

**Effect of surface acidity modulation on Pt/Al₂O₃ single atom catalyst for
carbon monoxide oxidation and methanol decomposition**

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Abstract

With ideal metal utilization efficiency and homogeneous active sites, single atom catalysts (SACs) have attracted extensive attention in heterogeneous catalysis field. The performance of SACs is highly dependent on the local coordination environment of metal single atoms. However, few works reported the effect of surface acidity modification on the performance of SACs such as Pt SACs which have been widely studied nowadays. In this work, a Pt/Al₂O₃ SAC has been successfully prepared using a bayerite Al(OH)₃ as support through simple IWI method for Pt loading. Through post-modification of Pt/Al₂O₃ with acidic WO₃ and basic MgO, the surface acidity of Pt/Al₂O₃ was tuned. Activity of CO oxidation and methanol decomposition on the modified catalysts has been evaluated. It was found that the catalytic performance was highly related to the surface acidity of Pt SACs. Basic MgO modified Pt/Al₂O₃ performed better in CO oxidation under the reaction condition with H₂O. Acidic WO₃ modified Pt/Al₂O₃ showed superior activity in methanol decomposition. Detailed characterization and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) study suggested that the positive H₂O effect on CO oxidation was due to the mitigated formation of bicarbonate species on Pt/Al₂O₃ and WO₃/Pt/Al₂O₃ catalysts and the promoted desorption of carbonate species from MgO/Pt/Al₂O₃. The superior methanol decomposition performance on WO₃/Pt/Al₂O₃ was owing to its abundant oxygen vacancies and high resistance to carbonate accumulation. This study highlights the importance of surface acidity modulation of Pt SACs in heterogeneous catalysis and suggests that fine-tuning the surface acidity can be an effective strategy in new SACs development.

Keywords

Platinum single atom catalyst; acidity modification; carbon monoxide oxidation; methanol decomposition; carbonate resistance

1. Introduction

As a rising star in material science, supported single atom catalysts (SACs) in which metal species are atomically dispersed on solid supports, have attracted extensive attention in various applications including biocatalysis, photocatalysis, electrocatalysis and thermal-catalysis [1]. Due to its relatively homogeneous active sites, SACs not only can show great benefits on improving catalytic activity but also can enhance selectivity in specific reactions. In addition, with maximum atomic utilization efficiency, SACs can contribute to more sustainable utilization of platinum group metals (PGMs), which are expensive, critical and difficult to have alternatives in multiple catalysis reactions [2, 3].

To increase the metal utilization efficiency and activity of supported Pt catalysts, Pt SAC on diverse supports have been developed and applied in many reactions, including hydrogenation [4], dehydrogenation [5], volatile organic compounds combustion [6, 7], the water-gas shift [8], CO oxidation [9], and alcohol decomposition [10]. For instance, Pt SACs on reducible metal oxide supports such as CeO_2 , FeO_x and MnO_x , or their derived catalysts showed superior catalytic performance for the hydrogenation of 3-nitrostyrene [11], CO oxidation [12-15], hydrocarbon oxidation [11, 16, 17], H_2 production from methanol decomposition [10, 18] and hydrocarbon reforming [19]. Pt SACs on irreducible metal oxide supports including ZrO_2 and Al_2O_3 also have been fabricated for various applications [20-22]. Zhang *et al.* reported that Pt single atom catalyst on mesoporous Al_2O_3 showed excellent performance and stability for *n*-hexane hydro-reforming, high activity for the selective hydrogenation of 1,3-butadiene, and superior stability in CO oxidation [21]. Liu *et al.* developed a methodology of electron-microscopy-based atom recognition statistics (EMARS) for determining the density of Pt single atoms on Al_2O_3 , and then concluded that the activity for aromatics production from hydrocarbon reforming quantitatively correlated with the density of Pt single-atoms [22].

A challenge in the development of efficient SACs is the modulation of metal local

coordination environment, which has been verified governing the catalytic performance in certain catalysis reactions [23-25]. Xu *et al.* claimed that propylene selectivity was highly related to the coordination number of Pt-O in Pt/CeO₂ for propyne semihydrogenation reaction [25]. With high-entropy oxides (HEOs) modification on Al₂O₃, Zhao *et al.* found that Pt-HEO/Al₂O₃ SAC exhibited superior stability against hydrothermal aging and long-term catalytic stability for CO oxidation comparing to the conventional Pt SACs [26]. Wang *et al.* reported a promotion effect of barium modification on hydrothermal stability of Pt/La-Al₂O₃ SAC for CO and C₃H₆ oxidation [27]. However, so far, there have been no known reports on studying the effects of surface acidity modification of Pt/Al₂O₃ SACs for CO oxidation and methanol decomposition. Therefore, in this work, through post-modification on Pt/Al₂O₃ SAC with acidic WO₃ and basic MgO, Pt/Al₂O₃ SACs with different surface acidity have been fabricated and applied in CO oxidation and methanol decomposition. By means of *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) of CO adsorption at room temperature, High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive x-ray spectroscopy (EDS) mapping, as well as extended X-ray absorption fine structure (EXAFS) of Pt L_{III}-edge, Pt single atom structure in the fabricated catalysts has been confirmed. Catalytic behaviors on Pt/Al₂O₃ SACs with different surface acidity property for CO oxidation and methanol decomposition have been investigated in detail. It was proposed that the CO oxidation and methanol decomposition performance was highly associated with the surface acidity of Pt SACs catalysts. Through systematic *in situ* DRIFTS study, the structure-activity relationship for both CO oxidation and methanol decomposition on different catalysts has also been discussed.

2. Experimental section

2.1. Materials

Commercial non-dispersible bayerite Al(OH)₃ support with a particle size of *ca.* 5-10 μm and

BET surface area of *ca.* 360 m²/g was obtained from Sasol. Platinum (IV) nitrate was purchased from Umicore Precious Metals Chemistry, LLC. Ammonium metatungstate hydrate (99.5%), magnesium nitrate (99.5%) and methanol (99.8%) were purchased from Alfa Aesar. 10% H₂/Ar, 10% CO/Ar, N₂ (99.999%), O₂ (99.999%) and Ar (99.999%) gas cylinders were purchased from Airgas. No further treatment was conducted on all chemicals and cylinders used in this work.

2.2. Catalyst preparation

An incipient wetness impregnation (IWI) method was adopted for the preparation of all samples. For Pt/Al₂O₃ catalyst, platinum (IV) nitrate solution with 1 wt.% Pt was added dropwise onto Al(OH)₃ support and then dried at 120 °C for 1 h. Followed by calcination at 550 °C for 2 h in air with a temperature ramp of 5 °C/min, the 1 wt.% Pt/Al₂O₃ catalyst was prepared. The WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts were obtained by dropwise adding ammonium metatungstate or magnesium nitrate solution (5 wt.% WO₃ or 5 wt.% MgO) onto Pt/Al₂O₃, followed by calcination at 550 °C for 2 h in air with a temperature ramp of 5 °C/min. The pure Al₂O₃ support was prepared by calcining Al(OH)₃ at 550 °C for 2 h, and WO₃/Al₂O₃ and MgO/Al₂O₃ reference samples were also prepared by skipping the Pt impregnation step.

2.3. Catalyst characterizations

X-ray powder diffraction (XRD) testing was performed on a PANalytical Empyrean diffractometer using a Cu K α X-rays (λ = 0.15406 nm). The collection range of XRD patterns was 10-80 °, and the scan speed was 6 °/min with a scan step of 0.067 °.

Nitrogen (N₂) adsorption-desorption isotherm analysis was performed on a Quantachrome Autosorb-iQ instrument with the samples degassed at 300 °C for 2 h under vacuum before measurement. Brunauer-Emmett-Teller (BET) surface areas were calculated using adsorption points in the relative pressures between 0.05 and 0.3. The pore size distribution was determined by non-local density functional theory (DFT) method.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive x-ray spectroscopy (EDS) mapping were performed on a JEOL-2100F equipment.

To determine the binding energies (BEs) of Al 2p, W 4f, Mg 2p, O 1s, Pt 4d, and C 1s for all the samples, X-ray photoelectron spectroscopy (XPS) analysis was conducted on a VG CLAM 4 MCD analyzer using Mg K- α ($h\nu = 1253.6$ eV) as an excitation source. All samples were degassed in the preparation chamber (10^{-5} Torr) for 0.5 h and then introduced into the analysis chamber (3×10^{-9} Torr) for XPS collection. The BE calibration was conducted using C 1s signal at 284.6 eV as reference.

