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Catalytic Hydrogenation Property of Methyl Benzoate to Benzyl Aldehyde over Manganese-Based Catalysts with Appropriate Oxygen Vacancies

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Abstract: The synthesis of benzaldehyde, a compound widely utilized in food, medicine, and cosmetics, was achieved through a one-step catalytic hydrogenation using the cost-effective raw material, methyl benzoate. This process aligns with the principles of atom economy and green production. Despite the development of numerous high-performance catalysts by scholars, the challenge remains in achieving lower reaction temperatures, ideally below 400 °C. In this study, a series of MnO_x/γ-Al₂O₃ catalysts were meticulously prepared using the precipitation-impregnation method. These catalysts featured supports calcined at various temperatures and distinct manganese active components. Characterization techniques such as X-ray diffraction (XRD), N₂ physical adsorption, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), H₂ temperature programmed reduction (H₂-TPR), and NH₃ temperature-programmed desorption (NH₃-TPD) were employed to analyze the structure and surface properties of the catalysts. Notably, the optimized reaction temperature was found to be 360 °C. The catalyst exhibited the most favorable performance when the calcination temperature of the support was 500 °C and the Mn/Al molar ratio reached 0.18. Under these conditions, the catalyst demonstrated the most suitable oxygen vacancy concentration, yielding impressive results: a conversion rate of 87.90% and a benzaldehyde selectivity of 86.1%. These achievements were attained at 360 °C, atmospheric pressure, a hydrogen to methyl benzoate molar ratio of 40:1, and a Gas Hourly Space Velocity (GHSV) of 800 h⁻¹. This research underscores the potential for optimizing catalysts to enhance the efficiency and sustainability of benzaldehyde synthesis.

Keywords: methyl benzoate; benzaldehyde; manganese based catalyst; catalytic hydrogenation; oxygen vacancy



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1. Introduction

Benzaldehyde is a significant organic intermediate, which is widely used in medicine [1], food [2], industry [3] and other fields. However, the benzaldehyde generated from natural pathways is not sufficient to meet market demand, and the product cost of the extraction process is relatively high. Therefore, the production of benzaldehyde through chemical industrial processes is the main path routes to obtain this type of organic intermediate. At present, the main routes of producing benzaldehyde in the chemical industry include chlorination hydrolysis [4], toluene oxidation [5], benzyl alcohol oxidation [6], styrene oxidation [7], etc. However, these path routes give rise to lots of problems, such as serious pollution, low yield, and difficulty in the catalyst recovery, which do not meet the requirements of green chemistry development.

Using methyl benzoate as a raw material to produce chloro-free benzaldehyde by selective hydrogenation has become a green chemical process for the manufacture of this

type of organic intermediate product. Methyl benzoate is a typical by-product in the production of dimethyl terephthalate, which has a wide range of sources and affordable low prices. The hydrogenation of methyl benzoate to benzaldehyde is characterized by simple operation, continuous production, high selectivity, low cost of raw materials and easy availability, which has practical significance and economic value. The development of a new process for the selective hydrogenation of benzoic acid or this kind of methyl benzoate by-product to produce chloro-free benzaldehyde exhibits good economic value.

The key issue for the market-oriented applications of benzaldehyde by the above mentioned green chemical process are the development of catalysts and the corresponding process optimization. Research in this aspect has shown that the hydrogenation activity of benzoic acid or benzaldehyde is associated with the redox properties of oxides [8–11] and the concentration of oxygen vacancies. Firstly, the alkaline metal oxides MgO and lanthanide metal oxides La₂O₃, Yb₂O₃, and Pr₆O₁₁, which have almost no redox properties, give rise to thermal decomposition, hydrogenolysis of benzoic acid (ester) and transition state salts, and therefore it is more likely for the excessive hydrogenation to generate by-products such as benzyl alcohol and benzene. Secondly, manganese-based compounds with a certain reduction ability and oxygen vacancies, such as γ -Mn₃O₄, MnO₂, and ZnMn₂O₄, exhibit high catalytic activity and selectivity at low temperatures. However, unfortunately the catalytic performance of this series of catalysts is uncontrollable, elevation in the temperature will more likely result in the formation of toluene. Furthermore, some other metal oxides such as Co₃O₄, Fe₃O₄, and Fe₂O₃ are more easily to be reduced than the manganese-based compounds, resulting in the poorer selectivity for the generation of benzaldehyde. Correspondingly, metal oxides with an appropriate redox capacity, such as ZrO₂ [12], ZnO [13], CeO₂ [14,15] and MnO [16], exhibited excellent catalytic activity, and simultaneously the by-product of toluene is inhibited by the low surface oxygen vacancies, therefore yielding the high selectivity of benzaldehyde. In addition, as mentioned above although various catalysts with high-performance have been developed, the reaction temperatures of these catalysts are all around 400 °C, which will result in higher energy consumption and higher production costs. At the same time, the cokes will be deposited on the surface of the catalyst, covering the active sites, thus resulting in the reduction of the catalytic stability and a quicker deactivation of the catalyst. Therefore, it is necessary to optimize the reaction conditions and improve the feasibility of the process through catalyst design and process improvement. Therefore, considering how to reduce the reaction temperature, while ensuring the product yields and stability is also the focus in this research.

In this work, manganese-based metal oxides with various active species and oxygen vacancies were developed to form a series of MnO_x/γ-Al₂O₃ catalysts. The catalytic performances were investigated by the hydrogenation of methyl benzoate to produce chloro-free benzaldehyde. The dependences of the catalytic activity and selectivity on the active sites of the catalysts fabricated by the calcination of support at various temperatures and various manganese loading amounts were investigated in detail.

