^{57}Fe 穆斯堡尔谱研究 Ir-Fe 催化剂用于 CO 选择氧化反应

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摘要: 采用不同浸渍顺序制备了三种 Ir-Fe 催化剂, 其 CO 选择氧化 (PROX) 反应活性差别很大, 其中共浸渍的 Ir-Fe 催化剂活性最高. 吸附量热研究表明, 三种催化剂的 H_2 和 CO 吸附存在差别. 通过对三种催化剂还原后、再氧化和反应后准原位 ^{57}Fe 穆斯堡尔谱的研究, 得到各种 Fe 物种信息. 结果表明, 三种制备方法影响催化剂中 Ir-Fe 相互作用强度, 导致催化剂中 Fe 物种的氧化还原性能不同. 催化剂中 $\text{Fe}^{2+}(\text{a})$ 的含量与 CO 转化率呈正比关系, $\text{Fe}^{2+}(\text{a})$ 是 PROX 反应过程中活化氧的活性中心. 浸渍顺序改变了 Ir-Fe 间相互作用强度, 从而改变 $\text{Fe}^{2+}(\text{a})$ 物种含量, 影响 PROX 反应活性. Ir-Fe 间的相互作用可以稳定活化氧的 $\text{Fe}^{2+}(\text{a})$ 物种, 为今后研究金属-金属间的相互作用提供借鉴.

关键词: 一氧化碳; 选择氧化; 铱; 铁; 准原位穆斯堡尔谱; 吸附量热; 金属-金属相互作用

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^{57}Fe Mössbauer Spectroscopy of Ir-Fe Catalysts for Preferential CO Oxidation in H_2

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Abstract: New insights on the interaction between Ir and Fe oxide are reported. Three Ir-Fe catalysts were prepared by different impregnation sequences of an Al_2O_3 support. Co-impregnation gave a better catalyst for the preferential CO oxidation in H_2 (PROX) reaction. Microcalorimetry data showed that the adsorption of CO and H_2 were different. Quasi in situ Mössbauer data of the three catalysts after reduction, reoxidation, and PROX reaction showed that a strong interaction between Ir and Fe affected the redox properties of the Ir-Fe catalysts. CO conversion was proportional to the concentration of the $\text{Fe}^{2+}(\text{a})$ species, thus, $\text{Fe}^{2+}(\text{a})$ was an active site in the PROX reaction. The impregnation sequence influenced the interaction between Ir and Fe and consequently, the amount of the active $\text{Fe}^{2+}(\text{a})$ species. A strong Ir-Fe interaction stabilized the active Fe^{2+} sites for activating O_2 .

Key words: carbon monoxide; selective oxidation; iridium; iron; quasi Mössbauer spectroscopy; microcalorimetry; metal-metal interaction

Preferential CO oxidation in H_2 (PROX) is a promising way to reduce the CO amount in the H_2 fuel for the polymeric electrolyte membrane fuel cell. Various supported noble metal-based catalysts for the PROX reaction of a H_2 gas have been widely investigated, and supported bimetallic

catalysts are considered the best. Several groups have reported that a higher activity for PROX at low temperatures was attained by the addition of a second metal such as Fe [1,2], Ce [3,4], Sn [5], and Ti [6,7]. A bifunctional catalytic mechanism has been suggested, in which noble metal sites

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and transition metal oxide sites allowed the adsorption of CO and O₂, respectively. In addition, since the addition of the second metal can change the reduction property of the catalyst and the electronic state of the noble metal, interactions between the noble metal and the second metal have been studied extensively. It has been pointed out that the adding of Fe species modified the adsorption of CO and electronic interactions between Pt and Fe [8]. Ko et al. [9] reported that PtNi catalysts prepared by different impregnation sequence had different activities. They attributed this difference to the different interactions between Pt and Ni caused by the different impregnation sequences. The metal-metal interaction appeared to change the adsorption of the gases.