X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) of Pt L_{III}-edge and W L_{III}-edge were measured in fluorescent mode for all catalysts and in transmission mode for all foils or oxide references at room temperature at 7-BM QAS beamline of the National Synchrotron Light Source II (NSLS-II), Brookhaven National Laboratory. Data was analyzed using Athena and Artemis software from the Demeter package. Pt and W foil were applied for energy calibration and drift correction of the monochromator. The processed EXAFS, $\chi(k)$, was weighted by k^2 for Pt L_{III}-edge and k^3 for W L_{III}-edge to amplify the high-k oscillations. For Fourier-transformed (FT) spectra, the k ranges between 3.0 to 11.0 Å⁻¹ for Pt L_{III}-edge and 2.0 to 12.0 Å⁻¹ for W L_{III}-edge were used, and the fitting in the R ranges for all catalysts were between 1.0 to 3.0 Å for Pt L_{III}-edge and 1.0 to 2.0 Å for W L_{III}-edge in Artemis software.

H₂ temperature-programmed reduction (H₂-TPR) was performed on a Quantachrome Autosorb-iQ instrument. Prior to test, 30 mg of the catalyst was treated in a flow of 5 vol.% O₂/He (40 sccm) at 300 °C for 1 h to remove the possible surface adsorbents and then cooled down to 30 °C. Afterwards, the temperature was increased from 40 to 500 °C linearly with a ramping rate of 10 °C/min in a flow of 10 vol.% H₂/Ar (30 sccm). A thermal conductivity

detector (TCD) was used to monitor the signal of H₂ consumption. Calculation of H₂ consumption was performed using CuO as a reference.

Pt dispersion of the samples were determined by a CO pulse titration experiment performed on Quantachrome Autosorb-iQ instrument as well. Typically, 50 mg sample was loaded into a U-shaped quartz reactor with an inner diameter of 8 mm. Afterwards, in order to obtain pure metallic Pt sites for CO adsorption, a typical pretreatment in 10% H₂/Ar flow at 400 °C for 1 h was conducted, followed by He purge at 400 °C for 30 min (avoiding the presence of residual adsorbed hydrogen) and cooling down to 25 °C. Afterwards, He was used as carried gas at 50 sccm, and successive doses of CO gas were introduced into the He stream by a calibrated injection valve (150 µL 5% CO/He per pulse) at 25 °C. The titration was considered as finished when the intensities of three peaks in a row kept constant.

In situ diffuse reflectance infrared Fourier transform spectroscopy (*in situ* DRIFTS) experiments were carried out on Nicolet iS50 FT-IR spectrometer with a liquid nitrogen-cooling MCT detector. Prior to *in situ* DRIFTS experiment, 20 mg sample was loaded into a high temperature IR cell (PIKE DiffusIR cell with ZnSe windows), followed with a treatment in 10% O₂/Ar flow (30 sccm) at 300 °C for 1 h. Subsequently, the sample was cooled to target temperature (25, 50, 100, 150, 200, 250, 300, or 350 °C) followed by Ar purge (50 sccm) for 30 min before collecting the background spectrum. The infrared spectra were collected by accumulating 100 scans at a spectral resolution of 4 cm⁻¹. For CO adsorption at 25 °C, 1% CO balanced with Ar was introduced into the cell for 30 min to achieve saturated CO adsorption on sample. Then, the flow of CO was discontinued, and the sample was exposed to Ar flow for 15 min to remove weakly adsorbed CO. For CO oxidation at 200 °C with/without water, 1% CO, 1% O₂ and 5% H₂O (when used) balanced with Ar were introduced into the cell for 60 min to achieve a steady-state CO oxidation on sample. Afterwards, the flow of CO was discontinued, and the sample was exposed to 1% O₂ and 5% H₂O (when used) balanced with

Ar for 30 min to react with surface adsorbed CO. For NH₃ adsorption/desorption experiments, the NH₃ adsorption was performed on the sample at 50 °C in the flow of 500 ppm NH₃ for 1 h. Then, the sample was purged by Ar for 30 min until the IR signals were stabilized. Afterwards, the desorption experiments were carried out in Ar flow with the temperature increased from 50 to 350 °C, respectively. For methanol decomposition at 240 °C, a flow of 10% CH₃OH balanced with Ar was introduced into the cell for 30 min until the IR signals were stabilized. Then, methanol desorption was carried out in Ar flow at 240 °C for 30 min after methanol was discontinued. The DRIFTS spectra were recorded during the whole methanol decomposition and desorption process.

2.4. Catalytic performance evaluation

Catalytic activity evaluation for CO oxidation and CH₃OH decomposition over all catalysts was carried out on a continuous flow fixed-bed quartz tubular microreactor (internal diameter = 4.0 mm). For CO oxidation, 25 mg of the catalyst (40-60 mesh) was diluted with 0.25 g of inert SiC (40-60 mesh) to minimize the effect of hot spots. The reactant mixture was composed of 1% CO, 1% O₂ and 5% H₂O (when used) (Ar balance), and the total flow was 83.33 sccm, thus giving a WHSV of 200,000 mL g⁻¹ h⁻¹. In the case of water vapor introduction, 5% H₂O was introduced by passing a carrier gas (Ar) through a water saturator at 60 °C. For CH₃OH decomposition, a flow of 10% CH₃OH balanced with Ar of 83.33 sccm obtained by passing a carrier gas (Ar) through a CH₃OH saturator at 35 °C was used, thus giving a WHSV of 50,000 mL g⁻¹ h⁻¹. Reactants and products were analyzed online by a Mass Spectrometer (MS, Hiden Analytical). The *m/z* ratios used for CO, O₂, CO₂, H₂ and CH₃OH detection were 28, 32, 44, 2 and 31, respectively. The reactant conversion was defined as $(c_{\text{inlet}} - c_{\text{outlet}})/c_{\text{inlet}} \times 100\%$, where c_{inlet} and c_{outlet} were the inlet and outlet CO/CH₃OH concentrations in the feed stream, respectively.

3. Results and discussion

3.1. Catalyst structure characterization

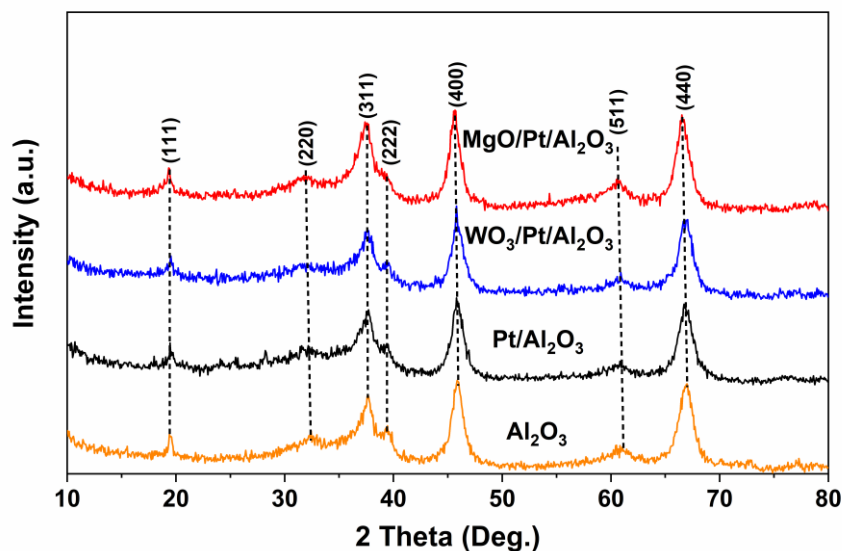


Fig. 1. XRD patterns of Al_2O_3 support, $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts.

Fig. 1 shows the XRD patterns of pristine Al_2O_3 support, $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts. For the Al_2O_3 support obtained from pre-calcination of bayerite $\text{Al}(\text{OH})_3$ at 550 °C, the formed Al_2O_3 showed an η - Al_2O_3 phase according to the Inorganic Crystal Structure Database (ICSD code 66558) [28]. It was reported that η - Al_2O_3 has very similar bulk structure to γ - Al_2O_3 , but due to the difference in surface Al coordination, η - Al_2O_3 has greater Lewis acidity than γ - Al_2O_3 [29]. Greater Lewis acidity and possibly more surface defects on η - Al_2O_3 should be beneficial in highly dispersing the loaded components comparing to that on the conventional γ - Al_2O_3 . For the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, no peaks indexed to Pt metal or Pt oxides were found from its XRD pattern, suggesting that the Pt species was highly dispersed on Al_2O_3 surface. It has to be noted that the diffraction peaks of η - Al_2O_3 in $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst showed weaker intensity and broader full width at half maximum (FWHM). This indicates that the impregnation of Pt nitrate onto bayerite $\text{Al}(\text{OH})_3$ followed by calcination actually hindered the growth of resulting Al_2O_3 crystallites to a certain extent (comparing to the pristine η - Al_2O_3) probably due to the strong interaction between highly dispersed Pt species and η - Al_2O_3 . This conclusion can be further confirmed by the calculated Al_2O_3 crystallite sizes according to

Scherrer equation using the FWHM of Al₂O₃ (400) peak, as shown in **Table 1**. The post-impregnation of acidic WO₃ and basic MgO onto Pt/Al₂O₃ catalyst did not obviously influence the Al₂O₃ crystal structure. The absence of typical diffraction peaks of WO₃ and MgO suggested that the W and Mg species were also highly dispersed without long-range order within WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts, respectively.

