

Catalytic Properties of Pt/Al₂O₃ Catalysts in the Aqueous-Phase Reforming of Ethylene Glycol: Effect of the Alumina Support¹

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Abstract—The influence of the alumina support on the catalytic activity of Pt/Al₂O₃ catalysts in aqueous phase reforming of ethylene glycol to hydrogen was studied. The catalysts were prepared by impregnation of γ -, δ -, and α -alumina with H₂PtCl₆. The highest rate of hydrogen production (452 $\mu\text{mol min}^{-1} \text{g}^{-1}$) obtained with the Pt/ α -Al₂O₃ catalyst can be related to the highest extent of dispersion of Pt on α -Al₂O₃. XPS, TEM-EDX and TPR-H₂ measurements showed the absence of chloride-containing surface complexes in the Pt/ α -Al₂O₃ catalyst. However, chloride-containing entities were found on the surface of Pt/ γ -Al₂O₃ and Pt/ δ -Al₂O₃ catalysts. When chloride ions are removed chlorinated Pt species facilitate the sintering of Pt crystallites and in this way affect the extent of Pt dispersion. Moreover, depending upon the particular crystalline form, alumina atoms have different coordination and alumina surfaces contain varying amounts of OH groups of different nature which affect the interaction between Pt and the support.

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The great challenge facing humankind during the next several decades is to develop sources of energy that are environmentally safe and that will meet energy needs. Resurgence in the chemistry and biochemistry of hydrogen, the simplest closed-shell molecule, has been spurred by recent scientific and practical interest in hydrogen as an energy carrier and potential transport fuel [1]. Hydrogen can be produced from hydrocarbons derived from biomass in a single-reactor aqueous-phase reforming (APR) using various transition metal catalysts at mild reaction conditions [2]. This process is energy saving because it eliminates the need to vaporize water and hydrocarbons derived from biomass. In addition, the APR process is operated at temperatures as low as 200–250°C, which are below those used in steam reforming or autothermal reforming. Under these conditions, the water gas shift reaction is thermodynamically favored with low amounts of CO found in the products.

Among the transition metal catalysts studied in the APR process, the rate of reforming decreases in the order: Pt, Ni > Ru > Rh, Pd > Ir. At the same time, the order of decreasing selectivity for hydrogen production is: Pd > Pt > Ni > Ru > Rh [3]. Due to a low cost and high activity nickel-based catalysts are widely used in a number of reforming processes. The problem with nickel-based catalysts is an increased contribution of methanation, which promotes the rapid growth of carbon deposits and leads to the catalyst deactiva-

tion and reactor plugging [3, 4]. Due to this reason Pt was identified as the most promising catalyst.

Ethylene glycol is a feed molecule suitable for studies of aqueous-phase reforming process because it contains the same functional groups as larger polyols, including C–C, C–O, C–H and O–H bonds, and also OH groups on adjacent carbon atoms. There are detailed studies of platinum catalysts for the aqueous-phase reforming of ethylene glycol [2, 3, 5–9] which indicated that alumina is a useful support for this process [5, 7]. Alumina is the most widely used as a carrier for industrial metal catalysts. Aluminas are generally prepared from aluminum trihydrate Al(OH)₃ or aluminum monohydrate AlOOH. Controlled calcination of the latter solid leads to a series of metastable polymorphs such as γ -Al₂O₃, δ -Al₂O₃, and θ -Al₂O₃, and to a thermodynamically stable α -Al₂O₃ [10, 11]. Lehnert and Claus reported that a mixture of γ -Al₂O₃, δ -Al₂O₃ and θ -Al₂O₃ (Puralox^{O,R}) was a better support than pure γ -alumina for platinum based catalysts in APR reforming of glycerol [12].

