Support effect in hydrogenation of methyl benzoate over supported manganese oxide catalysts

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Abstract

Manganese oxide supported on MgO, γ-Al$_2$O$_3$, SiO$_2$, ZrO$_2$, TiO$_2$ and SiO$_2$-Al$_2$O$_3$ catalysts were prepared. The effect of support on their catalytic behavior for hydrogenation of methyl benzoate to benzaldehyde was studied. The formation of toluene is suppressed on the supported catalysts due to the dilution of oxygen vacancies on the catalyst surface. The benzaldehyde yield of the supported catalysts follows the trend Mn/γ-Al$_2$O$_3$ > Mn/TiO$_2$ > Mn/ZrO$_2$ > Mn/SiO$_2$-Al$_2$O$_3$ > Mn/SiO$_2$ > Mn/MgO. XRD measurements show that the Mn nitrate precursor is essentially transformed to highly dispersed MnO$_2$ on the supports at calcination and subsequently to MnO under reaction conditions with an exception of Mn/MgO. TPR and XPS analyses suggest that a strong interaction between manganese oxide and the γ-Al$_2$O$_3$ support plays a positive role in the hydrogenation reaction.
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1. Introduction

Aromatic aldehydes are important intermediates in fine chemical industries, manufacturing pharmaceuticals, agrochemicals, perfumes and flavors [1]. Various processes have been used for the synthesis of aromatic aldehydes, e.g. partial oxidation of alkyl aromatics [2], halogenation of alkyl aromatics followed by hydrolysis [3], or halogenation of aromatic acids followed by hydrolysis, the so-called Rosenmund reduction [4]. However, all these technologies have their own drawbacks, such as low selectivity, low yield and production of a large amount of harmful wastes. The direct hydrogenation of carboxylic acids or carboxylic acid esters to corresponding aldehydes is a more preferable method of synthesizing aldehydes from the point view of green technology. Benzaldehyde was produced via this method with a high yield using chromium modified zirconia catalyst by Mitsubishi Chemicals in 1988 [5]. Later on, a large number of metal oxides, including alkali earth oxides, transition metal oxides and rare earth oxides, have been suggested for use as catalysts for the selective hydrogenation of benzoic acid and methyl benzoate [6–17].

Among these metal oxide catalysts, manganese oxide has shown good activity and selectivity to benzaldehyde at rather low temperature [11–16]. In the patent literature [11], the use of activated alumina support enhances the catalytic activity of manganese oxide. However, from the patent role of the individual oxides as catalyst or catalyst support in the hydrogenation reaction is unclear.

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In this work, the catalytic properties of a wide variety of bulk metal oxides and oxide supported manganese oxide catalysts in hydrogenation of methyl benzoate are studied. The catalysts are characterized by X-ray diffraction (XRD), temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS) and N_2 adsorption methods. The activity and selectivity of the catalysts are correlated with the characterization results to gain a better insight into the effect of the oxide supports on this type of catalyst.

2. Experimental

2.1. Preparation of catalysts

Supported manganese oxide catalysts were prepared by impregnation method. The supports used were commercial γ-Al_2O_3, SiO_2, SiO_2-Al_2O_3 (Si/Al = 1), TiO_2 (anatase), ZrO_2 (tetragonal), and MgO of chemical pure grade. Aqueous solution of $Mn(NO_3)_2 \cdot 4H_2O$ was applied to the dried supports until incipient wetness, followed by drying at $120\,^\circ$C for 3 h and calcining at $450\,^\circ$C for 3 h in air. For comparison purposes, bulk MnO_2, Mn_2O_3, and Mn_3O_4 were prepared according to the procedures in the literature [18]. MnO_2 was prepared by calcining $Mn(OH)_2$ at $500\,^\circ$C for 10 h in air. Mn_2O_3 was prepared by heating $MnCO_3 \cdot xH_2O$ in air consecutively for 3 h at $120\,^\circ$C, 8 h at $240\,^\circ$C and, finally, 8 h at $550\,^\circ$C. Mn_3O_4 was prepared by calcining $MnCO_3 \cdot xH_2O$ at $1000\,^\circ$C for 8 h in air.