Table 1. BET surface area, Al₂O₃ crystallite size ($D_{\text{Al}_2\text{O}_3}$), average pore size, and pore volume of different samples.

Sample	BET surface area ^a (m ² /g)	$D_{\text{Al}_2\text{O}_3}$ ^b (nm)	Average pore size ^c (nm)	Pore volume (cm ³ /g)	Pt dispersion ^d (%)
Al ₂ O ₃	273	6.4	3.2	0.33	-
Pt/Al ₂ O ₃	238	5.5	3.6	0.29	54.0
WO ₃ /Pt/Al ₂ O ₃	240	6.0	3.5	0.29	52.5
MgO/Pt/Al ₂ O ₃	202	6.1	3.8	0.26	30.1

^a Obtained using the BET method;

^b Estimated according to the Scherrer equation using the full width at half maximum (FWHM) of Al₂O₃ (400) peak;

^c Estimated according to the DFT method;

^d Obtained by CO pulse titration experiment for samples after pre-reduction by H₂ at 400 °C for 1 h.

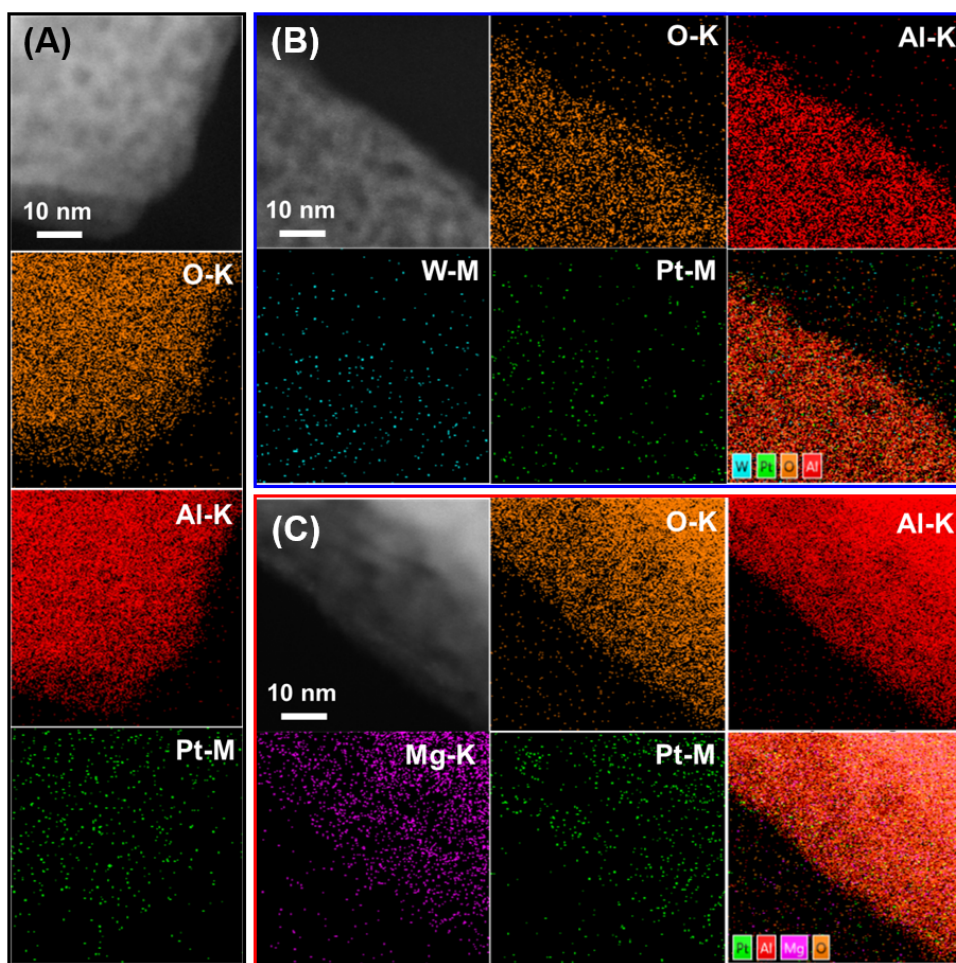


Fig. 2. HAADF-STEM and EDS mapping results for (A) Pt/Al₂O₃, (B) WO₃/Pt/Al₂O₃ and (C) MgO/Pt/Al₂O₃.

Fig. S1 (see Supplementary Material) shows the N₂ adsorption/desorption isotherms and pore size distribution of Al₂O₃, Pt/Al₂O₃, WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ samples. All the N₂ adsorption/desorption isotherms displayed as type II with a H1 hysteresis loop (**Fig. S1A**), which indicated the mesoporous characteristics of these materials [30]. As shown in **Fig. S1B**, all samples exhibited the most abundant pore structures around 3.8 nm, although the detailed pore size distributions showed slight difference. As shown in **Table 1**, the BET surface area for pristine Al₂O₃ was calculated as 273 m²/g, and the loading of Pt decreased the surface area to 238 m²/g probably due to the blocking of partial small pores. This can be confirmed by the slightly increased average pore size from 3.2 nm for Al₂O₃ to 3.6 nm for Pt/Al₂O₃. Upon the

post-impregnation of WO_3 , the BET surface area ($240 \text{ m}^2/\text{g}$) and average pore size (3.5 nm) barely changed, while the post-impregnation of MgO further decreased the surface area to $202 \text{ m}^2/\text{g}$ and increased the average pore size to 3.8 nm . The pore volumes also followed the same trend as BET surface areas, with Al_2O_3 showing the highest pore volume as $0.33 \text{ cm}^3/\text{g}$, $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ showing the medium pore volume as $0.29 \text{ cm}^3/\text{g}$, and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ showing the lowest pore volume as $0.26 \text{ cm}^3/\text{g}$. It was hypothesized that the impregnated MgO might not only block more small pores from Al_2O_3 but also cover portion of Pt species. This can be further confirmed by the Pt dispersion measurement using CO pulse titration, which indeed showed that $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ possessed lower Pt dispersion (30.1%) than $\text{Pt}/\text{Al}_2\text{O}_3$ (54.0%) and $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ (52.5%). To confirm the Pt dispersion state and the possible Pt tracking with post-impregnated W and Mg species, the HAADF-STEM images and EDS mapping results are shown in **Fig. 2**. As can be clearly seen from the HAADF-STEM images (**Figs. 2-3**), no apparent Pt particles could be observed on $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts, and meanwhile the Pt, W and Mg species were tracking well with Al and O, suggesting a high dispersion of Pt, W and Mg within all catalysts.

To further confirm the Pt dispersion state, aberration-corrected HAADF-STEM images for $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst have been collected. As shown in **Fig. 3e-3h**, the Pt atoms were singly dispersed on Al_2O_3 support within $\text{Pt}/\text{Al}_2\text{O}_3$. *In situ* DRIFTS of CO adsorption at 25°C on $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts was performed, and the results are shown in **Fig. 3i**. It can be clearly seen that, on all catalysts, only one dominant IR peak ascribed to CO linear vibrational mode at 2098 cm^{-1} could be observed [31-33], suggesting that the Pt species within these catalysts were highly dispersed as single atoms. Even after WO_3 and MgO post-impregnation and calcination again, the Pt single atoms were still stably present, although the CO adsorption peak intensity showed some decrease especially for $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ due to the covering of Pt species by MgO . **Fig. 3j** shows the pictures of all samples, in which the

pristine Al_2O_3 support displayed pure white color as usual, while $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts all showed light yellowish color, similar to that was observed by Zhang *et al.* for the 0.2 wt.% Pt single atoms loaded on mesoporous Al_2O_3 [21]. Usually, for $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts containing Pt nanoparticles, the sample color would be much darker such as dark gray or even black, which was not the case at all for the studied catalysts in this work. Above-mentioned results suggest that the Pt species within all catalysts was indeed highly dispersed on η - Al_2O_3 support as single atoms, which can be further verified by the following XAS results for Pt L_{III} -edge.