Our group has reported that Ir-Fe catalysts were highly active and selective for the PROX reaction [10–12]. The previous work focused on the different structure of the Ir-Fe catalyst that resulted in dramatic differences in the adsorption of CO and O₂, and led to different PROX activities. In addition, the interaction between Ir and Fe was explained by the changed reduction property of the catalyst. However, whether the metal-metal interaction affects the adsorption properties exclusively needs further investigation.

In the present work, new insight into the interaction between the noble metal (Ir) and Fe oxide was given in detail by quasi in situ Mössbauer spectroscopy. The preparation conditions of the three Ir-Fe catalysts, e.g., calcination temperatures and loading amounts of Ir and Fe, were different from that reported in Refs. [10,11] in order that the differences in the adsorption properties were less significant than that reported in Ref. [10]. Quantitative studies of the chemical state of the iron species in Ir-Fe/Al₂O₃ during PROX are still lacking, and the Ir-Fe interaction needs further investigation. It is widely accepted that Fe plays an important role in activating O₂ during the PROX reaction, so quasi in situ ⁵⁷Fe Mössbauer spectra were measured to show the influence of the interaction between Ir and Fe on the iron valence state due to the different impregnation sequences.

1 Experimental

1.1 Catalyst preparation

First, isotope ⁵⁷Fe powder was dissolved in concentrated nitric acid to prepare a ⁵⁷Fe(NO₃)₃ solution. Then ⁵⁷Fe(NO₃)₃ was used to replace a portion of Fe(NO₃)₃·9H₂O in the impregnation procedure so that ⁵⁷Fe was 40% of the total Fe amount in the IrFe catalyst. The three catalysts were prepared by impregnation. The Ir/Fe/Al₂O₃ catalyst was prepared by sequential incipient wetness impregnation. γ-Al₂O₃ (*A*_{BET} = 230 m²/g) was first impregnated with an

aqueous mixture of Fe(NO₃)₃ and ⁵⁷Fe(NO₃)₃, followed by drying at 80 °C and calcination at 300 °C for 5 h to obtain Fe/Al₂O₃. Then Ir was deposited on the Fe/Al₂O₃ by the same procedure with an aqueous solution of chloroiridic acid. The Ir/Fe/Al₂O₃ catalyst was obtained after calcination at 300 °C for 5 h. For comparison, the Fe/Ir/Al₂O₃ catalyst was obtained through an inverse impregnation sequence, and Ir-Fe/Al₂O₃ was prepared by co-impregnation of γ-Al₂O₃ with the three metal solutions. The drying and calcination conditions during the preparation of the Fe/Ir/Al₂O₃ and Ir-Fe/Al₂O₃ catalysts were the same as that of the Ir/Fe/Al₂O₃ catalyst. The Ir content for all the samples was fixed at 3 wt%, and the atomic ratio of Fe/Ir was 5.

1.2 Catalytic activity tests

The catalytic activities were evaluated in a fixed-bed reactor at atmospheric pressure. Before the test, the catalyst was reduced with hydrogen at 300 °C for 2 h. The Ir-Fe catalyst (100 mg) diluted with 100 mg SiC was loaded into the quartz reactor. The feed flow was 66.7 ml/min, which corresponded to a space velocity of 40 000 ml/(h·g). The feed mixtures comprised 2 vol% CO, 1 vol% O₂, 40 vol% H₂, and the remainder He for the PROX stream. The effluent gas was analyzed using an online gas chromatograph (Agilent GC-6890) equipped with a thermal conductivity detector. CO₂ and H₂O were detected as the only products. No methane was found under our experimental conditions.

CO conversion (*X*_{CO}) was calculated as $X_{\text{CO}} = ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/[\text{CO}]_{\text{in}}$. Selectivity (*S*) for CO₂ was defined as the ratio of the oxygen transformed into CO₂ to the total oxygen consumed: $S = 0.5 \times ([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})/([\text{O}]_{\text{in}} - [\text{O}]_{\text{out}})$.

