

Constructing surface active centres using Pd–Fe–O on zeolite for CO oxidation

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Abstract

Newly active centres for CO oxidation using Pd–M–O (M=Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Zr) on zeolite have been constructed. The derived co-impregnated Pd–Fe–O_x/NaZSM-5 catalyst not only showed high catalytic activity for low temperature CO oxidation, but was also a good kind of electrocatalyst for CO electrochemical stripping. It was probably because that the active centres including special oxygen species exhibit the high activity for CO oxidation. The typical 50% and 100% conversion temperatures of the co-impregnated Pd–Fe–O_x/NaZSM-5 catalyst for low temperature CO oxidation (T_{50} and T_{100}) were 29.1 and 47 °C, respectively. XRD and XPS characterizations indicated that the addition of Fe increased the dispersion of the active Pd species and Pd species were easy to enrich on the surface of the catalyst. A functional interface, bimetallic catalytic active centre, was formed on the surface of the catalyst, which contained a certain quantity of special oxygen species. The direct proofs of the existence of this kind of active oxygen species were given by our H₂-TPR and O₂-TPD experiments.

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1. Introduction

Constructing catalytic active sites on supports in order to satisfy the demands of catalytic reactions has received great attentions for its significant characteristic such as high activity, selectivity, easy separation and recycle usage in industry. The appearance of new porous materials results in extensive progress in the field. By designing and dispersing active components on selected supports with high surface area and special channel, one can construct desired active sites for special reaction. It is a key point for producing catalysts, especially for noble metal dispersed catalysts for CO oxidation. Low temperature CO oxidation has attracted considerable attentions because of its significance in academic research and practical applications [1]. More recently, since the fuel efficiency and emission level of fuel cell-based systems offer improvement over conventional power sources, fuel cell is expected to gain wide usage and as one of the most promising technologies for future global energy needs

for automotive and stationary applications [2]. However, poisoning by CO of the anode in a reformate fuelled or direct methanol PEM fuel cell is a potential problem. Pt or Ru was generally considered to be indispensable for a successfully electrocatalytic CO oxidation procedure [2]. Up to now, catalysts for CO oxidation were mainly focused on noble metals (such as Au, Pt, Rh, Pd, etc.) supported on reducible or on inert oxides [3]. Some catalysts based on ZSM-5 zeolite have been widely used in various processes such as the Fischer–Tropsch synthesis, reduction of NO_x with CO, and hydrocarbon aromatisation, etc. because of its excellent thermal stability, unique pore structure and great surface area [4]. However, it appeared to have extremely few attempts in fabricating catalysts based on zeolite for CO oxidation. Recently, there is a great progress in the study of Pd catalysts supported on metal oxides, but so far relatively high temperature (>200 °C) is still needed for CO elimination [5]. In addition, as to what kind of state of surface Pd species is involved in the reaction of CO oxidation and how the different Pd species vary during the reaction are still in dispute [6]. Furthermore, due to the limited resource of precious metal Pd, there is a strong motivation to develop cheap catalysts with low Pd-loading amount by introducing helpful additives or other techniques.

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In our previous work, a catalyst by construction of Pd on NaZSM-5 has been developed for low temperature CO oxidation. It was found that the minimum temperature for CO elimination on the Pd-NaZSM-5 catalyst was as low as 90 °C [7]. In this paper, a series of bi-component Pd-M-O_x/NaZSM-5 catalysts modified by various transition metals were designed by co-impregnation and sequential impregnation methods separately, among which the newly co-impregnated Pd-Fe-O_x/NaZSM-5 catalyst not only showed high catalytic activity for low temperature CO oxidation, but was also a good kind of electrocatalyst for CO electrochemical stripping.

2. Experimental

2.1. Preparation of catalysts

Pd-M-O_x/NaZSM-5 (M=Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Zr) catalysts were prepared by co-impregnation and sequential impregnation methods separately, following a procedure described in previous work (Pd wt.% = 0.8 and Me wt.% = 5) [8]. After sheet formatting, crushing and sifting, the catalysts of 60–80 meshes were ready for use.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) analysis was performed to verify the species in the catalysts. XRD patterns of the samples were recorded on a Rigaku D/MAX-RB X-ray diffractometer with a Cu K α target operated at 50 kV and 60 mA with a scanning speed of 0.5°/min and a scanning angle (2 θ) range of 25°–70°.

Chemical states of the atoms on the catalyst surface were investigated by X-ray photoelectron spectroscopy (XPS) on a VG ESCALAB 210 electron spectrometer (Mg K α radiation; $h\nu = 1253.6$ eV). XPS data were calibrated using the binding energy of C1s (284.60 eV) as the standard.