2.2. Catalyst characterization

XRD patterns were recorded on a Siemens D8 Advance X-ray diffractometer (Cu Kα radiation, 40 kV, 40 mA) with a scan speed of $8^\circ\,min^{-1}$ and a scan range of 10–80°. The surface areas of the oxides and the supported catalysts were measured by nitrogen adsorption at $-196\,^\circ$C using a Micromeritics ASAP 2000 instrument and calculated by BET method. XPS spectra were obtained with a Perkin-Elmer PHI 5000 ESCA system using Mg Kα radiation at 14 kV and 250 W. The vacuum of the specimen chamber was better than 5×10^{-7} Pa, and C_{1s} at 284.6 eV was taken as reference. TPR experiments were carried out on a Micromeritics ASAP 2900 instrument using 25 mg catalyst under a gas flow ($40\,ml\,min^{-1}$) of hydrogen

(10%) and argon (90%). The catalyst was pretreated in N_2 flow at $300\,^\circ$C for 3 h. The temperature was increased from 100 to $600\,^\circ$C with a ramp rate of $10\,^\circ$C min^{-1}. A thermal conductivity detector was used to monitor the hydrogen consumed during TPR course. CuO was used as a standard sample for the calibration of hydrogen consumption.

2.3. Activity measurement

The catalytic test was carried out in a fixed bed reactor with 600 mg of catalyst in the form of 20–40 mesh particles. The reaction was performed at $410\,^\circ$C and ambient pressure. Methyl benzoate (MB) was pumped to a vaporizer to mix with hydrogen (GHSV = $700\,h^{-1}$), and the mixture (H_2/MB = 20/1 vol.%) was preheated to $210\,^\circ$C before entering the reactor. Before the test, the catalyst was reduced at $260\,^\circ$C for 2 h, at $360\,^\circ$C for 3 h and, finally, at $420\,^\circ$C for 2 h in a H_2 flow ($30\,ml\,min^{-1}$). The reaction products were condensed and analyzed by means of a GC–MS (Finnigen Voyager) or a GC (HP 5890) equipped with a 30 m SE-54 capillary column and a flame ionization detector. The injector temperature was $260\,^\circ$C, and the column temperature was increased from 80 to $260\,^\circ$C with a ramp rate of $15\,^\circ$C min^{-1}.

3. Results and discussion

3.1. Catalytic behavior of various oxides

The conversion of methyl benzoate and product distribution on various metal oxides after reacting for 6 h at $410\,^\circ$C are listed in Table 1. The metal oxides of the main groups, such as MgO, γ-Al_2O_3, SiO_2-Al_2O_3 and SiO_2, are inactive for the reaction, whereas the transition metal oxides with some redox properties, such as TiO_2, ZrO_2 and manganese oxides, show rather high conversions of methyl benzoate (66–99%) and moderate selectivities to benzaldehyde (58–68%). ZrO_2 gives the highest yield of benzaldehyde among the oxides. The catalytic performance of different forms of manganese oxide in the reaction is similar, since these oxides are unstable in hydrogen at elevated temperature and they all reduce to MnO after catalyst pretreatment at $420\,^\circ$C in hydrogen. Fig. 1 shows the XRD patterns of the as-synthesized manganese oxides and

Table 1
Hydrogenation of methyl benzoate over various metal oxides

Catalyst	Conversion (%)	Selectivity (%)						BA yield (%)	Surface area ($m^2\,g^{-1}$)
		BA	B	T	BOH	ME	Others		
MgO	–	–	–	–	–	–	–	–	41.8
SiO_2	–	–	–	–	–	–	–	–	316
SiO_2-Al_2O_3	–	–	–	–	–	–	–	–	347
γ-Al_2O_3	–	–	–	–	–	–	–	–	110
TiO_2	66	62	10.9	4.4	2	2.3	18.4	41	107
ZrO_2	98.4	68.3	0.6	23.3	1.8	1.1	4.9	67.1	91
MnO_2	86.9	58.7	–	28.4	2.3	0.6	10	51	7.7
Mn_2O_3	98.9	58.2	–	26.7	1.7	0.6	12.8	57.2	16.9
Mn_3O_4	98.4	63.4	0.4	20.9	2.9	0.5	12.3	62.4	1.1

Reaction conditions: 600 mg catalyst; 410 °C; H_2 GHSV = 700 h^{-1}; H_2/methyl benzoate = 20/1 vol.%. BA: benzaldehyde; B: benzene; T: toluene; BOH: benzylalcohol; ME: methylbenzyl ether.

the oxides reduced at 420 °C. The diffraction patterns of the reduced oxides are typical of MnO.