Since a deeper understanding of the effect of various alumina forms on the catalytic activity is desirable, in this work we used different types of alumina to prepare Pt/Al₂O₃ catalysts and investigate the catalytic activity in APR ethylene glycol to hydrogen. The catalysts were prepared by impregnating γ -Al₂O₃, δ -Al₂O₃, and α -Al₂O₃ with H₂PtCl₆. The catalytic performance of Pt/Al₂O₃ catalysts with different phase compositions was studied in aqueous-phase reforming of ethylene glycol to hydrogen. Pt/Al₂O₃ catalysts were

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Table 1. Surface properties and ethylene glycol conversion on Pt/Al₂O₃ catalysts

Support	<i>S</i> _{BET} , m ² /g	<i>V</i> _p , cm ³ /g	Metal loading, wt %	CO uptake, μmol/g	Pt surface area, m ² /g _{cat}	Pt dispersion, %	Pt particle size, nm	<i>r</i> _{H₂} , μmol min ⁻¹ g _{cat} ⁻¹ /TOF, min ⁻¹
γ-Al ₂ O ₃	152.6	0.32	0.94	9.2	0.47	19.1	6.30	218/23.7
δ-Al ₂ O ₃	66.3	0.27	0.77	13.3	0.83	33.7	4.37	321/24.1
α-Al ₂ O ₃	13.4	0.04	0.61	17.9	1.41	57.1	3.25	452/25.2

Note: Pore volume *V*_p was calculated at the relative pressure of *P/P*₀ = 0.975. The values of metal loading were measured by ICP-AES analysis. Dispersion of Pt and Pt particles size were calculated from CO chemisorption. TOF – turnover frequency.

characterized using the methods of temperature programmed reaction in H₂ (TPR-H₂), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy with energy-dispersive X-ray analyser (TEM-EDX) and CO chemisorption measurements.

EXPERIMENTAL

Catalyst Preparation

Aluminum monohydrate (AlOOH) was heated to 550, 850, and 1050°C to yield γ-Al₂O₃, δ-Al₂O₃ and α-Al₂O₃ respectively. Platinum catalysts were prepared by incipient wetness impregnation of supports with an aqueous solution of H₂PtCl₆, followed by drying in air at 100°C for 12 h in an oven and heating to 550°C for 5 h at 5°C/min. The amount of platinum precursor was calculated to achieve a metal loading of 1 wt %. The actual platinum content in the catalysts was determined using the inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Catalyst Characterizations

The BET surface area for all samples was determined from nitrogen adsorption isotherms using the NOVA 4200e sorption analyzer. XRD measurements were carried out with RIGAKU diffractometer using CuK_α radiation. The extent of dispersion was measured by CO chemisorption with the ASAP 2000 equipment of Micromeritics, assuming CO/Pt = 1 and a surface area of 8 × 10⁻²⁰ m² per a Pt atom. Prior to CO chemisorption measurements the samples were reduced at 260°C in hydrogen. TPR-H₂ analysis of samples was conducted in a 5% H₂/N₂ flow at 30 ml/min. Before the measurements the samples were treated in flowing N₂ at 550°C for 1 h. The samples were then heated from 30 to 750°C at 10°C/min. Hydrogen consumption was measured using a thermal conductivity detector. X-ray photoelectron spectra were acquired with Thermo ESCALAB 250 spectrometer equipped with a hemispherical electron analyzer and AlK_α (*hν* = 1486.6 eV) 150 W X-ray source. The

samples were pressed into a pretreatment chamber and reduced in flowing H₂ at 260°C and then placed in the XPS analysis chamber. TEM images were obtained from FEI Tecnai 20 S-TWIN operating at 200 kV and equipped with an energy-dispersive X-ray analyzer.

Reaction Studies

The reaction was carried out in a fixed-bed stainless steel reactor (i.d. = 6 mm). The reaction conditions were as follows: 225°C, 29.5 kPa, a feed containing 10 wt % of ethylene glycol and a feed flow rate of 6 ml/h. The reactor was loaded with 0.6 g of the Pt/Al₂O₃ catalyst (20–40 mesh) which was then reduced in situ C under flowing hydrogen at 260°C. The effluent gas stream was analyzed on-line with an automatized gas chromatograph equipped with FID and TCD detectors and a methanizer. The effluent liquid was sampled periodically for the gas chromatography analysis.

