phenolic compounds in an alcohol solution, which exemplified the confining effect of the carbonaceous matrix to inhibit the aggregation of molybdenum nanoparticles during both the activation and reaction processes at a high temperature. The highest conversion efficiency and highest selectivities towards phenol and phenolics were obtained at 340°C under 2.8 MPa hydrogen pressure. Both demethoxylation and consecutive demethylation followed by a dehydroxylation proceeded concurrently to form phenol. Substitution of methyl or ethyl groups in phenol were from solvent methanol or ethanol. Moreover, no significant loss of catalytic activity even after three recycle times demonstrated that the core-shell structure of catalysts effectively offered the resistance to deactivation and sintering.

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