

# Catalytic oxidation of propene over Pd catalysts supported on CeO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and M/Al<sub>2</sub>O<sub>3</sub> oxides (M=Ce, Ti, Fe, Mn)

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## Introduction

Propene is among the most investigated probe molecules in the field of VOC catalytic oxidation, because of its high photochemical ozone creativity potential (POCP) [1]. Supported noble metals (Pt, Pd, Au) show high activity for VOC oxidation, although their use is limited because of the high price and deactivation due to sintering of the active phase and poisoning effects [2]. It is well-known that the support nature plays an important role in improving the activity and durability of supported noble metals. For Pd supported catalysts the oxidation activity strongly depends on the acid-base properties of the support [3,4] as well as on the metal-support interaction [5]. In the present study, the catalytic oxidation of propene was investigated over Pd catalysts supported over CeO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and M/Al<sub>2</sub>O<sub>3</sub> oxides (M=Ce, Ti, Fe, Mn). The propene oxidation activity of a conventional Pt/Al<sub>2</sub>O<sub>3</sub>, as reference, was also reported.

## Materials and Methods

Commercial oxides, CeO<sub>2</sub> (Aldrich), TiO<sub>2</sub> (Eurotitania) and Al<sub>2</sub>O<sub>3</sub> (Aldrich) were used as supports. Doped alumina oxides, M(5mol%)/Al<sub>2</sub>O<sub>3</sub>(95mol%), were prepared by wet impregnation with corresponding metal (Ce, Fe, Mn) nitrates or by grafting with Ti(iso-OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> in toluene solution and calcination at 500 °C for 3 h. Pd (0.8 wt%) and Pt (0.6 wt%) catalysts were prepared by impregnation method with Pd(NO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub> precursor, respectively. Then, the obtained powders were calcined at 400 °C for 4h. Characterizations by surface area measurements (BET method), X-ray diffraction (XRD), temperature programmed reduction/oxidation (TPR/TPO) and transmission electron microscopy (TEM) analyses were carried out. The activity tests were carried out in a tubular fixed-bed reactor under the reactive gas mixture containing 1000 ppm of C<sub>3</sub>H<sub>6</sub> and 9% O<sub>2</sub> in He at GHSV of 35,000 h<sup>-1</sup>.

## Results and Discussion

In Fig. 1, TPR curves of selected catalysts, Pd/CeO<sub>2</sub>, Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>, are displayed. Peaks corresponding to different types of PdO species were observed at different temperatures depending on the support. Very small PdO particles were detected over TiO<sub>2</sub>. A second peak appearing at 8 °C, also observed for Pd/Al<sub>2</sub>O<sub>3</sub>, was attributed to the reduction of bulky PdO particles [6]. For both catalysts, Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>, decomposition of β-hydride species takes place at 60 °C. Over CeO<sub>2</sub>, that is known to stabilize PdO, reduction occurred at higher temperature (25 °C). Moreover, a second peak, at 50 °C, ascribed to the reduction of ceria surface in contact with palladium was also observed.

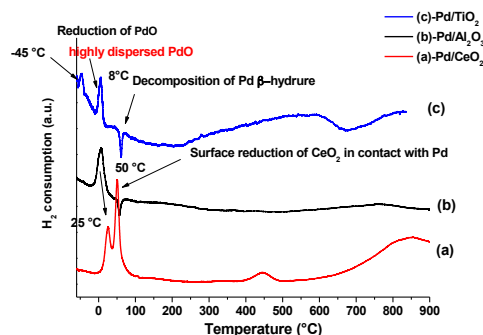


Fig. 1. TPR curves of Pd/CeO<sub>2</sub>, Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub> catalysts.

Above 300 °C CeO<sub>2</sub> and TiO<sub>2</sub> were reduced (surface reduction at around 400-500 °C, bulk reduction above 700 °C). In Fig. 2, the catalytic oxidation of C<sub>3</sub>H<sub>6</sub> over Pd supported catalysts, in terms of reaction rate at 135 °C, is compared. The addition of Ce and Fe improved the catalytic activity of Pd supported catalysts, while no positive effect was played by 5% of Ti and Mn. Pd/CeO<sub>2</sub> was scarcely active as compared to Pd/TiO<sub>2</sub>.

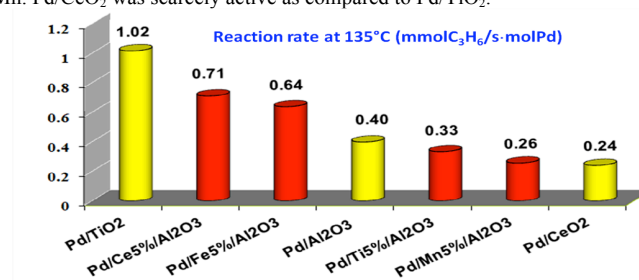


Fig. 2. Catalytic oxidation of C<sub>3</sub>H<sub>6</sub> over Pd supported catalysts: reaction rate (mmol C<sub>3</sub>H<sub>6</sub>/s·mol Pd) calculated at 135 °C.

**Significance:** Pd/TiO<sub>2</sub> and Pd/Ce5%/Al<sub>2</sub>O<sub>3</sub> were the best performing catalysts. The lower activity of Pd/CeO<sub>2</sub> was likely due to the ceria effect which stabilizes PdO preferentially to the active site, metallic Pd.

## References

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