

Selective Acetylene Hydrogenation over **Core-Shell Magnetic Pd-Supported** Catalysts in a Magnetically Stabilized Bed

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A novel magnetic microspherical catalyst support with enough mechanical strength was prepared through coating Al_2O_3 on a magnetic core of NiFe₂O₄ spinel ferrite using the oil drop method to synthesize magnetic Pd-supported catalyst for acetylene hydrogenation reaction. The synthesized core-shell composite Pd/Al₂O₃ catalyst shows high surface area and pore volume as well as sufficient saturated magnetization property, characterized by powder X-ray diffraction, low-temperature N2 adsorptiondesorption analysis, and magnetic measurements. Catalytic performance of this magnetic Pd/Al₂O₃ catalyst was measured for acetylene hydrogenation reaction in a magnetically stabilized bed (MSB) reactor under different operation conditions. Under the optimal conditions of 353 K, 1.5 MPa and a gas hourly space velocity of 12,000 h^{-1} , C_2H_2 conversion and C_2H_4 selectivity approximated 100% and 84%, respectively, over this magnetic Pd/Al₂O₃ catalyst in the MSB reactor, as a control over the commercial catalyst for hydrogenation reaction C_2H_2 conversion and C_2H_4 selectivity was near 37 and 64% under the similar conditions. Significant improvement of acetylene hydrogenation processes over this novel magnetic catalyst enlightens us a promising route to explore process intensification techniques through MSB. © 2008 American Institute of Chemical Engineers AIChE J, 54: 1358-1364, 2008

Keywords: magnetically stabilized bed, magnetic core-shell catalyst, selective acetylene hydrogenation, process intensification

Introduction

Magnetically stabilized bed (MSB) has the advantage of united characteristics of packed bed with conventional fluidized bed, for example, efficient interphase mass transfer properties, low pressure drop, high productivity, and the absence of particle clogging, 1-5 which attracts increasing interests in the field of petroleum chemical processes involving fine particles of catalyst besides the prior biotechnology processes. Using a magnetic amorphous Ni alloy catalyst, recently, a novel MSB reactor was proved to intensify successfully the purification process of caprolactam^{6,7} through effectively enhancing hydrogenation efficiency and reducing reactor volume and reaction temperature. However, the industrial application of MSB is restricted by the lack of appropriate magnetic catalysts for related reactions.

Selective catalytic hydrogenation of acetylene impurity $(\sim 0.3-3 \text{ vol }\%)$ has been the target of ethylene polymerization processes. It is known that acetylene hydrogenation

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produces ethylene, ethane, and C₄⁺ oligomers, which are the precursors to "green oil" often found in industrial processes. 8,9 This "green oil" tends to adhere to the catalyst surface and leads to a gradual decline in the activity and selectivity of the hydrogenation process, which results in shortened catalyst lifetime and necessitates more frequent regeneration of the catalyst, thereby leading to increased operating costs. In addition, mass and heat transfer property was the major factor that affects the selectivity for acetylene hydrogenation to a significant extent. Because the reaction order of acetylene hydrogenation is higher than that of ethylene hydrogenation, 9-11 restricted mass transfer adversely affects the selectivity of acetylene hydrogenation reaction. To maximize the mass transfer coefficient, different catalyst support with novel shapes involving trifoliate or gear, 12,13 rather than the traditional spherical or columnar shape, have been employed; however, little improvement on the reaction selectivity was achieved due to the inherent disadvantages of fixed bed reactors. Therefore, it is necessary to explore novel reactors to make acetylene hydrogenation process intensified.

Supported palladium catalysts with alumina, silicon dioxide, or honeycomb cordierite, are commonly used for the hydrogenation of highly unsaturated hydrocarbons such as alkynes and/or diolefins. 14-17 Promoters such as Group IB elements, 18-20 alkali, or alkaline earth metal elements 21,22 are added to enhance the hydrogenation selectivity of the catalyst and reduce the possibility of catalyst deactivation resulted from green oil formation. Although these supported palladium catalysts themselves are not magnetic, the core–shell structure makes it possible to produce composite catalysts with a magnetic core. For instance, TiO₂ coated on Zn_{0.35}Ni_{0.65}Fe₂O₄ spinel-like ferrite cores was reported as an active catalyst for the photooxidation of oxalate, 23 which enlighten us the probability to incorporate composite catalysts with a magnetic core in an MSB.