RESULTS

Catalytic Performance

Pt catalysts supported on γ-Al₂O₃, δ-Al₂O₃, and α-Al₂O₃ showed different activities in the APR of ethylene glycol (Table 1, last column). In addition to hydrogen, all the effluent gas streams typically contained CO, CO₂ and CH₄. The formation of higher alkanes was not detected. The selectivity to hydrogen [*S*_{H₂} = *n*_{H₂}/(*n*_{H₂} + *n*_{CO} + *n*_{CH₄})] under steady state conditions exceeded 90% and remained nearly constant in all experiments. The analysis of the liquid-phase products showed traces of by-products, such as methanol and ethanol. The Pt catalyst on α-Al₂O₃ with the lowest platinum loading (0.6% based on the ICP analysis) showed the highest catalytic activity (*r*_{H₂} = 452 μmol min⁻¹ g_{cat}⁻¹, Table 1). The yield of hydrogen decreased in the following order: Pt/α-Al₂O₃ > Pt/δ-Al₂O₃ > Pt/γ-Al₂O₃. The specific activities of the catalysts are given in Table 1. Since the values of specific activity are of the same

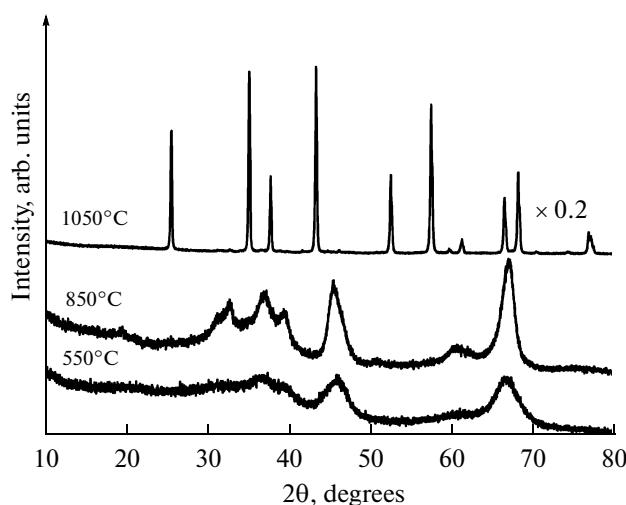


Fig. 1. X-ray diffraction patterns of alumina prepared by the calcination of AlOOH at different temperatures.

order, variations in activity are probably related to the differences in the number of active sites.

Catalysts Characterizations

Figure 1 presents XRD patterns of alumina prepared by heating AlOOH to 550, 850 and 1050°C. Based on the patterns, the increase in the calcination temperature changes the form of alumina. The sample heated to 550°C yields γ -Al₂O₃. Further heating to 850°C converts this to δ -Al₂O₃. When the temperature was increased to 1050°C corundum (α -Al₂O₃) was produced. This transformation sequence is in agreement with the set of routes described in literature [13]. The diffraction peaks of Pt/Al₂O₃ catalysts were the same as those of alumina supports. Pt particles seem to be fairly small as indicated by the absence of diffraction peaks corresponding to platinum.

Table 1 summarizes the BET surface areas of Pt/Al₂O₃ catalysts. As expected, an increase in the cal-

cination temperature of AlOOH decreases S_{BET} values and this effect was especially pronounced for the Pt/ α -Al₂O₃ sample. The pore volume was also decreased as evidenced by a value of 0.04 cm³/g found for the Pt/ α -Al₂O₃ catalyst,. The decrease in specific surface area and pore volume may lead to a low percentage of Pt anchored on α -Al₂O₃ (Table 1, column 4).