1.3 Catalyst characterization

The microcalorimetry study of CO, O₂, and H₂ adsorption was performed using a BT2.15 heat flux calorimeter. The calorimeter was connected to a gas handling and volumetric system with MKS 698A Baratron capacitance manometers for precision pressure measurements ($\pm 1.33 \times 10^{-2}$ Pa). Prior to CO, O₂, and H₂ adsorption, the sample was heated to 300 °C in 30 min and held at this temperature for 2 h in a special treatment cell under flowing H₂ (99.99%), followed by evacuation at 350 °C for 1 h. The adsorption was conducted at 40 °C. The detailed procedure has been described in [13].

Quasi in situ ⁵⁷Fe Mössbauer spectra of the Ir-Fe catalysts were recorded using a Topologic 500A spectrometer and a proportional counter at room temperature. ⁵⁷Co(Rh) moving in a constant acceleration mode was used as the radioactive source. The Doppler velocity of the spectrometer was calibrated with α-Fe foils. The spectra were fitted with Lor-

entzian peaks using MossWinn 3.0i [14], and the free recoil fraction was assumed to be the same for all iron species. Mössbauer parameters such as the isomer shift (IS), electric quadrupole splitting (QS), full linewidth at half maximum (LW), magnetic hyperfine field (H), and relative resonance areas of the different components of the absorption patterns (RI) were determined.

Before the ^{57}Fe Mössbauer measurement, each sample was loaded in a specially designed quartz reactor similar to that described in Ref. [15], which enabled measurements on samples treated under various atmospheres without exposing to air. The quartz reactor has two stopcocks at the ends and a side cell made of polymethyl methacrylate (PMMA). First, the sample placed in the quartz reactor was reduced at 300 °C for 2 h. After cooling to room temperature in He, both stopcocks were closed to seal the reactor filled with He. Then, the sample was poured into the side cell, and the Mössbauer spectra were measured. After reduction, the sample was subsequently treated in a feed mixture containing 2 vol% CO, 1 vol% O₂, 40 vol% H₂ in He at 80 °C for 1 h and then flushed by He for 0.5 h, followed by cooling to room temperature in He. Then, the Mössbauer measurements were performed.

2 Results and discussion

2.1 PROX reaction activity

Figure 1 compares the catalytic performance of the three catalysts. For Ir-Fe/Al₂O₃, the maximum CO conversion of 81% was obtained at 80 °C and the selectivity was 95%. With different impregnation sequence of the Ir and Fe precursors, the activity varied in the order Ir-Fe/Al₂O₃ > Fe/Ir/Al₂O₃ > Ir/Fe/Al₂O₃, and the selectivity for CO₂ also followed the same order. A maximum CO conversion of 73% was obtained at 100 °C for Fe/Ir/Al₂O₃. The CO conversion for Ir/Fe/Al₂O₃ did not exceed 50% in the whole temperature range. Compared with results reported in Ref. [10], both the CO conversion and selectivity due to Ir-Fe/Al₂O₃ were increased, and the order of activity and selectivity for the three catalysts were changed, which was due to the different calcination temperatures or loadings of Ir.

2.2 Microcalorimetry

It was reported that H₂ and CO were adsorbed on Ir, and O₂ on the iron species during the PROX reaction. In order to clarify whether the different adsorption properties of the three catalysts influenced CO conversion, we investigated H₂, CO, and O₂ adsorption on the three catalysts by microcalorimetry. Figure 2 shows the differential heats of H₂, CO,

Fig. 1. CO conversion and CO₂ selectivity as a function of reaction temperature over Ir-Fe/Al₂O₃ (1), Fe/Ir/Al₂O₃ (2), and Ir/Fe/Al₂O₃ (3).

