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Article

Enhanced CO oxidation over potassium-promoted Pt/Al₂O₃ catalysts: Kinetic and infrared spectroscopic study

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ABSTRACT

A series of K-promoted Pt/Al₂O₃ catalysts were tested for CO oxidation. It was found that the addition of K significantly enhanced the activity. A detailed kinetic study showed that the activation energies of the K-containing catalysts were lower than those of the K-free ones, particularly for catalysts with high Pt contents (51.6 kJ/mol for 0.42K-2.0Pt/Al₂O₃ and 63.6 kJ/mol for 2.0Pt/Al₂O₃). The CO reaction orders were higher for the K-containing catalysts (about -0.2) than for the K-free ones (about -0.5), with the former having much lower equilibrium constants for CO adsorption than the latter. In situ Fourier-transform infrared spectroscopy showed that surface CO desorption from the 0.42K-2.0Pt/Al₂O₃ catalyst was easier than from 2.0Pt/Al₂O₃. The promoting effect of K was therefore caused by weakening of the interactions between CO and surface Pt atoms. This decreased coverage of the catalyst with CO and facilitated competitive O₂ chemisorption on the Pt surface, and significantly lowered the reaction barrier between chemisorbed CO and O₂ species.

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1. Introduction

The catalytic oxidation of CO is an important reaction, not only because of its wide range of practical applications, such as indoor CO and automotive exhaust treatments [1,2], but also because of its high value in understanding some fundamental concepts in catalysis, such as structure-sensitivity relationships and reaction mechanisms. Noble metals, including Au [3–9], Pt [10–13], and Pd [14–16], and transition-metal compounds, including CuO [17–22] and Co₃O₄ [23,24], are the most commonly used catalysts for CO oxidation.

Although it is generally accepted that Au nanoclusters are the most active catalysts, because they can catalyze CO conversion to CO₂ at -70 °C [4], highly active Pt catalysts can also be obtained using reducible supports such as TiO₂ [25] and Fe₂O₃ [26]. The Pt activity strongly depends on the preparation

method. For example, Qiao et al. [27] synthesized a single-atom Pt₁/FeO_x catalyst, which was very active in CO oxidation. The enhanced activity was attributed to the partly vacant 5d orbitals of high-valent Pt atoms, which helped to reduce both the CO adsorption energy and the activation barrier for CO oxidation. Another strategy for improve the activities of Pt catalysts is promoter addition. Alkali metals such as Na and K effectively enhance the activities of Pt catalysts in various reactions such as CO oxidation and preferential CO oxidation (PROX) [28–30], the water-gas-shift reaction [31–33], HCHO oxidation [34], and oxidation of dichloromethane [35]. The role of the alkali metal depends on the reaction; it either weakens the interactions between CO and Pt and changes the CO adsorption sites in PROX over Pt/Al₂O₃ catalysts [28], results in the generation of alkali-stabilized Pt-OH_x species in Na- or K-promoted Pt/Al₂O₃ and Pt/SiO₂ catalysts for the water-gas-shift reaction [32], or

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generates surface Pt–O–K_x species in Pt/Al₂O₃ catalysts, which accelerate the decomposition of formate intermediates formed on the Al₂O₃ surface [35].

It is worth noting that evidence of the promoting effects of alkali metals on Pt catalysts is mostly based on spectroscopic results [28,34,35]. Although such evidence is relevant, it is desirable to perform kinetic studies, because they can provide useful information on reactions, such as the elementary steps, rate expressions, and reaction mechanisms. The roles of alkali metals could be clarified by comparing the kinetic behaviors of different catalysts (e.g., non-promoted and promoted catalysts). In the current work, we performed detailed kinetic studies of CO oxidation over a series of K-free and K-promoted Pt/Al₂O₃ catalysts. The obtained power-law rate expressions showed that the addition of K significantly influenced the reaction order with respect to CO, and that the apparent activation energy was lower on the K-containing catalysts than on the K-free ones. Rate equations based on reasonable elementary steps were derived and the calculated parameters such as intrinsic rate constants and equilibrium constants for CO and O₂ further illustrated that the addition of K to the catalyst weakened the interactions between CO and the catalyst surface and eased the reaction between chemisorbed CO and O₂. This conclusion was supported by in situ infrared spectroscopic results.

2. Experimental

2.1. Catalyst preparation

A series of K-promoted Pt/Al₂O₃ catalysts were prepared using an incipient wetness impregnation method. Commercial γ -Al₂O₃ with a surface area of about 180 m²/g was used as the support; it was calcined 500 °C for 4 h prior to use. The detailed preparation process was as follows. The γ -Al₂O₃ powder (10 g) was immersed in an appropriate volume of a mixed solution containing H₂PtCl₆ (1 mmol) and KNO₃ (2.6 mmol). The mixture was left to stand for 4 h, dried at 120 °C overnight, and calcined in static air at 500 °C for 4 h. The sample was washed three times with deionized water at room temperature, filtered, and dried at 120 °C overnight. This catalyst had a nominal Pt content of 2 wt%. Catalysts with various Pt loadings and K-free Pt/Al₂O₃ catalysts were prepared in a similar manner, but with no K addition for the K-free catalysts. The obtained catalysts are denoted by xK-yPt/Al₂O₃, where *x* and *y* are the contents (wt%) of K and Pt, respectively, in the catalyst.

2.2. Characterization

Inductively coupled plasma-atomic emission spectrometry (Optima 7300DV, Perkin Elmer) was used to determine the Pt and K contents of the catalysts. The Brunauer-Emmett-Teller (BET) surface areas of the catalysts were determined based on N₂ adsorption at liquid-nitrogen temperature (–196 °C), using a surface area analyzer (Quantachrome Autosorb-1). The catalysts were pretreated at 120 °C for 6 h in a vacuum before the BET measurements.