It is interesting to note that the catalytic activity and selectivity of the manganese oxides are very similar to those of ZrO_2 although their specific surface areas are much lower. Selective hydrogenation of methyl benzoate to benzaldehyde is a Mars and van Kreve-

Fig. 1. XRD patterns of manganese oxides before and after reaction: (a) MnO_2 before reaction; (b) Mn_2O_3 before reaction; (c) Mn_3O_4 before reaction; (d) MnO_2 after reaction; (e) Mn_2O_3 after reaction; (f) Mn_3O_4 after reaction.

len type reaction [19]. The initial step of the reaction is the adsorption of the benzoate molecule on an oxygen vacancy of the oxide catalyst, which results in the break of one C–O bond. Hydrogen from the nearby OH group hydrogenates the fragment to benzaldehyde, and the deposited oxygen is subsequently removed by hydrogen in the reaction mixture. The high activity of the manganese oxides implies that they are more reducible than the other oxides and a higher concentration of oxygen vacancy exists on the surface of the oxides after prereduction at 420 °C. However, the high concentration of oxygen vacancy may render a loss of both the oxygen atoms in the benzoate molecule and subsequently toluene is formed, leading to a reduction in selectivity to benzaldehyde [17].

3.2. Hydrogenation on supported manganese oxide catalysts

Manganese oxide catalysts supported on different oxides were prepared and tested. XRD patterns of the supported catalysts before and after reaction are illustrated in Fig. 2. After calcination at 450 °C, $Mn(NO_3)_2$ is decomposed to form MnO_2 species on the oxide supports. Under reaction conditions, MnO_2 is reduced to MnO, and the latter is the active component for the reaction. The diffraction peaks of both MnO_2 and MnO on the catalysts are very low and broad, which signals a rather high dispersion of the manganese oxides on the supports. The Mn/MgO catalyst is an exception. A stable complex oxide Mg_6MnO_8 is formed
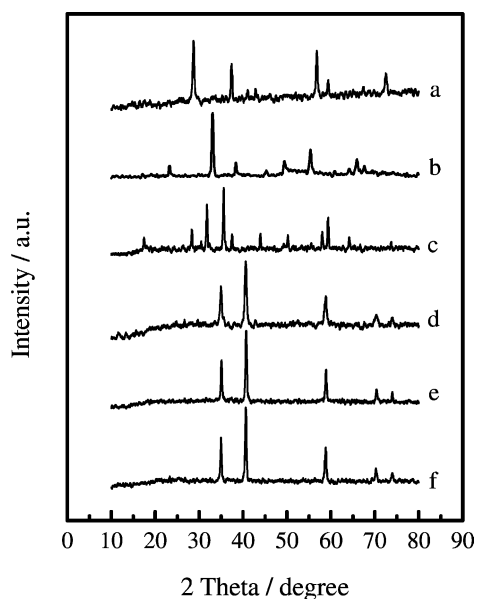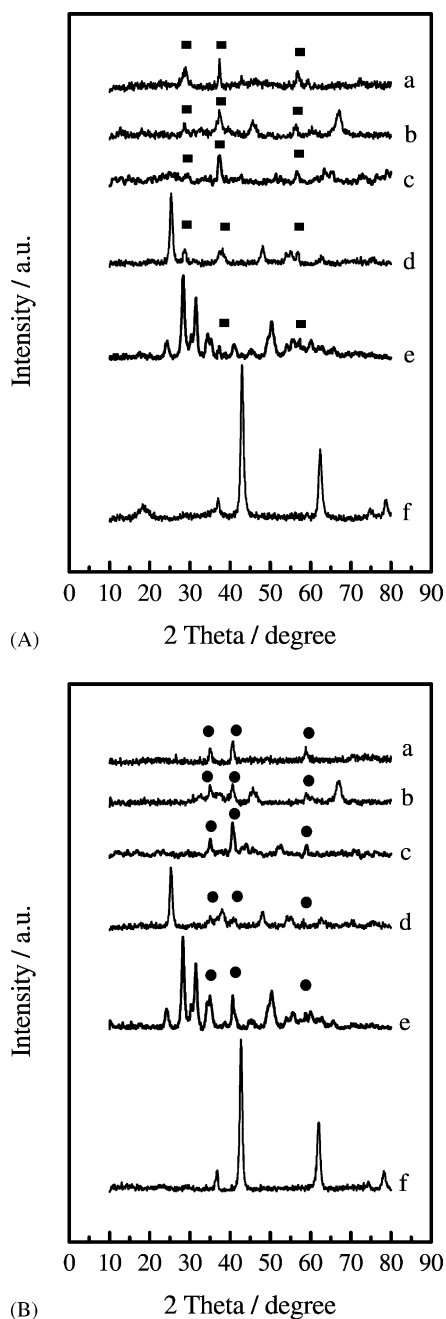
Fig. 2. XRD patterns of supported manganese oxide catalysts (A) before and (B) after reaction: (a) 10% Mn/SiO$_2$-Al$_2$O$_3$; (b) 10% Mn/γ-Al$_2$O$_3$; (c) 10% Mn/SiO$_2$; (d) 10% Mn/TiO$_2$; (e) 10% Mn/ZrO$_2$; (f) 10% Mn/MgO ((■) MnO$_2$; (●) MnO).

