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Green catalysis for selective CO oxidation in hydrogen for fuel cell

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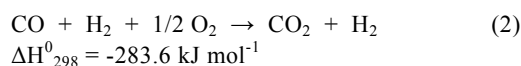
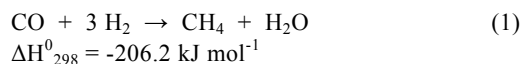
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Preferential oxidation of carbon monoxide in excess hydrogen (PROX) is one of the key processes for the production of clean hydrogen fuel for the polymer electrolyte membrane fuel cell (PEFC). Development of highly active and selective catalysts is among the most challenging works for decades. Platinum-based catalysts are regarded as the most promising candidates for this process.

However, the activities of Pt catalysts seriously suffer from the strong poisonous adsorption by CO substrate at low reaction temperature. This article addresses the present approaches to improve the catalytic performance under the low temperature. The focus in this article is the finding over the Pt/mesoporous silica catalyst. The high activity and selectivity of this catalyst has been attributed to the surface silanols in mesoporous silica. The perspectives of Pt/mesoporous silica in the PROX reaction are also presented.

Introduction

Polymer electrolyte membrane fuel cell (PEFC) uses the chemical energy of hydrogen to efficiently produce electricity with water as a by-product. In term of its high energy-efficiency and ultra-low emission of pollutants, the PEFC is regarded as one of the most promising candidates to replace the internal combustion engine in vehicles, and power supply in stationary and portable power applications.¹ The hydrogen fuel can be produced from fossil fuels (such as natural gas and coal) and other renewable resource such as biomass, solar and wind. However, in the medium term, pure hydrogen generated from renewable or sustainable energy sources will not be extensively available. At present, steam reforming, partial oxidation and auto-reforming of alcohols and hydrocarbons are still the major routes in the hydrogen production.^{1,2} The description for the whole process is shown in Fig. 1.³ A noticeable amount of CO, ca. 5-15 vol%, is formed together with the generation of H₂. By subsequent water-gas-shift (WGS) processes at high temperature (623-823 K) and low temperature range (473-573 K), the CO concentration can be reduced to 0.5-1 vol%.^{4,5} Unfortunately, Pt-based anodes are still extremely susceptible to the poisoning by the CO (>10 ppm) at their operation temperature (~353 K).^{1,6,7} Therefore, the delivery of clean H₂ to Pt anodes becomes the essential and imminent requirement for the application of PEFC. However, the complete reduction of CO cannot be accomplished by the WGS process due to the limitation in thermodynamic equilibrium.¹⁻⁵ To achieve the acceptable ppm level of CO concentration, methanation (Eq. (1)) and preferential oxidation of carbon monoxide (PROX) (Eq. (2)) are designed for the fine cleaning of hydrogen.⁴



However, the methanation of CO consumes rather higher amount of H₂, which decreases the total efficiency of fuel cells.¹ The PROX is regarded as the most effective and cost-efficient way to achieve the goal. The ideal solution is the direct integration of PROX process and PEFC as shown in Fig. 2. In order to approach this goal, the catalytic systems should match following key requirements:^{1,8}

- 1) Extremely high activity for CO oxidation. This deserves a priority due to the sensitivity of Pt anodes. In the stream containing 1 vol% CO, a conversion over 99.9% has to be achieved for the reduction to ppm level.
- 2) High selectivity for CO oxidation. The catalysts should be inert for the reverse water-gas-shift reaction, which hampers the deep reduction of CO in the presence of abundant H₂ and CO₂. In order to minimize the hydrogen loss, the catalysts are expected to be inactive for the side oxidation of H₂.
- 3) Wide operation temperature window. Since the PROX is placed between the low temperature WGS reactor and PEFC, the catalysts should be applicable from 353 K to the outlet temperature of low temperature WGS reactor.
- 4) Compatible with the operation parameters and conditions of upstream process. The catalysts should be resistant to the high concentration of CO₂ and steam from the upstream WGS processes, and preserve their performances to the

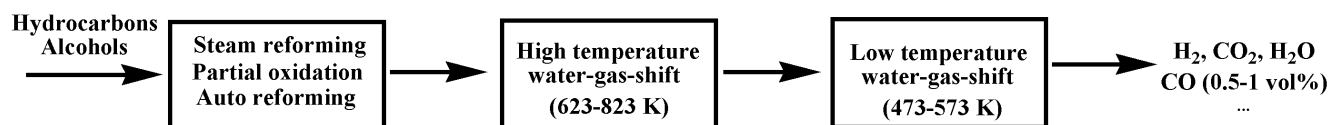


Fig. 1 The simplified description for the current production of hydrogen.