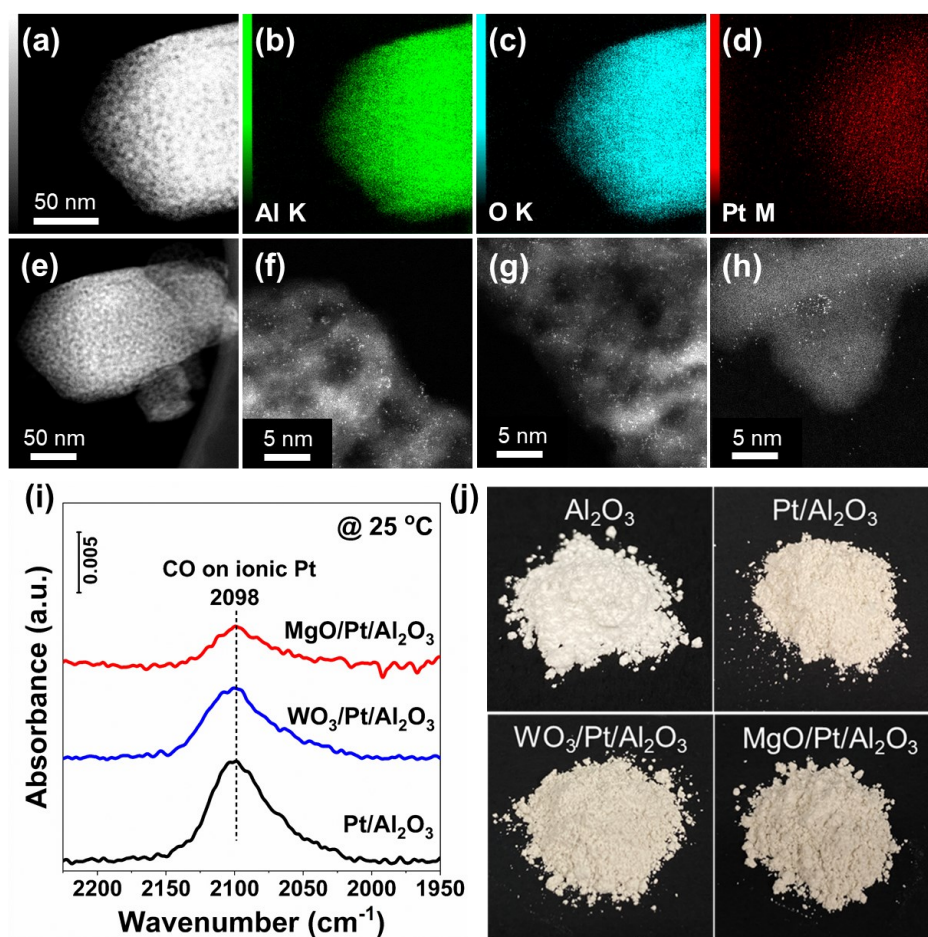


Fig. 3. (a-h) HAADF AC-STEM and EDS mapping results for $\text{Pt}/\text{Al}_2\text{O}_3$; (i) *In situ* DRIFTS of CO adsorption at 25 °C on $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$; and (j) Pictures of pristine Al_2O_3 support, as well as $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts.

Fig. 4A shows the normalized XANES for Pt L_{III} -edge in Pt foil, $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$,

273 and PtO₂ samples. It has to be noted that the XAS for Pt L_{III}-edge in WO₃/Pt/Al₂O₃ catalyst
 274 could not be measured due to the overlap of adsorption edge energy for W L_{II}-edge and Pt L_{III}-
 275 edge. From the white line intensity of normalized XANES for Pt L_{III}-edge, it can be concluded
 276 that the Pt species in Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts was in the highest oxidation state
 277 of Pt⁴⁺, which can also be confirmed by the first-order derivatives of XANES in **Fig. 4B** where
 278 the maximum value of first-order derivatives of Pt L_{III}-edge XANES for Pt/Al₂O₃ and
 279 MgO/Pt/Al₂O₃ catalysts were almost the same as that for PtO₂ reference. For easy comparison,
 280 **Fig. 4C** shows the Fourier transformed k^2 -weighted EXAFS oscillations in R space without
 281 vertical shift for Pt L_{III}-edge in Pt foil, Pt/Al₂O₃, MgO/Pt/Al₂O₃ and PtO₂ samples, and the
 282 corresponding EXAFS curve fitting results are presented in **Fig. S2** and **Table 2**. For Pt/Al₂O₃
 283 and MgO/Pt/Al₂O₃ catalysts, it was first confirmed that no metallic Pt-Pt was present. The first
 284 coordination shell can be ascribed to Pt-O with the bond length at 1.99 Å, slightly shorter than
 285 that in PtO₂ reference (2.02 Å). The second coordination shell can be ascribed to Pt-O-Al in
 286 Pt/Al₂O₃ at 3.20 Å and Pt-O-Al/Mg at 3.21 Å, both being longer than that of Pt-O-Pt in PtO₂
 287 reference (3.07 Å). Since Mg and Al are elements close to each other, it is very difficult to
 288 discern the two during the EXAFS curve fitting. However, the possible strong interaction
 289 between Pt and MgO can be verified by the coordination number of Pt-O-Al/Mg (6.0) in
 290 MgO/Pt/Al₂O₃, which was higher than that of Pt-O-Al (5.0) in Pt/Al₂O₃.

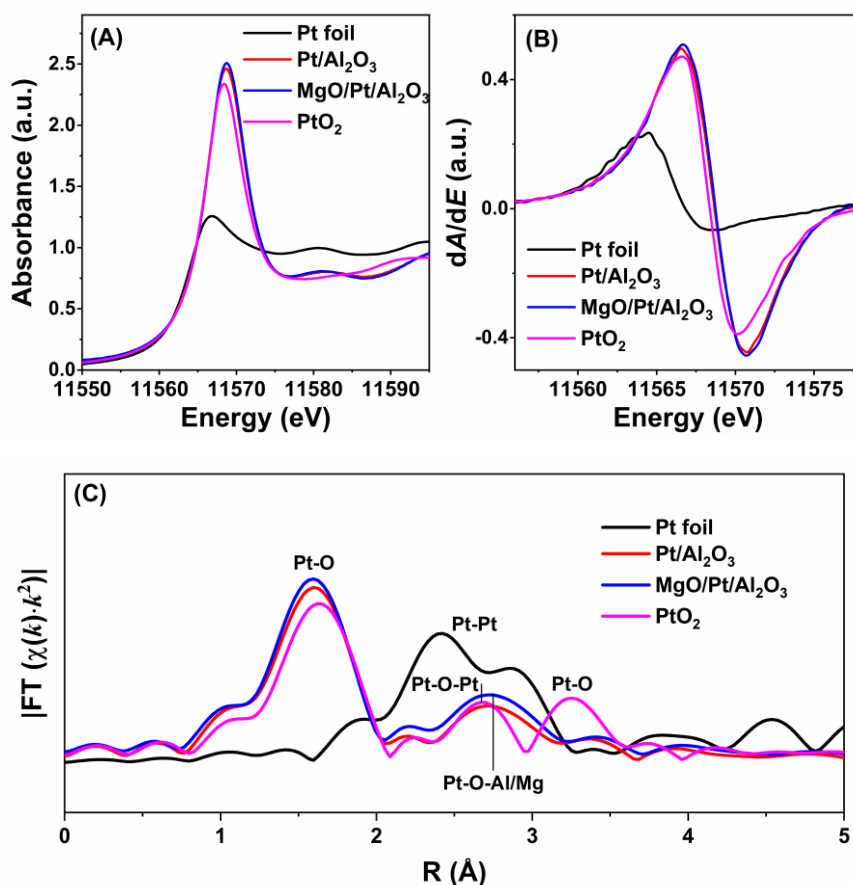


Fig. 4. (A) Normalized XANES, (B) first-order derivatives of XANES and (C) Fourier transformed k^2 -weighted EXAFS oscillations in R space for Pt L_{III}-edge in Pt foil, Pt/Al₂O₃, MgO/Pt/Al₂O₃ and PtO₂ samples.

Table 2. Pt L_{III}-edge EXAFS fitting parameters for Pt-based catalysts and Pt foil, PtO₂ references (k range = 3.0-11.0 $\text{\AA}^{-1}$ for Fourier transform)

Sample	Shell	CN	R ($\text{\AA}$)	ΔE_0 (eV)	σ^2 ($10^{-3} \text{\AA}^2$)	R factor
Pt foil	Pt-Pt	12.0 ± 0.9	2.76 ± 0.01	7.3 ± 0.6	4.12 ± 0.54	0.006
	Pt-O	6.0 ± 0.8	2.02 ± 0.01	10.7 ± 1.3	1.12 ± 1.54	
PtO ₂	Pt-O-Pt	6.0 ± 0.8	3.07 ± 0.04	6.2 ± 5.5	5.18 ± 2.17	0.012
	Pt-O	12.0 ± 1.5	3.71 ± 0.05	13.6 ± 2.5	6.33 ± 4.48	
Pt/Al ₂ O ₃	Pt-O	6.3 ± 1.1	1.99 ± 0.01	10.7 ± 1.3	0.47 ± 1.81	0.021
	Pt-O-Al	5.0 ± 2.4	3.20 ± 0.05	14.9 ± 5.5	0.94 ± 3.62	
MgO/Pt/Al ₂ O ₃	Pt-O	6.6 ± 0.9	1.99 ± 0.01	10.7 ± 1.3	0.65 ± 1.53	0.019
	Pt-O-Al/Mg	6.0 ± 1.4	3.21 ± 0.02	14.9 ± 5.5	0.94 ± 3.62	