The X-ray diffraction (XRD) patterns of the catalysts were

recorded using a powder diffractometer (PANalytical X'Pert PRO MPD), with Cu K α radiation, operated at 40 kV and 40 mA. The patterns were recorded in 2 θ range = 10°–80°, at a scanning speed of 0.15°/s.

High-resolution transmission electron microscopy (HRTEM) was performed using a JEM-2100F microscope with a field-emissive gun, operated at 200 kV, with a point resolution of 0.24 nm.

Pulse CO chemisorption was used to investigate Pt dispersion in the catalyst (Quantachrome CHEMBET-3000 instrument). Before the measurement, the sample was reduced in a 5% H₂–95% N₂ mixture with a total flow rate of 30 mL/min, at 300 °C for 1 h, followed by cooling to 30 °C in a pure He flow (99.999%, 30 mL/min). Pulses of CO were then fed into the stream of carrier gas (high-purity He, 99.999%, 30 mL/min) using a precision analytical syringe. The Pt dispersion was calculated based on the assumption that the CO/surface Pt atom ratio was 1, and the Pt particle size was calculated based on the equation $d_{Pt} \text{ (nm)} = 1.1/D$ (*D* = dispersion).

The oxidation states of the catalysts were determined using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi instrument), with an Al K α X-ray source (1486.6 eV) at a pressure of about 2×10^{-7} Pa at room temperature and a pass energy of 20 eV. The binding energy (BE) of the C 1s core level, i.e., 284.6 eV, was used as an internal standard. Before the measurements, the samples were pretreated inside the XPS chamber with an 10% O₂–90% Ar mixture (30 mL/min) at 300 °C for 0.5 h, followed by a 10% H₂–90% Ar mixture (30 mL/min) at 300 °C for 0.5 h. This in situ treatment was used to keep the chemical states of the catalysts the same as those under the catalyst-testing conditions (see section 2.3).

In situ Fourier-transform infrared (FTIR) spectra of the samples were recorded using a NEXUS670 spectrometer equipped with a mercury cadmium telluride detector. A self-supported wafer (diameter 16 mm) was placed in a quartz IR cell connected to the closed circulation system. The sample was pretreated under a pure O₂ flow (99.95%, 30 mL/min) at 300 °C for 0.5 h, followed by a pure H₂ flow (99.99%, 30 mL/min) at 300 °C for 0.5 h. It was then purged with pure He (99.95%, 30 mL/min) at 300 °C for 10 min and cooled to 40 °C; the background spectrum was then recorded. A pure CO flow (99.95%, 30 mL/min) or a mixture of 1% CO–1% O₂–98% N₂ (total flow rate 30 mL/min) was then introduced until saturated CO chemisorption was obtained. The sample was then purged with pure He to remove the gas-phase and physisorbed CO molecules, and the spectrum was recorded at 40 °C in a He flow. Temperature-dependent FTIR spectra were recorded during the reaction after holding each temperature point for 10 min.

2.3. Activity tests and kinetic study

Catalytic CO oxidation was performed using a fixed-bed microreactor with an inner diameter of 6 mm, using a catalyst (100 mg) of particle size 0.12–0.15 mm. The catalyst was diluted with quartz sand of the same mesh size to 0.25 mL. A thermocouple was placed in the middle of the catalyst bed to

monitor the reaction temperature. Before the reaction, the sample was pretreated with an 10% O₂–90% Ar mixture (30 mL/min) at 300 °C for 0.5 h (to clean the catalyst surface), followed by a 10% H₂–90% Ar mixture (30 mL/min) at 300 °C for 0.5 h (to reduce the catalyst). The catalyst was then cooled to a certain temperature and a feed gas containing 1% CO–1% O₂–98% N₂ was introduced. The total flow rate was 40 mL/min, which corresponds to a space velocity of 9600 h^{−1}. The CO concentration in the reactor effluent was determined using an Agilent 6850 gas chromatograph equipped with a thermal conductivity detector attached to an HP PLOT column (30 m × 0.32 mm × 12 μm).

The kinetic study was performed using the same fixed-bed reactor as was used for catalytic CO oxidation. The feed gases (i.e., CO, O₂, and N₂) were controlled using mass flow controllers and mixed before they reached the reactor inlet. In general, the reactor was operated at a CO conversion of less than 15% to ensure a differential mode. The reaction conversion was controlled by changing the catalyst load; it was diluted with quartz sand to a volume of 0.1 mL. The absence of mass transport resistances was checked based on the Weisz-Prater criterion for internal diffusion and Mears' criterion for external diffusion; the absence of heat transfer was checked based on Mears' criterion [36]. For the 0.42K-2Pt/Al₂O₃ catalyst, the calculated values under kinetic conditions were 4.30×10^{-4} for the Weisz-Prater criterion for internal diffusion, 7.94×10^{-4} for the Mears' criterion for external diffusion, and 2.97×10^{-5} for the Mears' criterion for heat transfer. The partial pressure dependences of the reaction rates were measured by adjusting the flow rate of 10% CO–90% Ar or 10% O₂–90% Ar while keeping the total flow rate at 120 mL/min, by adjusting the flow rate of pure Ar. The concentrations of CO and O₂ in the feed were varied between 0.1% and 3%. Each value was recorded after about 1 h as the reaction reached steady state. The CO₂ concentration in the outlet gas stream was determined using the Agilent 6850 gas chromatograph mentioned above.

The definition of CO conversion is as follows:

$$X_{\text{CO}} = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\% \quad (1)$$

where [CO]_{in} and [CO]_{out} are the CO concentrations in the inlet and outlet gas, respectively.

