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Effects of promotion of TiO_2 with alkaline earth metals on the chemisorptive properties and water–gas shift activity of supported platinum catalysts

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ABSTRACT

The effects of promotion of TiO_2 with Group II alkaline earth metals on the chemisorptive properties and water–gas shift (WGS) activity of dispersed platinum have been investigated over $Pt/TiO_2(x\%MO)$ catalysts of variable promoter type (M = Mg, Ca, Sr, Ba) and loading ($x = 0$–4 wt.%). DRIFTS experiments carried out using CO as a probe molecule showed that the presence of calcium does not affect appreciably adsorption on sites located on the surface of Pt crystallites, but results in the development of new, low-frequency bands in the $\nu(CO)$ region attributed to the creation and population of sites with increased electron density located at the metal–support interface. Results of H_2-TPD experiments indicated a weakening of the adsorption strength of these sites toward hydrogen with increasing CaO content. Catalytic performance tests and kinetic measurements showed that activity of alkaline earth metal-promoted catalysts depends appreciably on the nature and loading of the promoter, as well as on the calcination temperature employed for the preparation of doped TiO_2 supports. Optimal results were obtained for Pt catalyst supported on TiO_2 promoted with 1–2 wt.% CaO, the specific activity of which is 2–3 times higher, compared to that of the unpromoted catalyst. Optimized catalysts are characterized by increased activity and excellent stability under realistic reaction conditions and may be used efficiently in practical applications, provided that promoter loading, calcination temperature and operating conditions are properly selected.

1. Introduction

The catalytic properties of metal catalysts can be significantly influenced by the presence of small amounts of Group II alkanine earth metals, which may affect catalytic activity, selectivity to reaction products and/or long-term stability under reaction conditions. Examples of catalytic reactions that have been reported to be promoted by the presence of alkaline earth metals include ammonia synthesis over Fe- and Ru-based catalysts [1,2], gasification reactions over iron-group metals [3], selective catalytic reduction (SCR) of NO_x by hydrocarbons [4–6], oxidative coupling of methane [7], Friedel–Crafts alkylation reactions over HY zeolites [8], oxidation of propane over Au/Al_2O_3 catalysts [9] and selective oxidation of CO over Pt/Al_2O_3 catalyst [10]. In certain cases, alkaline earth metals have a negative effect on catalytic performance. For instance, addition of calcium decreases the activity of iron-based catalysts for Fischer–Tropsch synthesis (FTS) [11,12], whereas modification of $Au/\alpha\text{-}Fe_2O_3$ catalysts by MgO, CaO or BaO results in a decrease of their activity for the WGS reaction [13].

Depending on the catalytic system under consideration, alkaline earth metals may act as chemical promoters [1,2,5] by influencing, for example, the electron density [10,14,15] or oxidation state [16] of dispersed noble metal crystallites, and the acid–base properties of the support [7,10,17]. These additives may also act as structural promoters [9,18] by increasing the dispersion of the active phase [3,6,9] and by stabilizing the dispersed metallic phase [9] or the support [4] against sintering. For instance, the high activity and selectivity reported for the aromatization of hexane over Pt and Pd catalysts supported on aluminum-stabilized magnesium oxide has been attributed to the presence of small Pt clusters with an excess negative charge [19,20]. The improvement of the catalytic performance of Ru/TiO_2 catalysts for the partial oxidation of CH_4 to synthesis gas upon doping of TiO_2 with small amounts of Ca^{2+} has been related to stabilization of Ru in its metallic form, which enhances the direct conversion of methane to synthesis gas [16]. The beneficial effect of addition of alkali/alkaline earth metal oxides on the performance of Au/Al_2O_3 catalysts for propane oxidation has been attributed to the decrease of the size of gold particles and their stabilization against sintering [9]. The poisoning effect of calcium on the performance of V_2O_5/TiO_2 catalysts for the selective catalytic reduction of NO by NH_3 has been related to neutralization of Brønsted acid sites [21]. In general, addition of alkaline earths results in modification of the physicochemical and

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Table 1
Physicochemical characteristics of alkaline earth-promoted 0.5%Pt/TiO_2(*x*%MO) catalysts.