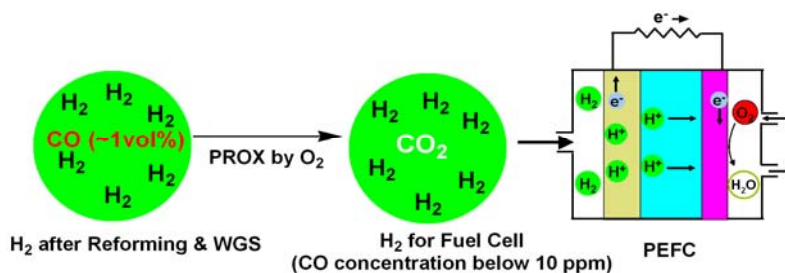


Fig. 2 The diagram of ideal PROX process for the deep purification of H₂ for PEFC.

fluctuations in the space velocities and start-stop operation cycles.

Various catalysts have been studied including precious metals (Ru,⁹⁻¹¹ Pd,^{3,9,12,13} Rh,¹⁴⁻¹⁶ Au¹⁷⁻²¹ and Pt²²⁻³⁰), non-precious metals (Cu³¹⁻³³ and Co^{31,34}) and the combination of multiple metallic systems. The traditional Ru-based catalysts are operated at 413-473 K and always accompanied with the methanation of H₂. Gold-based catalysts are rather active and selective at 353 K; however, the catalytic activities are still insufficient. Pt-based catalysts are the widely investigated and regarded as the promising candidates for this reaction. In fact, Pt/Al₂O₃ catalysts were used to remove carbon monoxide from hydrogen prior to ammonia synthesis as early as in the 1960s.³⁵⁻³⁷ Unfortunately, these conventional catalysts are not directly applicable to the present system because they cannot match the requirement for the operation temperature, and hence cannot be directly integrated with the PEFC. In general, the operation temperature window for the complete reduction of CO is 443-473 K for conventional Pt-based catalysts in PROX reaction. The extension to the lower temperature range has become the target for decades. What is the most challenging point for Pt-based catalysts at low reaction temperature? It is well recognized that the surface of Pt catalyst will soon be fully covered by adsorbed CO under a steady-state flow of CO and O₂, which prevents oxygen adsorption and hence suppresses the oxidation reaction.³⁸ This problem can only be overcome with temperature higher than 450 K, at which continuous desorption of adsorbed CO occurs

and gaseous O₂ may compete for these free adsorption sites.

Based on this understanding, the basic strategy is to promote the O₂ adsorption at low temperature, i.e. to transform the competitive Langmuir-Hinshelwood reaction pathway to non-competitive dual-site one. So far, the efforts in this area can be divided into following aspects (Fig. 3):

- 1) Incorporation of second metal or metal oxide as a promoter for the dissociation of O₂ (route a);
- 2) Usage of reducible support as the site for the activation of O₂ (route b);
- 3) Creation of new Pt structure to weaken the extremely strong interaction between metal and CO (route c);
- 4) Pursuit of new catalyst support (mesoporous silica) (route d), which is basically inspired by our work.

This paper gives examples of the ongoing research and advancement concerning the PROX reaction over Pt-based catalysts. The typical improvements in major catalyst systems have been referred. The results based on our recent work are also discussed, which reveals a newly proposed way for the oxidation of CO over the mesoporous silica. Furthermore, the perspectives of PROX reaction over mesoporous silica system are also presented.