2. Results and Discussion

2.1. Structure and Surface Species of Catalysts

The XRD patterns of catalysts with the support calcined at various temperature are showed in Figure 1a,c before and after reduction by hydrogen, respectively. The XRD patterns of catalysts with different amounts of manganese loading are showed in Figure 1b,d before and after reduction by hydrogen, respectively. For all the four figures, the diffraction peaks at $2\theta = 19.5^\circ$, 39.3° , 45.7° , and 66.6° are observed. These peaks can be considered as the typical γ-Al₂O₃ diffraction (JCPDF NO. 29-0003), corresponding to the (111), (222), (400), and (440) crystal facets of γ-Al₂O₃. As the calcination temperature of the support improved from 400 °C to 800 °C, a new diffraction peak of γ-Al₂O₃ appeared at $2\theta = 32.3^\circ$ for 700 °C and 800 °C calcined supports (Figure 1a). At the same time, the diffraction peaks at 45.7° shifts to the left upon calcination at 800 °C. This observation might be explained

by the lattice distortion of alumina caused by the high temperature calcination of the support [17–19]. At $2\theta = 28.7^\circ$, 37.3° , 42.8° , 56.7° , 59.4° , and 72.3° sharp diffraction peak were detected, which can be attributed to the generation of MnO_2 (JCPDF NO. 24-0735). Because the diffraction peaks of the α - MnO_2 phase and β - MnO_2 phase overlap at $2\theta = 29^\circ$ and 37° , both structures of MnO_2 crystalline phases might exist simultaneously in the catalysts [20]. In addition, low intensive diffraction peaks were detected at $2\theta = 32.9^\circ$, 55.1° , and 65.8° , which are attributed to the characteristic peaks of Mn_2O_3 (JCPDF NO. 76-0150). These results demonstrated that the crystalline phases of the catalysts are mainly composed of MnO_2 and Al_2O_3 and a small amount of Mn_2O_3 . More interestingly, if the calcination temperature of the support is higher than 600°C , the Mn_2O_3 phases in the catalyst cannot be observed. This may be explained by the high calcination temperature of the support, resulting in a decrease in the number of hydroxyl species on the surface, and then the interaction between Mn species and the support surface is affected during the impregnation process. From Figure 1b, it can be clearly observed that the diffraction peak of Mn_2O_3 gradually improved as the loading amount of Mn increases, indicating that increasing the loading amount of Mn will mainly result in the generation of Mn_2O_3 .

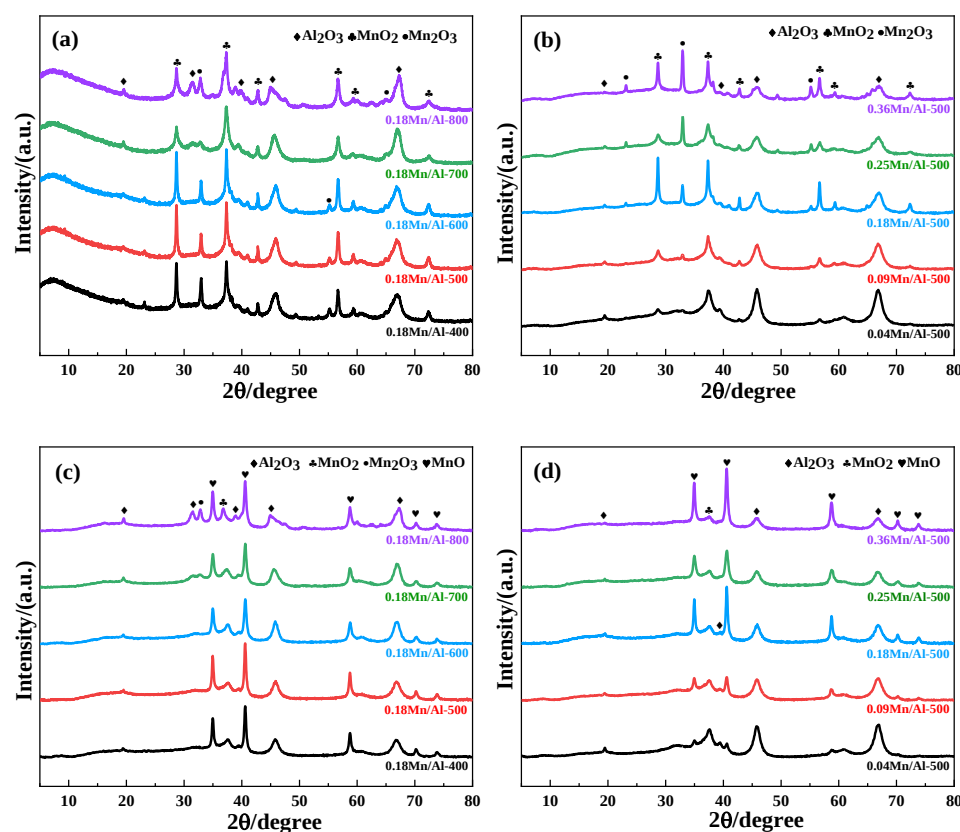


Figure 1. XRD patterns of catalysts with support calcined at various temperature: (a) before reduction, and (c) after reduction and different loading amounts: (b) before reduction and, (d) after reduction.