H₂ temperature-programmed reduction (H₂-TPR) of the catalyst was performed at atmospheric pressure in a conventional flow system built in our laboratory at a linearly programmed rate of 10 °C/min from 20 to 800 °C (5% H₂ in Ar stream, flow rate of 40 mL/min). Sample of 0.03 g was used for each run. The amount of the consumed H₂ was determined by a thermo-conductivity detector (TCD). Before each measurement, the samples were purged with dry air at 400 °C for 1 h.

O₂ temperature-programmed desorption (O₂-TPD) of the catalyst was performed at atmospheric pressure in the apparatus of AMI-100 at a linearly programmed rate of 30 °C/min from 20 to 800 °C. Sample of 0.1 g was used for each time. O₂ adsorption was conducted at room temperature (flow rate of 15 mL/min). The amount of the desorbed O₂ (He flow rate of 20 mL/min) was determined by on-line MS. Before each measurement, the samples were purged with He at 450 °C for 1 h.

2.3. Measurements of activity

The measurements of temperature program surface reaction of CO oxidation were performed in a fixed bed reactor (i.d. 5 mm) under atmospheric pressure. Then 150 mg of catalysts

with the average diameter of 0.5–1 mm was used each time. The catalysts were employed without any pretreatment. The total flow rate of the feed gas was 25 mL/min. The feed gas consisted of 0.8% of CO and 25.3% of O₂ in N₂ balanced. CO and O₂ in the reactant and product were analyzed on a gas chromatograph equipped with a Molecular Sieves 13X column and a thermal conductivity detector.

Cyclic voltammetry (CV) measurements of CO electrocatalytic oxidation were performed in an electrochemical cell holding a 0.5 M Na₂SO₄ solution at room temperature. The three-electrode system consisted of a catalyst modified glass carbon (GC) substrates as a working electrode, saturated calomel electrode (SCE) as a reference electrode and a platinum wire as the auxiliary electrode. The working electrode used in this study consisted of catalysts dispersed in polystyrene films deposited on GC substrates. In a typical preparation, a defined quantity of a suspension containing 5 mg of catalyst and 2 mg of polystyrene per milliliter of THF was spread on the clean surface of GC. All potentials reported here are referenced to the potential of SCE. Adsorption of CO on the electrode surface was carried out by bubbling CO gas for 15 min at 0.1 V. Before CO adlayer oxidation, the electrolyte was purged with highly purified nitrogen for 25 min to remove CO dissolved in the solution.

3. Results and discussion

3.1. Influence of auxiliary agent and preparation method

Fig. 1 showed the activity comparison for CO oxidation of the designed bi-component catalysts modified by various transition metals using co-impregnation and sequential impregnation methods, respectively. The results indicated that the activities were very sensitive to preparation procedures and pre-treatments. Performances of the co-impregnated catalysts were markedly superior to those of the sequential impregnated which were almost inactive. Activities for the co-impregnated catalysts decreased in the order of Pd-Fe > Pd-Co > Pd-Zr > Pd-Mn > Pd-Cr > Pd-Ni, Zn > Pd-Cu > Pd-Mo.

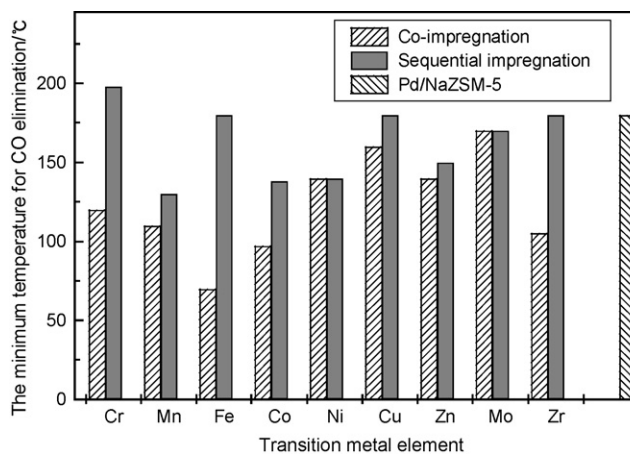


Fig. 1. CO oxidation over various Pd-M-O_x-NaZSM-5 catalysts prepared by different impregnation methods Pd loading amount = 0.8%, M content = 5%, (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Zr).

