Journal of Catalysis 260 (2008) 141–149

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Effects of alkali additives on the physicochemical characteristics and chemisorptive properties of Pt/TiO_2 catalysts

Paraskevi Panagiotopoulou, Dimitris I. Kondarides *

Department of Chemical Engineering, University of Patras, GR-26504 Patras, Greece

ARTICLE INFO

Article history:
Received 9 June 2008
Revised 23 August 2008
Accepted 21 September 2008
Available online 16 October 2008

Keywords:
Platinum
Titanium dioxide
Promotion
Alkali
Cesium
Sodium
Hydrogen
Carbon monoxide
TPD
TPR
DRIFTS
FTIR

ABSTRACT

The effects of alkali additives on the physicochemical and chemisorptive properties of 0.5% Pt/TiO_2 have been investigated over catalysts promoted with variable amounts of Na (0–0.2 wt%) or Cs (0–0.68 wt%) with the use of diffuse reflectance infrared spectroscopy (DRIFTS) and temperature-programmed (TPD, TPR) techniques. It has been found that addition of alkalis does not affect adsorption of CO and H_2 on the surface of Pt crystallites, indicating the absence of strong electronic-type interactions between these sites and the promoters. However, the presence of alkalis results in the creation and population of new sites with increased electron density, proposed to be located at perimetric sites of Pt crystallites, which are in contact with the support. The adsorption strength of these sites toward CO increases with increasing alkali content, which is evidenced by the development of new, low-frequency IR bands in the ν(CO) region. In contrast, addition of alkali results in weakening of hydrogen adsorption on sites located at the metal/support interface, which is reflected to a significant shift of the corresponding TPD peak toward lower temperatures. Results of CO-TPD experiments indicate that CO adsorbed on Pt interacts with hydroxyl groups associated with the support to yield formate, which decomposes during TPD to CO_2 and H_2. Thermal decomposition of formate is accomplished at lower temperatures in the presence of alkali. Finally, CO-TPR experiments indicate that the reducibility of TiO_2 is enhanced in the presence of alkali, which can be related to the creation of the new sites at the metal/support interface.

1. Introduction

Electropositive promoters, such as alkali and alkaline earth metals, are frequently used as additives in heterogeneous catalysis in order to improve catalytic activity, selectivity and/or durability. Well known examples of industrially important catalytic reactions promoted by alkalis are the Fischer–Tropsch synthesis of hydrocarbons and the ammonia synthesis from N_2 and H_2 [1]. In recent years, significant efforts have been made to modify catalytic performance of noble metal catalysts by chemical [2–12] or electrochemical [13–15] promotion with alkali metals, in order to change product distribution, to reduce the energy requirements (reaction temperature) or to decrease the amount of precious metal required for a specific reaction to occur. In most cases, it has been found that addition of alkalis results in a significant improvement of catalytic performance and that the promotional effect, which often depends on the size of the dopant atom, is maximized for a certain alkali content on the catalytic surface [2–15].

The ability of alkali additives to modify catalytic activity and/or selectivity can be understood by considering the effects induced by the promoting species on the chemisorptive properties of metal surfaces toward reactive molecules. These effects may originate from either electronic interactions, i.e., modification of electron density of alkali-promoted metal surfaces, and/or from electrostatic interactions associated with alkali-metal ions, and/or from site blockage [16–18]. Regarding the electronic-type effects, alkali metals are electron donors and, therefore, may act by enhancing chemisorption of electron acceptor species, such as carbon monoxide and oxygen, and/or by suppressing chemisorption of electron donors, such as olefins and hydrogen [13]. These issues have been investigated extensively in recent years, mainly with the use of carbon monoxide as probe molecule. Several fundamental studies conducted over single crystals of transition metals [17,19] and noble metals [17,18,20] have shown that the presence of alkali-metal atoms modifies adsorption characteristics of the metal surface toward CO leading to: (a) a dramatic increase in the binding energy of CO (strengthening of the metal–CO bond), which is reflected to the large shift in desorption temperature in TPD experiments, (b) a significant weakening of the carbon–oxygen bond, which is evidenced by the marked decrease in the frequency of the C–O stretch vibration, and (c) a shift in the electron binding energies of both core and valence levels. Qualitatively similar results have been obtained for alkali-promoted noble metal catalysts supported on SiO_2 [21–23], Al_2O_3 [8,24] or zeolite [25]. Additional effects of alkalis on

---

* Corresponding author. Fax: +30 2610 991527.
E-mail address: dimi@chemeng.upatras.gr (D.I. Kondarides).

0021-9517/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2008.09.014

Table 1
Physicochemical characteristics of alkali-promoted 0.5% Pt/TiO_2 catalysts.

Promoter type and nominal loading (wt%)		Alkali:Pt atomic ratio (nominal)	SSA[a] ($m^2\ g^{-1}$)	Surface alkali concentration (atom nm^{-2})	Anatase content[b] (%)	Platinum dispersion[c]	d_{Pt}[d] (Å)
None	0	0.0	29	0	48	0.87	12
Na	0.017	0.3	30	0.15	52	0.94	11
	0.06	1.0	27	0.58	56	1.01	10
	0.12	2.0	28	1.1	50	0.66	15
	0.20	3.4	28	1.9	56	0.81	13
Cs	0.17	0.5	30	0.26	50	0.78	13
	0.34	1.0	28	0.55	48	0.77	13
	0.68	2.0	28	1.1	59	0.74	14

[a] Specific surface area, estimated with the BET method.
[b] TiO_2 phase composition estimated from integral intensities of the anatase (101) and rutile (110) XRD reflections.
[c] Estimated from selective chemisorption of CO at room temperature.
[d] Mean crystallite size of dispersed Pt crystallites.

the properties of supported metal catalysts include modification of the acid/base characteristics of the support [4,11,12] and inhibition of spillover of adsorbed species [6,23].