when calcining at 450 °C, and unlike all the other catalysts it is irreducible during reaction.

The activity and selectivity of the supported manganese oxide catalysts for the hydrogenation of methyl benzoate are listed in Table 2. The yield of benzaldehyde increases insignificantly as the manganese oxide loading is increased from 10 to 20%. The selectivity to toluene of all the supported catalysts is suppressed, which may be explained by the dilution of the oxygen vacancies on the catalyst surface after supporting. In accordance to the catalytic activities of the supported manganese oxide catalysts, they can be divided into three categories. For most of the catalysts, such as Mn/TiO$_2$, Mn/ZrO$_2$, Mn/SiO$_2$ and Mn/SiO$_2$-Al$_2$O$_3$, their catalytic activity is likely an additive property of the two oxides. However, a marked "positive" support effect is observed in the case of Mn/γ-Al$_2$O$_3$. The conversion of methyl benzoate and selectivity to benzaldehyde on Mn/γ-Al$_2$O$_3$ catalyst are unexpectedly high, although γ-Al$_2$O$_3$ itself is inactive for the reaction. The yields of benzaldehyde on 10% Mn/γ-Al$_2$O$_3$ and 20% Mn/γ-Al$_2$O$_3$ are 73.6 and 74.0%, respectively, which are evidently higher than those on all the other catalysts. On the contrary, the activity of Mn/MgO is much lower than those of the other catalysts, implying the existence of a "negative" support effect. From the XRD results in Fig. 2, such a negative support effect is probably associated with the formation of the irreducible complex oxide Mg$_6$MnO$_8$ under reaction conditions.

For getting an even clearer picture of the interaction between the oxides, the hydrogenation reaction was carried out on mechanical mixtures of manganese oxide with the oxide supports as well. The reaction results are listed in Table 3. The activity and selectivity of the mechanical mixtures of the oxides are similar to those of the supported catalysts except Mn + γ-Al$_2$O$_3$ and Mn + MgO. The catalytic activity of Mn + γ-Al$_2$O$_3$ is two times less than that of the supported Mn/γ-Al$_2$O$_3$ catalyst, whereas the catalytic activity of Mn + MgO is 1.5 times higher than that of the supported Mn/MgO catalyst. Since the interaction between two oxides in mechanical mixtures is usually weaker than that in catalysts prepared by an impregnation method, the above observation further confirms that the positive or negative support effect of γ-Al$_2$O$_3$ or MgO originates from the strong interaction between manganese oxide and these two oxide supports.

Table 2
Hydrogenation of methyl benzoate over supported manganese oxide catalysts