The extent of Pt dispersion and the size of Pt particle calculated from CO chemisorptions measurements are also shown in Table 1. It can be seen that dispersion of Pt on Pt/ γ -Al₂O₃ catalyst was the lowest among the catalysts examined, even though it had a high BET surface area and a high loading of Pt. The order of increasing dispersion of Pt is: Pt/ γ -Al₂O₃ < Pt/ δ -Al₂O₃ < Pt/ α -Al₂O₃. As can be seen from Table 1, catalytic activity of Pt/Al₂O₃ catalysts increases with increased extent of platinum dispersion on alumina surface.

Figure 2 shows the TEM images of Pt/Al₂O₃ catalysts. Platinum particles could be observed clearly only in the images produced by Pt/ α -Al₂O₃. The dimensions of platinum particles estimated from the TEM image were in the range of 3 to 4 nm, similar to the Pt particle size range calculated from CO chemisorption. Table 2 shows the composition of Pt/Al₂O₃ catalysts as determined by EDX. Based on the data obtained for selected areas of Pt/ α -Al₂O₃ and Pt/ γ -Al₂O₃ catalyst the surface of Pt/ α -Al₂O₃ contains no chlorine atoms but includes an increased amount of Pt.

TPR-H₂

The reduction state of various samples was investigated by using TPR-H₂ method. The hydrogen consumption profiles as a function of temperature are plotted on Fig. 3. Unlike the alumina supports, Pt/alumina catalysts show reduction peaks at temperatures from 90 to 390°C (Fig. 3a). For all three catalysts a reduction peak at 370–390°C is observed. This peak is generated by the reduction of platinum oxides that strongly interact with the alumina supports. Some authors observed a middle-temperature peak at 210–250°C on Pt/ γ -Al₂O₃ and Pt/ δ -Al₂O₃ catalysts that was

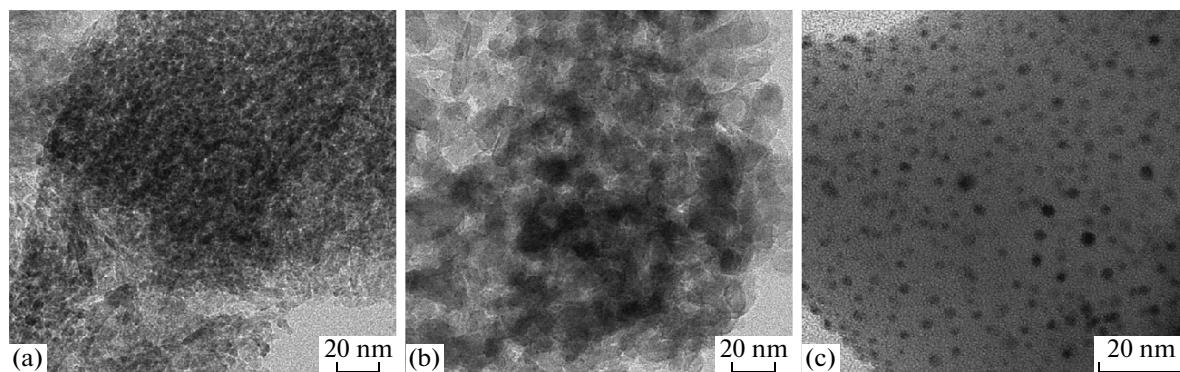


Fig. 2. TEM images of the Pt/Al₂O₃ catalysts: (a) Pt/ γ -Al₂O₃, (b) Pt/ δ -Al₂O₃, (c) Pt/ α -Al₂O₃.