The reaction rate (r_{CO}) is defined as

$$r_{\text{CO}} = \frac{N_{\text{CO}} \cdot X_{\text{CO}}}{W_{\text{cat}}} \quad (2)$$

where N_{CO} is the CO molar gas flow rate (mol/s), X_{CO} is the CO conversion, W_{cat} is the catalyst amount (g), and r_{CO} in mol_{CO}/(g_{cat}·s).

The power-law rate expressions were derived by linear regression fitting of the data (partial pressures and reaction rates) using the POLYMATH 5.1 program [37].

3. Results and discussion

3.1. Physical properties of catalysts

The general physical properties of the catalysts are summa-

Table 1

Physical properties of various catalysts.

Catalyst	Metal content (wt%)		S_{BET} (m ² /g)	Metal dispersion (%)	Pt particle size (nm)
	Pt	K			
0.1Pt/Al ₂ O ₃	0.15	—	180	56.1	2.0
0.02K-0.1Pt/Al ₂ O ₃	0.10	0.02	176	54.2	2.0
0.2Pt/Al ₂ O ₃	0.24	—	171	54.3	2.0
0.05K-0.2Pt/Al ₂ O ₃	0.23	0.05	173	55.6	2.0
1Pt/Al ₂ O ₃	1.15	—	174	47.0	2.5
0.23K-1Pt/Al ₂ O ₃	0.85	0.23	173	52.8	2.1
2Pt/Al ₂ O ₃	2.08	—	175	44.0	2.5
0.42K-2Pt/Al ₂ O ₃	2.15	0.42	166	56.0	2.0

rized in Table 1. All the catalysts have similar surface areas (166–180 m²/g). However, the actual contents of K in the catalysts are much lower than the nominal values, because most of the K salt was removed during washing. The Pt dispersion gradually decreases with increasing Pt content in the catalyst. For example, the Pt dispersion in 0.1Pt/Al₂O₃ is 56.1%, whereas that in 2Pt/Al₂O₃ is 44.0%. Moreover, the addition of K slightly enhances Pt dispersion; the 0.42K-2Pt/Al₂O₃ catalyst has a Pt dispersion of 56%, which is higher than that of 2Pt/Al₂O₃ (44%). Consequently, the calculated Pt particle size increases with increasing Pt content in the catalyst, ranging from 2.0 to 2.5 nm. However, the Pt dispersions of the K-promoted samples may have large deviations because of coverage of the Pt surface by K species.

The XRD patterns of the catalysts (not shown) show no distinct diffraction peaks from either Pt or K; this suggests that these species are highly dispersed.

Figure 1 shows representative TEM images of some samples. The presence of metallic Pt entities is verified by the measured d -space distances of the particles (Pt(111) = 0.226 nm). The detected Pt particle sizes in the investigated samples are similar (2–3 nm, based on analysis of more than 100 particles), and are consistent with the results obtained using CO chemisorption (Table 1).

3.2. Determination of oxidation states and surface compositions of catalysts

Fig. 1. TEM images of 0.2Pt/Al₂O₃ (a), 0.05K-0.2Pt/Al₂O₃ (b), 2.0Pt/Al₂O₃ (c), and 0.42K-2.0Pt/Al₂O₃ (d) catalysts.

The oxidation states of the catalysts were determined using XPS; the results are shown in Fig. 2. The Al 2p line overlaps with the Pt 4f one, therefore the Pt 4d line was used. Catalysts with low and high Pt contents (0.2 and 2.0 wt%) were examined. A broad band at bond energy (BE) = 310–322 eV is observed in the Pt 4d spectra of the samples (Fig. 2(a)). The peak was deconvoluted into two components with BEs = 313.8 and 316.3 eV. The peak at 313.8 eV is assigned to metallic Pt (Pt^0) [38], and that at 316.3 eV is typical of PtO species [39]. On addition of K to the catalysts, the Pt^0 peaks shift to higher BE (314.3 eV) compared with that of the K-free samples (313.8 eV). This shift suggests interactions between Pt and K species. The $\text{Pt}^0/\text{Pt}^{2+}$ ratios in these catalysts were also calculated, and are listed in Fig. 2. For the catalysts with low Pt contents, the $\text{Pt}^0/\text{Pt}^{2+}$ ratio in 0.05K-0.2Pt/ Al_2O_3 is 1.20, which is essentially the same as that in 0.2Pt/ Al_2O_3 (1.26). However, for catalysts with high Pt contents (2.0Pt/ Al_2O_3 and 0.42K-2.0Pt/ Al_2O_3), K addition significantly affects the surface compositions of Pt species; the $\text{Pt}^0/\text{Pt}^{2+}$ ratio (1.37) for 0.42K-2.0Pt/ Al_2O_3 is much lower than that for 2.0Pt/ Al_2O_3 (2.55). The lower $\text{Pt}^0/\text{Pt}^{2+}$ ratio strongly implies interactions between surface K and Pt species, resulting in Pt species remaining cationic. The broad peak in the O 1s spectra (Fig. 2(b)) can be deconvoluted into two peaks centered at BEs = 529.5 and 531.3 eV; these can be assigned to lattice oxygen species (O_{latt}) and adsorbed oxygen species or surface hydroxyl groups (O_{ads}) [40], respectively. The calculat-

ed $\text{O}_{\text{latt}}/\text{O}_{\text{ads}}$ ratios in the catalysts show that for samples with low Pt contents, these ratios are similar (0.20 for 0.2Pt/ Al_2O_3 and 0.22 for 0.05K-0.2Pt/ Al_2O_3), whereas for samples with high Pt contents, the ratio is higher for the K-containing catalyst than the K-free one (0.08 for 2.0Pt/ Al_2O_3 and 0.14 for 0.42K-2.0Pt/ Al_2O_3). These results suggest that the addition of K decreases the number of hydroxyl groups on the catalyst surface.