Catalyst	Conversion (%)	Selectivity (%)						BA yield (%)	Surface area (m^2 g^{-1})
		BA	B	T	BOH	ME	Others		
10% Mn/MgO	8.2	45.0	4.4	2.5	–	–	17	3.7	91.8
10% Mn/SiO$_2$	18.0	82.6	7.7	4.4	–	–	5.3	14.8	267
10% Mn/SiO$_2$-Al$_2$O$_3$	22.7	83.5	1.8	1.1	–	–	13.6	18.9	145
10% Mn/TiO$_2$	76.2	88.0	0.8	3	0.5	0.5	7.2	67.1	75.4
10% Mn/γ-Al$_2$O$_3$	91.2	80.8	0.5	5.3	6.4	2.0	5.0	73.6	73.9
10% Mn/ZrO$_2$	98.3	63.7	2.4	7.5	2.4	–	24.0	62.6	47.5
20% Mn/MgO	11.2	78.9	4.4	3.7	–	–	13.0	8.8	64
20% Mn/SiO$_2$	31.9	83.1	2.0	2.4	0.6	–	12.9	26.5	203
20% Mn/SiO$_2$-Al$_2$O$_3$	41.2	86.4	0.9	3.3	–	0.6	8.8	35.6	115
20% Mn/TiO$_2$	82.5	84.1	1.1	6	0.2	0.5	1.1	69.4	45.6
20% Mn/γ-Al$_2$O$_3$	90.9	81.4	0.2	6.7	5.8	1.7	8.6	74.0	78.1
20% Mn/ZrO$_2$	99.2	66.2	2	13.4	1.3	–	17.2	65.7	32.7

Reaction conditions: 600 mg catalyst; 410 °C; H$_2$ GHSV = 700 h^{-1}; H$_2$/methyl benzoate = 20/1 vol.%.

The specific surface areas of the supported catalysts were measured by N$_2$ adsorption method and given in Table 2 as well. Obviously, there is no direct correlation between the catalytic activity and specific surface area of the catalysts, suggesting that besides the textural properties of the catalysts the dispersion and chemical state of manganese oxide on the surface of the catalysts probably play a more important role in this selective hydrogenation reaction.

3.3. Effect of temperature and H$_2$

The activity and selectivity of MnO$_2$ and 10% Mn/γ-Al$_2$O$_3$ catalysts for the hydrogenation reaction at different reaction temperatures and H$_2$/methyl benzoate ratios are listed in Tables 4 and 5.

For both series of catalysts, the conversion of methyl benzoate is increased with reaction temperature, whereas the selectivity to benzaldehyde increases when the reaction temperature is increased from 350 to 370 °C and then decreases as the reaction temperature is further increased. The highest benzaldhyde yield is attained at 410 °C. The lower selectivity at 350 °C is due to the increased concentration of heavier aromatics such as phenyltoluene and diphenylmethane in the product, whereas the reduction in selectivity at higher temperatures is mainly associated with the increased concentration of toluene in the product. In the whole temperature region, the γ-Al$_2$O$_3$ supported catalyst is more selective to benzaldehyde than the unsupported manganese oxide catalyst due to the suppression of the formation of toluene and heavier aromatics. The selectivity and yield of benzaldehyde

Table 3
Hydrogenation of methyl benzoate over mixtures of oxides

Catalyst	Conversion (%)	Selectivity (%)						BA yield (%)
		BA	B	T	BOH	ME	Others	
10% Mn + MgO	12.0	81.8	0.6	1.4	–	0.6	9.6	9.8
10% Mn + SiO$_2$	16.3	82.7	3.9	2.1	–	1.3	10.0	13.5
10% Mn + SiO$_2$-Al$_2$O$_3$	21.5	69.4	3.7	2.8	–	–	18.5	14.9
10% Mn + γ-Al$_2$O$_3$	45.4	83.9	0.4	0.6	0.5	1.8	12.8	38.1
10% Mn + TiO$_2$	73.8	81.6	0.8	3.0	0.7	0.4	4.5	60.2
10% Mn + ZrO$_2$	99.0	62.0	0.3	20.7	–	–	18.0	61.4

Reaction conditions: 600 mg catalyst; 410 °C; H$_2$ GHSV = 700 h^{-1}; H$_2$/methyl benzoate = 20/1 vol.%.

Table 4
Hydrogenation of methyl benzoate over MnO_2 and $Mn/\gamma\text{-}Al_2O_3$ catalyst under different temperatures

Catalyst	T (°C)	Conversion (%)	Selectivity (%)						BA yield (%)
			BA	B	T	BOH	ME	Others	
MnO_2	350	23.0	78.2	–	2.5	5.0	–	14.3	18.0
	370	38.4	87.6	–	4.0	2.9	–	5.5	33.6
	390	74.7	69.9	0.3	16.7	3.4	–	9.7	52.2
	410	86.9	58.7	–	28.4	2.3	0.6	10.0	58.7
	430	92.0	48.4	0.5	30.0	2.4	1.4	17.3	46.8
$10\% Mn/\gamma\text{-}Al_2O_3$	350	13.6	82.2	–	2.4	0.6	–	14.8	11.2
	370	24.7	91.2	1.0	1.4	2.0	–	4.4	22.5
	390	52.8	90.7	0.6	0.7	3.5	–	4.5	47.9
	410	91.2	80.8	0.5	5.3	6.4	2.0	5.0	73.6
	430	92.3	71.8	0.5	11.8	5.9	2.1	7.9	66.3

Reaction conditions: 600 mg catalyst; 410 °C; H_2 GHSV $= 700\,h^{-1}$; H_2/methyl benzoate $= 20/1$ vol.%.