In Figure 1c,d, five diffraction peaks of (111), (200), (220), (311), and (222) crystalline facets of MnO (JCPDS NO. 71-1177) are observed at $2\theta = 34.9^\circ$, 40.5° , 58.6° , 70.1° , and 73.7° , respectively [21]. The main phase composition on the surface of the reduced catalysts with the calcination temperatures of 400°C , 500°C , and 600°C are γ - Al_2O_3 and MnO , as well as a small amount of un-reduced MnO_2 . However, the surface phase composition varied with the calcination temperature of the carrier, and increased to 700°C and 800°C . The deformation in the crystalline phase of γ - Al_2O_3 which resulted in the displacement in the diffraction peaks being observed. Moreover, the Mn_2O_3 crystalline phase is also formed on these two samples. In Figure 1d, the dependent in the intensity of XRD diffraction peak on the Mn loading amount is observed. It indicated that the Mn species are highly

dispersed on γ - Al_2O_3 . It is also observed that the intensity in the diffraction peak of MnO_2 at $2\theta = 37.5^\circ$ decreases as the loading amount of Mn species increases, demonstrating that most of the MnO_2 has been reduced to MnO . This result can be explained by the idea that the strong interaction between the support and the metal leads to a hard reduction of MnO_2 to MnO when the loading of Mn species is low.

2.2. Specific Surface Area and Pore Structure of Catalysts

The N_2 adsorption/desorption isotherms of $x\text{Mn}/\text{Al-T}$ catalysts are shown in Figure 2. From the graph, it can be seen that all catalysts exhibit an IV type isotherm with hysteresis loops. This observation indicates that all the catalysts possess a mesoporous structure which results in the capillary condensation phenomenon occurs during the adsorption-desorption process. As the calcination temperature of the support increases in Figure 2a, the starting point of the hysteresis loop shifts towards a higher pressure. This result indicates that the pore size of the catalysts is dependent on the calcination temperature of the supports. The specific surface area, pore volume, and pore size of the prepared $x\text{Mn}/\text{Al-T}$ catalysts are listed in Tables 1 and 2. The data in Table 1 reveals that the specific surface area of the catalysts gradually decrease with the increase in support calcination temperature. Table 2 shows that the amount of Mn loading does not generate a significant impact on the pore size of the catalysts. However, the specific surface area of the catalyst gradually decreases from $205 \text{ m}^2\cdot\text{g}^{-1}$ to $142 \text{ m}^2\cdot\text{g}^{-1}$. This result implies that higher amounts of Mn loading resulted in the aggregation of Mn species on the surface of the support and therefore large particles of the active species are formed which decrease the specific surface area.

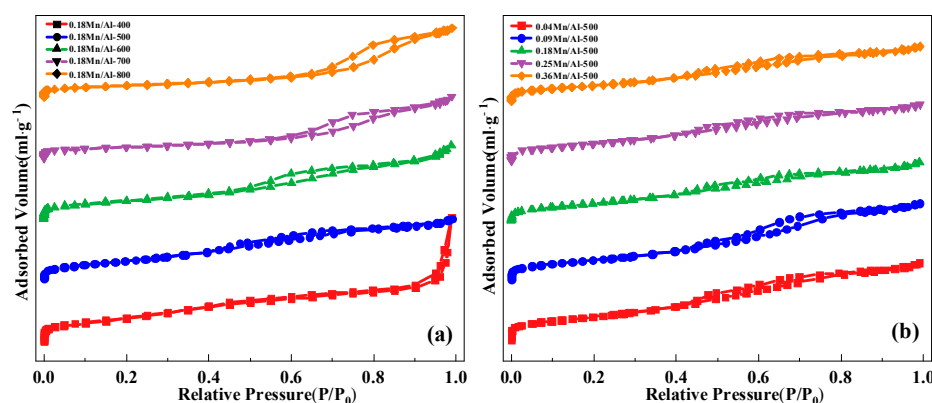


Figure 2. N_2 absorption-desorption isotherm of $x\text{Mn}/\text{Al-T}$ catalysts before reduction (a) support calcined at various temperatures, and (b) different Mn loading amounts.

Table 1. The physical properties of catalysts with support at various calcined temperatures.

Sample	BET Surface Area/ $\text{m}^2\cdot\text{g}^{-1}$ ¹	Pore Volume/ $\text{cm}^3\cdot\text{g}^{-1}$ ²	Average Pore Size/nm ³
0.18Mn/Al-400	220	0.39	5.54
0.18Mn/Al-500	170	0.23	6.14
0.18Mn/Al-600	157	0.27	6.31
0.18Mn/Al-700	93	0.24	6.56
0.18Mn/Al-800	98	0.26	7.80

¹ Surface area by Brunauer-Emmett-Teller (BET) method. ² Total pore volumes of $P/P_0 = 0.990$. ³ Average diameters were calculated by Barrett-Joyner-Halenda (BJH) method.

Table 2. The physical properties of catalysts at various loading amount of Mn species.

Sample	BET Surface Area/m ² ·g ^{−1} ¹	Pore Volume/cm ³ ·g ^{−1} ²	Average Pore Size/nm ³
0.04Mn/Al-500	205	0.30	5.93
0.09Mn/Al-500	180	0.30	6.78
0.18Mn/Al-500	170	0.23	6.14
0.25Mn/Al-500	158	0.22	5.68
0.36Mn/Al-500	142	0.22	6.19

¹ Surface area by Brunauer-Emmett-Teller(BET) method. ² Total pore volumes of P/P₀ = 0.990. ³ Average diameters were calculated by Barrett-Joyner-Halenda (BJH) method.

2.3. Surface Molecular Structure and Acid-Base Properties of Catalysts

The FT-IR spectra of xMn/Al-T catalysts are shown in Figure 3. It can be seen from the spectra that the typical absorbances are concentrated in the low wavenumber range of 450–1700 cm^{−1} and the high wavenumber range of 3000–3800 cm^{−1}. The strong and wide peaks appearing in the high wavenumber range can be assigned to the stretching vibration peaks of -OH on the surface of alumina and adsorbed water molecules. The peak near 1630 cm^{−1} belongs to the deformation vibration of the H-O bond of water molecules adsorbed by alumina. The absorbance from 450–750 cm^{−1} segment attributed to six coordinated Al^{VI}-O stretching vibration. The vibration peak near 820 cm^{−1} is attributed to the four coordinated Al^{IV}-O vibration. From Figure 3a,b, the peaks at 590 cm^{−1} become sharp compared with Al-500 in Figure 3a. This indicates that the positions of Mn-O and Al-O bonds overlap [22], and Mn components bind to the six coordinated Al^{VI}-O bonds.