In this article, the porous magnetic microspherical particles of NiFe₂O₄-Al₂O₃ with the core-shell structure were synthesized using the oil column method. This novel magnetic support was used to prepare Pd/NiFe₂O₄-Al₂O₃ catalysts, which were then employed in the selective hydrogenation of acetylene in an MSB reactor. The structure and properties of the catalyst were characterized by using X-ray powder diffraction (XRD), low-temperature N₂ adsorptiondesorption analysis and magnetic measurements. Effects of various operating parameters on acetylene hydrogenation were investigated as well as the service life of this magnetic Pd-supported catalyst. It is indicated that the MSB reactor incorporated with this magnetic core-shell Pd catalyst can significantly intensify the selective hydrogenation process of acetylene, which provides a promising route to explore novel process intensification technique using MSB reactors.

Experimental

Catalyst preparation

The magnetic core catalyst support was prepared by the oil drop method. Typically, the NiFe₂O₄ spinel particles were synthesized by traditional titration coprecipitation

method. The metal salts solution of Fe(NO₃)₃·9H₂O, FeCl₂·4H₂O, and Ni(NO₃)₂·6H₂O was prepared in 100 ml deionized water. Then the metal salts solution was added to 100 ml solutions contained 2 M NaOH and 0.125 M Na₂CO₃ in flasks under vigorous stirring. When the addition was complete, the mixtures were treated hydrothermally at 333 K for 24 h. After cooling to room temperature, the solid particles were collected by filtration and washed with deionized water subsequently, and then dried at 373 K for 10 h. Finally, the solid particles were calcined at 1373 K for 2 h, and the NiFe₂O₄ spinel particles were obtained after cooling to room temperature.

The NiFe₂O₄ spinel magnetic particles were crushed to powder form (1-3 μ m) and coated with a layer of SiO₂ by heterogeneous deposition method. NiFe2O4 spinel magnetic core was dispersed in deionized water with ultrasonic treatment for 30 min. The pH of the suspension was raised to 8-10 by adding dilute NaOH solution. The suspension was transferred into a 500-ml three-necked flask with vigorous mechanical stirring and heated to 85-95°C. Ten milliliters of 0.1 M Na₂SiO₃ and dilute HCl solutions were simultaneously added to the suspension. The pH of the suspension was maintained at 8-10 by controlling the titrating speed of the HCl, while the titrating speed of Na₂SiO₃ was kept constant. After titration, the suspension was aged for 1 h and cooled to room temperature. Then, the particles were washed five times with deionized water and absolute ethanol, dried at 80°C for 2 h, and calcined at 873 K for 4 h.

The NiFe₂O₄/SiO₂ magnetic-core particles were dispersed in an alumina sol solution containing hexamethylenetetramine, and the mixture was finally sprayed into hot oil. Then resulting gel-like spherical aluminum hydroxide particles were aged at 383–453 K for 5–10 h, washed with hot water, and dried at 393 K for 12 h, and subsequently calcined in air at 1373 K for 4 h. Spherical magnetic core–shell NiFe₂O₄-Al₂O₃ catalyst support particles were obtained with a diameter range of 50–450 μ m.

The magnetic Pd/NiFe₂O₄-Al₂O₃ catalyst was prepared by incipient wetness of the above support with H_2 PdCl₄ solution for 30–90 min, followed by drying at 373 K for 8 h and calcination in air at 723 K for 4 h. The procedure for Pd impregnation of the magnetic catalysts was the same as that used in the preparation of the commercial catalyst, and the loading was about 0.018 wt %. Before activity assessment, the catalyst was reduced in H_2 flow (30 ml min⁻¹) at 423 K for 2 h.

Characterization

Powder XRD data were collected on a Philips X'Pert Pro powder X-ray diffractometer under the following conditions: 40 kV, 30 mA, Cu K α radiation, with a scanning rate of 4° min⁻¹ in the range of $2\theta = 5-70^{\circ}$.

Low-temperature N_2 adsorption—desorption experiments were carried out using an accelerated surface area and porosimetry 2010 system. The samples were degassed at 343 K for 8 h. The specific surface area was calculated using the BET method based on the N_2 adsorption isotherm.

The magnetic properties of the samples were measured at room temperature using a JDM-13 vibrating sample magnetometer, manufactured by Jilin University.