3.3. Catalytic performance

Figure 3 shows the light-off curves for CO oxidation over various catalysts. The catalytic performances of 0.1Pt/ Al_2O_3 and 0.02K-0.1Pt/ Al_2O_3 are almost identical (Fig. 3(a)). With increasing K and Pt contents in the catalysts, the K-promoted samples show better performances than the K-free ones (Figs. 3(b)–(d)). This point is clearly illustrated by a comparison of the T_{50} temperatures (the temperature at which the CO conversion is 50%); ΔT_{50} ($= T_{50}$ on the K-containing sample $- T_{50}$ on the K-free sample) gradually increases with increasing K and Pt contents in the catalysts, strongly indicating that the addition of K significantly enhances the activity. The turnover frequencies (TOFs) were also calculated and compared with those reported in the literature. The TOF obtained on the 0.2Pt/ Al_2O_3 at 150 °C is 0.02 s^{-1} , which is lower than that reported by Allian et al. [41] (0.08 s^{-1}) on Pt/ Al_2O_3 catalysts with various Pt dispersions

Fig. 2. Pt 4d (a) and O 1s (b) XPS profiles of 0.2Pt/ Al_2O_3 , 0.05K-0.2Pt/ Al_2O_3 , 2.0Pt/ Al_2O_3 , and 0.42K-2.0Pt/ Al_2O_3 catalysts.

Fig. 3. Comparison of CO oxidations over various K-free and K-promoted Pt/Al₂O₃ catalysts.

from 0.05 to 0.87. The different TOFs may result from the different preparation methods. In Ref. [37], the Pt/Al₂O₃ catalysts were prepared by slurry impregnation and colloidal methods, whereas the catalysts used in the current work were prepared using an incipient wetness impregnation method.

3.4. Kinetic study

Kinetic investigations were conducted on four representative catalysts: 0.2Pt/Al₂O₃, 0.05K-0.2Pt/Al₂O₃, 2.0Pt/Al₂O₃, and 0.42K-2.0Pt/Al₂O₃. The partial pressures of CO and O₂ were varied between 0.304 and 3.04 kPa, and the reaction temperatures were kept low, to obtain reliable data. The detailed results are shown in Tables 2 and 3. These data were used to determine the dependences of the reaction rates on the CO and

O₂ partial pressures; the results are shown in Fig. 4. Generally, the reaction rate decreases with increasing CO partial pressure, and increases with increasing O₂ partial pressure. The apparent rate constants (k_{app}), and CO and O₂ reaction orders are listed in Table 4. The obtained power-law rate expressions are $r = 1.81 \times 10^{-7} p_{CO}^{-0.51} p_{O_2}^{0.73}$ for 0.2Pt/Al₂O₃, $r = 2.52 \times 10^{-7} p_{CO}^{-0.27} p_{O_2}^{0.59}$ for 0.05K-0.2Pt/Al₂O₃, $r = 2.56 \times 10^{-7} p_{CO}^{-0.53} p_{O_2}^{0.70}$ for 2.0Pt/Al₂O₃, and $r = 6.55 \times 10^{-7} p_{CO}^{-0.22} p_{O_2}^{0.63}$ for 0.42K-2.0Pt/Al₂O₃.

The activation energies for the catalysts were also calculated based on Arrhenius plots (Fig. 5(a)). The activation energies for 0.2Pt/Al₂O₃ and 2.0Pt/Al₂O₃ are similar (60–66 kJ/mol). The activation energies of the K-promoted samples are lower than those for the K-free ones (55.2 ± 5.6 kJ/mol for 0.05K-0.2Pt/Al₂O₃ and 51.6 ± 3.6 kJ/mol for

Table 2

Kinetic results for 0.2Pt/Al₂O₃ and 0.05K-0.2Pt/Al₂O₃ catalysts.

Partial pressure (kPa)		CO conversion* (%)		Reaction rate (10 ⁻⁷ mol/(g·s))	
CO	O ₂	0.2Pt/Al ₂ O ₃	0.05K-0.2Pt/Al ₂ O ₃	0.2Pt/Al ₂ O ₃	0.05K-0.2Pt/Al ₂ O ₃
1.013	0.304	1.8	3.5	0.64	1.25
1.013	0.507	3.9	4.6	1.39	1.64
1.013	1.013	4.9	7.4	1.75	2.64
1.013	2.027	9.2	10.8	3.28	3.86
1.013	3.040	8.3	22.0	2.96	7.86
0.304	1.013	32.9	31.2	3.52	3.34
0.507	1.013	13.3	16.4	2.38	2.93
2.028	1.013	1.7	3.6	1.21	2.57
3.040	1.013	1.0	1.6	1.07	1.71

* Reaction temperature = 170 °C; catalyst amount = 250 mg.

Table 3

Kinetic results for 2.0Pt/Al₂O₃ and 0.42K-2.0Pt/Al₂O₃ catalysts.

Partial pressure (kPa)		CO conversion* (%)		Reaction rate (10 ⁻⁷ mol/(g·s))	
CO	O ₂	2.0Pt/Al ₂ O ₃	0.42K-2.0Pt/Al ₂ O ₃	2.0Pt/Al ₂ O ₃	0.42K-2.0Pt/Al ₂ O ₃
1.013	0.304	1.6	5.1	0.95	3.03
1.013	0.507	2.3	6.8	1.37	4.04
1.013	1.013	3.3	12.7	1.96	7.56
1.013	2.027	5.8	16.4	3.45	9.76
1.013	3.040	8.3	22.0	4.94	13.1
0.304	1.013	20.5	48.8	3.66	8.72
0.507	1.013	9.4	26.2	2.80	7.80
2.028	1.013	2.1	4.4	2.50	5.24
3.040	1.013	1.7	2.8	3.04	5.00

* Reaction temperature = 150 °C; catalyst amount = 150 mg.

