MECHANISTIC STUDIES ON PREFERENTIAL OXIDATION OF CO IN H_2-RICH ATMOSPHERE OVER IRFE CATALYSTS
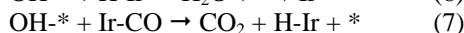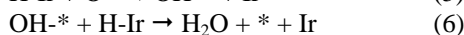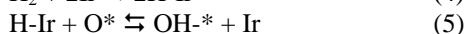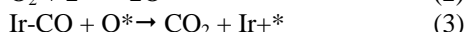
Kuo Liu, Junhu Wang and Tao Zhang

Mössbauer Effect Data Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Preferential oxidation of CO in H_2-rich stream (PROX) is becoming attractive with the fast development of the proton exchange membrane fuel cells. Among the PROX catalysts, bimetallic catalyst is one of the most effective candidates, such as PtFe[1-3] and IrFe[4-8] catalysts. In the present text, IrFe catalyst was chosen as a model catalyst for studying the mechanism of the PROX reaction on bimetallic catalysts.

IrFe bimetallic catalysts supported on SiO_2 was prepared by co-impregnation method.[6] It has been found that the presence of H_2, even in a slight excess (such as 2 %), could led to a large increase in the CO oxidation rate on $IrFe/SiO_2$.[7] In order to reveal the promotional role of Fe related with the presence of H_2, quasi in situ Mössbauer spectroscopy, in combination with microcalorimetry and in situ DRIFTS, was employed. The results showed that Fe^{3+} in the IrFe catalyst could be easily reduced to Fe^{n+} ($2 < n < 3$), Fe^{2+}, FeIr alloy and Fe^0 with the aid of Ir, and the low valence Fe species could also be easily oxidized when exposed to O_2. The relative amount of Fe^{2+} increased when increasing the H_2 concentration in the gas mixture, as shown in Figure 1, which was well consistent with the trend of the CO oxidation rate. In addition, Fe^0 remained intact in the oxidation atmosphere, probably because it was encapsulated by ferric oxide. The results above strongly suggested that Fe^{2+} was the active site for oxygen activation. During the PROX reaction, FeIr alloy disappeared due to oxidation, forming intimately contacted Fe^{2+} species and Ir particles. H_2 promoted CO oxidation by stabilizing Fe^{2+} in $IrFe/SiO_2$.

Based on the results of characterization and the steady state kinetic data in a microreactor, the microkinetic model which could predict the experimental results well was proposed.[8] The elementary steps (1) - (7) were involved in the PROX reaction, while the steps (1) - (3) were involved in CO oxidation:

$$CO + Ir \leftrightarrows Ir\text{-}CO \quad (1)$$
$$O_2 + 2* \rightarrow 2O* \quad (2)$$
$$Ir\text{-}CO + O* \rightarrow CO_2 + Ir+* \quad (3)$$
$$H_2 + 2Ir \leftrightarrows 2H\text{-}Ir \quad (4)$$
$$H\text{-}Ir + O* \leftrightarrows OH\text{-}* + Ir \quad (5)$$
$$OH\text{-}* + H\text{-}Ir \rightarrow H_2O + * + Ir \quad (6)$$
$$OH\text{-}* + Ir\text{-}CO \rightarrow CO_2 + H\text{-}Ir + * \quad (7)$$

Where * denotes Fe^{2+} species. The model suggested that for CO oxidation, no competitive adsorption between CO and O_2 was observed on IrFe catalyst. For CO oxidation, the surface reaction between adsorbed CO and O was rate limiting. For PROX, the reaction between adsorbed H and O for OH formation was rate determining, and the rate constant of step 7 was faster than step 3 (Table I), suggesting that the oxidation of adsorbed CO

by surface OH was the dominant pathway for CO_2 formation. According to the model, the increasing trend of OH coverage coincides with the increase of the CO oxidation rate, as shown in Figure 2. Thus, it can be concluded that the presence of H_2 increased the surface concentration of OH and hence lowered the activation energy and increased the reaction rate of PROX.

Therefore, H_2 not only stabilized Fe^{2+} species, but also increased OH groups on the surface, both of which could promote CO oxidation.

Table I: Rate constants for elementary steps for PROX.

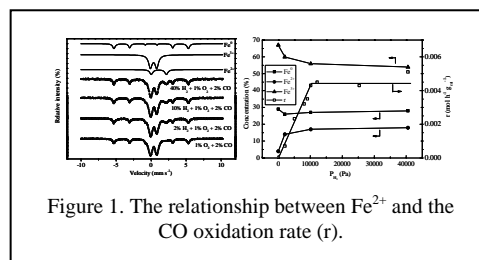| T (K)	333	353	373	393
k_1/k_{-1}	1.33×10^8	1.14×10^7	1.27×10^6	1.78×10^5
k_2	2000	2000	2000	2000
k_3	0.009	0.026	0.07	0.16
k_4/k_{-4}	1.08×10^4	3.88×10^3	1.56×10^3	6.85×10^2
k_5/k_{-5}	0.12	0.19	0.27	0.37
k_6	0.11	0.24	0.50	0.97
k_7	0.43	0.96	2.00	3.86

k: rate constant

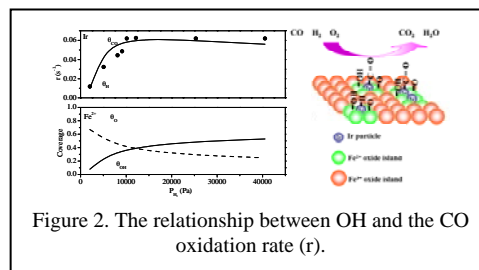Figure 1. The relationship between Fe^{2+} and the CO oxidation rate (r).

Figure 2. The relationship between OH and the CO oxidation rate (r).

[1] BT.Qiao et al., Nature Chem 3 (2011) 634-641
[2] Q.Fu et al., Science 328 (2010) 1141-1144
[3] J.Yin et al., Catal Lett 125 (2008) 76-82
[4] WS.Zhang et al., Catal Lett 121 (2008) 319-323
[5] WS.Zhang et al., Catal Today 131 (2008) 457-463
[6] WS.Zhang et al., Int J Hydrogen Energy 35 (2010) 3065-3071
[7] K.Liu et al., J Phys Chem C 114 (2010) 8533-8541
[8] K.Liu et al., Ind Eng Chem Res 50 (2011) 758-766