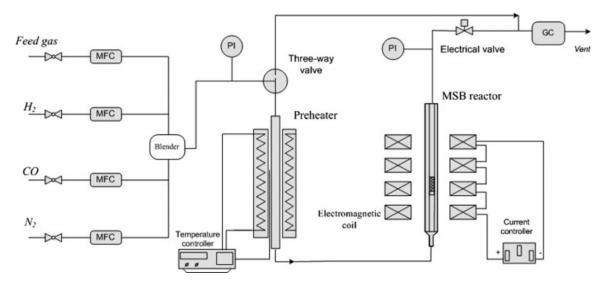


Figure 1. Diagram of the magnetically stabilized bed experimental facility.

Reaction performance and analytical procedures

The performance of magnetic Pd/NiFe₂O₄-Al₂O₃ catalysts was studied in a MSB experimental facility as shown in Figure 1. Its key section is the MSB reactor, which is encircled by four similar DC-powered copper wire coils. These coils are arranged at a fixed distance and can generate an axial and homogeneous magnetic field of up to 60 kA m⁻¹. The magnetic field intensity can be controlled by adjusting the current in these coils. To keep the magnetic field steady, the MSB reactor is not equipped with a heating unit, and the gas mixture is heated by a preheater with the temperature monitored by a K-type thermocouple inserted in the middle of the preheater.

As a control, the performance of a commercial catalyst was measured for acetylene hydrogenation reaction in a conventional quartz tubular reactor under the same operation conditions with those for magnetic catalysts. Size distributions of the commercial catalyst particles were kept similarly to those of synthesized magnetic catalysts. To make these experimental data comparable to those obtained in the MSB, the diameter of the conventional tubular reactor was maintained as the same as that of MSB reactor with the same amount of loaded catalyst weight.

A mixed gas feed with similar composition to that of the feed gas used in an industrial ethylene processing plant was used in the experiments as shown in Table 1. The reactant gas and the reaction effluent were analyzed on line by a Shimadzu GC-9A gas chromatograph with a hydrogen-air flame ionization detector.

The formulae for calculating C_2H_2 conversion $(X_{C_2H_2})$ and C_2H_4 selectivity $(S_{C_2H_4})$ are defined as follows:

$$X_{\text{C}_2\text{H}_2} = \frac{x_{\text{C}_2\text{H}_2}(\text{inlet}) - x_{\text{C}_2\text{H}_2}(\text{outlet})}{x_{\text{C}_2\text{H}_2}(\text{inlet})}$$

$$S_{\rm C_2H_4} = \frac{x_{\rm C_2H_4}({\rm outlet}) - x_{\rm C_2H_4}({\rm inlet})}{x_{\rm C_2H_2}({\rm inlet}) - x_{\rm C_2H_2}({\rm outlet})}$$

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where x is the molar fraction of the corresponding compound indicated by the subscript.

Results and Discussion

Characterization of Pd-supported magnetic core-shell catalyst

Figure 2 depicts the XRD pattern of the core-shell magnetic catalyst support calcinated at 1373 K containing 30 wt % magnetic NiFe₂O₄ spinel. The pattern shows the characteristic diffraction peaks of an NiFe₂O₄ spinel phase $(2\theta =$ 18.45°, 30.34°, 35.74°, 37.33°, 43.40°, 47.67°, 53.89°, 57.46° , 63.09° , 66.49°) and the monoclinic form of alumina θ -Al₂O₃ (2 θ = 19.48°, 31.30°, 32.80°, 36.73°, 38.94°, 44.89° , 50.63° , 59.83° , 67.45°). It is indicated that the spinel and alumina phases do not integrate with each other during the high temperature calcination and that nonmagnetic phases such as NiAl₂O₄ spinel are not formed. It is worthwhile to

Table 1. Compositions of the Feed Gas

Component	Content (%)	
H_2	17.35	
$\overline{\mathrm{CH}_{4}}$	33.77	
C_2H_6	8.12	
C_2H_4	40.30	
C_3H_8	0.40	
Δ -C ₃ ⁰	0.006	
${ m C_3H_6} \ i{ m -C_4^0} \ n{ m -C_4^0}$	10.85	
i - C_4^0	0.066	
n - \vec{C}^0_4	0.187	
PD	0.248	
C_2H_2	0.885	
$p-C_4^{=}$	0.171	
$n-C_4$	0.48	
i-C ₄ ⁼	0.788	
c - C_4	0.104	
C_5^0	0.067	
$i-C_{4}^{=}$ $c-C_{4}^{=}$ C_{5}^{0} $1,3-C_{4}^{=}$	3.089	
MA	0.383	
$C_5^=$	0.070	