and O₂ adsorption at 40 °C as a function of surface coverage. The saturation adsorption uptakes and initial heats of H₂, CO, and O₂ adsorption on the reduced catalysts are listed in Table 1. As can be seen from Table 1, initial heats were 45–60 kJ/mol for H₂ adsorption on the three catalysts, and 140–146 kJ/mol for CO adsorption. H₂ and CO adsorption on Ir/Fe/Al₂O₃ were slightly stronger than on the other two catalysts, which indicated that more Ir species were exposed on the surface due to the sequential impregnation of first Fe and then Ir. The stoichiometry CO/H₂ ≈ 2 revealed that the CO molecules interact with a surface Ir atom in a linear mode, which has been shown by an in situ DRIFT study [10,11,16]. CO uptakes on the three catalysts follow the order Ir-Fe/Al₂O₃ < Fe/Ir/Al₂O₃ < Ir/Fe/Al₂O₃, showing that the amount of Ir on the surface was influenced by the impregnation sequence. This trend was in an inverse order to that for CO oxidation activity since the weakening of CO adsorption benefits CO oxidation [8]. The previous study showed that FeO_x/Ir/Al₂O₃ was characterized by the almost full coverage of Ir with Fe₂O₃, thus, CO adsorption on the Ir sites was inhibited by the upper layer of Fe₂O₃, resulting in low CO conversion. However, in the present study, the differences in the adsorption property were not as large on the three catalysts as that reported previously [10,11]. In addition, similar amounts of O₂ adsorption for

Fig. 2. Differential heat of adsorption vs coverage of H₂ (a), CO (b), and O₂ (c) adsorbed separately on Ir-Fe/Al₂O₃ (■), Fe/Ir/Al₂O₃ (●), and Ir/Fe/Al₂O₃ (▲).

Table 1 Saturation uptakes and initial adsorption heats of CO, O₂, and H₂ on reduced Ir-Fe/Al₂O₃, Fe/Ir/Al₂O₃, and Ir/Fe/Al₂O₃

Catalyst	Differential heat (kJ/mol)			Coverage (μmol/g)		
	H ₂	CO	O ₂	H ₂	CO	O ₂
Ir-Fe/Al ₂ O ₃	60	140	404	24	58	205
Fe/Ir/Al ₂ O ₃	45	140	408	27	65	205
Ir/Fe/Al ₂ O ₃	55	146	428	35	75	210

the three catalysts have been observed.

2.3 Mössbauer spectroscopy

It is widely accepted that the activation of O₂ plays an important role in the PROX reaction, so it is worthwhile to study the state of the Fe species during the PROX reaction. Since Mössbauer is effective for the identification of the active phase or active sites of the catalyst components [17–19], we used the Mössbauer study to reveal the differences in the iron species in the three catalysts during the PROX reaction.

Figure 3 shows the in situ ⁵⁷Fe Mössbauer spectra of the three catalysts after reduction. The results showed marked differences in the reduction behavior, which showed that the

impregnation sequence influenced the reducibility of these catalysts. The spectra of Ir-Fe/Al₂O₃ and Fe/Ir/Al₂O₃ after reduction showed the presence of a six-line component, three quadrupole doublet components, and one singlet. The Mössbauer parameters of the components obtained by computer fitting the spectra are given in Table 2. The spectrum is composed of a doublet (IS = 0.58 mm/s and QS = 0.71 mm/s) for Feⁿ⁺ (2 < n < 3) [16], and a six-line component with a magnetic splitting corresponding to the magnetic field of 33.3 T, and with the isomer shift (IS = 0.00 mm/s) and quadrupole constant (QS = 0.00 mm/s) values for α-Fe⁰. The Mössbauer parameters (Fe²⁺(a), QS = 2.38 mm/s; Fe²⁺(b), QS = 1.55 mm/s) showed the presence of two different kinds of Fe²⁺. The two Fe²⁺ doublets have similar isomer shifts but different quadrupole splittings, and indicated Fe²⁺ in different positions in the aluminate [20]. Fe-Ir alloy appeared after reduction due to the strong interaction between the Ir and Fe species. However, the spectra of Fe/Ir/Al₂O₃ did not show Fe-Ir alloy, and the amount of zero valent iron was relatively less. The total amounts of the two kinds of Fe²⁺ was comparable with that of Ir/Fe/Al₂O₃. In contrast, the spectra of Ir/Fe/Al₂O₃ after reduction showed the presence of three quadrupole doublet components, which were attributed to two kinds of Fe²⁺ species in different positions in the aluminate and Fe³⁺. Neither Fe⁰ nor Fe-Ir alloy was observed for the Ir/Fe/Al₂O₃ catalyst. According to the Mössbauer results, the reducibility followed the order Ir-Fe/Al₂O₃ > Fe/Ir/Al₂O₃ > Ir/Fe/Al₂O₃, which was the trend for PROX activity. This phenomenon was attributed to the different interactions between Ir and Fe species due to the different impregnation sequences resulting in different reducibility of the iron oxide. Since the in-

Fig. 3. ⁵⁷Fe Mössbauer spectra of Ir-Fe/Al₂O₃, Fe/Ir/Al₂O₃, and Ir/Fe/Al₂O₃ after H₂ reduction at 300 °C for 2 h.

