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Article

Layered double hydroxide-like $\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ materials as supports for Ir catalysts: Promotional effects of Fe doping in selective hydrogenation of cinnamaldehyde

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ARTICLE INFO

Article history:

Received 5 December 2017

Accepted 2 February 2018

Published 5 May 2018

Keywords:

Ir catalyst

Layered double hydroxide

Fe doping

Support effect

Selective hydrogenation

Cinnamaldehyde

ABSTRACT

Supported Ir catalysts were prepared using layered double hydroxide-like materials, such as $\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$, containing Fe and Al species in varying amounts as supports. These Ir catalysts were applied for the selective hydrogenation of cinnamaldehyde (CAL). When x was changed from 0 (Ir/Mg₃Al) to 1 (Ir/Mg₃Fe), the rate of CAL hydrogenation reached a maximum at approximately $x = 0.25$, while the selectivity to unsaturated alcohol, i.e., cinnamyl alcohol, monotonously increased from 44.9% to 80.3%. Meanwhile, the size of the supported Ir particles did not change significantly with x , remaining at 1.7 ± 0.2 nm, as determined by transmission electron microscopy. The chemical state of Ir and Fe species in the Ir/Mg₃Al_{1-x}Fe_x catalysts was examined by temperature programmed reduction by H₂ and X-ray photoelectron spectroscopy. The surface of the supported Ir particles was also examined through the *in-situ* diffuse reflectance infrared Fourier-transform of a probe molecule of CO. On the basis of these characterization results, the effects of Fe doping to Mg₃Al on the structural and catalytic properties of Ir particles in selective CAL hydrogenation were discussed. The significant factors are the electron transfer from Fe²⁺ in the Mg₃Al_{1-x}Fe_x support to the dispersed Ir particles and the surface geometry.

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1. Introduction

Layered double hydroxides (LDHs) are promising materials as catalysts and support precursors because of their interesting physical and chemical properties [1]. LDH-supported metals are widely used as hydrogenation catalysts [2–4]. For example, Sangeetha *et al.* [3] reported that hydrotalcite MgAl-*MMO* (mixed metal oxide)-supported Pd catalyst showed higher ac-

tivity in the hydrogenation of nitrobenzene, as compared to MgO and $\gamma\text{-Al}_2\text{O}_3$ -supported Pd catalysts. The superior catalytic performance was ascribed to the presence of finely dispersed Pd nanoparticles and the basic nature of the hydrotalcite support. It was also reported that Pt/MgAl-*MMO* was active during the hydrogenation of xylose and sugars to the corresponding alcohols, showing better performance than Pt/ Al_2O_3 [4]. Furthermore, Mg-Al-Fe ternary hydrotalcite-like materials

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This work was supported by the National Key Research and Development Program of China (2016YFA0602900), National Natural Science Foundation of China (21603212, 21672204), Youth Innovation Promotion Association CAS (2016206), Jilin Provincial Science and Technology Program of China (20150204050GX), and Chinese Academy of Sciences President's International Fellowship Initiative (2018VCA0012).

DOI: 10.1016/S1872-2067(18)63042-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 5, May 2018

(MgAlFe-LDH) including the iron species in the Mg-Al hydrotalcite structure was reported to be active for photocatalysis [5], H₂S selective oxidation [6], and dehydrogenation of ethylbenzene [7,8].

In recent years, Ir catalysts have received particular attention with regard to hydrogenation reactions [9,10]. During the hydrogenation of alkenes, Rossi *et al.* [11] reported a magnetic Ir/Fe₃O₄@SiO₂-NH₂ catalyst that was more efficient compared to Rh and Pt catalysts. For the hydrogenation of ethyl pyruvate, the performance of Ir-based catalysts was influenced by the particle size, morphology, and support [12]. For ethene hydrogenation with Ir/MgO catalysts, better activity and stability were observed for the Ir clusters of 1 nm size [10]. Ir/ZrO₂·xH₂O showed a superior catalytic performance in the hydrogenation of halogenated aromatic nitro-compounds due to the formation of a hydrogen bond between the reactant and water, followed by the activation of the nitro group by water [13]. We showed Ir/TiO₂-FeO_x catalyst to be more active than Ir/TiO₂ in the selective hydrogenation of *o*-chloronitrobenzene, probably due to the strong interaction between Ir and FeO_x [14].

Recently, Ir catalysts were reported to be active for the selective hydrogenation of α,β -unsaturated carbonyl compounds such as crotonaldehyde, citral, and cinnamaldehyde (CAL) [15–21]. For controlling these reactions, the rates of hydrogenation, as well as the product selectivity are significant. In the hydrogenation of crotonaldehyde over Ir/TiO₂, the selectivity to crotyl alcohol was only 13% [15]. Ir/SiO₂ was more active than Au/SiO₂ in the hydrogenation of CAL. However, the selectivity to cinnamyl alcohol (COL; 57%) over Ir/SiO₂ was significantly lower than that (79%) over Au/SiO₂ [19]. Luo *et al.* [18] showed that, for the hydrogenation of crotonaldehyde over Ir/TiO₂ catalysts, the one that reduced at 300 °C was more active and selective. An effective strategy for improving the catalyst performance is to modify Ir catalysts by the addition of a second metal such as Fe [14,22,23]. For example, the selectivity to COL (83%) was significantly higher over Ir/FeO_x/SiO₂ compared to that with Ir/SiO₂ (57%) during CAL hydrogenation. However, the conversion of CAL achieved with the former was low (46%) [24]. For the hydrogenation of crotonaldehyde over Ir/SiO₂, the activity and the selectivity to crotyl alcohol were significantly enhanced by adding FeO_x, which was ascribed to the formation of new active sites at the Ir-FeO interface [25]. Although these results demonstrate the usefulness of Fe doping for the catalysis of the supported Ir catalysts, the functions and interactions of Fe dopant with active Ir species have not been clarified well.