Fig. 4. Dependences of reaction rates on CO and O₂ partial pressures. (a) 0.2Pt/Al₂O₃; (b) 0.05K-0.2Pt/Al₂O₃; (c) 2.0Pt/Al₂O₃; (d) 0.42K-2.0Pt/Al₂O₃.

Table 4

Apparent rate constants (k_{app}) and reaction orders for various catalysts.

Catalyst	k_{app} (10^{-7})	n	m
0.2Pt/Al ₂ O ₃	1.81 ± 0.34	-0.51 ± 0.12	0.73 ± 0.25
0.05K-0.2Pt/Al ₂ O ₃	2.52 ± 0.66	-0.27 ± 0.03	0.59 ± 0.06
2.0Pt/Al ₂ O ₃	2.56 ± 0.50	-0.53 ± 0.14	0.70 ± 0.12
0.42K-2.0Pt/Al ₂ O ₃	6.55 ± 0.42	-0.22 ± 0.08	0.63 ± 0.15

0.42K-2.0Pt/Al₂O₃). The obtained values are higher than those for Pt/SiO₂ (13–22 kJ/mol [42]) and Pt/TiO₂ (41.5 kJ/mol [43]), and are comparable with those obtained for Pt/Al₂O₃ (80–90 kJ/mol [41]; 65 kJ/mol [44]). The higher activation energies for 2.0Pt/Al₂O₃ and 0.2Pt/Al₂O₃ compared with those for their K-promoted counterparts suggest that the former are less active than the latter. Moreover, parity plots (Fig. 5(b)) indicate that the experimental reaction rates are in good agreement with the calculated values; this validates the derived rate ex-

pressions.

The elementary steps in CO oxidation over these catalysts were derived based on the rate expressions. The mechanisms of CO oxidation over Pt catalysts have been extensively studied, and various elementary steps have been proposed [41,45]. Classic Langmuir-Hinshelwood models have been used to deduce the elementary steps. For example, Djéga-Mariadassou and Boudart [45] proposed a reaction model in which molecular adsorption of O₂ was considered to be the sole kinetically relevant step and the reaction order of O₂ was 1. However, as the reaction orders of O₂ are 0.6–0.7, it is unlikely that chemisorption of O₂ on the Pt surface is the rate-determining step (RDS) in our study.

The following elementary steps are proposed to describe the reaction pathways over Pt/Al₂O₃ catalysts; they are similar to those proposed by Allian et al. [41].

This set of elementary steps includes: (1) competitive adsorptions of CO and O₂ on Pt surface atoms (reactions 1.1 and 1.2), where both reactions are equilibrium; (2) reaction between these two chemisorbed species, which is considered to be the RDS (reaction 1.3); (3) reaction of the remaining O adatom with another chemisorbed CO (reaction 1.4); and (4) desorption of CO₂ from the Pt surface (reaction 1.5).

A general rate reaction was derived based on the elementary steps represented by reactions 1.1–1.5:

Fig. 5. Arrhenius plots (a) and parity plots (b) for CO oxidation over various Pt/Al₂O₃ catalysts.

$$r = \frac{k_3 K_1 K_2 [\text{O}_2][\text{CO}]}{(1 + K_1[\text{CO}] + K_2[\text{O}_2])^2} \quad (\text{Eq. 1})$$

In the work by Allian et al. [41], it was assumed that chemisorbed CO species were the most abundant reactive intermediate therefore the rate expression could be simplified to $r = k_3 K_2 [\text{O}_2]/(K_1[\text{CO}])$ when $K_1[\text{CO}] \gg 1$ and $K_2[\text{O}_2] \ll 1$. This equation fits well with their findings that the reaction order of CO was -1 and that of O_2 was 1 . However, in the current work, the reaction orders for CO and O_2 are -0.3 to -0.5 and 0.6 to 0.7 , respectively, therefore the rate expression cannot be simplified as this does not fit the observed kinetics. We therefore propose that the CO coverage of the catalyst surface is high, but not saturated, and chemisorption of O_2 , although weak, is competitive with that of CO. The obtained expression (Eq. 1) is equivalent to a power-low rate $r = k_{\text{app}}[\text{CO}]^m[\text{O}_2]^n$, where m and n are the reaction orders of CO and O_2 , respectively. The chemisorption of CO on Pt is much stronger than that of O_2 ($K_1 \gg K_2$), therefore the contribution of $K_1[\text{CO}]$ in the denominator is much larger than that of $K_2[\text{O}_2]$; the reaction order m is therefore estimated to be in the range -1 to 0 , and the reaction order n is in the range 0 – 1 .