Although the valence state and local coordination structure of Pt species in WO₃/Pt/Al₂O₃ could not be determined by Pt L_{III}-edge XAS, the information of W species in this catalyst could actually be obtained using W L_{III}-edge XAS. **Fig. 5A** shows the normalized XANES for W L_{III}-edge in W foil, WO₃/Pt/Al₂O₃ and WO₃, which suggested that the W species in WO₃/Pt/Al₂O₃ catalyst possessed the oxidation state very close to that in WO₃. From the first-order derivatives of W L_{III}-edge XANES in **Fig. 5B**, the W species in WO₃/Pt/Al₂O₃ catalyst (with absorption edge energy at 10208.9 eV) showed slightly lower oxidation state than that in pure WO₃ (with absorption edge energy at 10209.2 eV). Furthermore, **Fig. 5C** shows the second-order derivatives of W L_{III}-edge XANES to better discern the two split peak positions in the white line. Accordingly, the gap energy between the two subpeaks at higher and lower energy positions could be determined, which was measured as 4.0 eV for WO₃ reference and 3.4 eV for WO₃/Pt/Al₂O₃ catalyst. It was reported that such gap energy between the two subpeaks for W L_{III}-edge XANES would decrease if the local coordination structure of W species changing from octahedron -WO₆ to tetrahedron -WO₄ [34]. Therefore, it can be concluded that, due to the high dispersion of W species within WO₃/Pt/Al₂O₃ catalyst (judged from XRD results), a portion of W species was present as tetrahedron -WO₄ besides of octahedron -WO₆ thus leading to rich defective W^{(6-δ)+}O_x sites with the average valence state lower than W⁶⁺O_x in pure WO₃. This can be verified by the W L_{III}-edge EXAFS results in R space (**Fig. 5D**) and the corresponding curve fitting results (**Fig. S3** and **Table S1**). For WO₃ reference, the first W-O shell possessed the coordination number as 6.0, with the W-O multiple scattering peak and the W-O-W coordination shell clearly showing up. However, for WO₃/Pt/Al₂O₃ catalyst, the W-O shell possessed the coordination number as 5.1, and no clear W-O multiple scattering peak and W-O-W coordination shell could be observed. This further confirmed that the WO_x species within WO₃/Pt/Al₂O₃ catalyst was indeed highly dispersed with rich defects, which was probably beneficial for reactant adsorption and activation during

certain catalysis reactions.

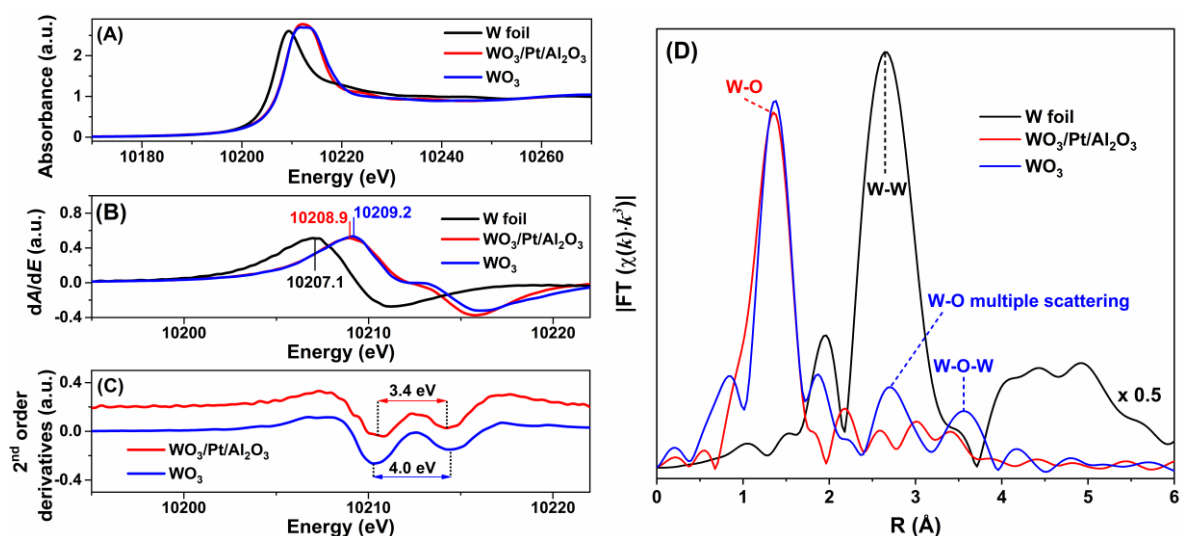


Fig. 5. (A) Normalized XANES, (B) first-order derivatives of XANES, (C) second-order derivatives of XANES, and (D) Fourier transformed k^3 -weighted EXAFS oscillations in R space for W L_{III}-edge in W foil, WO₃/Pt/Al₂O₃ and WO₃ samples.

3.2. Surface acidity characterization

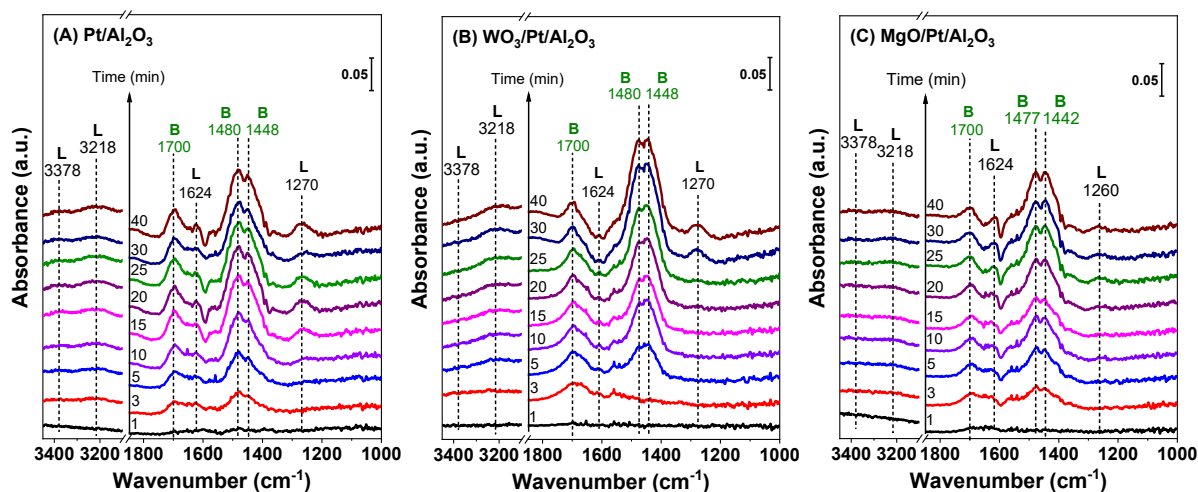


Fig. 6. *In situ* DRIFTS of NH₃ adsorption at 50 °C on Pt/Al₂O₃, WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts.

In order to characterize the surface acidity of different catalysts, *in situ* DRIFTS of NH₃ adsorption at 50 °C on Pt/Al₂O₃, WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ were performed, followed

by NH_3 desorption at elevated temperatures. As shown in **Fig. 6**, upon the introduction of NH_3 at 50 °C, the NH_3 adsorbed species bound to Lewis acid sites (1270/1260, 1624, 3218, and 3378 cm^{-1}) and NH_4^+ adsorbed species bound to Brønsted acid sites (1442/1448, 1477/1480, and 1700 cm^{-1}) both showed monotonic increase as a function of time and reached steady state after 30 min [35-37]. It is obvious that the intensity of the peaks at 1448 and 1480 cm^{-1} on $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ ascribed to NH_4^+ on Brønsted acid sites were much higher than those on $\text{Pt}/\text{Al}_2\text{O}_3$, indicating the improved surface acidity of catalyst by WO_3 addition. In contrast, both the NH_3 species bound to Lewis acid sites and NH_4^+ species bound to Brønsted acid sites on $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ showed some peak intensity decrease comparing to those on $\text{Pt}/\text{Al}_2\text{O}_3$, indicating that the basic MgO addition indeed decreased the surface acidity of catalyst to a certain extent. The *in situ* DRIFTS of NH_3 desorption at different temperatures (**Fig. S4**) also confirmed that the surface acid strength of the studied catalysts followed such sequence: $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3 > \text{Pt}/\text{Al}_2\text{O}_3 > \text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$.