After considering the above-mentioned previous works on the properties of LDH materials and the catalysis of the supported Ir catalysts in the selective hydrogenation of α,β -unsaturated carbonyl substrates, the authors have attempted to use interesting structural features of Mg-Al-Fe hydrotalcite-like materials to improve the performance of supported Ir catalysts, while shedding light on the possible functions of Fe species in the catalysis of supported Ir particles. Mg₃Al_{1-x}Fe_x-LDH samples were prepared by introducing Fe³⁺ into Mg₃Al-LDH through simple co-precipitation, while Ir was loaded onto these hydrotalcite-derived Mg₃Al_{1-x}Fe_x materials by incipient wetness

impregnation. The catalytic performance of the supported Ir samples thus prepared was investigated with the selective hydrogenation of CAL in water. It should be noted here that the activity and the selectivity to COL were improved significantly by doping Fe into the parent support material, Mg₃Al-LDH. These promotional effects of the Fe doping were examined by characterizing the supports and catalysts using X-ray diffraction (XRD), transmission electron microscopy (TEM), temperature programmed reduction by H₂ (H₂-TPR), X-ray photoelectron spectroscopy (XPS), and *in-situ* diffuse reflectance infrared Fourier-transform (DRIFT) of CO adsorption.

2. Experimental

2.1. Preparation of LDH supports and Ir catalysts

A series of Mg₃Al_{1-x}Fe_x-LDH ($x = 0, 0.25, 0.5, 0.75, 1$) samples were prepared by the co-precipitation method. Required amounts of Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, and Fe(NO₃)₃·9H₂O were added to 50 mL of distilled water under stirring (solution A), in which $[Mg^{2+}]/([Al^{3+}] + [Fe^{3+}]) = 3$ and $([Mg^{2+}] + [Al^{3+}] + [Fe^{3+}]) = 1$ mol/L. Another solution (solution B) of NaOH (0.5 mol/L) and Na₂CO₃ (1.6 mol/L) was prepared. Solutions A and B were added dropwise (1 mL/min) to a 250 mL round-bottom flask under stirring at 35 °C at a pH of 9.5, resulting in the formation of precipitates. The suspension obtained was aged in a water bath at 65 °C for 18 h under stirring. Subsequently, the precipitates were separated by filtration, washed repeatedly with distilled water, and dried at 100 °C.

Ir-supported catalysts were prepared by the incipient wetness impregnation method with a nominal Ir content of 3 wt%. One gram of the support was impregnated with 2 mL of IrCl₃ aqueous solution. The resultant mixture was dried at 80 °C for 12 h. Subsequently, the sample thus obtained was reduced at 300 °C by H₂ for 2 h before reaction. The supported Ir catalysts were prepared using various Mg₃Al_{1-x}Fe_x ($x = 0, 0.25, 0.5, 0.75, 1$) supports.

2.2. Characterization

The structure of the LDH supports and supported Ir catalysts prepared were characterized by XRD (Bruker D8, Cu K α , 40 kV and 40 mA). The (110) plane was used to calculate parameter *a*, corresponding to the cation-cation distance in the hydroxide layers. The (003) and (006) planes were used to determine parameter *c*, related to the total thickness of the layer and the interlayer distance [26]. The average crystal size in *c* direction was calculated from (003) and (006) planes using Scherrer's equation. The size of supported Ir particles was examined by TEM on JEOL JEM-2010 instrument, with an accelerating voltage of 200 kV. The catalyst sample was dispersed in ethanol under ultrasonic conditions for 10 min, subsequently being dropped onto a carbon film on a copper grid. TPR experiments with H₂ were carried out on a multi-purpose adsorption instrument (TP-5080) with 50 mg of sample. The reduction was conducted in a 10% H₂/N₂ stream at a heating rate of 10 °C/min. Hydrogen consumption was detected using a

thermal conductivity detector. The properties of the exposed Ir and Fe species were examined by XPS (VG Microtech 3000 Multilab). The binding energy correction was made by using C 1s peak at 284.6 eV as reference. Nicolet iS50 spectrometer with an MCT detector was used to perform the *in-situ* diffuse reflectance infrared Fourier-transform (DRIFT) spectra of the CO adsorbed on catalyst samples. Firstly, the samples were reduced *in-situ* with 10% H₂/Ar at a flow rate of 50 mL/min for 1 h. Subsequently, the flowing gas was changed to He, while the sample was cooled to 30 °C. After the background spectrum was collected, the sample was exposed to 10% CO/He for 1 h, followed by purging with He for an additional 15 min. Finally, the spectra were recorded. The actual Ir loading was measured by ICP-OES (Thermo Scientific ICAP6000, USA). The amounts of Ir measured were in agreement with the nominal value of 3.0 wt% (with a deviation < 5%) for all the Ir/Mg₃Al_{1-x}Fe_x catalysts prepared.