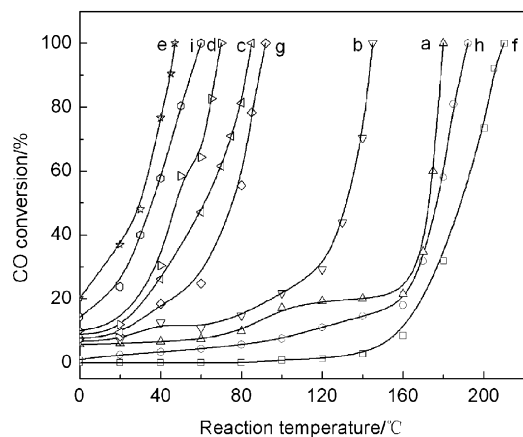


Fig. 2. Relation between reaction temperature and conversion for CO oxidation over Pd–Fe–O_x/NaZSM-5 catalysts with different Fe-loadings (a) 0.8Pd/NaZSM-5; (b) 0.8Pd–0.5Fe–O_x/NaZSM-5; (c) 0.8Pd–2.5O_x/NaZSM-5; (d) 0.8Pd–5Fe–O_x/NaZSM-5; (e) 0.8Pd–10Fe–O_x/NaZSM-5; (f) 10Fe/NaZSM-5; (g) catalyst e reduced by H₂ at 400 °C for 3 h; (h) 0.8Pd/Al₂O₃; (i) 0.8Pd–18Fe–O_x/NaZSM-5.

3.2. Influence of Fe content on CO oxidation activity

In order to elucidate the excellent properties of co-impregnated catalysts and reveal the relationship between material structure and catalytic performance, co-impregnated Pd–Fe–O_x/NaZSM-5 catalysts with different Pd–Fe compositions were prepared, on which effects of preparation process and reaction conditions for CO oxidation have been investigated in detail. Fig. 2 illustrated the results of CO oxidation over Pd–Fe–O_x/NaZSM-5 catalysts with various Fe loadings. No reactivity for CO oxidation is observed with NaZSM-5 zeolite alone at below 250 °C. It is clearly indicated that either Pd/NaZSM-5 or Fe/NaZSM-5 catalyst individual shows low activity. The light-off temperature (T_{50}) of Pd/NaZSM-5 and Fe/NaZSM-5 are 173.1 and 189.1 °C, which correspond to the minimum CO complete oxidation temperature (T_{100}) of catalysts (a and f), 180 and 210 °C, respectively. The Pd–Fe bimetal catalysts exhibit relatively higher activity than that of Pd or Fe single supported ones. The addition of a small quantity of Fe will enhance the performance of Pd/NaZSM-5 markedly (b). Fig. 2 also elucidated that the catalytic activity correlated to Fe loading amounts, and it enhances monotonously with the increase of Fe loadings. Fifty percent conversion temperatures (T_{50}) are 132.6, 60.6, 46.3, and 29.1 °C for the catalysts with 0.5%, 2.5%, 5%, and 10% of Fe, respectively, and the minimum 100% conversion temperatures (T_{100}) are 145, 85, 70, and 47 °C (b–e), respectively. However, when the Fe loading amount reached 18%, the activity of Pd–Fe–O_x/NaZSM-5 catalyst decreased. Its T_{50} is 42 °C and T_{100} is 60 °C.

3.3. Characterization of catalysts

3.3.1. XRD

Fig. 3 showed the XRD patterns of the series of Pd–Fe–O_x/NaZSM-5 catalysts. It is clear that all of the samples

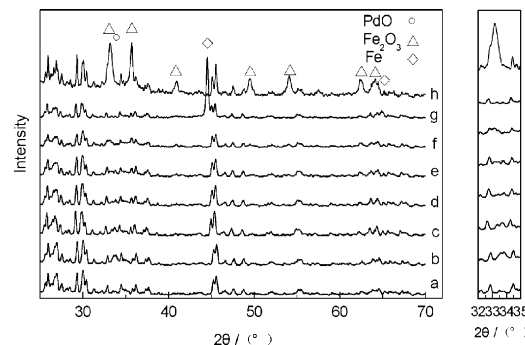


Fig. 3. XRD patterns of different Pd–Fe–O_x/NaZSM-5 catalysts (a) NaZSM-5 type zeolite; (b) 0.8Pd/NaZSM-5; (c) 0.8Pd–0.5Fe–O_x/NaZSM-5; (d) 0.8Pd–2.5Fe–O_x/NaZSM-5; (e) 0.8Pd–5Fe–O_x/NaZSM-5; (f) 0.8Pd–10Fe–O_x/NaZSM-5; (g) catalyst (f) reduced by H₂ at 400 °C for 3 h; (h) 0.8Pd–18Fe–O_x/NaZSM-5.

contain the framework of NaZSM-5 zeolite (a). A characteristic diffraction peak of PdO particles appears at 33.87° (2θ) in the 0.8Pd/NaZSM-5 catalyst (b), which corresponds to the (1 0 1) face, while for the catalysts containing Fe₂O₃, the intensity of the PdO peak is relatively weak. The PdO characteristic diffraction peak still weakens gradually accompanied by the increase of the Fe-loading amounts, and when Fe-loading amount reaches 2.5%, the peak of PdO disappears. According to polycrystalline X-ray diffraction theory, the more Fe-loadings, the smaller the dimension of PdO particles is. That is to say, the addition of Fe₂O₃ improved the dispersion of PdO species over NaZSM-5, which may be one of the reasons for the high activity of Pd–Fe bimetal catalysts. This conclusion is in good agreement with the XPS results to be stated below.