Table 5
Hydrogenation of methyl benzoate over 10% $Mn/\gamma\text{-}Al_2O_3$ catalyst at different H_2/methyl benzoate ratios

H_2:MB	Conversion (%)	Selectivity (%)						BA yield (%)
		BA	B	T	BOH	ME	Others	
5:1	26.5	89.4	2.0	1.1	3	–	4.5	23.7
10:1	69.8	81.6	1.3	5.0	7.1	–	5.0	56.9
20:1	91.2	80.8	0.5	5.3	6.4	2.0	5.0	73.6
30:1	80.1	86.8	0.4	2.0	6.7	2.1	2.0	69.5

Reaction conditions: 600 mg catalyst; 410 °C; H_2 GHSV $= 700\,h^{-1}$.

on 10% $Mn/\gamma\text{-}Al_2O_3$ catalyst at 410 °C reach 80.8 and 73.6%, respectively.

The ratio of H_2 and methyl benzoate in the reactant affects the activity and selectivity of 10% $Mn/\gamma\text{-}Al_2O_3$ as well. The highest yield of benzaldehyde is attained at a H_2/methyl benzoate ratio of 20:1. Further increasing the H_2/methyl benzoate ratio improves the selectivity to benzaldehyde but reduces the conversion of methyl benzoate.

3.4. TPR and XPS results

The TPR profiles of the supported manganese oxide catalysts are illustrated in Fig. 3. The 10% Mn/MgO catalyst is irreducible before 600 °C due to the formation of the complex oxide. All the other supported catalysts show a two-step reduction. The two reduction peaks on the profile correspond to subsequent reduction of MnO_2 to Mn_2O_3/Mn_3O_4 and MnO. The reduction peak temperatures and the total H_2 con-
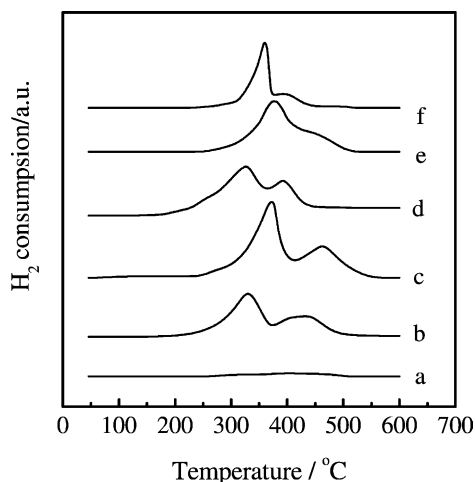

Fig. 3. TPR profiles of various supported manganese oxide catalysts: (a) 10% Mn/MgO; (b) 10% Mn/SiO_2; (c) 10% $Mn/\gamma\text{-}Al_2O_3$; (d) 10% Mn/ZrO_2; (e) 10% Mn/TiO_2; (f) 10% $Mn/SiO_2\text{-}Al_2O_3$.

Table 6
TPR data for supported manganese oxide catalysts

Catalyst	T (°C)		H_2 consumption (O/Mn)
	I	II	
10% Mn/ZrO$_2$	323	394	0.89
10% Mn/SiO$_2$-Al$_2$O$_3$	360	409	0.90
10% Mn/SiO$_2$	328	434	0.87
10% Mn/TiO$_2$	375	434	0.91
10% Mn/γ-Al$_2$O$_3$	370	467	0.95

sumption expressed as O/M ratio are summarized in Table 6.

The O/Mn values in Table 6 indicate the presence of a small fraction of Mn_2O_3 phase along with MnO_2 phase on all the supported catalysts before reduction. Nevertheless, this small amount of dispersed Mn_2O_3 species is not detected in XRD measurement. The reduction peak temperatures of Mn/γ-Al$_2$O$_3$ are higher than those of the other supported catalysts, suggesting the occurrence of a stronger interaction between the manganese oxide and the γ-Al$_2$O$_3$ support.