Table 2 ^{57}Fe Mössbauer parameters of reduced Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 at room temperature

Catalyst	Chemical state	IS ^a (mm/s)	QS ^b (mm/s)	H ^c (T)	RI ^d (%)
Ir-Fe/ Al_2O_3	Fe^{n+}	0.43	1.00		15
	Fe^0	0.00	0.00	33.4	31
	$\text{Fe}^{2+}(\text{a})$	1.00	2.38		15
	Fe-Ir	0.09			4
	$\text{Fe}^{2+}(\text{b})$	1.04	1.55		35
Fe/Ir/ Al_2O_3	Fe^{n+}	0.47	0.85		27
	Fe^0	0.00	0.00	33.3	18
	$\text{Fe}^{2+}(\text{a})$	1.02	2.40		20
	$\text{Fe}^{2+}(\text{b})$	0.99	1.67		35
	Fe^{3+}	0.36	1.14		24
Ir/Fe/ Al_2O_3	$\text{Fe}^{2+}(\text{a})$	1.09	2.22		29
	$\text{Fe}^{2+}(\text{b})$	1.02	1.56		47

^aIsomer shift relative to $\alpha\text{-Fe}$. ^bElectric quadrupole splitting. ^cMagnetic field. ^dRelative intensity (Uncertainty is $\pm 5\%$ of reported value).

teraction between Ir and Fe can accelerate the reduction of Fe oxide [10], the order of the strength of the Ir-Fe interaction would be Ir-Fe/ Al_2O_3 > Fe/Ir/ Al_2O_3 > Ir/Fe/ Al_2O_3 .

To elucidate the redox property of the different iron components in the three catalysts, Mössbauer spectra of the three reduced catalysts after treating with O_2 at the reaction temperature were also obtained. It can be seen from Fig. 4 and Table 3 that in the Ir-Fe/ Al_2O_3 and Fe/Ir/ Al_2O_3 catalysts, zero-valence iron still existed that cannot be oxidized to Fe^{3+} or Fe^{2+} . The Fe^0 in the reduced Ir-Fe catalyst has a large particle size and was not in a highly dispersed state as suggested by the existence of a magnetic field (33.0 T). Wang et al. [21] pointed out that a critical size existed below which the iron can be fully oxidized, whereas for particles larger than the critical size (~ 8 nm), an iron/iron-oxide structure was found. We accordingly proposed that only some outer layers of these large Fe^0 particles had been oxidized upon exposing to the 1% O_2 atmosphere at 80 °C for 1 h, while the cores of the Fe^0 particles were encapsulated by ferric oxide and not oxidized. Surprisingly, the $\text{Fe}^{2+}(\text{a})$ species was not oxidized to Fe^{3+} completely in the Ir/Fe/ Al_2O_3 and Fe/Ir/ Al_2O_3 catalysts. We attributed the stabilization of $\text{Fe}^{2+}(\text{a})$ to the interaction between Fe and the aluminate support, or that this part of $\text{Fe}^{2+}(\text{a})$ was covered by iron oxide. Our group has reported in a previous paper [16] that for a Fe/ SiO_2 catalyst, most of the Fe^{2+} was stable after treating in O_2 due to an interaction between Fe and the silicate support. Since the low valence Fe species that cannot be reoxidized do not activate O_2 during the PROX reaction, it is obvious that not all of the $\text{Fe}^{2+}(\text{a})$ was active for activating O_2 on the Ir/Fe/ Al_2O_3 and Fe/Ir/ Al_2O_3 catalysts. Therefore, the possible active sites for activating O_2 in PROX are $\text{Fe}^{2+}(\text{a})$, $\text{Fe}^{2+}(\text{b})$, or Fe^0 for Ir-Fe/ Al_2O_3 and Fe/Ir/ Al_2O_3 , and