2.3. Activity measurements

A catalyst sample was reduced at 300 °C in H₂ stream for 2 h before the activity test of CAL hydrogenation. A stainless-steel autoclave reactor (50 mL) was charged with 0.5 mL of CAL, 0.1 g of reduced catalyst, and 5 mL of water. The reduced catalyst was transferred into the solvent directly without exposure to atmosphere. The reactor was sealed and purged with H₂ several times to remove the air and insert into a water bath for 15 min. Subsequently, H₂ (3 MPa) was introduced into the reactor to initiate the reaction with continuous stirring. After the reaction was completed, the reactor was cooled in an ice-water bath and carefully depressurized. The liquid products were analyzed and identified by gas chromatograph (Shimadzu GC-2010, Rtx-50) and gas chromatograph-mass spectrometer (Agilent 5890, HP-5). *O*-Xylene was used as an internal standard for quantitative analysis. The total conversion of CAL was calculated by $1 - m_{\text{CAL}}/(m_{\text{CAL}} + m_{\text{HCAL}} + m_{\text{COL}} + m_{\text{HCOL}})$, where m_x was the moles of the product x detected: cinnamaldehyde (CAL), hydrocinnamaldehyde (HCAL), cinnamyl alcohol (COL), hydrocinnamyl alcohol (HCOL). The selectivity to x was determined by m_x divided by the total amount of the products of HCAL, COL, and HCOL. The rate of CAL hydrogenation was the moles of CAL reacted per unit time per unit mol of Ir.

3. Results and discussion

3.1. Characterization of supports and supported Ir catalysts

XRD patterns of Mg₃Al_{1-x}Fe_x-LDH ($x = 0-1$) samples pre-

Fig. 1. XRD patterns of Mg₃Al-LDH (1), Mg₃Al_{0.75}Fe_{0.25}-LDH (2), Mg₃Al_{0.5}Fe_{0.5}-LDH (3), Mg₃Al_{0.25}Fe_{0.75}-LDH (4), and Mg₃Fe-LDH (5).

pared are shown in Fig. 1, which indicate the structure of layered double hydroxides (JCPDS 41-1428) for all the samples. The diffraction peaks at 2θ angles of 11.8°, 23.4°, 60.6°, and 61.8° correspond to (003), (006), (110), and (113) planes of the hydrotalcite-like structure, respectively [5,27]. No diffraction peaks were observed for separate Fe oxides, confirming that all Fe species were incorporated into the hydrotalcite structure. Table 1 provides the lattice parameters for all the samples. It can be seen that $d_{(003)} = 2d_{(006)}$, indicating that the samples have an ideal layered structure [5,27]. The cell parameter a was found to increase with an increase in Fe content, probably due to the difference in the size of cations between Fe³⁺ (0.065 nm) and Al³⁺ (0.054 nm). This also indicated that Fe³⁺ species successfully replaced Al³⁺ ones in the lattices [5]. Moreover, parameter c decreased with increasing Fe content, which could be ascribed to a change in the electrostatic interaction between the hydrotalcite-like layer and the interlayer, when the other metal (Fe³⁺ in the present case) was introduced into the hydrotalcite structure. The crystallite size calculated by (110) diffraction line broadening was found to increase with the Fe content.

Iridium was deposited onto the Mg₃Al_{1-x}Fe_x-LDH samples and reduced at 300 °C. Fig. 2 shows the XRD patterns of the supported Ir catalysts. Ir/Mg₃Al and Ir/Mg₃Al_{0.75}Fe_{0.25} catalysts continued to show some diffraction lines of the layered double hydroxides, implying that the hydrotalcite structure remained in these two catalysts. The diffraction peaks of Ir/Mg₃Al_{0.75}Fe_{0.25} were very weak, indicating the partial destruction of the hydrotalcite structure. For Ir/Mg₃Al_{0.5}Fe_{0.5}, Ir/Mg₃Al_{0.25}Fe_{0.75}, and Ir/Mg₃Fe catalysts containing larger amounts of Fe species, the XRD diffraction lines assigned to

Table 1

XRD structural parameters of Mg₃Al_{1-x}Fe_x-LDH samples.

Sample	$d_{(003)}/\text{\AA}$	$d_{(006)}/\text{\AA}$	$d_{(110)}/\text{\AA}$	c^a/nm	$a^a/\text{\AA}$	$D_{(110)}^b/\text{nm}$
Mg ₃ Al-LDH	7.5416	3.8415	1.5257	2.262	3.051	21.2
Mg ₃ Al _{0.75} Fe _{0.25} -LDH	7.5304	3.8302	1.5279	2.244	3.056	22.2
Mg ₃ Al _{0.5} Fe _{0.5} -LDH	7.5205	3.8262	1.5372	2.262	3.074	26.0
Mg ₃ Al _{0.25} Fe _{0.75} -LDH	7.5147	3.8160	1.5428	2.278	3.086	25.2
Mg ₃ Fe-LDH	7.4782	3.8085	1.5471	2.243	3.094	26.0

^a $c = 3d_{(003)}$, $a = 2d_{(110)}$.

^b Calculated by (110) diffraction line broadening via the Scherrer equation.

Fig. 2. XRD patterns of the reduced Ir/Mg₃Al (1), Ir/Mg₃Al_{0.75}Fe_{0.25} (2), Ir/Mg₃Al_{0.5}Fe_{0.5} (3), Ir/Mg₃Al_{0.25}Fe_{0.75} (4), and Ir/Mg₃Fe (5) catalysts.