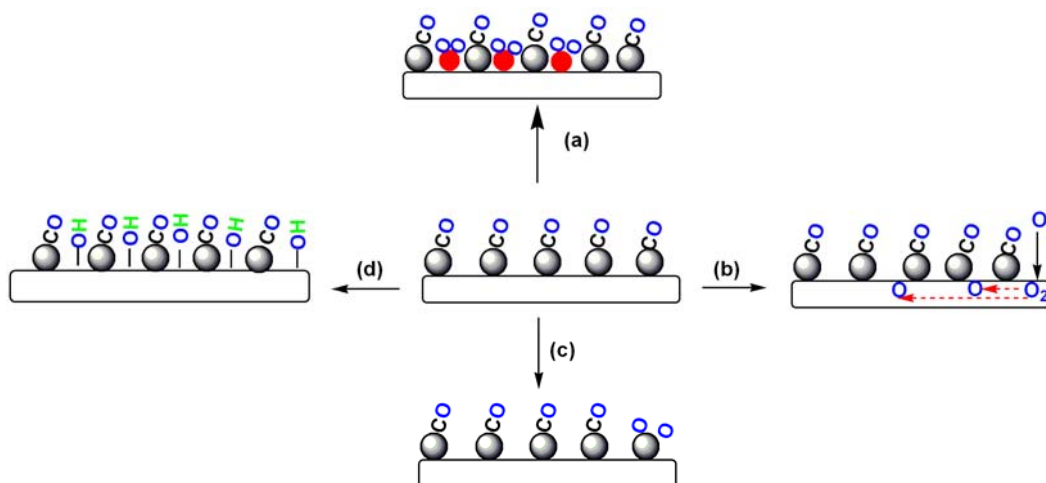


Fig. 3 Reported strategies for the improvements of Pt-based catalysts.

1. Representative improvements for the catalyst systems

1.1 Incorporation of promoter for activation of O₂

The direct way to realize the dual-site reaction pathway is to incorporate some metal or metal oxide, which are capable of O₂ dissociation. The reported formulations include MnO_x/Pt/Al₂O₃,³⁹ Ce₂O₃/Pt/Al₂O₃,⁴⁰ SnO_x-Pt/Al₂O₃,^{41,42} and Fe-Pt/Al₂O₃(or TiO₂).⁴³⁻⁴⁶ Compared with the supported monometallic Pt catalysts, the light-off temperatures are shifted to lower range over the promoted systems in usual CO oxidation reaction, which proves the contribution from improved O₂ activation. However, the complete CO reduction still cannot be achieved over these systems at low temperature. For example, MnO_x/Pt/Al₂O₃ (0.35 wt% Pt - 15 wt% Mn) shows ca. 90% CO conversion at 413 K in the PROX reaction despite the high oxygen storage of MnO_x species.³⁹ SnO₂-Pt/Al₂O₃ (1 wt% Pt-3 wt% Sn) can achieve ca. 100% CO conversion at 383 K with excess O₂ conditions (O₂/CO = 1.5).⁴¹ A series of Fe promoted Pt/zeolite catalysts have been reported to exhibit higher activity.^{23,26,27,47-49} The Fe-Pt bimetallic (4 wt% Pt-0.5-2 wt% Fe) systems on mordenite zeolite show complete CO reduction between 373-403 K under the condition of excess O₂/CO = 1. The reaction has been proposed to proceed through the “bifunctional mechanism” as shown in Fig. 4(b), where Pt acts as CO adsorption site and Fe site serves as O₂ activation site, respectively.²⁶

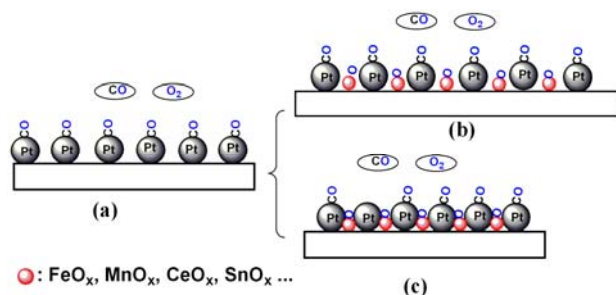


Fig. 4 Incorporation of metal or metal oxide species for the dissociation of O₂: (a) mono-metal without promoter, (b) neighbouring bimetallic system, (c) intimate bimetallic system.

Depending on the pretreatment conditions, Fe species can be presented as metal oxide strongly intimated with Pt or metallic form in metal-Pt alloy (Fig. 4(c)).^{26,42,44,48} It is reported that the bond strength between CO and Pt can be weakened due to the increase of Pt 5d-vacancy by alloying effect with metallic Fe.⁴⁸ Besides improved O₂ activation capability, such intimate interaction can also suppress the CO adsorption on Pt as characterized by chemisorption and DRIFT-IR results.^{42,44,48} Furthermore, the effect of Fe promoter also depends on the type of support. The Fe promoted Pt/Al₂O₃ catalysts do not exhibit such high activity and selectivity at low temperature. The cages of mordenite and ZSM-5 zeolites are speculated to play positive roles in reaction including the restricted space for fabrication of highly dispersed Pt nanoparticles and also “special reaction space” for CO oxidation. The effect of zeolites architecture