The present investigation was undertaken in order to develop an understanding of the effects of alkali promotion on the physicochemical and chemisorptive properties of Pt/TiO_2 catalysts, which have been found to be very active for the low-temperature water–gas shift (WGS) reaction [26–29]. Results of the present study provide the basis for explaining the enhanced WGS activity of alkali-promoted Pt/TiO_2 catalysts, which will be discussed in a forthcoming publication.

2. Experimental

2.1. Catalyst preparation and characterization

Alkali-promoted TiO_2 carriers were prepared by impregnation of titanium dioxide powder (Degussa P25) with an aqueous solution of the corresponding alkali precursor salt ($NaNO_3$, $CsNO_3$). Typically, 5 g of TiO_2 were added under continuous stirring in 50 mL of water containing the desired amount of the salt, at natural solution pH. The resulting slurry was heated slowly at 70 °C under continuous stirring and maintained at that temperature until nearly all the water evaporated. The solid residue was dried at 110 °C for 24 h and subsequently calcined in air at 600 °C for 3 h. The promoter concentration of samples thus prepared varied in the ranges of 0–0.20 wt% (0–1.9 atoms nm^{-2}) and 0–0.68 wt% (0–1.1 atoms nm^{-2}) for Na and Cs dopants, respectively (Table 1).

Dispersed platinum catalysts (0.5 wt% Pt) were prepared employing the wet impregnation method with the use of the above carriers and $(NH_3)_2Pt(NO_2)_2$ (Alfa) as platinum precursor salt. Materials were characterized with respect to their specific surface area, anatase content, primary crystallite size of TiO_2 and Pt dispersion, employing nitrogen physisorption at the temperature of liquid nitrogen (BET method), X-ray diffraction (XRD) and selective chemisorption of CO at room temperature. Details on the equipment and procedures used for catalyst preparation and characterization can be found elsewhere [26].

2.2. In situ FTIR spectroscopy

Fourier transform infrared (FTIR) experiments were carried out using a Nicolet 740 FTIR spectrometer equipped with a diffuse reflectance (DRIFT) cell (Spectra Tech), an MCTB detector and a KBr beam splitter. The cell is directly connected to a flow system, equipped with mass flow controllers and a set of valves which allow control of feed gas composition [28]. In a typical experiment, the catalyst powder was heated at 450 °C under He flow for 10 min and then reduced in flowing hydrogen (20% H_2 in He) at 300 °C for 60 min. The reduced sample was flushed with He at 450 °C for 10 min and subsequently cooled down to room temperature (RT). During the cooling stage, background spectra were collected at temperatures of interest. The flow was then switched to a gas mixture of 1% CO in He at RT for 30 min. Finally, the system was purged with He for 10 min and temperature was stepwise increased up to 450 °C. Spectra were recorded 3 min after reaching the desired temperature. In all experiments, the total flow through the DRIFT cell was 30 cm^3/min.

2.3. Temperature-programmed desorption of H_2 or CO

Temperature-programmed desorption (TPD) experiments were carried out using an apparatus and following the procedures described in detail elsewhere [30]. In a typical experiment, an amount of 200 mg of freshly prepared catalyst ($0.18 < d < 0.25$ mm) was placed in a quartz microreactor, heated at 500 °C under He flow for 15 min and then reduced *in situ* at 300 °C for 30 min under flowing hydrogen. The catalyst was heated again at 500 °C under He flow for 15 min, in order to remove adsorbed species from the catalyst surface, and then cooled down to 25 °C. The flow was then switched to the adsorbing gas, H_2 or CO (1% in He), for 15 min, followed by purging with He for 10 min at RT. After this step, temperature was increased linearly ($\beta = 30\,°C/min$) up to 650 °C and TPD patterns were recorded with the use of a mass spectrometer (Fisons, SXP Elite 300H) connected on-line to the reactor outlet. Responses of the mass spectrometer were calibrated against standard mixtures of accurately known composition. When necessary (e.g. CO_2–CO signals), the cracking coefficient determined in separate experiments was also taken into account in the calculations of gas effluent concentrations.

2.4. Temperature-programmed reduction experiments

Temperature-programmed reduction (TPR) experiments were carried out using carbon monoxide (CO-TPR) as reducing agent, following the procedure described elsewhere [26]. In a typical experiment, 200 mg of the catalyst were placed in a quartz microreactor and treated at 300 °C with a flowing 2% O_2/He mixture for 30 min. The sample was then heated under He flow at 500 °C for 15 min and subsequently cooled down to room temperature. TPR experiments were then carried out over the pre-oxidized samples by switching the feed composition from He to 0.25% CO/He (40 cm^3/min), left at 25 °C for 10 min, and then heating linearly ($\beta = 30\,°C/min$) at 650 °C. A mass spectrometer (Omnistar/Pfeiffer Vacuum) was used for on-line monitoring of TPR effluent gas. The transient-MS signals at $m/z = 2$ (H_2), 15 (CH_4), 18 (H_2O), 28 (CO)