Table 2. Composition of the Pt/Al₂O₃ catalysts as determined by TEM-EDX

Sample	Al (K)	Pt (L)	Cl (K)	O (K)
	atom %			
Pt/γ-Al ₂ O ₃	34.48	0.21	0.57	64.73
Pt/α-Al ₂ O ₃	42.00	1.11	undetected	56.88

attributed to the reduction of oxy- or hydroxychlorinated Pt species [14, 15–17]. But the present authors could not find this peak in the profile obtained for the Pt/α-Al₂O₃ catalyst. Instead, a low temperature peak assignable to the reduction of Pt oxides appears at 93°C [14, 18]. This suggests that in the Pt/α-Al₂O₃ catalyst, platinum exists as an oxidized species rather than as oxy- or hydroxychlorinated entity. In the case of the Pt/δ-Al₂O₃ catalyst, a peak at 243°C with a shoulder at 128°C was observed. The latter can be related to the reduction of oxidized Pt species. It is suggested that the amount of oxidized platinum on Pt/Al₂O₃ increases with increasing calcination temperature, contrary to the behavior of oxy- or hydroxychlorinated Pt species.

Furthermore, the TPR-H₂ profile of the Pt/γ-Al₂O₃ catalyst exhibits a broad reduction peak near 610°C. Based on the reduction profiles of γ-Al₂O₃ (Fig. 3b) the peak can be caused by the dehydroxylation of the alumina surface. As shown in Fig. 3b, the intensity of the peak decreases when the calcination temperature is increased, and at 1050°C the peak disappears completely.

XPS

To provide further insight into the effect of the alumina form on the distribution of Pt species, XPS tech-

nique was used with spectra shown in Fig. 4. The unreduced catalysts contain peaks due to platinum species and there is overlap between these peaks and those for Al 2p.

After curve fitting procedures a broad peak in the spectra of Pt/Al₂O₃ could be resolved into three components. The peak with a binding energy of ca. 74.3 eV can be ascribed to Al 2p. Other peaks are related to Pt species on the catalyst surface. As shown in Table 3, the peak with a binding energy of 75.4–75.6 eV and 73.2 eV could be attributed to the presence of oxychlorinated Pt species and hydroxychlorinated Pt species, respectively. The photoemission doublet observed at 73.9–75.0 eV and around 73.0 eV could be assigned to the oxidized Pt species. As expected, XPS measurements indicated that no chlorine was present in the Pt/α-Al₂O₃ catalyst. This finding was supported by EDX data. As shown in Table 3, the amount of chlorine on the surface of Pt/Al₂O₃ catalysts decreases as the temperature used on heating AlOOH increases. The observation is also consistent with the TPR results. It was reported that chlorine is nearly always present in the proximity of platinum atoms on the surface of γ-Al₂O₃ and the presence of Cl[–] and OH[–] groups on the support favors migration of Pt species during the oxidizing treatment [14, 17]. It can be thus inferred that the presence of chlorine strongly influences the dispersion of platinum on the surface of alumina support, and in this way the catalytic performance. Moreover, for the Pt/α-Al₂O₃ catalyst, the peak at 73.0 eV related to oxidized Pt species was shifted to lower binding energy values, suggesting that a strong interaction with the support results in the formation of Pt species with a lower oxidation degree [19].

Table 3 is also supplemented with the data on composition of the surface platinum species on Pt/Al₂O₃ catalysts derived from the XPS spectra. The ratio of