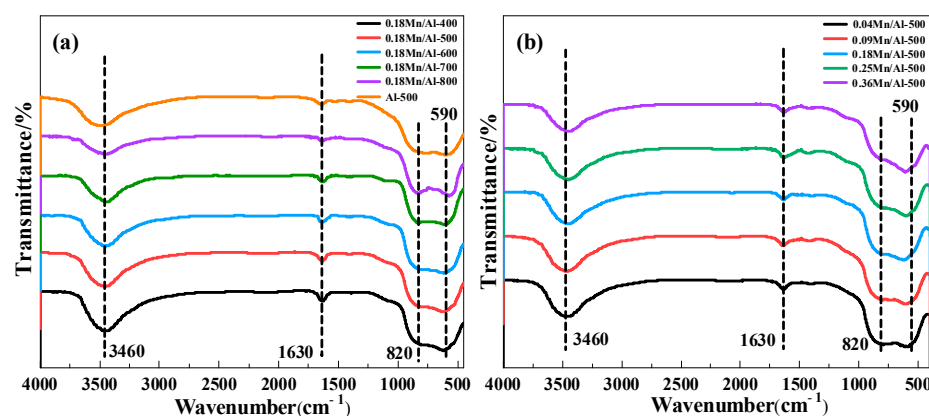


Figure 3. FT-IR spectra of xMn/Al-T catalysts before reduction with: (a) support calcined at various temperatures; (b) various Mn loading amounts.

In order to make clear the surface acidity of the xMn/Al-T catalysts, NH₃-TPD measurements were conducted. From Figure 4a, three desorption peaks of NH₃ can be clearly observed, corresponding to weak acid sites near 110 °C, moderately strong acid sites near 200 °C, and strong acid sites near 380 °C, respectively [23,24]. It can be seen that the acid content of the medium strength acid and strong acid center increase with the calcination temperature of the support increasing from 400 °C to 600 °C. When the temperature is further increased from 600 °C to 800 °C, the acid content decreases. This result also indicates that the different surface states caused by the calcination temperature affect the interaction between Mn species and Al surface hydroxyl species or electronic states, resulting in different surface states of the catalysts and affecting its acidity. The quantities of weak acid sites show a trend of first decreasing and then increasing with the increase of loading amount. The minimum is reached when Mn/Al is 0.09. On the contrary, the moderate strength and strong acid sites continue to decrease. When Mn/Al is 0.36, the moderate strength acid sites disappear, which may be because the Mn species uniformly cover the surface and neutralize the moderate strength acid sites on the support [25–27]. It is also worth noting

that when Mn/Al is 0.36, a strong acid site appears around 650 °C. Overall, the surface acidic site of the catalyst plays an important role for the selectivity of the target products. Appropriate modulated acidic sites favor for the selectivity of the target product [28].

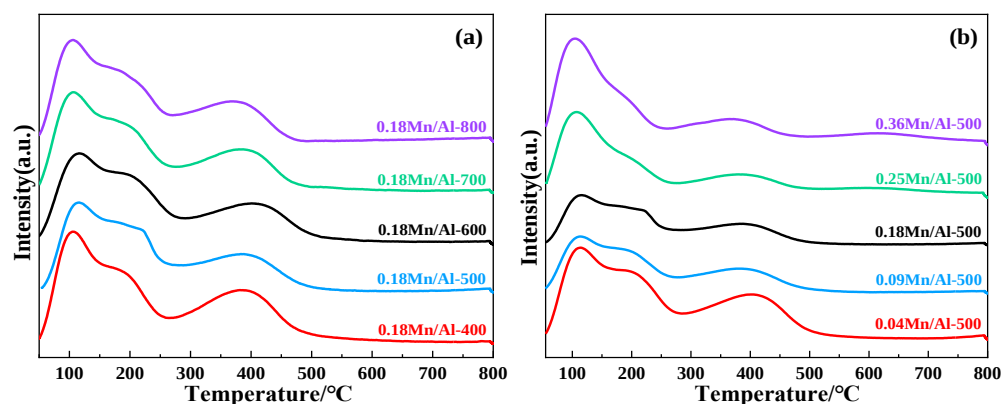


Figure 4. NH_3 -TPD curves of xMn/Al-T catalysts before reduction: (a) support calcined at various temperatures; (b) various Mn loading amounts.

2.4. Surface Chemical Composition and Redox Properties of the Catalyst

X-ray photoelectron spectroscopy (XPS) proves to be an exceptionally practical method for conducting qualitative, quantitative, and structural analyses of solid surfaces. Through the examination of XPS spectra for catalysts, valuable information regarding the chemical and elemental composition, oxidation state, and surface energy distribution can be derived. In Figure 5, the Mn2p spectra of xMn/Al-T catalysts are presented both before and after reduction. The primary signal peaks of Mn2p_{3/2} (around 641.5 eV) and Mn2p_{1/2} (around 653.0 eV) can be observed in the figure, encapsulating the oxidation state of Mn. In Figure 5a,b, the oxidation state of Mn before reduction manifests as Mn(IV) (around 653.28 eV and 642.98 eV) and Mn(III) (approximately 649.08 eV and 641.38 eV) [29,30], respectively. From Figure 5c,d, it can be seen that after reduction, Mn(II) (near 652.22 eV and 640.95 eV) appeared, along with Mn(IV) (around 653.58 eV and 643.00 eV) and satellite peaks (approximately 654.88 eV and 644.5 eV) [31–33].

