

## Alkali-Promoted Pt/TiO<sub>2</sub> Opens a New Pathway to Formaldehyde Oxidation at Ambient Temperatures

Catalytic oxidation of formaldehyde (HCHO) to CO<sub>2</sub> under ambient conditions is of great interest for indoor HCHO purification. Pt/TiO<sub>2</sub> catalysts have low activity and stability for the total oxidation of HCHO at room temperature. Here, we report that the addition of alkali ions significantly promotes the activity of Pt/TiO<sub>2</sub> catalysts for the HCHO oxidation reaction by inducing an atomically dispersed Pt-O(OH)x-alkali species and opening a new low-temperature reaction pathway. Accordingly, the atomically dispersed Pt-O(OH)x-alkali species could effectively activate H<sub>2</sub>O and then catalyze a simple reaction between surface OH and formate species to total oxidation products.

Figure 1 shows the conversion of HCHO to CO<sub>2</sub> as a function of temperature over 1% Pt/TiO<sub>2</sub> and 2% Na-1% Pt/TiO<sub>2</sub> samples at a GHSV of 120,000 h<sup>-1</sup> and HCHO inlet of 600 ppm. All gas streams were humidified to around RH = 50%. Before each activity test, the samples were reduced in H<sub>2</sub> at 300°C for 30 min. The Na-free catalyst had low activity for the HCHO oxidation reaction, with HCHO conversion being only ca. 19% at 15°C. The addition of alkali ions significantly promoted the activity of Pt/TiO<sub>2</sub>, and 100% HCHO conversion to

CO<sub>2</sub> and H<sub>2</sub>O was measured over 2% Na-1% Pt/TiO<sub>2</sub> at 15°C. The 2% Na-promoted sample also had excellent stability as confirmed by long isothermal tests. At a GHSV of 300,000 h<sup>-1</sup> and with other reaction conditions being the same, approximately 80% HCHO conversion was maintained over a 72 h-long test, as shown in Fig. 1 (inset). Li and K were equally effective promoters as Na and imparted the same high activity and stability to the Pt species.

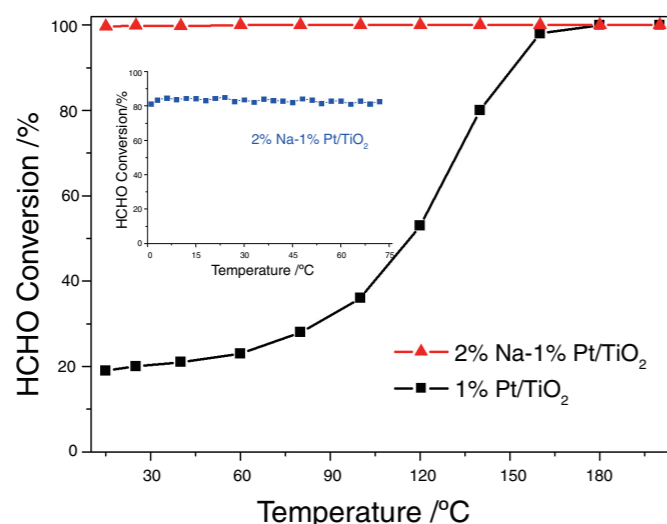


Figure 1: HCHO conversion over 1% Pt/TiO<sub>2</sub> and 2% Na-1% Pt/TiO<sub>2</sub> catalysts as a function of temperature. Reaction conditions: HCHO 600 ppm, O<sub>2</sub> 20 vol.%, RH: ~50%, He balance, total flow rate of 50 cm<sup>3</sup> min<sup>-1</sup>, and GHSV 120,000 h<sup>-1</sup> (inset: stability test of 2% Na-1% Pt/TiO<sub>2</sub> at 25°C, GHSV 300,000 h<sup>-1</sup> with other reaction conditions being the same).