was also investigated, and difference among various zeolites was observed as following: Pt/A>Pt/mordenite>Pt/X. Moreover, dependence of oxidation activity on the pore diameter of A zeolite was also observed. The higher catalytic performance of Pt/3A was attributed to the “shape selectivity” by the dimension of 3 Å pore diameter, which may inhibit the admission of CO₂ molecule and suppress the reverse water-gas-shift side reaction.^{3,23} Further efforts have been made to prepare bimetallic systems with uniform composition between Pt and promoters, which can improve the cooperative effects between CO adsorption and O₂ activation sites.^{50,51} By using organometallic precursors (Pt₅Fe₂(1,5-cyclooctadiene)(CO)₁₂ or PtFe₂(1,5-cyclooctadiene)(CO)₈), the cluster-derived 1 wt% PtFe/SiO₂ catalysts show a relatively uniform Fe:Pt composition and particle-size distribution, which result in higher activity and selectivity than the 1 wt% Fe-Pt/SiO₂ catalyst prepared by the incipient wetness impregnation method.⁵⁰

1.2 Usage of reducible support

Besides the incorporation of promoters for Pt over inert Al₂O₃ and zeolite support, the usage of reducible-oxidizable support is an alternative route to provide the sites for O₂ activation. Ceria is a typical and representative of such type of support due to the well-known high oxygen storage capacity (OSC) of CeO₂,⁵² which can improve the oxygen supply and subsequent oxidation reaction. As expected, Pt/CeO₂ (0.54 wt% Pt) showed ca. 100% CO conversion at 373 K with a stoichiometric O₂/CO ratio in the absence of H₂.³⁰ Although the CO conversion was improved in the presence of H₂ at the low temperature range (<353 K), it decreased with further higher reaction temperature and far from the complete CO reduction.³⁰ As noted above, the reaction follows the modified non-competitive Langmuir-Hinshelwood pathway, i.e. the O atoms are activated by the ceria support and react with adsorbed CO through spill-over or at the metal-support interface. The participation of surface oxygen from the support has already been proved from the observation of zero-order oxygen pressure dependence and also the oxygen-exchange measurements between C¹⁶O and ¹⁸O-predosed catalysts.⁵³⁻⁵⁵ The decreased CO conversion in PROX is attributed to the competitive side oxidation of H₂, which occurs between the surface O atoms of ceria support and spill-over H atoms from Pt. The side reaction becomes more severe with higher OSC. The doping of ZrO₂ to CeO₂ improved the OSC and oxygen mobility of CeO₂,^{8,56} and was able to oxidize CO even in absence of O₂.⁸ However, the CO conversions over the Pt/CeO₂-ZrO₂ (1.0 wt%) in PROX was much lower than those of Pt/CeO₂. In contrast, the O₂ conversions were always ca. 100%, indicative of more serious H₂ oxidation side reaction. This may suggest that it is very important to control the O₂ activation to avoid the competitive side reaction in PROX. Nevertheless, the controversy over the reaction mechanism still remains. It is proposed that the reaction may occur through the low temperature water-gas-shift route, i.e., the gas phase O₂ is not only limited to the activation by the re-oxidation of reducible support, but also be transformed into the surface water on the ceria surface that is reactive with CO

on the Pt surface.⁵⁷⁻⁵⁹ Nonetheless, the redox properties of supports always lead to the serious competitive side oxidation of H₂. Furthermore, the CeO₂ support is not resistant to the CO₂ due to the carbonation effect.^{30,58} These weaknesses manifest the intrinsic disadvantages of this type of material in the practical PROX reactions.

1.3 New Pt structure with weakened CO adsorption

Bimetallic noble metal systems of Pt-Ru and Pt-Pd have been reported to show high CO-tolerance in electrocatalysis.^{60,61} These combinations are naturally incorporated into the heterogenous catalysis application. In such systems, the catalysts work in the bifunctional way: the more oxophilic metal (with lower CO coverage, e.g. Ru) serves as an oxygen activator, which improves the oxidation of adsorbed CO on less oxophilic Pt center. The typical reported formulations include Pt-Ru/Mordenite,⁶² Pt-Ru/SiO₂,⁶³ and Pt-Ru/Al₂O₃.⁶⁴ The metals can be presented as in monometallic particles and segregated intra-particles (alloy); the latter may weaken adsorption strength between CO and Pt. Another way is to directly weaken the interaction between Pt and CO by the addition of alkali base metal species.⁶⁵⁻⁶⁷ However, it is difficult to control the state and interaction of the components, while the improvement in catalytic performance is also limited.