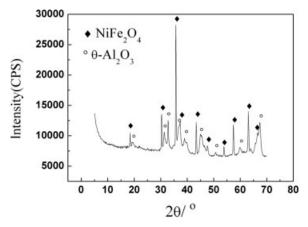
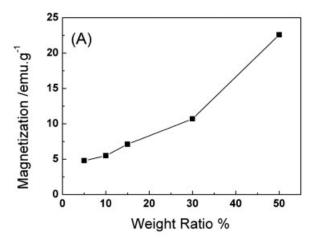


Figure 2. XRD pattern of the magnetic core-shell NiFe₂O₄-Al₂O₃ catalyst support calcined at 1373 K.

note that the characteristic diffraction peaks of α -Al₂O₃ were not detected in the catalyst supports, although α -Al₂O₃ is generally formed by calcination of hydrated alumina precursors at 1373 K. Thus, it is suggested that the presence of the NiFe₂O₄ spinel phase can restrict the transformation from θ -Al₂O₃ to α -Al₂O₃. As a control, a commercial catalyst (denoted as catalyst A in the context) that is commonly used in the front-end hydrogenation reaction was also studied by X-ray diffraction. The results showed that the support of the commercial catalyst is mainly composed of rhombohedral α -Al₂O₃ (as shown in Figure S1 in the Supporting Information).

Table 2 lists the surface area, pore volume, and average pore size of the magnetic core—shell NiFe₂O₄-Al₂O₃ catalyst calcined at different temperatures together with the related data for catalyst A. It is shown that the surface area and pore volume of the magnetic alumina catalyst decreased with increasing calcination temperature, whereas the average pore size increased. Previous work⁹ indicated that low surface areas and large pore volumes enhanced the selectivity of the catalyst and extended the catalyst life; hence, the magnetic core—shell support calcined at 1373 K was chosen to prepare hydrogenation catalyst. It should be noted that the surface area and pore volume of the magnetic alumina support calcined at 1373 K are significantly larger than the corresponding values for catalyst A, whilst the average pore sizes of these two materials are comparable.

Figure 3A shows the specific saturated magnetization at room temperature of the core-shell magnetic alumina supports with different contents of NiFe₂O₄ calcinated at 1373 K. As expected, the specific saturation magnetization of the



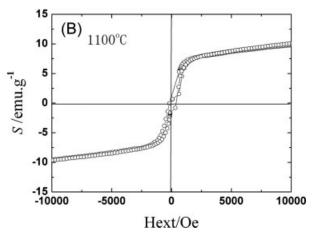


Figure 3. A: Specific saturated magnetization of magnetic core–shell NiFe₂O₄-Al₂O₃ catalyst supports with different contents of NiFe₂O₄ after calcination at 1373 K. B: Hysteresis loop for the magnetic core–shell NiFe₂O₄-Al₂O₃ catalyst support with NiFe₂O₄ content of 30 wt %.

material increased with increasing loading of the magnetic core. When the magnetic core content in the alumina support exceeded 30 wt %, however, the mechanical strength of the support decreased markedly and the support could be easily crushed. To meet the requirements of both magnetic performance and mechanical strength, the optimum content of the magnetic core is selected as 30 wt %. The hysteresis loop of the magnetic alumina support with this optimal composition (Figure 3B) shows that the saturation magnetization of the material reaches a value of 11.2 emu g⁻¹, which is suitable for the application in an MSB reactor.

Table 2. Textural Properties of the Magnetic Core-Shell NiFe₂O₄-Al₂O₃ Catalyst Supports and Catalyst A

Catalyst or Support	Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Average Pore Size (nm)
Magnetic Al ₂ O ₃ support calcined at 973 K	158	0.93	23.49
Magnetic Al ₂ O ₃ support calcined at 1173 K	101	0.83	32.88
Magnetic Al ₂ O ₃ support calcined at 1273 K	72	0.65	31.57
Magnetic Al ₂ O ₃ support calcined at 1373 K	46	0.39	35.61
Catalyst A	23	0.19	36.78

Effects of operation conditions in the MSB reactor on hydrogenation reaction

Operation conditions of the MSB reactor were determined according to the cold model experiments in a gas-solid MSB reactor, which classified three possible operating regimes dependent on the reaction parameters including the magnetic field intensity, the catalyst particle size, and the gas flow velocity. Three operating regimes comprise the particulate regime, the chain regime, and the magnetically condensed regime, among which the chain regime is superior to provide good heat and mass transfer property and low pressure drop even when the particles are very small.^{24,25} Therefore, during the catalytic activity assessment, the MSB reactor was maintained under the chain regime by adjusting the magnetic field intensity as necessary.