The analysis of the figures reveals that the various Mn active components and the calcination temperature of the supports do not have a significant impact on the shift of the Mn2p peak. However, comparing the Mn2p spectra before and after reduction, the predominant portion of surface Mn species is now comprised of Mn(II), while Mn(III) on the surface disappeared after reduction. This result indicates that all of Mn(III) has been reduced to Mn(II). Additionally, There is also a small amount of Mn(IV) on the surface.

According to the literature, the catalytic performance of Mn-based catalysts in the selective hydrogenation of methyl benzoate to benzaldehyde appears to be closely linked to the reducibility of manganese oxide species [18,20,34]. To investigate this, the reduction performance of these manganese species on the catalyst was examined using hydrogen temperature programmed reduction (H_2 -TPR). The H_2 -TPR spectra of catalysts with various calcination temperatures and different Mn active components are shown in Figure 6a and Figure 6b, respectively. From Figure 6a, it can be observed that within the range of 50–550 °C, there are two H_2 consumption peaks for 0.18Mn/Al-400, 0.18Mn/Al-600, 0.18Mn/Al-700, and 0.18Mn/Al-800 catalysts, while there is a single H_2 consumption peak for 0.18Mn/Al-500 catalyst. In Figure 6b, within the temperature range of 50–550 °C, only 0.18Mn/Al-500 and 0.36Mn/Al-500 catalysts display one H_2 consumption peak, while 0.04Mn/Al-500, 0.09Mn/Al-500, and 0.25Mn/Al-500 catalysts exhibit two H_2 consumption peaks.

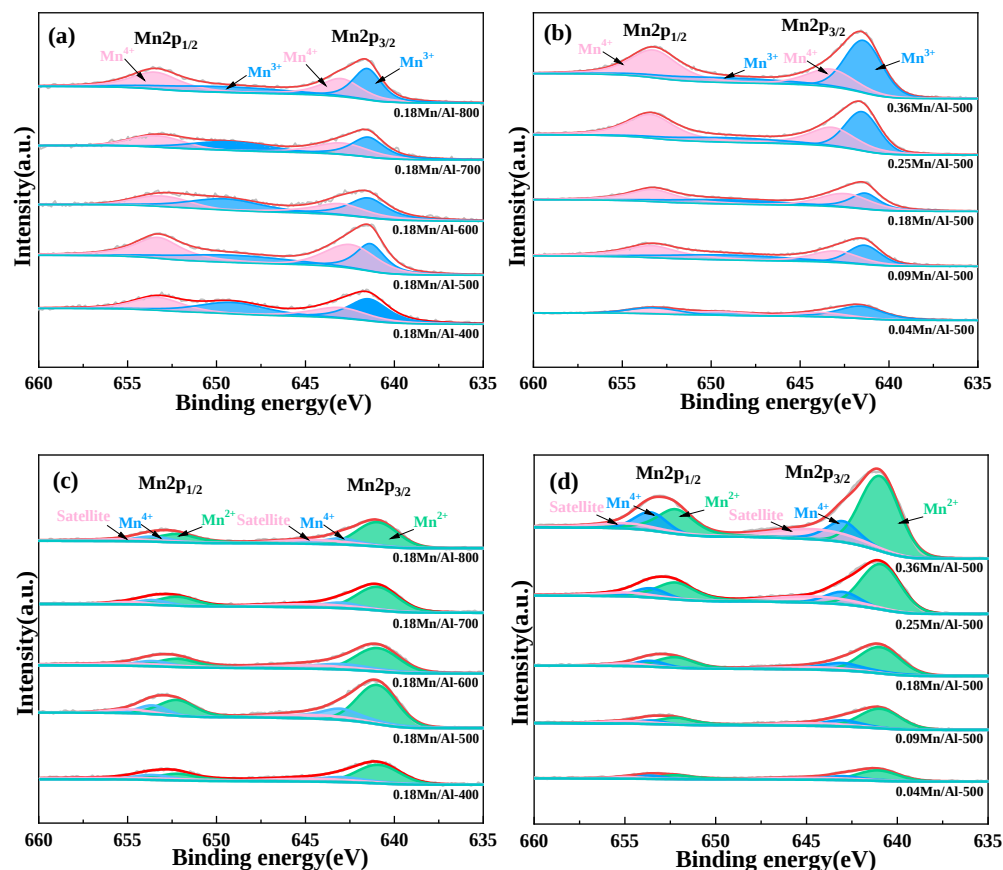


Figure 5. XPS patterns for Mn2p of catalysts with support calcined at various temperature: (a) before reduction, and (c) after reduction and different loading amounts: (b) before reduction, and (d) after reduction.

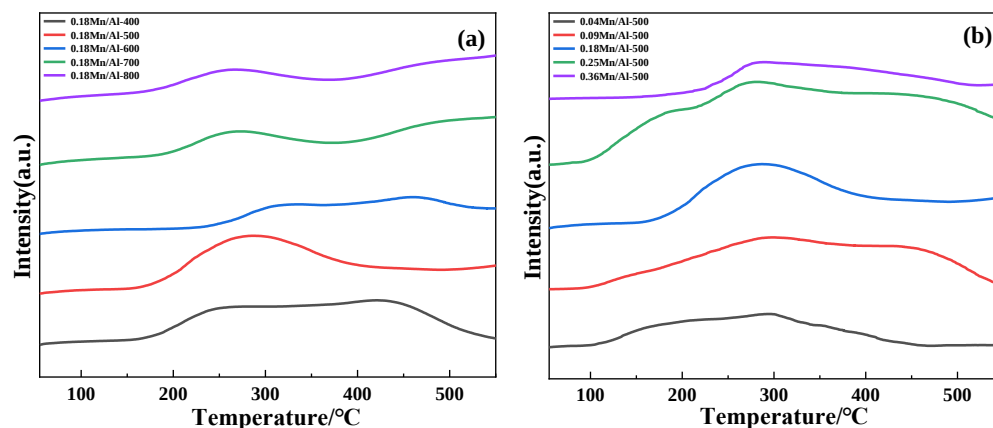


Figure 6. H₂-TPR patterns of catalysts before reduction: (a) support calcined at various temperatures (b) different Mn loading amounts.