3.3. Catalyst reducibility characterization

To study the reducibility of Pt species, H_2 -TPR profiles were measured for Al_2O_3 support, $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts. As shown in **Fig. 7**, the pure Al_2O_3 support did not have obvious H_2 consumption up to 500 °C. For all Pt containing catalysts, three H_2 consumption bands showed up, at *ca.* 94-110, 214-223, and 390-460 °C. According to literature [38, 39], the first peak was attributed to the reduction of adsorbed surface oxygen species, and the second one and third one were assigned to the reduction of PtO_x species weakly and strongly interacting with Al_2O_3 support. As verified above, Pt was present as single atoms within the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst, therefore the reduction peaks for PtO_x species in this work can be actually assigned to the reduction of Pt-O-Al species specifically. Different from the intense reduction of weakly interacted PtO_x species from Pt particles loaded on Al_2O_3 as reported elsewhere [38, 39], much more intense reduction peak for PtO_x species strongly interacting

with Al_2O_3 support was observed on the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst in this work, which was mainly due to the atomic dispersion of Pt species on $\eta\text{-Al}_2\text{O}_3$ to form Pt-O-Al bonds. After modification by WO_3 and MgO , the first and second reduction peaks for $\text{Pt}/\text{Al}_2\text{O}_3$ slightly shifted to higher temperatures, possibly indicating some enhanced interaction between Pt and Al_2O_3 upon the WO_3 or MgO addition. In addition, with the continuous reduction of Pt-O in Pt-O-Al/Mg/W bonds, broad reduction peaks showed up for all catalysts. By quantitatively analyzing the reduction peaks in H_2 -TPR profiles, the H_2 consumption for different species was calculated and the results are shown in **Table S2**. The H_2 consumption on $\text{Pt}/\text{Al}_2\text{O}_3$ ($122.3 \mu\text{mol/g}$) was greatly increased after WO_3 addition ($167.3 \mu\text{mol/g}$), while it was decreased after MgO modification ($70.1 \mu\text{mol/g}$). Different interactions between Pt and WO_3 or MgO should be present, resulting in the different reducibility of Pt species.

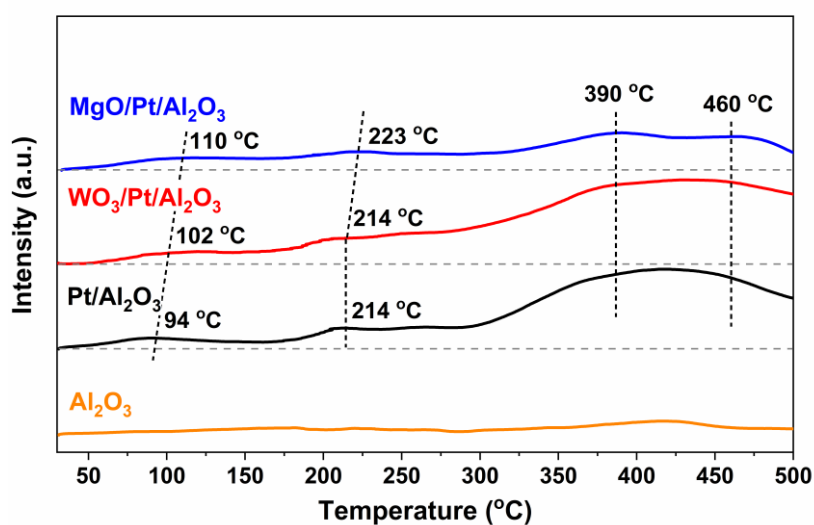


Fig. 7. H_2 -TPR profiles of Al_2O_3 support, $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts.

3.4. Surface property characterization

Surface species and surface element compositions on different catalysts were determined by XPS technique. **Fig. 8** illustrates the Pt 4d and O 1s XPS spectra, and the surface element compositions and $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$ ratio are summarized in **Table S3**. As expected, with the loading of

WO₃ and MgO onto Pt/Al₂O₃, both surface Al and Pt concentrations decreased to a certain extent due to the covering of Pt/Al₂O₃ surface, particularly after MgO loading. The trend of surface Pt concentration was in consistence with Pt dispersion on all catalysts measured by CO pulse titration. It can be clearly seen from **Fig. 8A** that only Pt⁴⁺ species were present in Pt/Al₂O₃ and WO₃/Pt/Al₂O₃ catalysts [40]. It should be noted that it was not possible to discern the Pt species in MgO/Pt/Al₂O₃ catalyst due to the overlap of Pt 4f/4d with Mg_{Auger} and Al 2p signals. As for the O 1s XPS (**Fig. 8B**), the asymmetrical O 1s spectrum for each catalyst could be deconvoluted into two components, with the surface lattice oxygen (O_{latt}) species at BE = 530.9 eV and the surface adsorbed oxygen (O_{ads}) species at BE = 532.5 eV [41, 42]. As shown in **Table S3**, the surface O_{ads}/O_{latt} molar ratio decreased in the order of WO₃/Pt/Al₂O₃ (0.77) > MgO/Pt/Al₂O₃ (0.32) > Pt/Al₂O₃ (0.17). A higher concentration of O_{ads} species could be related to a higher density of surface oxygen vacancy (O_{vac}) on a particular catalyst. Since WO₃ and MgO were highly dispersed once loaded onto Pt/Al₂O₃, it was reasonable that higher concentration of O_{vac} could be formed on WO₃ and MgO modified catalysts thus possibly leading to the formation of more O_{ads} species especially the acidic hydroxyls on WO₃/Pt/Al₂O₃ and basic hydroxyls on MgO/Pt/Al₂O₃.

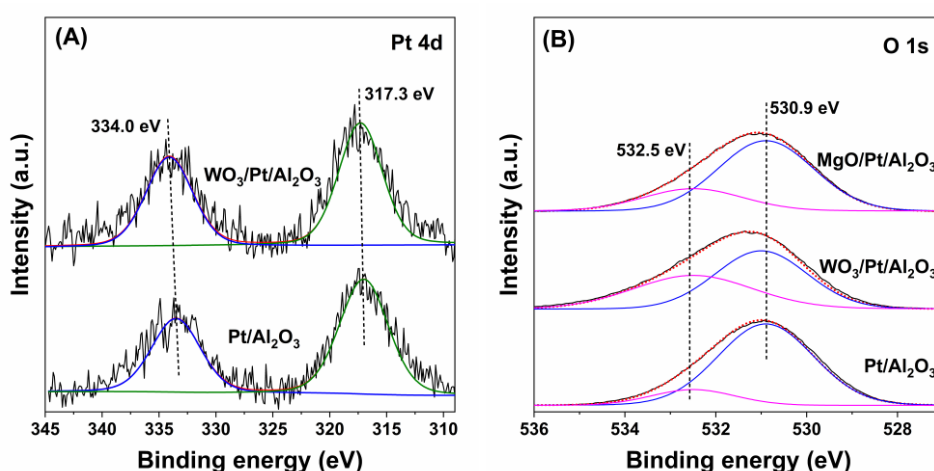


Fig. 8. (A) Pt 4d XPS and (B) O 1s XPS for Pt/Al₂O₃, WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts.

3.5. Catalytic performance for CO oxidation

To evaluate the catalytic performance of different catalysts, the supports including Al₂O₃, and WO₃, MgO modified Al₂O₃ were first tested for CO oxidation (**Fig. S5**). For the supports without Pt, their catalytic CO oxidation performance was very poor as expected, following such sequence: WO₃/Al₂O₃ > MgO/Al₂O₃ > Al₂O₃. Upon 1% Pt loading, the CO oxidation performance showed significant enhancement, with the T₅₀ (the temperature at which the CO conversion reaching 50%) decreased by *ca.* 150 °C. However, as shown in **Fig. 9**, for the CO oxidation in dry condition, the WO₃ and MgO modification for Pt/Al₂O₃ catalyst showed some negative effect on CO oxidation performance, possibly due to the covering of partial Pt sites during the post-impregnation procedure. Yet, it is interesting to see that the introduction of 5% H₂O into the CO oxidation reaction stream showed positive effect on improving the catalytic performance, and the H₂O promotion effect was much more significant on MgO/Pt/Al₂O₃ catalyst than that on Pt/Al₂O₃ and WO₃/Pt/Al₂O₃ catalysts. In most practical applications involving CO oxidation such as the diesel oxidation catalysts and three-way catalysts for vehicle emission control, the reaction conditions always contain H₂O, and using basic metal oxides such as MgO to modify the Pt based catalysts should be an effective way to enhance the CO oxidation performance. The promotion effect of MgO addition on Pt/Al₂O₃ catalyst for CO oxidation can be well explained using the *in situ* DRIFTS results as described below. To check the stability of Pt single atoms after CO oxidation at 300 °C, *in situ* DRIFTS of CO adsorption on the spent Pt/Al₂O₃ catalyst was collected at 25 °C and shown in **Fig. S6A**. Other than a dominant peak at 2098 cm⁻¹ for CO adsorption on Pt single atoms, a shoulder peak at 2050 cm⁻¹ due to the CO adsorption on Pt clusters also showed up on the spent catalyst, suggesting that a portion of Pt single atoms had transformed into Pt clusters during the CO oxidation reaction.