MgO and Mg₃Al-LDH disappeared, suggesting that the Mg₃Al-LDH structure was destroyed during the reduction. Most of the Fe³⁺ species were likely to be reduced. Moreover, the small quantity of remaining Fe³⁺ was unable to support the hydrotalcite structure. Fig. 3 shows the TEM images of the reduced Ir/Mg₃Al_{1-x}Fe_x catalysts. Iridium nanoparticles were well dispersed on the supports, with the average size of Ir particles being 1.7 ± 0.2 nm for all the catalysts. In other words, the introduction of Fe into the parent Mg₃Al-LDH support affected

Fig. 3. TEM images and particle size distribution of the reduced catalysts of Ir/Mg₃Al (a), Ir/Mg₃Al_{0.75}Fe_{0.25} (b), Ir/Mg₃Al_{0.5}Fe_{0.5} (c), Ir/Mg₃Al_{0.25}Fe_{0.75} (d), and Ir/Mg₃Fe (e).

Scheme 1. Reaction pathways for the hydrogenation of cinnamaldehyde.

the degree of Ir dispersion slightly in the reduced catalysts. For Ir/Mg₃Al ($x = 0$), the distribution was narrow, with an average Ir particles size of approximately 1.5 nm. For Ir/Mg₃Fe ($x = 1$), the particle distribution was slightly broader, with the average particle size of Ir being approximately 1.8 nm.

3.2. Catalytic performance of Ir/Mg₃Al_{1-x}Fe_x catalysts

The catalytic performance of the above-mentioned Ir/Mg₃Al_{1-x}Fe_x samples was tested in a model reaction of selective hydrogenation of CAL, in which C=C and C=O were hydrogenated to COL and HCAL, respectively, and subsequently to the fully hydrogenated product of HCOL (Scheme 1). It is important to control the product selectivity, as well as the rate of reaction for such selective hydrogenation. The results obtained are summarized in Table 2. For the Ir/Mg₃Al catalyst including no Fe species, the CAL conversion was 17.6%, while the COL selectivity was 44.9%. When a small amount of Fe was introduced (Ir/Mg₃Al_{0.75}Fe_{0.25}), the CAL conversion and the COL selectivity were enhanced to 59.8% and 68.2%, by factors of 3.4 and 1.5, respectively. When the Fe content was further increased, the CAL conversion decreased to 30.0% for Ir/Mg₃Fe catalyst, while the COL selectivity increased to 80.3% for the same catalyst. The catalytic activity of Ir/Mg₃Fe continued to be higher than that of Ir/Mg₃Al. The introduction of Fe species to hydrotalcite-like Mg₃Al support can improve the overall activity and COL selectivity of the supported Ir catalyst (Fig. 3).

Fig. 4 shows the variation of CAL conversion and product selectivity with reaction time for two selected catalysts, Ir/Mg₃Al and Ir/Mg₃Fe. For the former catalyst, the CAL conversion increased slowly, reaching 50.6% in 10 h, at which point the COL selectivity was 44.0%. However, for the latter, the conversion reached 94.4% within 5 h, with a higher COL selectivity of 79.1%. It was observed that the product selectivity

Table 2
Results of CAL hydrogenation over Ir/Mg₃Al_{1-x}Fe_x catalysts.

Catalyst	Conversion (%)	Selectivity ^a (%)			Rate ^b (h ⁻¹)
		HCAL	COL	HCOL	
Ir/Mg ₃ Al	17.6	52.6	44.9	2.5	45
Ir/Mg ₃ Al _{0.75} Fe _{0.25}	59.8	27.1	68.2	4.7	152
Ir/Mg ₃ Al _{0.5} Fe _{0.5}	47.0	29.8	66.9	3.3	120
Ir/Mg ₃ Al _{0.25} Fe _{0.75}	31.0	24.4	73.8	1.8	79
Ir/Mg ₃ Fe	30.0	18.0	80.3	1.7	76

Reaction conditions: catalyst, 0.1 g; CAL, 0.5 mL; H₂O, 5 mL; H₂, 3 MPa; 1 h; 60 °C.

^a COL: cinnamyl alcohol; HCAL: hydrocinnamaldehyde; HCOL: hydrocinnamyl alcohol.

^b Mole of CAL reacted per hour per unit mole of Ir.

Fig. 4. Variation in conversion and selectivity with reaction time for cinnamaldehyde hydrogenation over Ir/Mg₃Al (a) and Ir/Mg₃Fe catalysts (b). Reaction conditions: catalyst, 0.1 g; CAL, 0.5 mL; H₂O, 5 mL; 60 °C; H₂, 3 MPa.

ty did not change significantly at the initial stage of the reaction (up to 40%–60% conversion), after which the selectivity to HCOL decreased, while that to COL remained unchanged, and that to HCOL increased. This suggests that the final product, HCOL, is mainly produced from HCOL, instead of COL. This tendency is common for the two catalysts with and without Fe. These results mean that CAL, COL, and HCOL are competitively adsorbed on the Ir/Mg₃Al_{1-x}Fe_x catalysts. When the CAL conversion is low (the CAL concentration is high), the substrate molecules are likely to be mainly adsorbed, with parallel hydrogenation reactions occurring to COL and HCOL. Thus, the selectivity to these two products does not change significantly. After a certain high CAL conversion, the concentration of CAL becomes low. Then, the adsorption of HCOL and the hydrogenation of HCOL to HCOL should occur. A similar phenomenon was reported over Co/ZSM-5 catalyst in a previous work [28].