To evaluate the performance of the magnetic core-shell Pd/NiFe₂O₄-Al₂O₃ catalyst, a series of tests were carried out in the experimental MSB facility under operation conditions ranged within a GHSV of 1.0×10^4 to 3.0×10^5 h⁻¹, a reaction temperature of 313-373 K, a system pressure of 0.1-3.0 MPa, and a magnetic field intensity of 0-40 kA m⁻¹.

Figure 4A shows the variation in C₂H₂ conversion and C₂H₄ selectivity as a function of the temperature for acetylene hydrogenation reaction in the MSB reactor. The results show that the performance of the magnetic core Pd-supported catalyst depends strongly on the reaction temperature. The C₂H₂ conversion increases with temperature, whilst the C₂H₄ selectivity decreases. C₂H₂ almost totally conversed at the temperature higher than 343 K, while the C₂H₄ selectivity approximates to 100% in the temperature range of 313-343 K but decreases sharply above 343 K. This is consistent with other work in the literature, 26 which showed that the rate of C₂H₄ hydrogenation was affected by the amount of C₂H₂ adsorbed on the catalyst surface. The rate of C₂H₄ hydrogenation is relatively low and the C2H4 selectivity relatively high in the presence of small amount of C₂H₂, whereas when C₂H₂ is no longer present, the rate of C₂H₄ hydrogenation is high and the C₂H₄ selectivity therefore decreases sharply.

Figure 4B indicates the effect of system pressure on the catalyst performance. Both C₂H₂ concentration at the outlet and C₂H₄ selectivity decrease with increasing system pressure. According to the kinetics equations for C₂H₄ and C₂H₂ hydrogenation reactions derived by Bond,²⁷ C₂H₄ tends to convert into C₂H₆ at high pressures, so that the C₂H₄ selectivity decreases with increasing system pressure. Taking into account the actual situation in industrial ethylene units, it is reasonable to select the optimal working pressures in the range 2.0-4.0 MPa for a front-end hydrogenation reactor.

Figure 4C shows the effect of gas hourly space velocity on the performance of the magnetic core Pd/Al₂O₃ catalyst. It can be seen that the C₂H₄ selectivity is very low at low space velocities but increases markedly with increasing space velocity up to $6000~h^{-1}$ and then remains relatively constant even under a space velocity as high as 24,000 h⁻¹. This behavior is distinctly different from that observed in a traditional fixed bed reactor in which the acetylene conversion is low at high space velocity. This high C₂H₄ selectivity is attributed to the unique feature of the MSB reactor,

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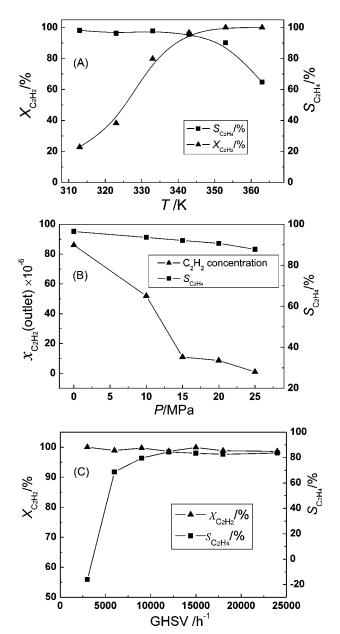


Figure 4. Relationship between the performance of the magnetic Pd-supported catalyst and operation conditions: (A) reaction temperature (P = 1.5 MPa, GHSV = $10,000 h^{-1}$, H = 25 kA m^{-1}); (B) system pressure (T = 343 K, GHSV = 8000 h^{-1} , $H = 25 \text{ kA m}^{-1}$); (C) space velocity ($T = 348 \text{ K}, P = 1.5 \text{ MPa}, H = 25 \text{ kA m}^{-1}$).

that is, its good heat and mass transfer property and high contact efficiency is beneficial for small magnetic particles to operate at high space velocities without excess pressure drop. 28,29

Additionally, the relationship between the catalyst performance and the space velocity reflects the fact of reaction competitions in acetylene hydrogenation processes. As mentioned earlier, acetylene hydrogenation processes involve the series reactions from acetylene to ethane with ethylene as the