Promoter type (MO) and nominal loading (wt.%)		M:Pt atomic ratio (nominal)	Calcination temperature (°C)	SSA ($m^2\,g^{-1}$)	Anatase content (%)	CO chemisorption	
						CO:Pt ratio	d_{Pt} (nm)
None	0	0	600	29	48	0.67	1.5
CaO	0.14	1	600	35	64	1.02	0.9
	0.43	3	600	36	70	1.07	0.8
	1.0	7	600	36	69	1.07	0.7
	2.0	14	600	39	73	1.05	1.0
	4.0	28	600	36	72	0.96	1.1
	2.0	14	500	40	75	0.80	1.3
	2.0	14	700	28	61	0.81	1.3
	2.0	14	900	8	0	0.73	1.4
SrO	0.5	1.9	600	37	71	0.97	1.1
	2.0	7.5	600	36	72	0.97	1.1
BaO	0.5	1.3	600	37	66	0.84	1.2
	2.0	5.1	600	35	71	0.95	1.1
MgO	0.5	4.9	600	33	65	1.06	1.0
	2.0	19.4	600	33	68	1.08	0.9

chemisorptive properties of catalytic materials in a manner that depends on both the nature and loading of alkaline earth promoter and the metal catalyst employed. For instance, low levels of calcium have been reported to increase catalytic activity for the oxidative dehydrogenation of isobutene, while higher levels act as a poison for chromium oxide catalysts supported on Al_2O_3 [22].

In our previous studies [23,24], we have investigated the effects of alkali (Li, Na, K, Cs) promotion of the support on the chemisorptive properties and water–gas shift (WGS) activity of noble metal catalysts (Pt, Ru, Pd) dispersed on TiO_2 [23,24]. It has been found that catalytic performance can be significantly improved with the addition of the appropriate amount of alkali. The enhancement of WGS activity has been attributed to strong interactions between the added alkali and the TiO_2 surface, which leads to the creation of new, catalytically active sites located at the metal–support interface [25]. In order to find out if the same holds for alkaline earths metals, their promoting effects on the WGS activity of Pt/TiO_2 catalysts is investigated in the present study. Results are discussed by considering the effects of alkaline earth metal-induced alterations of the support on the physicochemical characteristics and chemisorptive properties of Pt/TiO_2 catalysts.

2. Experimental

2.1. Catalyst preparation and characterization

Alkaline earth metal-promoted TiO_2 supports, denoted in the following as TiO_2(*x*%MO) (M = Mg, Ca, Sr, Ba), were prepared employing the wet impregnation method followed by calcination in air at 500–900 °C [16,26]. Briefly, a known amount of the alkaline earth metal-precursor ($Mg(NO_3)_2{\cdot}6H_2O$, CaO, $Sr(NO_3)_2$, $Ba(NO_3)_2$) was dissolved in water. The solution pH was adjusted at pH 1 with the use of HNO_3 in order to enable dissolution of CaO. The solution was then added into an aqueous suspension of TiO_2 (Degussa P25) under continuous stirring. The resulting mixture was heated slowly at 70 °C 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 the desired temperature (500–900 °C) for 5 h. The promoter concentration of samples thus prepared varied in the range of 0–4.0 wt.% MO (Table 1). Dispersed platinum catalysts were prepared employing the wet impregnation method with the use of $(NH_3)_2Pt(NO_2)_2$ (Alfa) as metal precursor salt and the above TiO_2(*x*%MO) powders as supports [27]. The solid residue obtained following evaporation of water was dried at 110 °C for 24 h and then reduced at 300 °C in H_2 flow for 2 h. The nominal metal loading of all catalysts thus prepared was 0.5 wt.% Pt.

The specific surface area (SSA) of synthesized catalysts was measured employing nitrogen physisorption at the temperature of liquid nitrogen (B.E.T. method). The anatase-to-rutile content and the primary crystallite size of TiO_2 (d_{TiO_2}) were determined with the use of X-ray diffraction (XRD). Platinum dispersion (D_{Pt}) and mean crystallite size (d_{Pt}) were estimated by selective chemisorption of CO at room temperature. Details on the apparatuses, methods and procedures used for catalyst characterization can be found elsewhere [27].

Temperature-programmed desorption (TPD) experiments were carried out over freshly prepared catalysts as described in detail elsewhere [23]. Briefly, an amount of catalyst (200 mg) was reduced *in situ* with hydrogen at 300 °C, purged with He flow at 500 °C to remove adsorbed species from the catalyst surface and then cooled down to room temperature (RT) under He flow. This was followed by adsorption of hydrogen at 25 °C for 15 min, purging with He for 10 min and linear increase of temperature ($\beta = 30\,°C\,min^{-1}$) to 650 °C under He flow (40 $cm^3\,min^{-1}$). A mass spectrometer (Fisons, SXP Elite 300H) was used for on-line monitoring of the TPD patterns.

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 was directly connected to a flow system, equipped with mass flow controllers and a set of valves, which allowed 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 was subsequently cooled down to RT. During the cooling stage, background spectra were collected at temperatures of interest. The flow was then switched to a gas mixture consisting 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 FTIR experiments presented here, the total flow rate through the DRIFT cell was 30 $cm^3\,min^{-1}$.

2.2. Catalytic performance tests and kinetic measurements

Catalytic performance tests and kinetic measurements have been carried out using an apparatus, which consists of a flow measuring and control system, a quartz microreactor and an on-line