The catalytic performance of the present Ir/Mg₃Fe is com-

Fig. 5. H₂-TPR profiles of Ir/Mg₃Al (1), Ir/Mg₃Al_{0.75}Fe_{0.25} (2), (c) Ir/Mg₃Al_{0.5}Fe_{0.5} (3), (d) Ir/Mg₃Al_{0.25}Fe_{0.75} (4), and Ir/Mg₃Fe (5) catalysts.

pared with those of other supported Ir catalysts reported in the literature (Table 3). Ir/Mg₃Fe catalyst is active at a lower reaction temperature. The conversion obtained is similar or better than those at higher temperatures. The rate of CAL hydrogenation with CoIr/SiO₂ is much higher than that of our Ir catalysts, while the selectivity to COL is comparable.

3.3. Features of Ir/Mg₃Al_{1-x}Fe_x catalysts

To examine the above-mentioned promotion effect of Fe doping on the performance of Ir/Mg₃Al_{1-x}Fe_x catalysts in CAL hydrogenation, these were further subjected to H₂-TPR, XPS, and CO adsorption measurements. Fig. 5 provides the profiles of the H₂-TPR collected. For Ir/Mg₃Al with no Fe species, a broad H₂ consumption can be seen, with a peak at 130 °C that is assigned to the reduction of IrO₂, along with two overlapping peaks from 310 to 460 °C that are attributable to the reduction of interlayer NO₃⁻ into NO and/or the decomposition of the intercalated CO₃²⁻ anions [14,32]. With the addition of Fe (Ir/Mg₃Al_{0.75}Fe_{0.25}), two clear peaks appeared in a range of 110–220 °C, in which the one at around 116–125 °C was assigned to the reduction of IrO₂ and Fe³⁺ species close to Ir, while the other one at around 144–170 °C was assigned to the reduction of isolated Fe³⁺ to Fe²⁺. These two peaks became larger with increasing Fe content. The reduction temperature observed for Fe³⁺ to Fe²⁺ was lower than that reported in the literature [14], suggesting that the existence of Ir promotes the reduction of Fe³⁺ species [23] because hydrogen atoms split from the surface of Ir⁰ nanoparticles to Fe³⁺ species, causing their reduction [33,34]. In addition, there was a reduction peak

Table 3

Comparison of the catalytic performance among Ir/Mg₃Fe and other catalysts.

Catalyst	Solvent	H ₂ (MPa)	T (°C)	t (h)	Rate (h ⁻¹)	Conversion (%)	Sel. to COL (%)	Ref.
Ir/FeO _x /SiO ₂	Ethanol	0.62	90	5.5	17.5	40	86	[24]
Au-Ir/TiO ₂	<i>i</i> -PrOH/H ₂ O	2	100	10	14.3	98	75	[21]
Ir/H-MoO _x	Ethanol/H ₂ O	2	100	2	223.9	99	93	[29]
Ir/C	<i>i</i> -PrOH	2	100	5	73.3	60	97	[30]
CoIr/SiO ₂	Ethanol	2	50	1.2	935.1	80.6	79.5	[31]
Ir/Mg ₃ Fe	H ₂ O	3	60	5	144.2	94.4	79.1	This work

at around 340–390 °C, indicative of the reduction of interlayer NO_3^- into NO and/or the decomposition of the intercalated CO_3^{2-} anions. The reduction peak shifted to lower temperatures with increasing Fe content, while the amount of H_2 consumed did not vary significantly among the catalysts. Another broad H_2 consumption was observed at higher temperatures due to the reduction of Fe^{2+} or Fe^{3+} to Fe^0 , with the peak position shifting to lower temperatures with increasing Fe content [32,35]. This reduction began to occur at approximately 400 °C, even for the Ir/Mg₃Fe catalyst. Therefore, it was unlikely for the present Ir/Mg₃Al_{1-x}Fe_x catalysts to be reduced at a lower temperature of 300 °C. The H_2 -TPR results showed that all Ir and Fe cations incorporated in the catalysts were not completely reduced to the corresponding zero-valent species. The H_2 consumption occurs by the reduction of various species at similar temperatures for the present catalyst samples, making it difficult to estimate the degree of reduction of Ir and Fe species.

The Ir/Mg₃Al_{1-x}Fe_x catalysts were subsequently subjected to XPS measurement to examine the valence state of Ir and Fe species on their surface. The XPS results obtained are shown in Fig. 6 and Table 4. For Ir/Mg₃Al, two peaks at binding energies (BEs) of 60.8 and 62.3 eV were attributed to Ir⁰ and Ir⁴⁺ 4f_{7/2}, respectively. These peaks of Ir species shifted to lower BE values with an increase in the amount of Fe dopant to the parent support, which were 60.2 and 61.7 eV for Ir/Mg₃Fe catalyst, respectively. However, the ratio of Ir⁰/(Ir⁰ + Ir⁴⁺) barely changed with the Fe content, indicating that the Ir⁰/Ir⁴⁺ ratio was insignificant for the change of catalytic activity observed on the Fe doping. Fig. 6(b) shows that the increase in Fe content in the support causes a blue shift in the Fe 2p peak and an increase in the peak ratio of Fe²⁺/(Fe²⁺ + Fe³⁺). The formation of a larger amount of Fe²⁺ species with increasing Fe content is in agreement with the results of H_2 -TPR mentioned above. The present XPS results indicate that electron transfer occurs from Fe²⁺ to Ir, resulting in the formation of electron-rich Ir species and electron-deficient Fe species. Further, Table 4 shows that the Fe²⁺/Ir⁰ ratio increased with increasing Fe content, suggesting that the reduced Fe²⁺ species may migrate onto the Ir⁰ surface during reduction. As mentioned above (Table 2), the impact of Fe loading to the parent Mg₃Al support on CAL conversion was optimized at certain Fe content (Ir/Mg₃Al_{0.75}Fe_{0.25}). The enhanced activity of Ir/Mg₃Al_{0.75}Fe_{0.25}, as compared to Ir/Mg₃Al, may be ascribed to electron transfer from the Fe species to the active Ir ones. The electron transfer provides electron-rich Ir and electron-deficient Fe species on the surface of catalysts. It might be easier for a CAL molecule to be adsorbed on such electron-rich Ir sites with its C=O bond, relative to the adsorption with its C=C bond. The total amount of CAL mole-