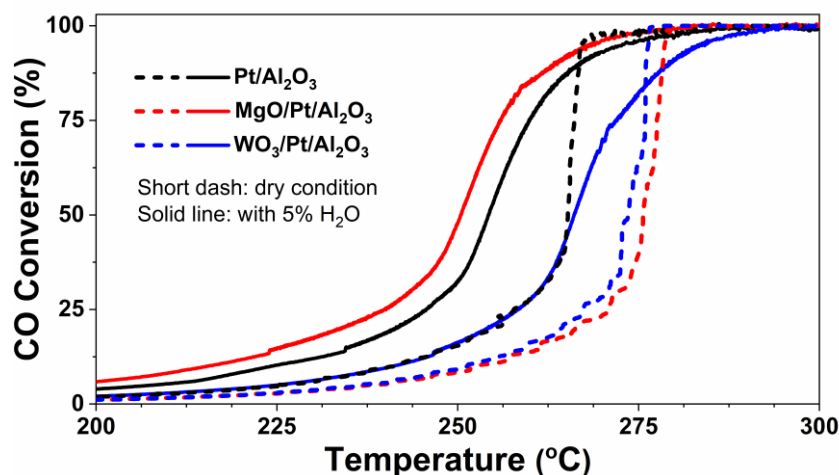


Fig. 9. CO oxidation activity on Pt/Al₂O₃, WO₃/Pt/Al₂O₃, MgO/Pt/Al₂O₃ catalysts without and with the presence of H₂O in the reaction stream. Conditions: [CO] = [O₂] = 1%, 5% H₂O if used, balanced with Ar, WHSV of 200,000 mL·g_{cat}⁻¹·h⁻¹, temperature ramp of 2 °C/min from 200 to 300 °C.

3.6. *In situ* DRIFTS study for CO oxidation

In situ DRIFTS experiments of CO oxidation under conditions without and with H₂O were performed at 200 °C on all catalysts. It can be observed from **Figs. S7** and **10** that adsorbates appeared on all the catalysts after the exposure to reaction flow. For CO oxidation on Pt/Al₂O₃ under dry condition (**Fig. S7A**), the appearance of bands at 2172 and 2067 cm⁻¹ was due to the gas phase CO and CO adsorbed on Pt sites [13, 14], and bands at 1655 and 1440 cm⁻¹ were attributed to the surface bicarbonate species on Al₂O₃ support [43], where the bicarbonate came from the CO₂ produced in CO oxidation. Comparing to Pt/Al₂O₃, less adsorbed CO and bicarbonate species were observed on WO₃/Pt/Al₂O₃ under dry CO oxidation condition (**Fig. S7B**) due to a less exposure of Pt and Al₂O₃ and the enhanced surface acidity as well. As depicted in **Fig. S7C**, on MgO/Pt/Al₂O₃, less CO species adsorbed on Pt sites was also observed comparing to that on Pt/Al₂O₃. However, more bicarbonate species was present on MgO/Pt/Al₂O₃ probably due to the enhanced surface basicity, also with a new band at 1590 cm⁻¹ corresponding to formate species showing up [44]. As shown in **Fig. S8**, after cutting off

CO (in dry condition), the CO adsorbed species on Pt sites disappeared rapidly, and the adsorbed carbonates could partially desorb from the catalysts. It should be noted that there was still a large amount of residual carbonates on the catalysts even after flowing O₂ for 40 min especially on MgO/Pt/Al₂O₃, which might block the Pt active sites from efficient catalytic cycling. Comparing to CO oxidation under dry condition, as shown in **Fig. 10**, clear bands at 2352 cm⁻¹ due to adsorbed CO₂ appeared on all the catalysts with the presence of H₂O in reaction stream at the same temperature (200 °C), indicating an improved catalytic activity for CO oxidation to CO₂ by H₂O. This agreed well with the CO oxidation results in **Fig. 9**. Interestingly, instead of abundant surface bicarbonate species, very little formate species (1592 and 1377 cm⁻¹) on Pt/Al₂O₃ (**Fig. 10A**) and almost no species on WO₃/Pt/Al₂O₃ (**Fig. 10B**) were observed under the testing condition with H₂O. In other words, the addition of H₂O inhibited the formation of bicarbonates on these two catalysts, which could help the cycling of Pt sites during CO oxidation. Different from Pt/Al₂O₃ and WO₃/Pt/Al₂O₃, both bicarbonates and formate species were largely present on MgO/Pt/Al₂O₃ due to its basic nature (**Fig. 10C**). However, the carbonate species desorbed quickly on MgO/Pt/Al₂O₃ once the CO was cut off (**Fig. S9**). This result suggests that the introduced H₂O promoted the desorption of formed carbonate species and possibly formed reactive hydroxyls as well, thus facilitating the CO oxidation cycle significantly on the MgO/Pt/Al₂O₃ catalyst. It has been reported that OH species not only can participate as a reactant for CO oxidation but also can act as a promoter when they are located at/or nearby Pt sites,[32] with which the CO oxidation can follow H₂O-mediated Langmuir-Hinshelwood mechanism.[45] Due to the basic nature of MgO, abundant reactive hydroxyls could be formed on MgO/Pt/Al₂O₃ surface with which the CO oxidation activity could be largely enhanced due to the improved O₂ activation in the presence of H₂O, even though the *in situ* formed bicarbonates and formate species might block some Pt sites.

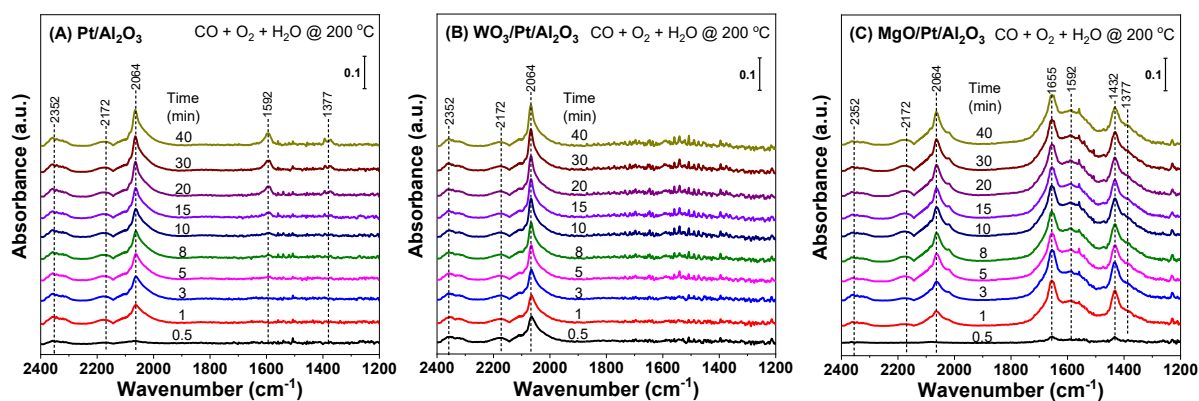


Figure 10. *In situ* DRIFTS of CO oxidation as a function of exposure time to CO + O₂ + H₂O flow at 200 °C on the samples.

3.7. Catalytic performance for methanol decomposition

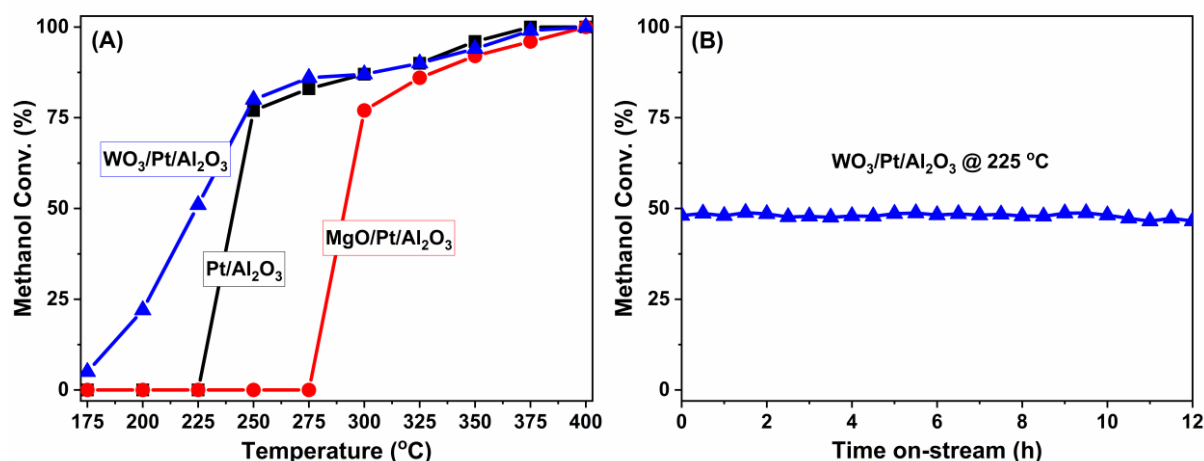


Fig. 11. (A) Methanol decomposition activity on Pt/Al₂O₃, WO₃/Pt/Al₂O₃, and MgO/Pt/Al₂O₃; (B) Catalytic stability of WO₃/Pt/Al₂O₃ catalyst for methanol decomposition at 225 °C. Conditions: 10% CH₃OH, balanced with Ar, WHSV = 50,000 mL·g_{cat}⁻¹·h⁻¹.