Table 1: Fitting parameters of the curve-fitted  $k^3$ -weighted EXAFS analysis of 1% Pt/TiO<sub>2</sub> and 2% Na-1% Pt/TiO<sub>2</sub> catalysts

Samples	Shell	CN	R(Å) (±0.01)	DW(Å)	R factor
Pt-foil	Pt-Pt	12.0±2.3	2.77	0.77±0.010	0.8
PtO <sub>2</sub>	Pt-O	6.0±1.2	2.02	0.061±0.020	3.0
	Pt-O-Pt	4.0±1.0	3.14	0.061±0.012	
1 Pt/TiO <sub>2</sub> <sup>a</sup>	Pt-O	3.7±1.2	2.02	0.061±0.020	0.6
	Pt-Cl	2.3±1.0	2.30	0.051±0.057	
2 Na-1Pt <sup>a</sup>	Pt-O	5.4±1.2	2.02	0.061±0.020	8.7
1 Pt-TiO <sub>2</sub> <sup>b</sup>	Pt-Pt	5.6±1.2	2.77	0.097±0.010	1.3
2 Na-1Pt <sup>b</sup>	Pt-Pt	2.4±0.5	2.77	0.097±0.010	7.2
1 Pt/TiO <sub>2</sub> <sup>c</sup>	Pt-Pt	4.7±1.0	2.77	0.097±0.010	0.4
	Pt-Cl	0.6±0.2	2.30	0.051±0.057	
2 Na-1Pt <sup>c</sup>	Pt-O	2.8±0.6	2.02	0.092±0.010	9.8

a: Samples calcined in static air, 400°C, 2 h; b: Samples after *in situ* H<sub>2</sub> reduction in 10% H<sub>2</sub>/Ar at 300°C for 30 min; c: Samples exposed to ambient air after H<sub>2</sub> reduction.

XAFS measurements were conducted to study the structure of samples before/after Na addition and after H<sub>2</sub> reduction under atmospheric pressure. Fitting parameters of the curve-fitted  $k^3$ -weighted EXAFS analysis of 1% Pt/TiO<sub>2</sub> and 2% Na-1% Pt/TiO<sub>2</sub> catalysts are given in Table 1. Prior to H<sub>2</sub> reduction, all Pt was coordinated with O or Cl, and the Pt-Pt coordination was zero on all catalysts. After *in situ* H<sub>2</sub> reduction at 300°C, all Pt species were reduced to the metallic phase, yet the Pt-Pt coordination number was clearly lowered with 2% Na addition. Once the pre-reduced catalysts were exposed to air, as in realistic operation for HCHO oxidation, surface structures were changed due to oxygen adsorption [1]. The Na-free Pt/TiO<sub>2</sub> sample showed a Pt-Pt coordination shell as in Pt metal and a small residual Pt-Cl coordination shell. With 2% Na added, only a Pt-O shell was detected, indicating that 2% Na addition can completely suppress the formation of Pt-Pt bonds in the presence of O<sub>2</sub> and induce atomically dispersed Pt-O species on the TiO<sub>2</sub> surface.

The atomically dispersed Pt-O(OH)x-Na species induced by Na addition could easily activate H<sub>2</sub>O and then open a new pathway for HCHO oxidation under

ambient conditions. The HCHO oxidation reaction on Na-free samples follows the formate (HCOO<sup>-</sup>) decomposition route (HCHO → HCOO<sup>-</sup> → CO → CO<sub>2</sub>), with formate decomposing into CO being the rate determining step [2]. In contrast, the HCHO oxidation over the Na-promoted Pt/TiO<sub>2</sub> catalyst follows a simple pathway with reaction between surface OH and formate species to total oxidation products (HCHO → HCOO + OH → H<sub>2</sub>O + CO<sub>2</sub>), thus greatly enhancing the HCHO oxidation activity.

### REFERENCES

- [1] C. Zhang, F. Liu, Y. Zhai, H. Ariga, N. Yi, Y. Liu, K. Asakura, M. F.-Stephanopoulos and H. He, *Angew. Chem. Int. Ed.* **51**, 9628 (2012).
- [2] C. Zhang, H. He and K. Tanaka, *Appl. Catal. B* **65**, 37 (2006).

### BEAMLINES

BL-12C and BL-7C

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