It can also be seen from Fig. 3 that the hematite type Fe₂O₃ is easy to be dispersed over the zeolite too. When the content of Fe is less than 10%, no characteristic diffraction peaks of Fe₂O₃ are observed. When Fe content reaches 10%, weak diffraction peaks of Fe₂O₃ were observed at 33.11, 35.61, 40.83, 49.41 and 54.00° (2θ), which corresponded to the (1 0 4), (1 1 0), (1 1 3), (0 2 4) and (1 1 6) faces, respectively. However, when Fe content raised to 18%, diffraction peaks are the narrowest and sharpest as compared with catalyst f, which indicates that the diameter of Fe₂O₃ particles becomes larger in terms of polycrystalline X-ray diffraction theory. It should be noted that due to the Pd–Fe–O_x/NaZSM-5 catalyst was prepared by co-impregnation method, too much Fe addition will lead to large Fe₂O₃ particles, which may embed the Pd oxide and decrease the catalytic activity (Fig. 2i).

3.3.2. XPS

In general, heterogeneous reaction occurred on the surface of catalyst and the surface composition is often different from that in bulk. To demonstrate active phases of the bimetallic catalysts involved in CO oxidation and variation of the surface species during catalytic reaction in detail, XPS was used to investigate chemical states of surface atoms in catalysts as well as composition and related distribution of the surface elements. Effect of different Pd states on their catalytic abilities has been observed. The spectra data of Pd3d_{5/2}, Fe2p_{3/2} and O1s, corresponding

Table 1
XPS data of different Pd–Fe–O_x/NaZSM-5 catalysts

Catalyst	Pd3d _{5/2}		Fe2p _{3/2}		O1s	
	B.E. (eV)	[at]%	B.E. (eV)	[at]%	B.E. (eV)	[at]%
0.8Pd/ <i>r</i> -Al ₂ O ₃	336.50	0.175	–	–	531.50	62.51
0.8Pd/NaZSM-5	337.40	0.181	–	–	533.42	64.83
0.8Pd–0.5Fe–O _x /NaZSM-5	337.42	0.188	711.41	1.480	533.35	64.79
0.8Pd–2.5Fe–O _x /NaZSM-5	337.56	0.246	711.29	2.002	533.28	64.62
0.8Pd–5Fe–O _x /NaZSM-5	337.61	0.279	711.11	2.149	533.30 529.85	60.83 0.01
0.8Pd–10Fe–O _x /NaZSM-5	337.65	0.292	711.04	2.203	533.29 529.91	60.38 1.21
0.8Pd–10Fe–O _x /NaZSM-5 ^a	335.40	0.249	711.34 706.87	0.729 0.121	533.10	26.25
0.8Pd–18Fe–O _x /NaZSM-5	336.16	0.294	711.01	9.560	533.22 530.50	37.91 23.70

^a Catalyst of 0.8Pd–10Fe–O_x/NaZSM-5 reduced by H₂ at 400 °C for 3 h.

binding energies (B.E.) of each atom and the derived surface atomic ratios ([at]%) in the different catalysts are summarized in Table 1.

Table 1 showed that the Pd3d_{5/2} binding energies of the various Pd–Fe–O_x/NaZSM-5 catalysts are at 337.40–337.65 eV. This is an unusual and interesting result. In order to verify this experiment, we deposited Pd on the surface of *r*-Al₂O₃, SiO₂ and the zeolite of 5A, NaY, 13X. It was found that the binding energy of Pd3d_{5/2} on these supports is around 336.4 eV (Fig. 4), and we did not find any Pd3d_{5/2} at such a high binding energy region in former time. After compared the results with Refs. [9] and [10], we assigned the binding energies of Pd3d_{5/2} at 337.40–337.65 eV for the Pd–Fe–O_x/NaZSM-5 catalyst to PdO₂. The existence of Pd⁴⁺ may be formed during the preparation process and it could be stabilized by NaZSM-5 zeolite through its special space structure.