Fig. 6. XPS results of (a) Ir 4f and (b) Fe 2p for Ir/Mg₃Al (1), Ir/Mg₃Al_{0.75}Fe_{0.25} (2), Ir/Mg₃Al_{0.5}Fe_{0.5} (3), Ir/Mg₃Al_{0.25}Fe_{0.75} (4), and Ir/Mg₃Fe catalysts (5).

cules that could be adsorbed might be increased because of lower steric hindrance for adsorption with the C=O bond compared to the C=C bond attached to the benzene ring. In addition, the presence of electron-deficient Fe²⁺ species close to the active Ir sites would also facilitate the adsorption of CAL with the C=O bond (as discussed later). Those factors would increase the amount of CAL molecules adsorbed, thus enhancing the total rate of hydrogenation (conversion) with the doping of a small amount of Fe species. When the amount of Fe dopant is further increased, some exposed active Ir sites would be blocked by excess Fe species migrating onto the surface of Ir particles, as suggested by the XPS. It was reported that the addition of Fe to Pt-OMC (ordered mesoporous carbons) could improve the conversion of CAL, as well as the selectivity to COL, due to the formation of Pt-Fe alloy and the charge-transfer between Pt and Fe [36]. The conversion of some α,β -unsaturated aldehydes reaches a maximum at a certain optimum Fe content [23,37]. A small amount of Fe (0.2 wt%) is necessary for promoting the activity of Pt in the hydrogenation of citral, while a larger amount (> 0.3 wt%) causes a sharp reduction in the conversion, due to the blockage of metal active sites by the excess Fe [37].

The surface of Ir nanoparticles supported on MgAl_{1-x}Fe_x materials was further examined by the *in-situ* DRIFT spectra of CO adsorbed on them (Fig. 7). It indicates that the strength of the absorption band of CO molecules is comparable among the catalyst samples examined. Therefore, the surface coverage of CO molecules adsorbed on these samples is similar under the adsorption conditions used. A broad absorption band was ob-

Table 4

Binding energy values of supported Ir catalysts and surface atomic ratios of Fe²⁺/Fe³⁺ and Fe/Ir.

Sample	Ir ⁰ 4f _{7/2} (eV)	Ir ⁴⁺ 4f _{7/2} (eV)	Fe ²⁺ 2p _{3/2} (eV)	Fe ³⁺ 2p _{3/2} (eV)	Surface atomic ratio *		
					Ir ⁰ /(Ir ⁰ + Ir ⁴⁺)	Fe ²⁺ /(Fe ²⁺ + Fe ³⁺)	Fe ²⁺ /Ir ⁰
Ir/Mg ₃ Al	60.8	62.3	—	—	0.60	—	—
Ir/Mg ₃ Al _{0.75} Fe _{0.25}	60.6	62.1	709.6	712.3	0.57	0.40	1.37
Ir/Mg ₃ Al _{0.5} Fe _{0.5}	60.5	62.0	709.8	712.3	0.57	0.40	1.61
Ir/Mg ₃ Al _{0.25} Fe _{0.75}	60.4	61.9	709.8	712.3	0.59	0.55	3.45
Ir/Mg ₃ Fe	60.2	61.7	709.9	712.3	0.54	0.62	5.56

* Calculated from their XPS areas.

served at 2058–2069 cm^{-1} for all the samples, which can be attributed to linearly adsorbed CO on Ir^0 sites [38,39]. This CO absorption band was observed to shift towards a higher wave-number with increasing Fe content, with the extent of this blue shift being 11 cm^{-1} from $\text{Ir}/\text{Mg}_3\text{Al}$ (2058 cm^{-1}) through $\text{Ir}/\text{Mg}_3\text{Fe}$ (2069 cm^{-1}). This is contradictory to the expectation of a red-shift for the CO absorption band. According to the XPS result, the electron transfer occurs from Fe^{2+} to Ir^0 with the addition of Fe. It was reported for Ga-modified $\text{Pd}/\text{MgO}-\text{Al}_2\text{O}_3$ sample that the electron transfer occurred from Pd^0 to Ga (XPS) and the CO-IR absorption band red-shifted, instead of blue-shifting, with the addition of Ga to $\text{Pd}/\text{MgO}-\text{Al}_2\text{O}_3$ [40]. This means, the CO-IR absorption depends not only on the electron transfer, but also on other factors, such as the change in geometric structure of metal species and dipole-dipole effect [41]. Strong dipole-dipole effect existed for CO molecules adsorbed on metal particles smaller than 2 nm, being more significant on the reduced sample than the oxidized one [41]. It was also reported for the $\text{Pd}-\text{Sn}/\text{SiO}_2$ catalyst that when the amount of Sn additive increased from 1.5% to 2%, the size of Pd particles barely changed (5.9 vs. 5.7 nm), with the XPS showing no electron transfer between Pd and Sn species. However, the CO-IR absorption band indicated a red-shift from 2091 to 2084 cm^{-1} [42]. For the present $\text{Ir}/\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ catalysts, the previous results indicate that the blue-shift of CO-IR absorption band observed should be due to the difference in the surface geometry of Ir particles and/or dipole-dipole coupling of CO species adsorbed on their surface with the addition of Fe species, in which the electron transfer occurs from Fe^{2+} to Ir species.