Table 3. Effect of Magnetic Field Intensity on the Performance of the Magnetic Core Pd/Al₂O₃ Catalyst

H (kA m ⁻¹)	$X_{C_2H_2}$ (%)	$S_{C_2H_4}$ (%)
10	84.6	62.9
20	97.8	81.7
30	98.5	83.6
40	98.2	83.4

Reaction conditions: T = 343 K, P = 1.5 MPa, GHSV = 9,000 h⁻¹.

intermediate and the paralleled reactions from acetylene to ethylene and from ethylene to ethane. $^{30-32}$ Increase the space velocity makes the residence time shortened, which reduces the probability of ethane formation and consequently enhance the C_2H_4 selectivity. Although under much high space velocity, the residence time is too short to provide enough reaction time for C_2H_2 hydrogenation to C_2H_4 , so that the C_2H_2 conversion would be reduced. As far as industrial ethylene units are considered, a space velocity in the range of 6000-18,000 h^{-1} appropriates the practical application in a front-end hydrogenation reactor.

Furthermore, the performance of magnetic catalyst was measured under different magnetic field intensity. As listed in Table 3, acetylene conversion was only 84.6% when the magnetic field intensity was relatively low (10 kA m⁻¹), which is not so high enough to prevent the catalyst particles from carrying out of the apparatus. Under higher magnetic field intensities (20-30 kA m⁻¹), the MSB operates stably in the above-mentioned chain regime with uniform porosity, which are beneficial to adsorption of reactants and desorption of products so as to achieve high acetylene conversion and ethylene selectivity. No significant improvement in catalyst performance is obtained by further increasing the magnetic field intensity; moreover, very high magnetic field intensities lead to increased capital and operating costs. Thus, in the view of practical applications, the optimal magnetic field intensity is in the range 20–30 kA m⁻¹.

Comparison of magnetic Pd-supported catalyst with the commercial catalyst

Based on the effects of operation conditions on catalyst performance, the optimal reaction condition was selected as T = 353 K, P = 1.5 MPa, H = 25 kA m⁻¹, under which the performance of magnetic Pd/Al₂O₃ catalyst was measured and compared with that of commercial catalyst A containing 0.018 wt % Pd and about 99 wt % alumina. Table 4 lists the

acetylene conversion and ethylene selectivity over the magnetic Pd/Al_2O_3 catalyst and the catalyst A under the same reaction temperature and system pressure but different space velocity. It is indicated that over the magnetic Pd/Al_2O_3 catalyst both acetylene conversion and ethylene selectivity are markedly superior at high space velocities (12000 h⁻¹ and above), although its advantage over catalyst A is not so significant at low space velocities.

Inspired by the process intensification concept of chemical processes, a number of investigations have been reported to improve catalytic reactor performance via novel modes of operations. For instance, improving product selectivities in a parallel-series reaction by feeding one reactant through the reactor by step-wise reactant dosing.³³ Increasing the rates and improving the selectivity of catalytic reactions was achieved by using ultrasonic and microwave technology.³⁴

MSB reactors have the advantages of efficient interphase mass transfer properties and high productivity; however, its practical application is constrained by the nonmagnetic property of most catalysts. Improvement of acetylene hydrogenation processes in this article illuminates that catalysts coated on a magnetic core are available to operate in MSB reactors as well as provide a promising route to explore process intensification techniques through MSB.

Conclusions

Core-shell Al₂O₃ microsphere particles with a diameter of 50–450 μm were successfully prepared by spray-coating alumina solution on the magnetic core of NiFe₂O₄ spinel ferrite. Using impregnation method, Pd catalyst was supported on the magnetic core-shell Al₂O₃ microsphere particles, which displayed high surface area and pore volume and sufficient saturated magnetization property that appropriated for operation in a MSB reactor. Optimal operation conditions were determined through catalytic performance assessment for acetylene hydrogenation reaction over this magnetic Pd/ Al₂O₃ catalyst in an MSB reactor. When compared with the commercial catalyst for hydrogenation reaction operated under the same conditions of 353 K and 1.5 MPa, this magnetic Pd/Al₂O₃ catalyst incorporated with the MSB reactor significantly enhanced the productivity and achieved the C₂H₂ conversion close to 100% and the C₂H₄ selectivity of 84%, whereas the commercial catalyst showed C₂H₂ conversion and C₂H₄ selectivity near 37 and 64%, respectively. These results not only provide an available procedure to synthesize magnetic core-shell catalysts suitable for operation in MSB reactor, but also enlighten us potentially wide applica-