Very recently, a Ru-Pt core-shell (Ru@Pt) structure has been designed.^{64,68} Compared with the traditional Pt-Ru alloy and mixture of monometallic particles, the core-shell structure is characteristic of confined Ru core covered with an approximately thin monolayer-thick shell of Pt atoms. The full characterization results (XRD, TEM, XPS and FT-IR) validate only 1-2 Pt monolayer is exposed on the surface. For the 1000 ppm CO feeds, CO is reduced to ppm level from room temperature over the Ru@Pt/Al₂O₃ (1 wt% Pt loading, O₂/CO = 5) catalysts, which is distinctly superior to the PtRu alloy and Ru+Pt monometallic mixture counterparts. Since the Ru is buried in the core, the traditional bifunctional mechanism is not operative. This means the electronic structure of Pt surface should be modified by the Ru core. The Ru substrate has a lateral compression on Pt monolayer and decreases the interaction between Pt and adsorbates.^{64,68} Moreover, the interaction between Pt-monolayer and Ru core downshifts the *d*-band center. Both effects contribute to the weakened interaction strength between Pt surface and adsorbates, and significantly destabilize CO on Pt. This leads to lower CO saturation coverage and provides much more CO-free sites for activation of other reactants. The density-function-theory (DFT) calculations show 2/3 monolayer of the pure Pt(111) surface is covered with CO at saturation state, whereas only 1/2 monolayer of Pt (Ru@Pt) is covered with CO. The CO-free sites decrease the H₂ dissociation energy barrier and contributes to an O₂ dissociation route assisted by H. These interpret the high CO oxidation activity of Ru@Pt architecture at low reaction temperatures.

2. Promotional effect of mesoporous silica for PROX reaction

The basic start point of current strategy is to improve the O₂ activation by weakening the CO adsorption on Pt or adding reducible promoter. However, the improved O₂ activation always results in the competition of H₂ oxidation, which suppresses the CO oxidation. So far, the architecture with precise controlled O₂ activation capability still requires more efforts. Among the reported results, the reduction of CO still require temperature around 373 K or high excess O₂/CO ratio.^{49,68} Hence, there still remains a challenge of catalyst design for high activity and selectivity from the low temperature (< 373 K). Instead of exploring new Pt architecture, we put our efforts into the pursuit of a support.

Since the discovery of FSM-16,^{69,70} MCM-41⁷¹ and SBA-15⁷² in the last decades, mesoporous silicas have been extensively investigated for applications in catalysis.^{73,74} The mesoporous silicas are characteristic of ordered pores (2-10 nm) with high surface area (ca. 500-1000 m² g⁻¹), which are attractive as catalysts and supports. However, the understanding the role of mesoporous silica is generally limited to give higher dispersion of active sites than over the conventional silica. From the viewpoint of molecular level, the participation of mesoporous silica in the catalytic reactions is through the silanols (or hydroxyl groups) on the surface. If the surface silanols can participate in the CO oxidation, the limitation of O₂ activation on the activity can be decreased. Inspired by this point, we investigate the PROX reaction over the Pt/mesoporous silica.

2.1 Unique superior catalytic performance of Pt/FSM-16.

Pt nanoparticles and nanowires (5 wt% Pt loading) are synthesized in several types of mesoporous silica (FSM-16, MCM-41 and HMM-1) as previously reported.⁷⁵ The surface area and dispersion of Pt nanoparticles over mesoporous silica are higher than those of conventional SiO₂- and Al₂O₃-supported catalysts (Table 1).

Table 1 Structural parameters of representative catalysts.

materials	Surface area (BET, m ² g ⁻¹) ^a	Pore diameter (BJH, nm) ^b	Pore volume (mLg ⁻¹)	CO/Pt
Pt(p)/FSM-16	944	2.7	0.77	0.24
Pt(w)/FSM-16	878	2.7	0.68	0.09
Pt(p)/HMM-1	661	3.0	0.58	0.31
Pt/SiO ₂				0.13
Pt/Al ₂ O ₃				0.17

^a Brunauer-Emmet-Teller surface area. ^b Barrett-Joyner-Halenda method.

Table 2 Catalytic performances of various catalysts at the operation temperature of PEFC.