For the results of CO-IR (Fig. 7), the high-frequency band at 2069 cm^{-1} can be assigned to the CO adsorbed on high-coordinate Ir sites (planes), while the low-frequency band at 2058 cm^{-1} is assigned to CO on low-coordinate Ir sites (edges, corners, etc.) [41]. This means the doping of Fe species to parent Mg_3Al support changes the surface geometry of the

Fig. 7. In-situ DRIFT spectra of CO adsorbed on $\text{Ir}/\text{Mg}_3\text{Al}$ (1), $\text{Ir}/\text{Mg}_3\text{Al}_{0.75}\text{Fe}_{0.25}$ (2), $\text{Ir}/\text{Mg}_3\text{Al}_{0.5}\text{Fe}_{0.5}$ (3), $\text{Ir}/\text{Mg}_3\text{Al}_{0.25}\text{Fe}_{0.75}$ (4), and $\text{Ir}/\text{Mg}_3\text{Fe}$ (5) catalysts.

supported Ir particles. It was also reported for Pt catalysts that the absorption band at ca. 2086 cm^{-1} corresponded to CO molecules adsorbed on the terraces of the metallic platinum clusters, while that at a lower frequency (2050–2060 cm^{-1}) corresponded to CO molecules adsorbed on steps and corners [43,44].

As mentioned above, in CAL hydrogenation, the selectivity to COL is significantly higher for $\text{Ir}/\text{Mg}_3\text{Fe}$ catalyst as compared to the $\text{Ir}/\text{Mg}_3\text{Al}$ with no Fe species (Table 2). The relationship thus observed between the type of exposed Ir^0 sites and the COL selectivity is in accordance with the literature. In general, the high-coordination terrace sites are beneficial for CAL adsorption with its C=O bond, instead of the C=C bond attached to a large phenyl group, leading to the improvement of the COL selectivity [45]. It should be noted that the size of Ir nanoparticles on various support materials is similar, as confirmed by TEM in Fig. 3. This means that the introduction of Fe species to the parent Mg_3Al support material does not change the size of the Ir nanoparticles supported thereby. Instead, it modifies their surface geometry and electronic properties. The surface of the supported Ir particles exposed the Ir^0 and Ir^+ species, while the relative amounts of the exposed Ir species did not depend on Fe doping (Table 4). Therefore, the size and Ir^0/Ir^+ ratio of the supported Ir particles are not significant factors in determining the conversion and/or the product selectivity in the present CAL hydrogenation over $\text{Ir}/\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ catalysts. Another factor responsible for the increase of COL selectivity with the Fe content may be the presence of Fe^{n+} species on the surface of the catalysts. It is observed that Fe^{2+} species with a local positive charge would act as electrophilic sites for the polarization and activation of the C=O bond in the CAL molecule with a lone pair of electrons in its oxygen atom [23,46]. For the $\text{Ir}/\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ catalysts in the present study, the exposed Fe^{n+} species existing close to the Ir species may facilitate the hydrogenation of C=O, enhancing the selectivity to COL as observed. The amount of these functional Fe^{n+} species is likely to increase with increasing Fe content. However, the presence of excess Fe causes the blockage of active Ir sites, thus decreasing the total rate of CAL hydrogenation as discussed above.

4. Conclusions

In CAL hydrogenation of over 3 wt% Ir catalysts supported on LDH-like material of $\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$, the rate of hydrogenation and the product selectivity were observed to depend on the composition of support used. When the content of Fe species was increased from $x = 0$ to 1, the rate of hydrogenation was maximized at around $x = 0.25$, while the COL selectivity was monotonously enhanced from 44.9% to 80.3%. The COL selectivity did not change with conversion, while those of HCAL and HCOL started to decrease and increase, respectively, at a certain conversion. These changes in product selectivity were the same for $\text{Ir}/\text{Mg}_3\text{Al}$ and $\text{Ir}/\text{Mg}_3\text{Fe}$ catalysts, in which the final product of HCOL was mainly produced from HCAL. Although the catalytic performance varied among the $\text{Ir}/\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ catalysts ($x = 0-1$), the sizes of their supported Ir particles were comparable, being in the range of 1.7 ± 0.2 nm. In addition, the

relative amounts of Ir⁰ and Ir⁺ species exposed on their surface did not change due to Fe doping. When the Fe content in the Mg₃Al_{1-x}Fe_x support was increased, the ratio of surface Fe²⁺ to Fe³⁺ species increased, and the XPS binding energy of Ir species shifted to a lower binding energy, indicating electron transfer from Fe²⁺ to Ir species in the Ir/Mg₃Al_{1-x}Fe_x catalysts. Furthermore, the surface geometry of the supported Ir particles was suggested to be dependent on the Mg₃Al_{1-x}Fe_x support used, which exposed low-coordination (step, corner, and kink) and high-coordination (terrace) Ir sites for the catalysts with low and high Fe content *x* in the support, respectively. These electronic and geometric modifications were induced for supported Ir particles due to Fe doping, which increased the likelihood of the occurrence of adsorption and hydrogenation of the carbonyl group of CAL, enhancing the selectivity to COL. The presence of exposed Feⁿ⁺ species close to active Ir ones also helps facilitate the adsorption and hydrogenation of the C=O bond of CAL molecule. However, some exposed active Ir sites were covered by excess Fe species. Therefore, the total activity was maximized at a certain amount of Fe species loaded.