If we take a close look at the kinetic behaviors of the catalysts, obvious differences can be observed. First, the apparent rate constants k_{app} (Table 4) for the K-promoted catalysts are 2.52×10^{-7} for $0.05\text{K-0.2Pt/Al}_2\text{O}_3$ and 6.55×10^{-7} for $0.42\text{K-2.0Pt/Al}_2\text{O}_3$; these are much larger than those for the K-free catalysts (1.81×10^{-7} for $0.2\text{Pt/Al}_2\text{O}_3$ and 2.56×10^{-7} for $2.0\text{Pt/Al}_2\text{O}_3$). These results suggest that K promotes the reaction. Secondly, the reaction orders of CO are about -0.5 for the K-free samples, i.e., much lower than those for the K-containing ones (about -0.2). According to Eq. 1, a lower reaction order implies stronger interactions between CO molecules and the catalyst surface. Thirdly, the reaction orders of O_2 for the K-promoted samples are slightly lower than those for the K-free ones, implying that K promotion accelerates competitive O_2 chemisorption on the Pt surface. This enhancement of O_2 chemisorption is probably the result of lower CO coverage of the Pt surface as a result of K promotion. The proposed elementary steps (reactions 1.1–1.5) suggest that the differences between the reaction orders of CO and O_2 must be related to changes in their equilibrium constants (K_1 for CO and K_2 for O_2) and the intrinsic rate constant k_3 . The kinetic parameters (K_1 , K_2 , and k_3) were therefore calculated based on Eq. 1 and the data in Tables 2 and 3, using POLYMATH 5.1. The regressed results are listed in Table 5. The intrinsic rate constant k_3 for $0.2\text{Pt/Al}_2\text{O}_3$ ($1.99 \mu\text{mol}/(\text{g}\cdot\text{s})$) is close to that for $0.05\text{K-0.2Pt/Al}_2\text{O}_3$ ($2.09 \mu\text{mol}/(\text{g}\cdot\text{s})$), suggesting similar intrinsic activation energies for these catalysts. However, k_3 for $2.0\text{Pt/Al}_2\text{O}_3$ ($2.90 \mu\text{mol}/(\text{g}\cdot\text{s})$) is only half that for $0.42\text{K-2.0Pt/Al}_2\text{O}_3$ ($5.86 \mu\text{mol}/(\text{g}\cdot\text{s})$), suggesting a higher intrinsic activation energy. These observations are consistent with the apparent activation energies (k_{app}). The addition of K significantly affects the CO equilibrium constant (K_1). For $0.2\text{Pt/Al}_2\text{O}_3$, K_1 is 11.7 kPa^{-1} , which is almost twice that for $0.05\text{K-0.2Pt/Al}_2\text{O}_3$ (5.95 kPa^{-1}). Similar results were obtained for $2.0\text{Pt/Al}_2\text{O}_3$ and $0.42\text{K-2.0Pt/Al}_2\text{O}_3$ (10.14 kPa^{-1} vs 4.84

Table 5

Kinetic parameters for various catalysts, derived from Eq. 1.

Catalyst	$k_3/(\mu\text{mol}/(\text{g}\cdot\text{s}))$	K_1/kPa^{-1}	K_2/kPa^{-1}
$0.2\text{Pt/Al}_2\text{O}_3^{\text{a}}$	1.99 ± 0.34	11.7 ± 1.2	1.34 ± 0.24
$0.05\text{K-0.2Pt/Al}_2\text{O}_3^{\text{a}}$	2.09 ± 0.51	5.95 ± 0.72	1.58 ± 0.31
$2.0\text{Pt/Al}_2\text{O}_3^{\text{b}}$	2.90 ± 0.26	10.1 ± 1.5	1.02 ± 0.18
$0.42\text{K-2.0Pt/Al}_2\text{O}_3^{\text{b}}$	5.86 ± 0.68	4.84 ± 0.67	1.28 ± 0.27

^a Reaction temperature = 170°C .^b Reaction temperature = 150°C .

kPa^{-1}). The lower K_1 values for the K-containing samples indicate a lower adsorption heat (ΔH) compared with those of the K-free samples. The adsorption heat for linear adsorbed CO on the Pt surface is significantly lowered by K addition to the catalyst, as reported by Derrouiche et al. [46]. For the O_2 equilibrium constant (K_2), addition of K slightly enhances K_2 . For example, K_2 is 1.58 kPa^{-1} for $0.05\text{K-0.2Pt/Al}_2\text{O}_3$ and that for $0.2\text{Pt/Al}_2\text{O}_3$ is 1.34 kPa^{-1} . These findings clearly indicate that K addition significantly suppresses CO chemisorption (a lower K_1), but slightly enhances O_2 chemisorption (a higher K_2). Moreover, K_1 is much larger than K_2 , suggesting that the interactions between CO and the catalyst surface are much stronger than those between O_2 and the catalyst surface; this is understandable, because CO molecules are easily chemisorbed on Pt, with a high heat of adsorption [47].

3.5. In situ FTIR spectroscopic studies

Although the kinetic results give direct evidence on the promoting effect of K addition on CO oxidation, spectroscopic results on CO chemisorption are desirable because CO adsorption is often used as a probe for investigating catalyst structures and interactions between CO and metals. There are distinct differences between the kinetics of the $2.0\text{Pt/Al}_2\text{O}_3$ and $0.42\text{K-2.0Pt/Al}_2\text{O}_3$ catalysts; therefore, it is interesting to compare their CO chemisorption behaviors using FTIR spectroscopy. Parallel experiments on CO + O_2 chemisorption were also performed to investigate the effect of O_2 on the chemisorption behaviors.

Fig. 6(a) shows the spectrum for CO chemisorption on $2.0\text{Pt/Al}_2\text{O}_3$. A strong band at 2047 cm^{-1} and a weak, broad band at about 1816 cm^{-1} are observed, together with a very weak shoulder at about 2085 cm^{-1} ; these can be assigned to linear CO on Pt^0 sites (L-CO), bridging CO on Pt^0 sites (B-CO), and linear CO on Pt^{2+} , respectively [48]. These spectra are consistent with the findings reported by Alexeev et al. [48] and Kuriyama et al. [28]. CO adsorption on different Pt species is consistent with the XPS results (Fig. 2(a)), and clearly confirms the presence of both Pt^0 and Pt^{2+} species in the catalyst. The intensities of all these bands decrease with increasing temperature, but they have not completely disappeared at 180°C . L-CO adsorption on Pt is very strong, and it can only be completely removed at 400°C [48]. In addition, the L-CO band at 2047 cm^{-1} shifts slightly to lower wavenumbers (about 4 cm^{-1}) with increasing temperature; this can be explained by a decrease in the dipole-dipole coupling between adsorbed CO molecules resulting from a decrease in the CO surface coverage

Fig. 6. In situ FTIR spectra of 2.0Pt/Al₂O₃ catalyst under exposure to CO (a) and CO-O₂ (b) at different temperatures. (1) 40 °C; (2) 60 °C; (3) 800 °C; (4) 100 °C; (5) 120 °C; (6) 140 °C; (7) 160 °C; (8) 180 °C.