Table 4. Comparison Between the Magnetic Pd/Al₂O₃ Catalyst and the Commercial Catalyst A

Space Velocity (h ⁻¹)	$X_{C_2H_2}$ (%)		$S_{C_2H_4}$ (%)	
	Magnetic Pd/Al ₂ O ₃	Catalyst A	Magnetic Pd/Al ₂ O ₃	Catalyst A
3,000	100	100	-11.2	-65.8
6,000	100	92.7	68.0	23.5
9,000	100	78.1	80.6	46.9
12,000	100	36.6	83.7	63.8
18,000	98.6	13.8	84.2	65.5
24,000	95.1	2.7	82.6	70.1

Reaction conditions: T = 353 K, P = 1.5 MPa, $H = 25 \text{ kA m}^{-1}$.

tions of MSB in the development of novel process intensification techniques.

Notation

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X_{C_2H_2} = C_2H_2 conversion (%)
 S_{\text{C}_{2}\text{H}_{2}} = \text{C}_{2}\text{H}_{4} selectivity (%) x_{\text{C}_{2}\text{H}_{2}} (inlet) = \text{C}_{2}\text{H}_{2} concentration at inlet of reactor (mol %)
x_{C_2H_2} (outlet) = C_2H_2 concentration at outlet of reactor (mol %)
x_{C_2H_4} (inlet) = C_2H_4 concentration at inlet of reactor (mol %)
x_{C_2H_4} (outlet) = C_2H_4 concentration at outlet of reactor (mol %)
                S = \text{saturation magnetization (emu g}^{-1}

S = \text{saturation field intensity (kA m}^{-1})
               H = \text{magnetic field intensity (kA m}^2)
                T = \text{temperature } (K)
                P = pressure (MPa)
         GHSV = gas hourly space velocity (h^{-1})
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Literature Cited

- 1. Mark AB, George IK, David JG. Dried calcium alginate/magnetite spheres: a new support for chromatographic separations and enzyme immobilization. Biotechnol Bioeng. 2004;27:137-145.
- 2. Hristov J. Magnetic field assisted fluidization: a unified approach, Part 2: Solids batch gas-fluidized beds: versions and rheology. Rev Chem Eng. 2003;19:1-132.
- 3. Hristov J. Magnetic field assisted fluidization: a unified approach, Part 5: A hydrodynamic treatise on liquid-solid fluidized beds. Rev Chem Eng. 2006;22:195-375.
- 4. Li W, Zong BN, Li XF, Meng XK, Zhang JL. Interphase mass transfer in G-L-S magnetically stabilized bed with amorphous alloy SRNA-4 catalyst. Chin J Chem Eng. 2006;14:734-739.
- 5. Rosensweig RE, Ciprios G. Process for magnetically stabilizing a fluidized bed containing nonmagnetizable particles and a magnetizable fluid. United States Patent 4,668,379 (1987).
- 6. Meng XK, Mu XH, Zong BN, Min E, Zhu ZH, Fu SB, Luo YB. Purification of caprolactam in magnetically stabilized bed reactor. Catal Today. 2003;79:21-27.
- 7. Pan ZY, Dong MH, Meng XK, Zhang XX, Mu XH, Zong BN. Integration of magnetically stabilized bed and amorphous nickel alloy catalyst for CO methanation. Chem Eng Sci. 2007;62:2712–2717.
- 8. McGown WT, Kemball C, Whan DA. Hydrogenation of acetylene in excess ethylene on an alumina-supported palladium catalyst at atmospheric pressure in a spinning basket reactor. J Catal. 1978;51: 173-184
- 9. Moses JM, Weiss AH, Matusek K, Guczi L. The effect of catalyst treatment on the selective hydrogenation of acetylene over palladium/alumina. J Catal. 1984:86:417-426.
- 10. Tan WH, Peng SY, Tan CY. Kinetic study of consecutive hydrogenation of acetylene. Chin J Appl Chem. 1988;1:47-51.
- 11. Schbib NS, Garcia MA, Gigola CE, Errazu AF. Kinetics of frontend acetylene hydrogenation in ethylene production. Ind Eng Chem Res. 1996;35:1496-1505.
- 12. Zhao Y, Cai YS, Ge SY, Li PS. Pressure drop and intra-particle diffusion for non-cylindrical extruded catalyst particles in a trickle bed. Petrochem Technol. 1990;19:380-386.