According to references [34–36], the reduction of supported Mn species occurs in two steps: (i) $\text{MnO}_2/\text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4$, and (ii) $\text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$. Consequently, the first peak near 280 °C can be attributed to the reduction of surface Mn species composed of MnO_2 and Mn_2O_3 to Mn_3O_4 in step (i), while the second peak near 420 °C corresponds to the reduction of Mn_3O_4 to MnO in step (ii). Notably, the 0.18Mn/Al-500 catalyst displays only one H₂ consumption peak, possibly owing to the oxidation state of Mn components on the catalyst's surface, resulting in varied binding states of interaction between Mn species and the support $\gamma\text{-Al}_2\text{O}_3$. And the Mn active component is more easily reduced to

MnO_x, causing the overlap of the two peaks, indicating that the catalysts have almost been completely reduced below 400 °C. In Figure 6a, the reduction peak area clearly shows that the 0.18Mn/Al-500 catalyst consumes the highest amount of H₂ near 280 °C. This reveals that the support calcined at a lower temperature can obtain more active manganese oxide species. Although the H₂ consumption peak of the 0.25Mn/Al-500 catalyst in Figure 6b is large, its reduction at 420 °C remains incomplete. More interestingly, except for the 0.18Mn/Al-500 catalyst, all the other catalysts are not completely reduced below 420 °C, implying a significant impact on the performance of these catalysts.

2.5. Evaluation of Reaction Performance and Correlation with Surface Properties

The reaction performance of catalysts with varying calcination temperatures and diverse active components, was assessed in the selective hydrogenation of methyl benzoate to benzaldehyde in Tables 3 and 4, respectively. In order to ensure uniformity in Mn active component processing with an identical unit of raw material MB, while ensuring the ratio of hydrogen to MB remains unchanged in Table 4, the feed rate of raw material MB and different gas velocity during H₂ intake are set.

Table 3. Effects of support at different calcined temperature on the catalytic for hydrogenation of MB over 0.18Mn/Al-T (T = 400, 500, 600, 700, 800) catalyst ^a.

Catalyst	Conversion/%	Selectivity/%				
		Benzaldehyde	Toluene	Benzyl Alcohol	MBE	Others
0.18Mn/Al-400	90.6	68.00	17.89	9.97	2.02	2.12
0.18Mn/Al-500	87.9	86.11	1.63	6.45	5.03	0.78
0.18Mn/Al-600	89.5	71.94	9.83	11.95	2.37	3.91
0.18Mn/Al-700	75.4	79.36	10.13	5.76	3.74	1.01
0.18Mn/Al-800	60.9	91.80	2.19	3.89	2.10	0.02

^a Catalyst: 0.18Mn/Al-T; T = 360 °C; H₂/MB (mol:mol) = 40; GHSV = 800 h⁻¹.

Table 4. Effects of different capacity on the catalytic for hydrogenation of MB over xMn/Al-T (x = 0.04, 0.09, 0.18, 0.25, 0.36) catalyst ^a.

Catalyst	Conversion/%	Selectivity/%				
		Benzaldehyde	Toluene	Benzyl Alcohol	MBE	Others
0.04Mn/Al-500	86.4	86.91	0.56	3.17	5.10	4.26
0.09Mn/Al-500	93.3	71.53	4.88	9.44	13.89	0.26
0.18Mn/Al-500	87.9	86.11	1.63	6.45	5.03	0.78
0.25Mn/Al-500	94.4	78.44	4.01	13.69	1.02	2.84
0.36Mn/Al-500	55.7	89.63	1.48	5.44	0.40	3.05

^a Catalyst: xMn/Al-500 (x = 0.04, 0.09, 0.18, 0.25, 0.36); T = 360 °C; H₂/MB (mol:mol) = 40; GHSV = 168 h⁻¹, 400 h⁻¹, 800 h⁻¹, 1130 h⁻¹, 1600 h⁻¹.

From the data in Table 3, the catalyst activity remains relatively stable when the support calcination temperature is below 600 °C, with minimal variation in MB conversion. The selectivity of benzaldehyde peaks at 86% when the support calcination temperature is 500 °C. After the calcination temperature of the support exceeds 700 °C, the activity of the catalyst significantly decreases. Combining N₂ physical adsorption characterization, it becomes apparent that excessively high calcination temperatures result in larger grains and lower specific surface area. This alteration in the interaction relationship between the support and Mn species leads to a decrease in the redox ability of the catalysts, consequently, there is a reduction in the concentration of oxygen vacancies on the catalyst's surface, causing the decrease in catalytic activity.

From the catalytic performance data of different amounts of active component catalysts in Table 4, it can be seen that in the case of Mn/Al ≤ 0.25, the catalyst has high conversion rate. However, the activity of the 0.36Mn/Al-500 catalyst declines. This suggests that

a relatively suitable concentration of oxygen vacancies can be achieved with supports calcined at 500 °C, resulting in high catalytic activity. But for the 0.36Mn/Al-500 catalyst, combined with NH₃-TPD characterization, it can be observed that excessive Mn loading can lead to the formation of a stronger acids on the catalyst surface, thereby reducing the catalyst's activity.