It can also be seen from Table 1 that the introduction of Fe into Pd–NaZSM-5 system changed the electronic environment

about Pd species. The binding energies of PdO₂ gradually go up with the increase of Fe-loadings, which may be explained by the fact that the introduction of Fe to Pd–NaZSM-5 system brings the strong mutual effect among Fe, Pd and NaZSM-5, which may decrease the surrounding electron cloud density about Pd. In addition, the surface Pd content increases with the increase of Fe content, which implies the higher Pd dispersion. This conclusion agrees quite well with the XRD results mentioned above. According to XPS in Table 1, Pd species formed on 0.8Pd/*r*-Al₂O₃ are clearly Pd(II)O supported on alumina which has no special space like that of NaZSM-5 and have almost the same dispersion with 0.8Pd/NaZSM-5. The above results and the related difference in activity (Fig. 2, curves a and h) suggested that Pd⁴⁺ existing in special space of NaZSM-5 is important for its high catalytic activity for CO oxidation.

The introduction of Fe into Pd–NaZSM-5 system also changed the electronic environment about Fe species. The binding energies of Fe2p_{3/2} of the Pd–Fe bimetal zeolite catalyst are at 711.01–711.41 eV and it gradually decrease with the increasing Fe content, which may also be interpreted as that stated above. High Fe-loading results in the higher Fe electron cloud density and the stronger Pd–Fe–NaZSM-5 mutual effect, which decreases the B.E. of Fe.

However, when Fe loading amount reached 18%, although the surface Pd amount still increased ([at]%=0.294), the Pd species changed from PdO₂ to PdO, which is not beneficial to enhance the activity (Fig. 2i).

The binding energy of O1s in Al₂O₃ lies in 531.50 eV, which can be assigned to the lattice oxygen of Al₂O₃ [11,12]. For all NaZSM-5 zeolite catalysts, the binding energies of O1s are at 533.10–533.42 eV which can be identified as the zeolite lattice oxygen combining the results of Ref. [10]. When Fe-loading raised to 5%, a faded diffraction peak of O1s appears at 529.85 eV. When it increases, the peak intensity is greatly enhanced, so it can be ascribed to the oxygen of the active centre Pd–Fe–O.

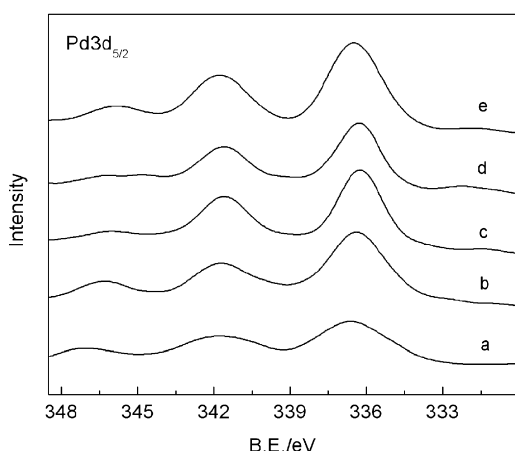


Fig. 4. XPS spectra of different Pd catalysts with various supports (a) Pd/Al₂O₃; (b) Pd/SiO₂; (c) Pd/5A; (d) Pd/13X; (e) Pd/NaY.

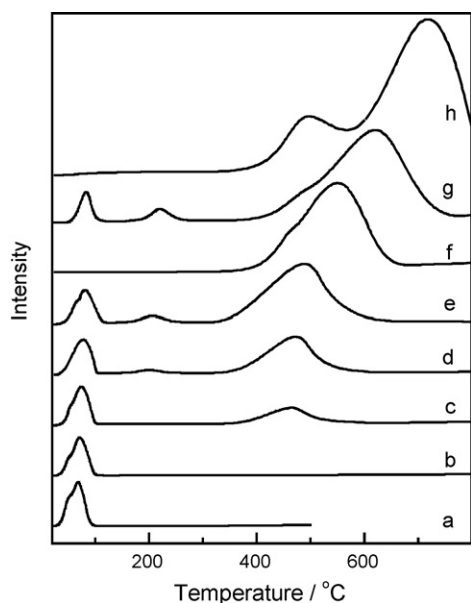


Fig. 5. H_2 -TPR profiles of different Pd-Fe- O_x /NaZSM-5 catalysts (a) 0.8Pd/NaZSM-5; (b) 0.8Pd-0.5Fe- O_x /NaZSM-5; (c) 0.8Pd-2.5Fe- O_x /NaZSM-5; (d) 0.8Pd-5Fe- O_x /NaZSM-5; (e) 0.8Pd-10Fe- O_x /NaZSM-5; (f) 10Fe/NaZSM-5; (g) 0.8Pd-18Fe- O_x /NaZSM-5; (h) Fe_2O_3 .