[48]. In contrast, the B-CO band shows a significant red-shift with increasing temperature. When the catalysts are exposed to a mixture of CO-O₂ (Fig. 6(b)), spectra with peaks of almost identical shapes and positions are observed. The spectra of 0.42K-2.0Pt/Al₂O₃ are similar to those of 2.0Pt/Al₂O₃, for both CO and CO-O₂ (Fig. 7). It is worth noting that the spectra of 0.42K-2.0Pt/Al₂O₃ are different from those reported for other K-promoted Pt/Al₂O₃ catalysts [28,46], i.e., a band at about 1760 cm⁻¹ was observed; this was assigned to three-coordinated CO species on Pt atoms interacting with K species [46]. The absence of such a band at 1760 cm⁻¹ in our work might be caused by the low K content in the catalyst. Note that the catalyst in the current work has a K/Pt molar ratio of 1, whereas the K/Pt ratios of the catalysts in refs. [28] and [46] were 10. The much higher K/Pt ratio may result in more inter-

active K-O-Pt species in the reported catalysts, which would make CO chemisorption on these species more distinct.

Although the features of the FTIR spectra of the investigated catalysts are similar, the peak intensities of the bands change at high temperatures, and the rates at which the band intensities decrease are different. We therefore calculated the normalized peak areas of the L-CO and B-CO bands in the catalysts. Fig. 8 compares the band areas of L-CO and B-CO under exposure to CO and CO-O₂ on the 2.0Pt/Al₂O₃ and 0.42K-2.0Pt/Al₂O₃ catalysts. For the chemisorbed L-CO species (Fig. 8(a)), the area for the 0.42K-2.0Pt/Al₂O₃ catalyst is significantly lower than that for 2.0Pt/Al₂O₃. Moreover, chemisorbed L-CO is not completely removed at 180 °C from 2.0Pt/Al₂O₃, but is completely removed from 0.42K-2.0Pt/Al₂O₃. These results clearly suggest that the presence of K in the catalyst suppresses CO chemisorp-

Fig. 7. In situ FTIR spectra of 0.42K-2.0Pt/Al₂O₃ catalyst under exposure to CO (a) and CO-O₂ (b) at different temperatures. (1) 40 °C; (2) 60 °C; (3) 800 °C; (4) 100 °C; (5) 120 °C; (6) 140 °C; (7) 160 °C; (8) 180 °C.

Fig. 8. Comparison of peak areas for CO adsorption over 2.0Pt/Al₂O₃ (1) and 0.42K-2.0Pt/Al₂O₃ (2) catalysts under exposure to CO and CO-O₂ at different temperatures. (a) and (b) L-CO; (c) and (d) B-CO; (e) and (f) total (L-CO + B-CO).

tion and weakens the interactions between CO and the catalyst surface; this is in good agreement with the findings reported in the literature [28,46]. For the chemisorbed B-CO species (Fig. 8(c)), the presence of K in the catalyst enhances CO chemisorption, particularly at low temperatures (<100 °C). This phenomenon has also been reported in the literature; Derrouiche et al. [46] found that the heat of adsorption of a major B-CO species was significantly larger in the presence than in the absence of K. Note that the contribution of B-CO is much lower than that of the L-CO, therefore the total L-CO + B-CO peak areas are higher for 2.0Pt/Al₂O₃ than for 0.42K-2.0Pt/Al₂O₃ (Fig. 8(e)); this observation is not consistent with the Pt dispersion measurements (Table 1), because the pulsed CO chemisorption results show that the Pt particles in 0.42K-2Pt/Al₂O₃ are smaller (higher amount of chemisorbed CO) than those in 2Pt/Al₂O₃ (lower amount of chemisorbed CO). This inconsistency may arise from the different temperatures used for CO chemisorption in the two sets of experiments (40 °C for IR spectroscopy and 30 °C for the Pt dispersion measurements); alternatively there may be considerable errors in the Pt dispersions results because of the low Pt loadings in the catalysts.

When the catalysts are exposed to a CO-O₂ mixture (Figs. 8(b), (d), and (f)), the general features are similar to those in a CO environment. However, the addition of O₂ further accelerates CO desorption. The temperature for complete removal of L-CO shifts to 160 °C, and that for B-CO shifts to 140 °C. These are about 20 °C lower than those in a CO environment. This difference implies that the adsorptions of CO and O₂ are competitive, and coadsorption of O₂ weakens the interactions between CO and the surface. In addition, note that the total area of the CO peak for 0.42K-2.0Pt/Al₂O₃ (Fig. 8(f)) is slightly lower

than that for 2.0Pt/Al₂O₃, indicating that O₂ coverage on the catalyst surface is quite low.