Catalyst	CO conversion (%)	Selectivity (%)
Pt/SiO ₂	18.8	64.1
Pt/Al ₂ O ₃	37.6	55.0
Pt(w)/FSM-16 ^a	75.6	59.5
Pt(p)/HMM-1	21.0	>99.5
Pt(p)/FSM-16 ^b	>99.5	50.0

Reaction conditions: 353 K, CO 1%, O₂ 1%, N₂ 5%, H₂ balance, SV 12000 ml g⁻¹ h⁻¹, 0.1 MPa. ^a Pt(p): Pt nanoparticles; ^b Pt(w): Pt nanowires

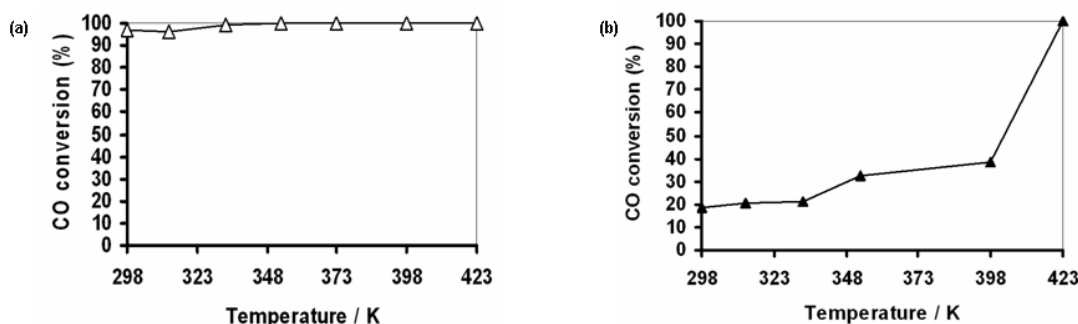


Fig. 5 (a) PROX over Pt(p)/FSM-16 under stoichiometric condition. Reaction conditions: CO 1%, O₂ 0.5%, N₂ 5%, H₂ balance, SV 12000 ml g⁻¹ h⁻¹, 0.1 MPa. (b) Usual CO oxidation over Pt(p)/FSM-16. Reaction conditions: CO 1%, O₂ 1%, N₂ 5%, He balance, SV 12000 ml g⁻¹ h⁻¹, 0.1 MPa.

The Pt nanoparticles over FSM-16 (5 wt% Pt loading) show unprecedented high activity. As shown in Table 2, Pt(p)/FSM-16 provides remarkably higher activity of ca. 100% CO conversion at 353 K under the conditions of twice excess O₂ (O₂/CO = 1) over the stoichiometry (CO/O₂ = 1/2). In contrast, SiO₂-, Al₂O₃- and HMM-1 supported catalysts show CO conversion less than 30% under the same reaction conditions, and require 423 K or even higher temperature to remove majority of CO.²⁵ In particular, Pt(p)/FSM-16 gives ca. 100% conversion of CO from 313 K to 423 K,²⁵ thus showing that this is one of the most active catalysts for PROX. The reported Pt catalysts always require excess O₂ (O₂/CO > 1/2) because the H₂ oxidation (H₂ + 1/2 O₂ → H₂O) consumes the O₂. As shown in Fig. 5a, in the stoichiometric O₂/CO (1/2) gas flow mixture, Pt(p)/FSM-16 shows CO conversions over 95% at 298-423 K. This indicates that the CO selectivity is over 95% for Pt(p)/FSM-16.

For the mesoporous type silica, FSM-16 and MCM-41 show the similar catalytic performance, perhaps due to the similar structure. However, the performance of Pt(p)/organosilica HMM-1 is even lower than those of Pt/Al₂O₃ and Pt/SiO₂ despite its higher Pt dispersion. This poses a question: what is the decisive factor for the activity?

For Pt(p)/FSM-16, 2.5 nm Pt particles inside the internal mesopore are observed in the TEM and STEM images. The Pt/Al₂O₃ and Pt/SiO₂ have a broad particle-size distribution

from 3 to 7 nm. However, the temperature-programmed CO desorption (CO-TPD) experiments show the interaction between CO and Pt is quite similar on different catalysts. Moreover, the CO conversion on Pt(p)/FSM-16 undergoes a sharp decrease if the reaction is carried out in the absence of H₂ (Fig. 5b). This indicates the reaction mechanism of PROX over Pt(p)/FSM-16 is totally different from the usual CO oxidation, and the difference in the Pt morphology is not responsible for the different activities.