3.3.3. H_2 -TPR

Fig. 5 showed the H_2 -TPR patterns of the series of Pd-Fe- O_x /NaZSM-5 catalysts. Patterns below $100^\circ C$ represent the reduction peak of Pd oxide. It is clear that all the peaks of the Pd oxide for the series of Pd-Fe- O_x /NaZSM-5 catalysts are asymmetrical if Fe content varies in the range of 0–10%. It means that more than one Pd species is reduced, which strongly supported the XPS conclusion stated above. The peak moved towards high temperature with the increase of Fe loading amount, which suggested that the addition of Fe into Pd-NaZSM-5 system increased the stabilization of Pd oxide. When the Fe loading amount reached 18%, the peak seemed symmetrical, which indicated only one kind of Pd species was reduced.

From Fig. 5, it can also be seen that H_2 -consumed patterns of Fe_2O_3 emerged at 487 and $719^\circ C$. However, when supported on NaZSM-5 zeolite, the reduction of Fe_2O_3 becomes easy. The existence of Pd species further lowered the reduction temperature of Fe_2O_3 , which may be attributed to the activity under the reaction conditions.

To be interesting, when Fe content reached 2.5%, a broad H_2 -consumed peak was detected in the range of 330 – $600^\circ C$. The intensity of this H_2 -consumed peak gradually enhanced with the increase of Fe amount (see Fig. 5). It was due to the reduction of the special oxygen species. The reduction peak of lattice oxygen of pure Fe_2O_3 appeared at both 487 and $719^\circ C$. Therefore, the special oxygen species in the active centres exhibit the different property in comparison with the lattice oxygen of pure Fe_2O_3 . The special oxygen species were more active and more easily reduced by hydrogen, compared to the lattice oxygen of pure Fe_2O_3 . The conclusion agrees quite well with the O_2 -TPD results stated below. The special oxygen species could play an important role in the oxidation of CO. When the Fe loading

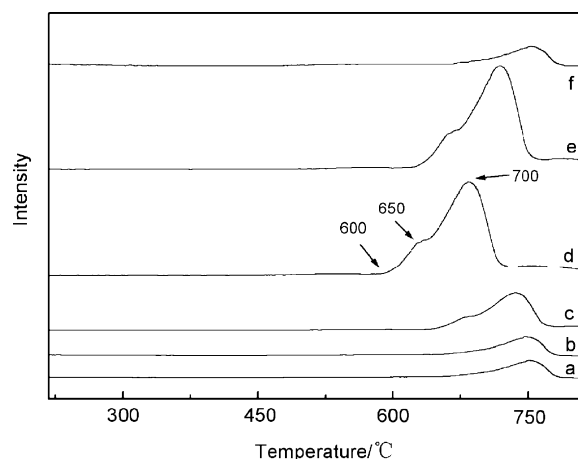


Fig. 6. O_2 -TPD profiles of different Pd-Fe- O_x /NaZSM-5 catalysts (a) 0.8Pd/NaZSM-5; (b) 0.8Pd-0.5Fe- O_x /NaZSM-5; (c) 0.8Pd-2.5Fe- O_x /NaZSM-5; (d) 0.8Pd-10Fe- O_x /NaZSM-5; (e) 0.8Pd-18Fe- O_x /NaZSM-5; (f) 10Fe/NaZSM-5.

amount increased, the peak moved toward higher temperature. It seems to be not beneficial to the oxidation of CO. But the desorption amount of the special oxygen species was small at the low loading amount of Fe.

3.3.4. O_2 -TPD

O_2 -TPD profiles of the different Pd-Fe- O_x /NaZSM-5 catalysts are shown in Fig. 6. The O_2 -TPD peak for the Pd/NaZSM-5 or Fe/NaZSM-5 catalyst appeared at 750 and $755^\circ C$, respectively. It was also shown that a shoulder peak emerged on the left of the O_2 -desorption peak of catalyst modified by appropriate amount of Fe, which indicated that catalyst structure has changed. It can be due to the fact that the addition of Fe produced some mutual effect among Pd species, Fe promoter and NaZSM-5 support, which changed the local microtexture of the Pd-Fe- O_x /NaZSM-5 catalyst. The special oxygen species were formed at the active centres on the surface of the catalyst, which can markedly increased the activity. When the Fe loading amount increased, the desorption of oxygen species became more easily and the desorption amount is larger. It was indicated that the special oxygen species were more active with the increase of the loading amount of Fe, which is beneficial to the enhancement of the activity of the catalysts. The 0.8Pd-10Fe- O_x /NaZSM-5 catalyst showed the lowest O_2 -desorption temperature ($700^\circ C$). Nevertheless, when Fe loading amount increased to 18%, the temperature of O_2 -desorption peak increased as compared with that of 0.8Pd-10Fe- O_x /NaZSM-5 catalyst, which indicated that too much Fe is not suitable for further enhancing the catalytic activity.