XPS spectra of some representative reduced catalysts with a Mn loading 3 wt.% were recorded instead of the supported catalysts with Mn loadings of 10 and 20 wt.%, because the sensitivity of the measurement of electron binding energy shift related to surface interactions is decreased with increasing loading [20]. In the literature [20–22], it has been reported that the shifts in binding energy of surface metal oxides on alumina substrate reflect the interaction of the metal oxides with the alumina environment. The Mn $2p_{3/2}$ electron binding energies of Mn^{2+} compounds are in the range of 640.6–641.7 eV [20]. The binding energy of the Mn $2p_{3/2}$ electrons of the reduced Mn/γ-Al$_2$O$_3$ catalyst in Fig. 4 is obviously higher than those observed for the other supported catalysts, which is again in agreement with the suggestion on a stronger interaction between the surface Mn species and the γ-Al$_2$O$_3$ support.

In the preparation of supported catalysts, the support pH at the point of zero charge (PZC) may influence the molecular structure of the surface active species [23,24]. The pH values of the supports used in this work decrease in the order of MgO > γ-Al$_2$O$_3$ > TiO$_2$ ∼ ZrO$_2$ > SiO$_2$ > SiO$_2$-Al$_2$O$_3$. The higher pH values of MgO and γ-Al$_2$O$_3$ could lead to a stronger interaction between the support and the acidic Mn
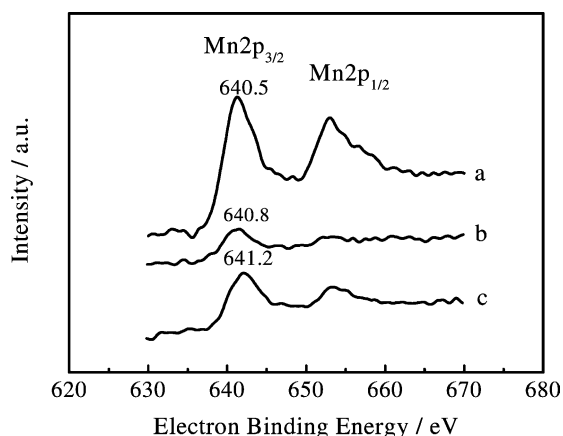

Fig. 4. XPS spectra of the supported catalysts reduced in hydrogen: (a) 3% Mn/ZrO$_2$; (b) 3% Mn/SiO$_2$; (c) 3% Mn/γ-Al$_2$O$_3$.

nitrate precursor. This may explain the cause of the variations in the structure or electronic state of the manganese oxide active species on the catalysts and ultimately the differences in catalytic behavior.

4. Conclusions

The catalytic performance of bulk oxides and supported manganese oxide catalysts for hydrogenation of methyl benzoate to benzaldehyde were studied. Transition metal oxides, such as ZrO$_2$, TiO$_2$ and manganese oxides with redox properties are active for the reaction, whereas oxides of the main groups, such as MgO, γ-Al$_2$O$_3$, SiO$_2$ and SiO$_2$-Al$_2$O$_3$, are inactive. γ-Al$_2$O$_3$ is a good support for this type of catalyst. The selectivity to benzaldehyde on Mn/γ-Al$_2$O$_3$ catalyst is improved considerably in comparison to the bulk manganese oxides due to suppression of the formation of toluene and other heavier aromatics. The benzaldehyde yield of the supported manganese oxide catalysts follows the order of Mn/γ-Al$_2$O$_3$ > Mn/TiO$_2$ > Mn/ZrO$_2$ > Mn/SiO$_2$-Al$_2$O$_3$ > Mn/SiO$_2$ > Mn/MgO. Under our reaction conditions, the conversion of methyl benzoate, selectivity to benzaldehyde and benzaldehyde yield on 10% Mn/γ-Al$_2$O$_3$ catalyst are 91.2, 80.8 and 73.6%, respectively.

XRD measurements show that manganese oxide on the supported catalysts is reduced to highly dispersed

MnO under reaction conditions with the exception of Mn/MgO, in which an irreducible complex oxide Mg_6MnO_8 is formed. TPR and XPS analyses reveal the occurrence of a strong interaction between the γ-Al_2O_3 support and the surface manganese oxide, that may explain the positive support effect of γ-Al_2O_3.

Acknowledgements

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