In summary, catalytic activity is controlled by the interaction between γ -Al₂O₃ and active components MnO_x. Both strong and weak interactions influence the oxidation state of Mn species, the redox ability, and acidity on the catalyst's surface. The redox ability further impacts the surface oxygen vacancy concentration, ultimately affecting the catalyst's activity.

The main reaction path of methyl benzoate hydrogenation reaction (Figure 7) follows the Mars-van-Krevelen [37] mechanism, which means lattice oxygen on the Mn-supported catalyst's surface and the resulting oxygen vacancy are pivotal to the reaction [37]. Initially, during H₂ reduction before the reaction, H₂ is dissociated and adsorbed on the catalyst surface, combining with surface oxygen atoms to form H₂O and generate oxygen vacancies. The concentration of these oxygen vacancies is interdependent with the oxidation state of the active species after reduction due to the interaction between the active components and the support. In addition, the transition metal Mn has a special d-empty orbital, which is easy to accept the pair electrons on the carbonyl oxygen, facilitating adsorption and activation of the molecule. Simultaneously, the oxygen atom on the ester group of methyl benzoate supplemented the oxygen vacancy on the catalyst surface, and the catalyst regained the oxidation performance. At a certain temperature, C-O bond of the ester group in methyl formate breaks, forming a transition state of carboxylate and methoxy group.

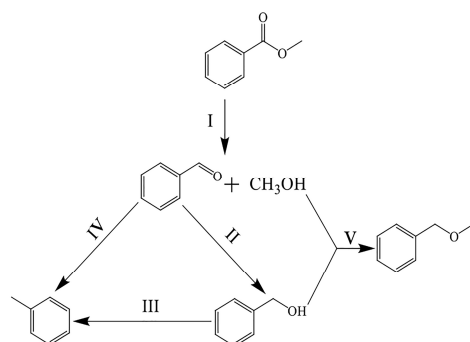


Figure 7. The reaction routes for the products in the hydrogenation of methyl benzoate.

The proposed activation path of H₂ during the reaction involves dissociation on the catalyst surface. The hydrogen atoms are either combined with the transition state carboxylate to form benzaldehyde or reacted with oxygen atoms to form H₂O, leaving the oxygen vacancy behind. Consequently, the conversion rate of methyl benzoate and the selectivity of the product are closely related to the Mn species on the catalyst surface and the resultant oxygen vacancy. The concentration of surface oxygen vacancies also influences the selectivity of other products. If the concentration of oxygen vacancy on the catalyst surface is too high, more benzaldehyde will be further hydrogenated to produce toluene and benzyl alcohol (the occurrence of steps II and IV). Table 3 illustrates that while there is no significant difference in catalyst conversion prepared with support calcination at 500 °C and 600 °C, the selectivity for benzaldehyde, toluene, and benzyl alcohol in the product distribution differs significantly. This suggests distinct surface properties for catalysts obtained under these conditions, confirming observations from H₂-TPR. Thus, active manganese oxide species and an appropriate oxygen vacancy concentration can be obtained by catalysts prepared at a low calcination temperature of the support.

In Step II, benzyl alcohol is formed by the nucleophilic mechanism of benzaldehyde adsorption on the activated carbonyl group at the Mn species/support interface. The interface properties and the degree of metal dispersion are crucial in determining benzyl alcohol

formation [38]. Benzyl methyl ether is formed by the dehydration reaction of benzyl alcohol and methanol on the catalyst surface (Step V). Toluene originates from the deoxidation of benzyl alcohol on the oxygen vacancy (Step III) and the secondary hydrogenation of benzaldehyde (Step IV). In Table 3, the conversion of the catalysts prepared by the support calcination at 400 °C and 600 °C is about 90%, the selectivity difference of benzaldehyde is about 4%, the selectivity of benzyl alcohol is about 2%, but the selectivity difference of toluene is about 8%, indicating that toluene is obtained by benzaldehyde and benzyl alcohol, rather than only by benzaldehyde or benzyl alcohol.

It is also worth noting that changes in the interaction between the support and the metal can also lead to changes in the surface acidity of the catalyst. The surface acid strength and acid quantities of the catalyst also have a significant impact on the product selectivity. If the surface acidity is too strong, it will cause the transition state carboxylate to be adsorbed on the surface and be difficult to be desorbed, resulting in a decrease in benzaldehyde selectivity. Combined with NH_3 -TPD characterization, due to the higher strength of acidic sites in 0.18Mn/Al-600, the selectivity of by-products toluene and benzyl alcohol is relatively higher compared to 0.18Mn/Al-500. In addition, the enhancement of moderate strong acids and strong acid quantities leads to further hydrogenation of benzaldehyde along the direction of path II→path V (Figure 7), thus increasing the selectivity of benzyl alcohol and benzyl methyl ether. Combined with NH_3 -TPD characterization, due to more quantities of moderate strong acids and strong acid in 0.09Mn/Al-500, the selectivity of MBE is higher than in 0.25Mn/Al-500.

Therefore, different calcination temperatures of $\gamma\text{-Al}_2\text{O}_3$ and various loading amounts of Mn regulate the acidity of the catalyst surface by changing the interaction relationship between $\gamma\text{-Al}_2\text{O}_3$ and the active components of Mn. The distinction is that the former has a greater impact on the strength of acidity, while the latter has a greater impact on the quantities of acidity. Overall, benzaldehyde is the first order reaction product of methyl benzoate hydrogenation, benzyl alcohol and toluene are the second order reaction products, and benzyl methyl ether is the third order reaction product. These reaction products are synergistically affected by the acidity and oxygen vacancy concentration on the surface of the catalysts.