2.2 Mechanistic study of PROX by the isotope tracer method

IR spectra of CO adsorption (30 Torr) over Pt catalysts at 298 K were shown in Fig. 6a. All the typical three samples, active Pt(p)/FSM-16 and inactive Pt(p)/HMM-1 and Pt/SiO₂, show a linear CO frequency on Pt at 2088 cm⁻¹ (Fig. 6a). However, small gaseous CO₂ peaks were observed at ca. 2350 cm⁻¹ over Pt(p)/FSM-16 in the enlarged range of 2400-2200 cm⁻¹ (Fig. 6b). Furthermore, in the adsorption of ¹³CO or a mixture of ¹²CO and ¹³CO, gaseous ¹³CO₂ peak was also observed at 2280 cm⁻¹. As a strong comparison, none of CO₂ peak was observed in the CO adsorption over the inactive Pt(p)/HMM-1 or Pt/SiO₂ catalyst. It should be noted that no oxygen source was presented except the FSM-16 support in the adsorption of ¹²CO or ¹³CO. The most reasonable explanation is that the oxygen of silica in FSM-16 is incorporated into CO₂ in the CO adsorption.

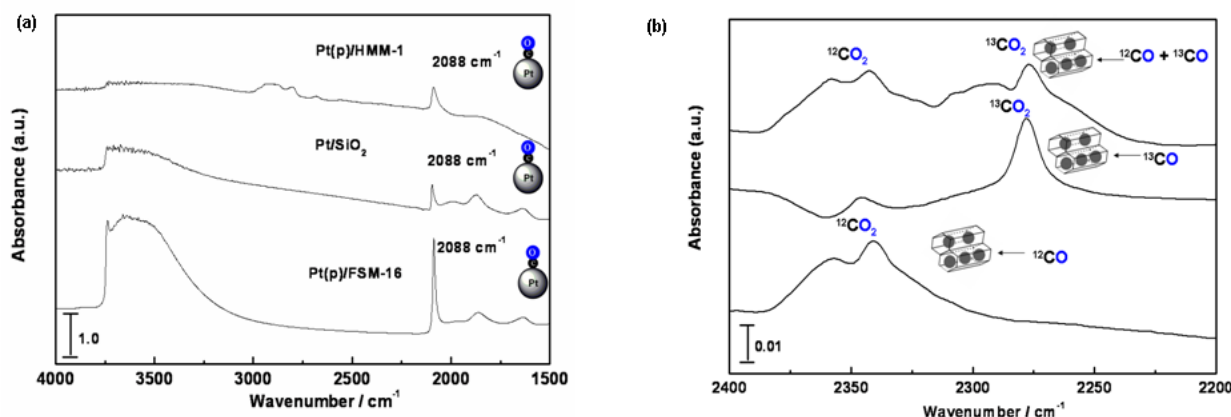


Fig. 6 (a) IR spectra of ¹²CO adsorption over Pt(p)/FSM-16, Pt/SiO₂ and Pt(p)/HMM-1. (b) Formation of gaseous ¹²CO₂ or ¹³CO₂ formed in the adsorption of ¹²CO and ¹³CO over the Pt(p)/FSM-16.

Table 3 The variation of CO and CO₂ peak over Pt(p)/FSM-16 during the sequential adsorption of CO, ¹⁸O₂ and D₂.

atmosphere	CO	CO ₂	C ¹⁶ O ¹⁸ O (2331 cm ⁻¹)
CO	2088 cm ⁻¹	2350 cm ⁻¹	Not observed
CO + ¹⁸ O ₂	2088 cm ⁻¹	2350 cm ⁻¹	Not observed
CO + ¹⁸ O ₂ + D ₂	2084 cm ⁻¹	2350 cm ⁻¹	Not observed

Sequential adsorption of CO (10 Torr), ¹⁸O₂ (10 Torr), and D₂ (60 Torr).

CO, and the OD band reflects the spill-over process in the PROX atmosphere.

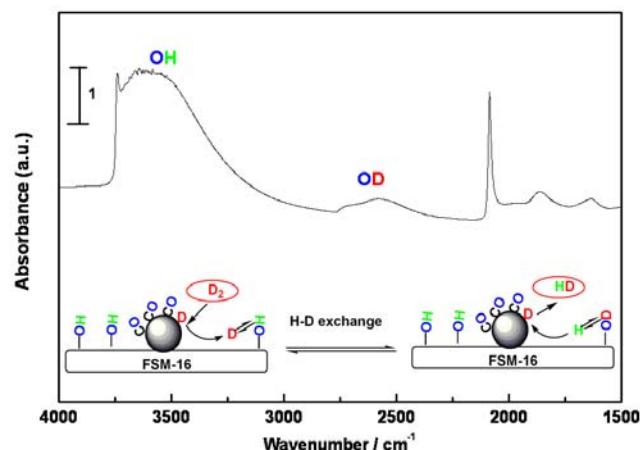


Fig. 7 H-D exchange over Pt(p)/FSM-16 in the sequential adsorption of CO (10 Torr) and D₂ (10 Torr).