- 13. Yang YY. Progress in the catalyst for selective hydrogenation of C2 and C₃ fractions. Petrochem Technol. 2001 (Suppl.);30:26-30.
- 14. Borodzinki A. Selective hydrogenation of ethyne in ethene-rich streams on palladium catalysts, Part 1: Effect of changes to the catalyst during reaction. Catal Rev-Sci Eng. 2006;48:91-144.
- 15. Flick K, Herion C, Allmann HM. Supported palladium catalyst for selective catalytic hydrogenation of acetylene in hydrocarbonaceous streams. United States Patent 5,856,262 (1999).
- 16. Shi CK, Jang BWL. Nonthermal RF plasma modifications on Pd/γ-Al₂O₃ for selective hydrogenation of acetylene in the presence of ethylene. Ind Eng Chem Res. 2006;45:5879-5884.
- 17. Liu XX, Zhao BY, Riegel H, Chien JL. Novel catalyst and process for hydrogenation of unsaturated hydrocarbons. United States Patent 4,762,956 (1988).
- 18. Lamberov AA, Egorova SR, Il'yasov IR, Gil'manov KK, Trifonov SV, Shatilov VM, Ziyatdinov AS. Changes in the course of reaction and regeneration of a Pd-Ag/Al₂O₃ catalyst for the selective hydrogenation of acetylene. Kinet Catal. 2007;48:136-142.
- 19. Khan NA, Shaikhutdinov S, Freund HJ. Acetylene and ethylene hydrogenation on alumina supported Pd-Ag model catalysts. Catal Lett. 2006;108:159-164.
- 20. Blankenship SA, Voight RW, Perkins JA, Fried JE. Process for selective hydrogenation of acetylene in an ethylene purification process. United States Patent 6,509,292 (2003).
- 21. Park YH, Price GL. Potassium promoter for palladium on alumina selective hydrogenation catalysts. J Chem Soc Chem Commun. 1991; 17:1188-1189
- 22. Park YH, Price GL. Promotional effects of potassium on palladium/ alumina selective hydrogenation catalysts. Ind Eng Chem Res. 1992;31:469-474.
- 23. Shchukin DG, Kulak AI, Sviridov DV. Magnetic photocatalysts of the core-shell type. Photochem Photobiol Sci. 2002;1:742-744.
- 24. Lu XS. Bed expansion of a G-L-S magnetic fluidized bed with fine ferro-particles. Eng Chem Metall. 1999;20:129-135.
- 25. Zong BN. Amorphous Ni alloy hydrogenation catalyst and magnetically stabilized bed reaction technology. Catal Surveys Asia. 2007;11:87-94.
- 26. Wang SH, He XO. Ethylene Process and Technology. Beijing, China: Petrochemical Press, 2000:513-550.
- 27. Bond GC, Wells PB. The hydrogenation of acetylene. I. The reaction of acetylene with hydrogen catalyzed by alumina-supported platinum. J Catal. 1965;4:211-219.
- 28. Levenspiel O, Kamhoiz K. Enhancing the characteristics of magnetically stabilized fluidized beds. United States Patent 4,272,893 (1981).
- 29. Arnaldos J, Casal J. Study and modeling of mass transfer in magnetically stabilized fluidized beds. Int J Heat Mass Tran. 1987;30: 1525-1529.
- 30. Bond GC, Wells PB. The hydrogenation of acetylene. II. The reaction of acetylene with hydrogen catalyzed by alumina-supported platinum. J Catal. 1966;5:65-73.
- 31. Yang CS. Technology for eliminating acetylene in ethylene plant. Ethylene Ind. 1996;1:27-44.
- 32. Pradier CM, Mazina M, Berthier Y, Oudar J. Hydrogenation of acetylene on palladium. J Mol Catal A: Chem. 1994;89:211-220.
- 33. Morbidelli M, Gavriidilis A, Varma A. Catalyst Design: Optimal Distribution of Catalyst in Pellets, Reactors and Membranes. Cambridge: Cambridge University Press, 2001.
- 34. Mikkola JP, Kuusists J, Aumo J, Salmi T. In: Derouane EG, editor. Principles and Methods for Accelerated Catalyst Design and Testing. Dordreche: Kluwer, 2002:333-335.

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