3.4. Influence of H_2 reduction on activity

In order to investigate the influence of pre-reduction to catalytic performance, some of the 0.8Pd-10Fe- O_x /NaZSM-5 catalyst were further reduced at $400^\circ C$ in the stream of hydrogen gas with a rate of 25 mL/min for 3 h, and then cooled in hydrogen atmosphere to room temperature. Before test, the 0.8Pd-10Fe- O_x /NaZSM-5 catalysts reduced by H_2 were further

purged with argon gas for 5 h. It is shown that the performance of the reduced catalyst (Fig. 2g) is lower compared with the unreduced 0.8Pd–10Fe–O_x/NaZSM-5. Its T_{50} datum is 75.4 °C and T_{100} is 92 °C.

Results of XRD characterization indicated that the Fe crystalline in the bulk phase of reduced 0.8Pd–10Fe–O_x/NaZSM-5 catalyst presents in the form of α -Fe (Fig. 3g). XPS characterization proved that in the surface of 0.8Pd–10Fe–O_x/NaZSM-5 catalyst, Fe existed as the form of Fe⁰ and Fe oxide (the standard B.E. of Fe₂O₃ and Fe₃O₄ is very close, so it is difficult to distinguish) (Table 1). Table 1 also shows that Pd species in the reduced catalyst exists as Pd⁰. Our previous work revealed that H₂-reduction of Pd–NaZSM-5 would convert the surface Pd⁴⁺ gradually to Pd²⁺ and Pd⁰, which will decrease the catalytic performance [7]. Combined with the catalytic experiment results, we consider that the deactivation of reduced Pd–Fe–O_x/NaZSM-5 catalyst is mostly associated with the change of the chemical states of the Fe₂O₃ and Pd species.

3.5. Influence of gas hourly space velocity on activity

Our experiments conformed that gas hourly space velocity of the feed gas affects the performance of CO oxidation greatly. Fig. 7 gave the relation between space velocity and the CO conversion of the 0.8Pd–10Fe–O_x/NaZSM-5 catalysts. From Fig. 7, at the same reaction temperature, the CO conversion decreased with the increasing space velocity. Moreover, at the same CO conversion, the reaction temperature gradually rose with the increase of space velocity. As a consequence, it is obvious that the apparent activities of the Pd–Fe–O_x/NaZSM-5 catalyst decreased with the rising space velocity, which may be a result of the shortened contact time.

3.6. Effects of moisture on the activity and stability of CO oxidation

In this work, we also studied the effect of moisture on the catalyst activity in order to clarify the controversial effects of moisture on CO oxidation. The result is shown in Fig. 8. It is denoted that the Pd–Fe bimetal catalyst is sensitive

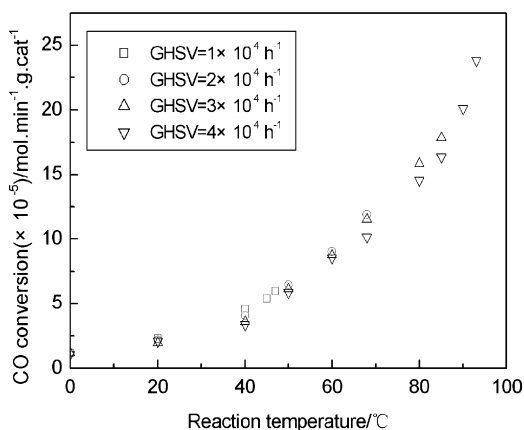


Fig. 7. Influence of gas hourly space velocity on CO oxidation of 0.8Pd–10Fe–O_x/NaZSM-5 catalyst.

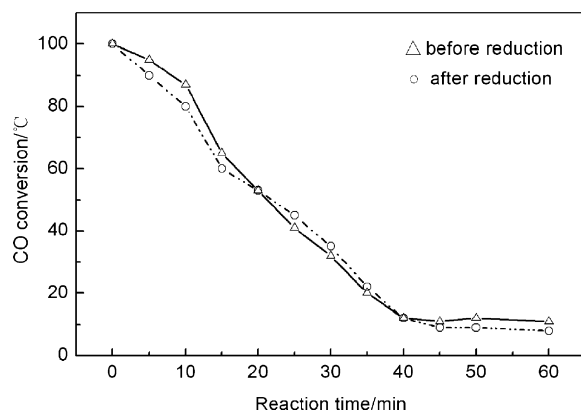


Fig. 8. Effect of moisture on the catalytic performance of 0.8Pd–10Fe–O_x/NaZSM-5 for CO oxidation.

to moisture. Although the directly calcined and the reduced Pd–Fe–O_x/NaZSM-5 catalysts can completely convert CO to CO₂ at room temperature, the high activity for CO complete elimination can only maintain for less than 40 min at 25 °C and subsequently deactivates almost completely, which may be arisen from the occupation of active sites by H₂O molecules introduced to the feed gas. The detailed mechanism of deactivation is not clear and further study is in progress.