Fig. 4. ^{57}Fe Mössbauer spectra of Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 after 1 % O_2 treatment at 80 °C for 1 h.**Table 3** ^{57}Fe Mössbauer parameters of Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 after exposure to O_2 at 80 °C for 1 h

Catalyst	Chemical state	IS (mm/s)	QS (mm/s)	H (T)	RI (%)
Ir-Fe/ Al_2O_3	Fe^{3+}	0.33	1.08		80
	Fe^0	0.00	0.00	33.4	20
Fe/Ir/ Al_2O_3	Fe^{3+}	0.32	1.09		80
	Fe^0	0.00	0.00	33.3	13
	$\text{Fe}^{2+}(\text{a})$	1.07	2.14		6
Ir/Fe/ Al_2O_3	Fe^{3+}	0.32	1.08		81
	$\text{Fe}^{2+}(\text{a})$	1.09	2.15		19

$\text{Fe}^{2+}(\text{a})$ or $\text{Fe}^{2+}(\text{b})$ for Ir/Fe/ Al_2O_3 .

Mössbauer spectra of the three catalysts after the PROX reaction were also conducted. As can be seen from Fig. 5 and Table 4, the spectra of Ir-Fe/ Al_2O_3 and Fe/Ir/ Al_2O_3 catalysts was well fitted into Fe^0 , $\text{Fe}^{2+}(\text{a})$, and Fe^{3+} . The exposure of the reduced catalysts to the PROX gas mixture at 80 °C converted $\text{Fe}^{2+}(\text{b})$ and Fe-Ir alloy completely to Fe^{3+} , accompanied by the decrease of $\text{Fe}^{2+}(\text{a})$ and Fe^0 . When Ir/Fe/ Al_2O_3 was subjected to the PROX gas mixture at 80 °C, $\text{Fe}^{2+}(\text{b})$ disappeared completely, and the amount of $\text{Fe}^{2+}(\text{a})$ decreased by 7%. The amount of Fe^0 after the PROX reaction was the same as that after reoxidation, which indicated the possibility that the Fe^0 species was covered by other iron species and did not take part in the reaction. According to the results above, it is deduced that $\text{Fe}^{2+}(\text{a})$ was the active site for activating O_2 during the PROX reaction on the three catalysts. It has been reported by Kotobuki et al. [22] that Fe^{2+} played the role of activating O_2 during PROX over a PtFe catalyst.

As discussed above, not all the $\text{Fe}^{2+}(\text{a})$ present was active because a certain amount of $\text{Fe}^{2+}(\text{a})$ cannot be reoxidized, as shown in Fig. 5. The amount of $\text{Fe}^{2+}(\text{a})$ that was active for

Fig. 5. ^{57}Fe Mössbauer spectra of Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 after PROX reaction at 80 °C for 1 h.

Table 4 ^{57}Fe Mössbauer parameters of Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 after PROX reaction at 80 °C for 1 h

Catalyst	Chemical state	IS (mm/s)	QS (mm/s)	H (T)	RI (%)
Ir-Fe/ Al_2O_3	Fe^{3+}	0.32	1.09		61
	Fe^0	0.00	0.00	33.4	22
	$\text{Fe}^{2+}(\text{a})$	1.10	2.10		17
Fe/Ir/ Al_2O_3	Fe^{3+}	0.32	1.10		70
	Fe^0	0.00	0.00	33.3	15
	$\text{Fe}^{2+}(\text{a})$	1.08	2.11		15
Ir/Fe/ Al_2O_3	Fe^{3+}	0.31	1.11		78
	$\text{Fe}^{2+}(\text{a})$	1.11	2.06		22

O_2 activation can be calculated. The amount of $\text{Fe}^{2+}(\text{a})$ in the Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 catalysts after the PROX reaction were 17%, 15%, and 22%, while after the re-oxidation, namely, for the inactive $\text{Fe}^{2+}(\text{a})$, the amounts were 0, 6%, and 19%, respectively. Thus, the amounts of the active $\text{Fe}^{2+}(\text{a})$ in the Ir-Fe/ Al_2O_3 , Fe/Ir/ Al_2O_3 , and Ir/Fe/ Al_2O_3 catalysts were 17%, 9%, and 3%, respectively.