The analyses based on the FTIR results are in excellent agreement with the kinetic results. The addition of K to the catalysts results in significant suppression of CO chemisorption and consequently a lower adsorption equilibrium constant (K_1) for both CO and CO-O₂ adsorptions (Table 5). However, the addition of O₂ only changes the CO adsorption, because the equilibrium constant (K_2) for O₂ chemisorption is very low, therefore O₂ adsorption is weak (Table 5). Although the results of the current work provide convincing evidence for the role of K, the nature of the surface species (Pt-O-K) remains unclear. Nevertheless, some progress has been made. For example, in our previous work [35], a surface species Pt-O-K_x ($x \approx 2$) was proposed for K-promoted Pt/Al₂O₃ catalysts, based on the surface compositions of K and Pt. Moreover, using density functional theory calculations, Zhai et al. [32] proposed that a PtK₆O₄(OH)₂ species was the most active in the water-gas-shift reaction over a K-promoted Pt/Al₂O₃ catalyst. The authors [32] concluded that the role of the alkali metal (Na and K) was to generate and stabilize Pt-OH_x species, which could be activated by CO at low temperatures. Although the structures of the active sites could not be determined in the current work, the participation of such Pt-associated hydroxyl groups in CO oxidation cannot be ruled out. Xu et al. [49] observed direct evidence for the interfacial oxidation of CO with hydroxyls over a FeO(111)/Pt(111) inverse model catalyst, and they concluded that an interfacial CO_{ads} + OH_{ads} reaction producing CO₂ occurred easily at the Pt-oxide interface at low temperatures.

4. Conclusions

A combination of detailed kinetic and spectroscopic investigations clarified the role of K in the enhancement of CO oxidation over Pt/Al₂O₃ catalysts. The addition of K significantly weakens CO chemisorption, leading to a lower equilibrium constant compared with that of the K-free sample. Such weakened interactions between CO and the catalyst surface lower the surface coverage by CO, facilitate competitive O₂ chemisorption on the Pt surface, and significantly lower the reaction barrier between chemisorbed CO and O₂ species.

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Graphical Abstract

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Enhanced CO oxidation over potassium-promoted Pt/Al₂O₃ catalysts: Kinetic and infrared spectroscopic study

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The promoting effect of K addition was caused by weakening of the interactions between CO and surface Pt atoms. This decreased surface coverage by CO and facilitated competitive O₂ chemisorption on the Pt surface.

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K改性的Pt/Al₂O₃催化剂上CO氧化反应: 反应动力学和红外光谱研究

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摘要: CO氧化不仅具有重要的实用价值, 而且在基础研究中被用于考察反应机理及催化剂结构敏感性等一些重要问题, 因此, 该反应在催化领域具有重要意义. Pt基催化剂被广泛应用于CO氧化反应. 其催化活性取决于催化剂的制备方法. 其中, 碱金属如Na、K等助剂的添加可有效促进催化活性, 红外光谱证据表明, 其促进作用在于碱金属的添加可降低CO与表面Pt原子的相互作用. 尽管如此, 催化剂上反应动力学证据却十分缺乏. 反应动力学的研究可以提供一些本征反应信息如反应基元步骤、反应速率表达式以及反应机理等. 通过对比不同催化剂之间的反应动力学行为, 可以进一步解释碱金属对催化剂结构以及反应行为的影响. 因此在本工作中, 我们制备了一系列以K为助剂的Pt/Al₂O₃催化剂, 并进行了CO氧化的反应动力学研究, 考察了助剂对CO反应级数和反应活化能的影响. 结合原位红外光谱表征, 进一步揭示了助剂在反应中的作用.

通过对比不同Pt和K含量的催化剂上CO氧化反应活性, 我们发现, K的添加能促进反应活性, 且随着催化剂中K含量的增加, 促进程度越明显. 例如, 0.42K-2Pt/Al₂O₃上 T_{50} 温度比对应的2Pt/Al₂O₃降低了30 °C. 不同催化剂上CO氧化的反应动力学实验表明, 反应速率随着CO的分压的增加而降低; 但随着O₂分压的增加而增大. 幂函数反应速率表达式推导得到的反应级数发现, 对于含K的催化剂其CO的反应级数(约为-0.2)明显比不含K的催化剂(约为-0.5)中高, 说明K的添加减弱了CO与表面Pt原子之间的吸附能力. 但对O₂的反应级数影响较小. 例如: 在0.42K-2.0Pt/Al₂O₃上反应速率表达式为 $r = 6.55 \times 10^{-7} p_{\text{CO}}^{-0.22} p_{\text{O}_2}^{0.63}$; 而在2.0Pt/Al₂O₃上为 $r = 2.56 \times 10^{-7} p_{\text{CO}}^{-0.53} p_{\text{O}_2}^{0.70}$. 表观反应活化能的计算表明, 含K的催化剂上表观反应活化能较低, 进一步说明K的添加有利于反应进行. 根据反应速率表达式, 我们进行了基元步骤的推导, 并计算了反应动力学参数. 结果发现, 与不含K的催化剂相比, 含K的催化剂中本征反应速率常数明显增加, 而CO吸附平衡常数降低了一半, 表明K的存在使CO在Pt表面上的覆盖度降低. 我们还通过原位红外光谱对比了催化剂上CO吸附行为的差异. 数据表明, 与不含K的催化剂相比, K的添加一方面降低了CO在催化剂表面的吸附量(峰面积变小); 另一方面显著降低了CO在Pt表面上的脱附温度, 说明两者之间的相互作用力减弱.

综上所述, 通过反应动力学和红外光谱实验, 我们认为K助剂与表面Pt原子相互作用后生成了较为稳定的Pt-O-K物种. 尽管该物种的具体结构目前还不明确, 但我们的实验证据表明, 该物种的存在可以有效减弱CO与表面Pt原子之间的相互作用, 降低CO的表面覆盖度并有利于O₂在Pt表面的竞争吸附, 从而降低了表面吸附的CO与O₂之间反应的能垒, 促进了反应性能.

关键词: CO氧化; 钾; 反应动力学; Pt/Al₂O₃催化剂; 促进作用

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