3. Experiment

3.1. Preparation of Catalyst

To prepare different $\text{MnO}_x/\gamma\text{-Al}_2\text{O}_3$ catalysts, firstly various supports were calcined at different temperatures. A certain amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in deionized water. Ammonia was added dropwise to the sample with continuous stirring until the pH reached 11. The resulting precipitate was filtered and washed to neutral, and dried in an oven at 120 °C for 12 h. After that, it is calcined at different temperatures for 3 h in the muffle furnace. Then Al_2O_3 supports at various calcined temperatures were obtained. Next, the incipient wetness impregnation method was used to impregnate 50 wt.% $\text{Mn}(\text{NO}_3)_2$ in the $\gamma\text{-Al}_2\text{O}_3$ separately. For supports at different calcination temperatures, the molar ratio of Mn/Al was controlled at 0.18. Meanwhile, only when the calcination temperature of the support was 500 °C, the ratio of Mn/Al was controlled within the range of 0.04–0.36. After impregnation, the samples were dried again at 120 °C for 12 h, and they were calcined at 500 °C for 3 h. Finally, catalysts were compressed and crushed to obtain 20–40 mesh particles. The prepared catalysts were represented as xMn/Al-T (x = 0.04, 0.09, 0.18, 0.25, 0.36, x represents different manganese loading amount; T = 400 °C, 500 °C, 600 °C, 700 °C, 800 °C, T represents the calcination temperature of different Al_2O_3 supports, denoted as 0.04Mn/Al-T, 0.09Mn/Al-T, 0.18Mn/Al-T, 0.25Mn/Al-T, 0.36Mn/Al-T, respectively).

3.2. Catalyst Performance Evaluation

Gas phase hydrogenation of Methyl benzoate (MB) was carried out in a continuous flow fixed bed reactor (inner diameter: 10 mm, length: 500 mm, provided by Xuentian Research Institute, Qingdao, China) under atmospheric pressure. The reaction temperature

was controlled by a temperature controller and measured by a K-type thermocouple. Before the reaction, the catalysts needed to be reduced for 2 h in a mixed atmosphere of H₂ and N₂ (H₂:N₂ = 1:10, mol/mol) at 360 °C, and finally reduced for 2 h in a 100% H₂ atmosphere at 420 °C. MB was gasified at 360 °C and mixed with H₂ (H₂:MB = 40:1, mol/mol) and pumped into the reactor. GHSV was maintained at 800 h^{−1}. The obtained products were collected by condensation and analyzed by Shimadzu 2030 gas chromatography. FID was selected as the detector and operated a 50 m HP-5 capillary column.

3.3. Characterization of Catalyst

Conducting Cu K α ray (λ = 0.15406 nm), the crystal structure of the samples was tested by DX-2500X-ray diffractometer (Rigaku, Tokyo, Japan). The tube current and tube voltage are 40 mA and 40 kV, respectively. Scan rate is 8°/min with 5–80° range. In order to reveal the oxidation states of Mn on the catalyst surface, XPS spectra were recorded on the Perkin Elmer PHI5000C ESCA system. In this experiment, Al K α X-rays ($h\nu$ = 1486.6 eV) was regarded as excitation source (150 W), and the peak position of C1s (284.6 eV) was employed as the reference. The porous structure of the samples was tested by autosorb-S1 specific surface area and pore size automatic analyzer (Quantachrome, Norcross, GA, USA). Before testing, the sample was degassed under vacuum at 300 °C for 3 h, and then N₂ adsorption/desorption tests were conducted at −196 °C. According to the N₂ isothermal adsorption/desorption curve of the samples, the specific surface area of the sample was calculated by the Brunauer-Emmett-Teller (BET) equation, and the pore volume and pore size were obtained by the Barrett-Joyner-Halenda equation. The FT-IR characterization of the catalyst was carried out on the Nicolet AVATAR 370DTGS Fourier transform infrared spectrometer. The relevant test is to mix Potassium bromide (KBr) and catalyst evenly, which were pressed and tested in the range of 4000~400 cm^{−1}. The programmed temperature reduction (H₂-TPR) of the catalyst was carried out on a Chem BET Pulsar TPR/TPD instrument (USA). The relevant testing methods and conditions are as follows: Firstly, 50 mg of the catalyst was loaded it into the corresponding sample tube. The argon gas was injected, and the catalyst was pre-treated at 5 °C/min heating rate from room temperature to 100 °C. After processing for 30 min, the temperature is lowered to room temperature. The argon gas was replaced by 5% H₂/Ar for programmed temperature reduction treatment (50–550 °C). In addition, the determination of catalyst surface acidity involves the sample adsorbed in NH₃ atmosphere for 30 min after the gas pre-treatment, followed by blowing with He for 1 h, and finally performing the desorption at a rising rate of 5 °C/min. The desorption peak signal is also detected on the TCD detector.

4. Conclusions

In our research, we have found that the manganese-based catalyst synthesized through the precipitation-impregnation method exhibits excellent catalytic performance in the gas-phase hydrogenation of methyl benzoate to chloro-free benzaldehyde. This catalyst not only allows for a reduction in the optimal reaction temperature by approximately 40 °C, but also provides opportunities for adjusting and optimizing the catalyst structure. This optimization involves the calcination temperature of the support and the active components of manganese, resulting in the development of high-performance catalysts. Our findings indicate that by adjusting the interaction between manganese active components and the support, it becomes possible to alter the catalyst surface acidity, redox properties, and suitable oxygen vacancies, thus providing valuable insights for the optimization of manganese-based catalysts.

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