As an efficient hydrogen carrier, methanol is relatively inexpensive and can be manufactured from a variety of sources [10, 46]. Looking for highly effective catalysts for methanol decomposition to release H₂ quickly is of significant importance. Therefore, the Pt/Al₂O₃, WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts were also tested for methanol direct decomposition reaction. As shown in **Fig. 11A**, WO₃/Pt/Al₂O₃ catalyst showed much higher methanol

decomposition activity than Pt/Al₂O₃ catalyst below 250 °C, while the MgO/Pt/Al₂O₃ catalyst showed much lower methanol decomposition activity than Pt/Al₂O₃ catalyst (with the T₅₀ of methanol conversion shifted *ca.* 50 °C to higher temperature range). It is obvious that the addition of acidic WO₃ significantly improved the catalytic performance of Pt/Al₂O₃ catalyst for methanol decomposition, and such excellent methanol decomposition activity on WO₃/Pt/Al₂O₃ catalyst could be well maintained during the long-term catalytic stability testing at 225 °C (**Fig. 11B**). To reveal the stability of Pt single atoms during long-term methanol decomposition at 225 °C for 12 h, *in situ* DRIFTS of CO adsorption on the spent WO₃/Pt/Al₂O₃ catalyst was conducted at 25 °C. As shown in **Fig. S6B**, a shoulder peak for CO adsorption on Pt clusters was observed on the spent catalyst, implying that a portion of Pt single atoms were transformed into Pt clusters probably due to the *in situ* reduction by the produced H₂ in methanol decomposition. It was reported that Pt single-atoms were more active in methanol decomposition than Pt clusters.[10] Based on the undetectable decline of methanol decomposition activity in the long-term testing, there should be only a very small portion of Pt single-atoms converted into clusters during this process. To understand the intrinsic mechanisms of promotion effect from WO₃ and inhibition effect from MgO on Pt/Al₂O₃ catalyst for methanol decomposition, systematic *in situ* DRIFTS of methanol decomposition and desorption was performed as described below in detail.

3.8. *In situ* DRIFTS study for methanol decomposition

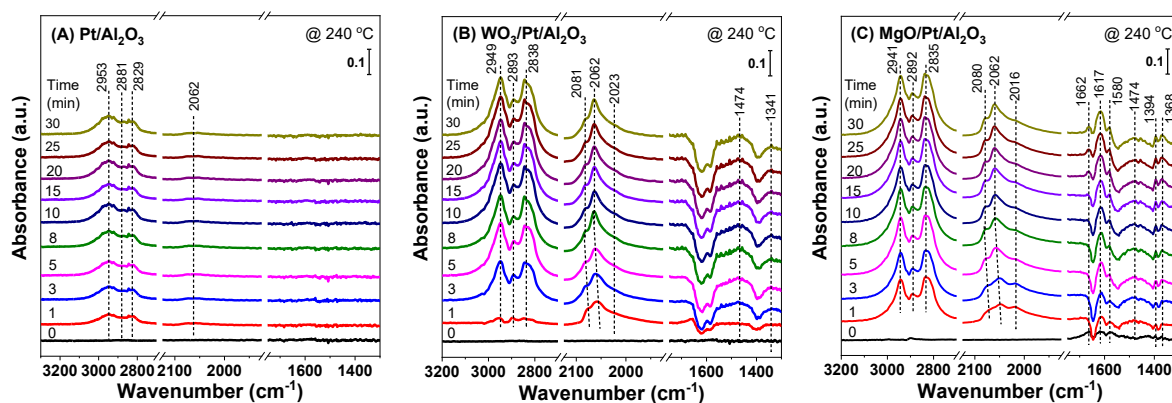


Fig. 12. *In situ* DRIFTS of methanol decomposition at 240 °C on Pt/Al₂O₃, WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts.

In situ DRIFTS of methanol decomposition at 240 °C over the catalysts are shown in **Fig. 12**. As shown in **Fig. 12A**, once exposure to methanol, the bands at 2828-2949 cm⁻¹ attributed to the C-H vibration of methoxy group and the bands at 2062 cm⁻¹ assigned to CO linearly adsorbed on Pt sites appeared immediately on Pt/Al₂O₃ [47]. After modification by WO₃ and MgO, the adsorption of methoxy group and CO species showed obvious increase. As indicated by O 1s XPS results, WO₃ and MgO modified Pt/Al₂O₃ catalysts possessed more O_{vac} than Pt/Al₂O₃, which could be considered responsible for the higher adsorption of methanol and *in situ* formed CO species on them. In addition, different from that on Pt/Al₂O₃, the bands at 1474 and 1341/1368 cm⁻¹ ascribed to C-O vibration within methoxy group was observed on both WO₃/Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts probably due to the intense adsorption of methanol (**Fig. 12A and 12B**). Comparing to Pt/Al₂O₃ and WO₃/Pt/Al₂O₃, the peaks at 1662, 1617, 1580 and 1394 cm⁻¹ showed up on MgO/Pt/Al₂O₃ due to the OCO stretching mode of carbonate species formed during methanol decomposition [47]. Once cutting off the methanol, as depicted in **Fig. 13**, the adsorbed methoxy group decreased, but the adsorbed CO species remained over all the catalysts. Similar to the situation for CO oxidation under dry condition, the formed carbonate species on MgO/Pt/Al₂O₃ was quite stable even after Ar purge at 240 °C for 30 min. As discussed above, the stable and strongly adsorbed carbonate species could block the active Pt sites on MgO/Pt/Al₂O₃ once the CO₂ was generated from CO oxidation, thus resulting in the low catalytic activity. Similarly, the poisoning of Pt sites by the *in situ* formed carbonate species in methanol decomposition would also lead to the low activity of MgO/Pt/Al₂O₃ catalyst. In short summary, comparing to Pt/Al₂O₃ and MgO/Pt/Al₂O₃ catalysts, the abundant O_{vac} for methanol adsorption, rich Pt active sites with high Pt dispersion, as well as more acidic catalyst surface for high carbonate resistance simultaneously contributed to the

superior methanol decomposition activity on $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ catalyst.

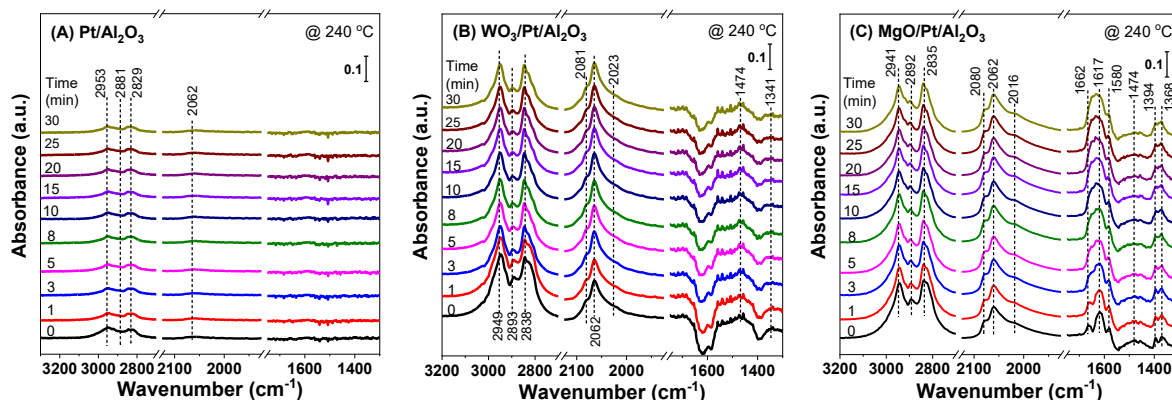


Fig. 13. *In situ* DRIFTS of methanol desorption at 240 °C for $\text{Pt}/\text{Al}_2\text{O}_3$, $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts.

4. Conclusion

$\text{Pt}/\text{Al}_2\text{O}_3$ single atom catalyst was successfully prepared using bayerite $\text{Al}(\text{OH})_3$ as support through simple IWI method for Pt loading. With surface acidity modification on $\text{Pt}/\text{Al}_2\text{O}_3$ by highly dispersed WO_3 and MgO , different catalytic behaviors were achieved on the catalysts in CO oxidation and methanol decomposition. Significant positive effect of H_2O on CO oxidation was observed on the $\text{Pt}/\text{Al}_2\text{O}_3$ based catalysts, particularly on the basic MgO modified $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$ catalyst which performed the best CO oxidation activity under reaction condition with H_2O . With acidic WO_3 modification, the $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ catalyst exhibited the best methanol decomposition activity among all the studied catalysts. By detailed *in situ* DRIFTS study, it was concluded that the positive H_2O effect on CO oxidation activity was attributed to the inhibition of bicarbonate species formation on $\text{Pt}/\text{Al}_2\text{O}_3$ and $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ catalysts and promoted carbonate desorption from $\text{MgO}/\text{Pt}/\text{Al}_2\text{O}_3$. The superior methanol decomposition activity on $\text{WO}_3/\text{Pt}/\text{Al}_2\text{O}_3$ was closely associated with its abundant oxygen vacancies and high resistance to carbonate accumulation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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