2.3 Overall mechanism for PROX reaction over Pt(p)/FSM-16

Combining the catalytic performances and the IR results, we propose that the surface OH on FSM-16 is highly reactive toward CO adsorbed on Pt nanoparticles at the interface of Pt and FSM-16. As depicted in Fig. 8, the OH groups attacks CO on Pt to form CO₂ and H₂, and a vacant site is formed on FSM-16. O₂ is adsorbed on FSM-16 and suggested to form the OH groups with the assistance of spill-over hydrogen from Pt.

Perspectives and prospects

According to the present results, it can be concluded that the difference between mesoporous silica and conventional amorphous silica is not only in their physical parameters, but also in their reactivity in surface silanols. Since the high activity and selectivity of Pt/mesoporous silica is related with the surface silanols in FSM-16 and MCM-41, following questions arise naturally:

- 1) Which type of surface silanols is closely related with the superior catalytic performances? In general, there are three types of surface silanols (free, geminal and hydrogen-bonded silanols) on the mesoporous silica. We have revealed the involvement of surface silanols in the reaction. However, we have no more information about the possible different activities among these silanol groups.

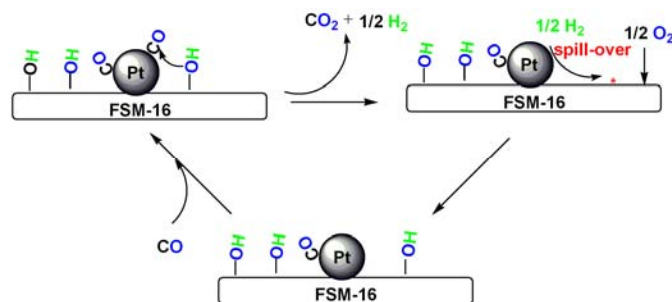


Fig. 8 Proposed mechanism for PROX over Pt(p)/FSM-16.

2) What is the effect of pore size on the catalytic performance?
The pore diameter may influence the encapsulation of Pt nanoparticles into the mesopore, which affects the proximity between metal sites and surface silanols. On the other hand, the distribution of silanols is different as the function of pore size,^{76,77} which can give more clarifications about the catalytic role of surface silanols.

3) How about the catalytic performance of other mesoporous silicas? FSM-16 (MCM-41) is one of the representative materials in the mesoporous silica family. Can we observe such promotional effect on other typical mesoporous silica? This will improve the understanding of the catalytic role of mesoporous silica not only from the viewpoint of structure but also from their possible intrinsic different reactivity in surface silanols.

4) How can we decrease the Pt loading to a practical level? It has been reported that the introduction of Al into mesoporous silica can improve the activity of Au catalysts in CO oxidation.⁷⁸ Since the incorporation of Al will change the type and interaction of surface silanols, similar effect may also be observed on the Pt/mesoporous silica in PROX reaction.

5) Why is there remarkable difference between siliceous FSM-16 and organic-inorganic HMM-1 silica?

We have just opened the application of mesoporous silica in PROX reaction. The ongoing and forthcoming investigations will promote the catalytic performance and improve understanding the intrinsic catalytic role of mesoporous silica. We hope it will be helpful not only for PROX reaction but also for the general understanding of these materials in wide applications.

Conclusions

In general, the PROX reaction and normal CO oxidation are regarded to follow the same competitive Langmuir-Hinshelwood reaction mechanism. As a result, one of the crucial problems for Pt-based catalysts in the PROX reaction is to create the CO-free sites for the selective and controlled activation of gas phase O₂. The reported methods include the introduction of O₂ activator, usage of reducible support and designed structure for weaker CO adsorption. Despite these efforts, further efforts are still required for the innovation of extremely high active, selective and stable catalyst systems. At the same time, the controversy and unresolved problems still remain in the basic research on this process, e.g. the reaction intermediate, variation of surface species plus their real roles in reaction, the origin of the deactivation and the possibly transformed states under different reaction condition (space velocity, O₂/CO ratio and concentration, etc.). The application of mesoporous silica in PROX opens a new potential way for the resolution. The most valuable and interesting finding is that the surface silanols in mesoporous silica can play as the "oxidant" to initiate the CO reaction. This may release the confliction in the modification for the adsorption between CO and Pt, in which too much weakened adsorption will accelerate the side oxidation of H₂. Compared with the system with O₂ activator, it also decreases the side reaction at higher temperature. Joint efforts from above

mentioned methods will help to approach the final resolutions for PROX process.

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Notes and references

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