To better show the relation between the active $\text{Fe}^{2+}(\text{a})$ concentration and CO oxidation rate, we plotted CO conversion as a function of active $\text{Fe}^{2+}(\text{a})$ concentration in Fig. 6. After the PROX reaction, the amount of $\text{Fe}^{2+}(\text{a})$ for O_2 activation followed the order Ir-Fe/ Al_2O_3 > Fe/Ir/ Al_2O_3 > Ir/Fe/ Al_2O_3 . This trend is the same as that for the activity, which showed that $\text{Fe}^{2+}(\text{a})$ in the Ir-Fe catalysts can be related with the catalytic activity. It can be seen clearly in Fig. 6 that CO conversion was proportional to the amount of $\text{Fe}^{2+}(\text{a})$. This is consistent with reports that with PtFe [22,23] and PtSn [5] catalysts, low valent Fe or Sn played

Fig. 6. CO conversion in PROX versus active $\text{Fe}^{2+}(\text{a})$ concentration determined by ^{57}Fe Mössbauer spectroscopy.

the key role of activating O_2 in the PROX reaction. Although it was proposed that about 10% Fe-Ir alloy was observed in Ir-Fe/ SiO_2 which formed Ir and Fe^{2+} for activating CO and O_2 , respectively [16], only a very small amount of Fe-Ir alloy was formed after reduction of the Ir-Fe/ Al_2O_3 catalyst. This was probably due to the much stronger interaction of Fe and Al_2O_3 than that of Fe and SiO_2 .

In the present study, the interaction between Ir and Fe on Ir-Fe/ Al_2O_3 or Fe/Ir/ Al_2O_3 was much stronger than that on Ir/Fe/ Al_2O_3 . This was possibly because the strong metal-support interaction between Fe and Al_2O_3 weakened the interaction between Ir and Fe when the support was first impregnated with Fe. The strong interaction between Ir and Fe accelerated the reduction and reoxidation of the iron oxide, which promoted CO conversion. Thus, a stronger interaction between Ir and Fe resulted in more active $\text{Fe}^{2+}(\text{a})$ sites being retained. Nevertheless, although it is widely accepted [24] that an alloy can provide intimately connected binary sites for activating CO and O_2 , respectively, an Fe-Ir alloy was not necessary for PROX on the Ir-Fe catalysts supported on Al_2O_3 .

3 Conclusions

Three Fe-promoted Ir/ Al_2O_3 catalysts were prepared by different impregnation sequences. The co-impregnated Ir-Fe/ Al_2O_3 was better than Fe/Ir/ Al_2O_3 and Ir/Fe/ Al_2O_3 prepared by sequential impregnation of Ir and Fe, and vice versa. Mössbauer spectra showed that reducibility followed the same order as PROX activity and selectivity, which was Ir-Fe/ Al_2O_3 > Fe/Ir/ Al_2O_3 > Ir/Fe/ Al_2O_3 . This trend indicated significantly different interactions between Ir and Fe and metal-support interactions, which resulted in different redox properties of the iron species. The CO uptakes on the three catalysts follow the order Ir-Fe/ Al_2O_3 < Fe/Ir/ Al_2O_3 < Ir/Fe/ Al_2O_3 , showing that the Ir-Fe interaction weakened the

adsorption of CO and promote CO oxidation. The amount of the active $\text{Fe}^{2+}(\text{a})$ species during PROX followed the same trend as CO conversion, indicating that $\text{Fe}^{2+}(\text{a})$ was the active site for activating O_2 during PROX. The different impregnation sequences influenced CO conversion by resulting in different amounts of $\text{Fe}^{2+}(\text{a})$, which was due to different interactions between Ir and Fe.

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