3.7. Catalytic CO electro-oxidation

Conventional Pt-based materials were the commonly used catalysts for CO electrochemical oxidation. In our present work, a Pd-based electrode derived from Pd–Fe–O_x/NaZSM-5 nanoparticle was developed for the first time and successfully applied to CO electro-oxidation (Fig. 9). No characteristic CV peak of CO oxidation was observed on 0.8Pd/r-Al₂O₃ film. There were obvious changes in the CV morphology with different Pd–Fe compositions. As the amounts of Fe increase, a well-defined CV peak of CO oxidation is achieved on 0.8Pd–2.5Fe–O_x/NaZSM-5 in the potential region of

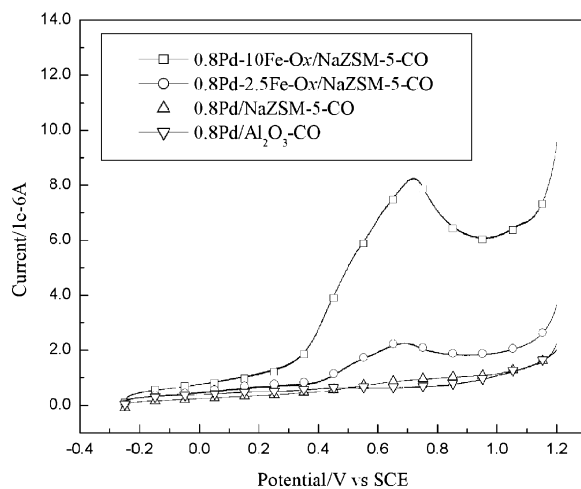


Fig. 9. CO stripping voltammograms on different working electrodes modified by various catalysts in a 0.5M Na₂SO₄ solution with potential sweep rate of 100 mV s⁻¹ at room temperature.

0.37–0.86 V, with the increase of the charge in the double-layer region. The further Fe decoration induced more double-layer charge. As previously noticed on Pt-based electrodes [13], it indicated the formation of oxygen-like species on the surface at more negative potentials, which played an important role in progressively lowering the onset potential of irreversible CO electro-oxidation. 0.8Pd–10Fe–O_x/NaZSM-5 showed the lowest onset potential (0.32 V) as well as the max total amount of charge (*Q*) for CO oxidation, indicating its super electrochemical property. According to H₂-TPR and O₂-TPD results stated above, the introduction of Fe into Pd–zeolite system produced some active oxygen, such as special oxygen species, which may be beneficial to CO reaction under electrochemical environment. Different from Pt electrode [13,14], the CO stripping peak on the zeolite catalysts is quite broad. The probable reason is that oxidation of CO_{ad} in the special cages of NaZSM-5 is a slow process. In comparison with Pt-based electrodes, the chemically modified electrodes used in this work are easy to be fabricated and rather inexpensive, which will provide tremendous opportunities for CO electrocatalytic oxidation in fundamental research and many practical applications.

4. Conclusions

In conclusion, artificial design of surface active centres using Pd–M–O (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Zr) on zeolite, including special Pd chemical environments and special oxygen species, has been achieved by our experiment. The designed co-impregnated Pd–Fe–O_x/NaZSM-5 catalyst not only showed excellent performance for CO oxidation at low temperature but was also successfully applied to CO electro-oxidation. The typical 50% and 100% conversion temperatures of the co-impregnated Pd–Fe–O_x/NaZSM-5 catalyst for low temperature CO oxidation (*T*₅₀ and *T*₁₀₀) were 29.1 and 47 °C, respectively. And the typical onset potential of the co-impregnated Pd–Fe–O_x/NaZSM-5 catalyst for CO electro-oxidation was

0.32 V. XRD showed that Pd species are highly dispersed on the surface of NaZSM-5 zeolite, which is strongly dependent upon the amounts of Fe-loading and the interaction among Pd species, Fe promoter and NaZSM-5 support. XPS characterization indicated that the addition of Fe increased the dispersion of the active Pd species and Pd species was easy to enrich on the surface of the catalyst. The direct proofs of bimetallic catalytic active centres on the surface of the catalyst, which contained a certain quantity of special oxygen species, were given by our H₂-TPR and O₂-TPD experiments.

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