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Graphical Abstract

Chin. J. Catal., 2018, 39: 988–996 doi: 10.1016/S1872-2067(18)63042-6

Layered double hydroxide-like Mg₃Al_{1-x}Fe_x materials as supports for Ir catalysts: Promotional effects of Fe doping in selective hydrogenation of cinnamaldehyde

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The doping of Fe to Ir/Mg₃Al could improve its activity and selectivity in cinnamaldehyde hydrogenation owing to the electronic interaction of Fe–Ir and the change in the geometrical structure of Ir active species.

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类水滑石 $\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ 负载 Ir 催化剂在肉桂醛加氢反应中的应用：Fe 的促进作用

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摘要: 水滑石类化合物 (LDH) 的层板金属阳离子组成具有可调变性, 通过将具有变价特性的过渡金属定量引入 LDH 层板, 经热处理后可以得到具有高比表面积和层板金属原子级分散的混合金属氧化物, 后者可广泛用作催化剂载体。如三元 Mg-Al-Fe 类水滑石材料在光催化、 H_2S 选择性氧化和乙苯脱氢等反应中表现出较好的活性。Ir 催化剂在 α,β -不饱和醛加氢反应中具有较好的活性, Fe 修饰 Ir 催化剂可提高不饱和醇选择性, 但有关 Fe 的作用以及 Fe 与活性组分 Ir 间的相互作用本质还不是很清楚。

本文以类水滑石材料 $\text{Mg}_3\text{Al}_{1-x}\text{Fe}_x$ 为载体, 采用等体积浸渍法制备了 Ir 催化剂, 并用于肉桂醛加氢反应, 通过考察 Fe 的加入对 Ir 电子和几何结构的影响揭示了 Fe 的加入对活性和选择性的影响规律。结果表明, 当 x 从 0 (Ir/ Mg_3Al) 增加到 1 (Ir/ Mg_3Fe) 时, 肉桂醛加氢的反应速率在 $x=0.25$ 时达到最大值, 肉桂醇选择性从 44.9% 增加到 80.3%, 且不随肉桂醛转化率的增加而改变。透射电镜结果表明, Ir 纳米粒子的粒径随着 x 的增加未发生明显变化, 均为 1.7 ± 0.2 nm。H₂ 程序升温还原结果发现 Ir 可以促进 Fe^{3+} 的还原且两者之间存在相互作用。X 射线光电子能谱结果表明, Fe 的掺杂没有改变催化剂表面 Ir^0 和 Ir^{4+} 含量的比值, 但当 Fe 含量增加时, $\text{Fe}^{2+} 2p_{3/2}$ 向高结合能方向偏移, 且 $\text{Ir}^0 4f_{7/2}$ 向低结合能方向偏移, 说明电子从 Fe^{2+} 转移到 Ir, 形成了富电子的 Ir 物种和缺电子的 Fe 物种。富电子的 Ir 物种有利于肉桂醛分子中的 C=O 键在其表面吸附, 并且和 Ir 相邻的 Fe^{n+} 物种可以作为亲电位点吸附肉桂醛分子中氧, 从而极化和活化 C=O 键, 因而催化剂活性和选择性增大。采用吸附 CO 红外光谱表征了催化剂表面的几何结构, 2058–2069 cm^{-1} 处出现了 CO 吸附峰, 归属于 Ir^0 表面 CO 的线性吸附, 高波数 2069 cm^{-1} 的吸附峰归属于 CO 在高配位 Ir 位点 (平台) 的吸附, 低波数 2058 cm^{-1} 的吸附峰归属于 CO 在低配位 Ir 位点 (台阶、角、楞) 的吸附。随着 Fe 含量的增加, CO 吸附峰蓝移 11 cm^{-1} , 表明 Fe 的加入改变了催化剂表面 Ir 的几何结构, 低配位 Ir 位点减少, 高配位 Ir 位点增多。高配位 Ir 位点 (平台) 有利于肉桂醛分子中 C=O 键的吸附, 从而提高了肉桂醇的选择性。总之, Fe 的加入虽然没有明显改变 Ir 纳米粒子的粒径, 但却改变了其电子和几何结构, 从而提高了催化剂活性和选择性。

关键词: 铱催化剂; 水滑石; 铁掺杂; 载体影响; 选择性加氢; 肉桂醛

收稿日期: 2017-12-05. 接受日期: 2018-02-02. 出版日期: 2018-05-05.

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基金来源: 国家重点研发计划 (2016YFA0602900); 国家自然科学基金 (21603212, 21672204); 中国科学院青年创新促进会 (2016206); 吉林省科技发展规划 (20150204050GX); 中国科学院国际人才计划 (2018VCA0012).

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