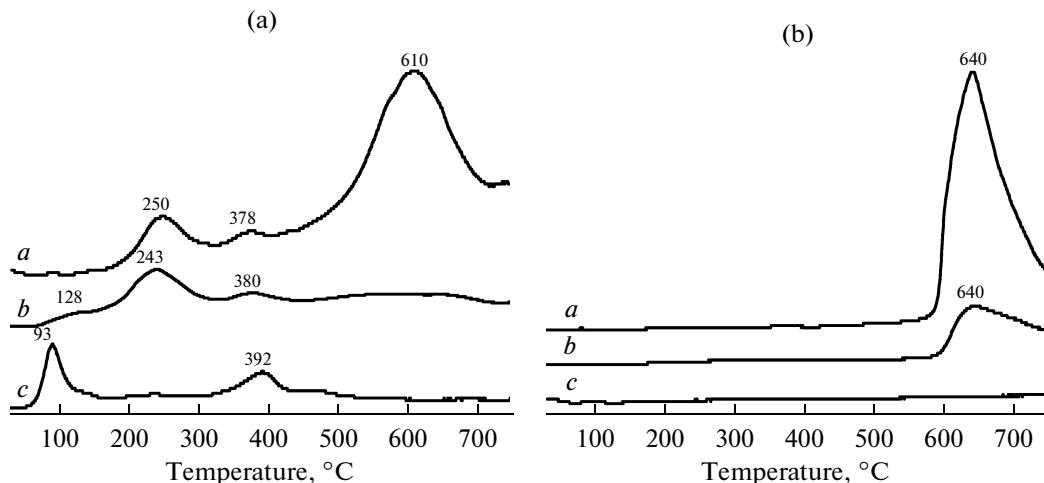


Fig. 3. (a) TPR profiles of Pt/Al₂O₃ catalysts with alumina calcined at 550 (a), 850 (b) and 1050°C (c). (b) TPR profiles of Al₂O₃ prepared by calcinations of AlOOH at 550 (a), 850 (b) and 1050°C (c).

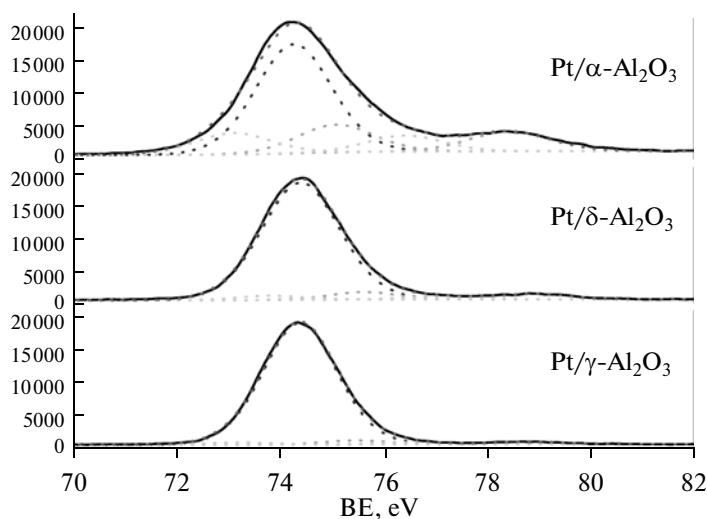


Fig. 4. Pt 4f XPS spectra of the unreduced Pt/Al₂O₃ catalysts. Solid lines—experimental data, dot lines—simulation.

peak area of platinum species to that of alumina in the Pt/α-Al₂O₃ sample was calculated to be 0.80, while it was only about 0.14 and 0.08 for the samples of Pt/δ-Al₂O₃ and Pt/γ-Al₂O₃, respectively. Obviously the surface of the Pt/α-Al₂O₃ catalyst is enriched in platinum species compared to that of Pt/γ-Al₂O₃ and Pt/δ-Al₂O₃ catalysts. This conclusion is consistent with the results of CO chemisorption measurements.

DISCUSSION

By comparing different Pt/Al₂O₃ samples it can be concluded that the highest rate of hydrogen production (452 $\mu\text{mol min}^{-1} \text{g}^{-1}$) shows the Pt/α-Al₂O₃ catalyst and this observation can be attributed to the highest extent of dispersion of Pt on α-Al₂O₃. From the XPS, TEM-EDX and TPR-H₂ measurements the presence of chlorine in Pt/γ-Al₂O₃ and its absence in Pt/α-Al₂O₃ are evident. The amount of chlorine in Pt/Al₂O₃ decreases with increasing calcination temperature of AlOOH. A usual transformation sequences that occur upon heating the aluminum hydroxides impregnated with H₂PtCl₆, involve conversion of platinate to [Pt(IV)(OH)_xCl_y]_s by oxygen treatment at

about 300°C followed by transformation into [Pt(IV)O_xCl_y]_s at higher temperatures (between 450 and 600°C) [15]. However, when a chlorinated Pt catalyst is treated in a dry and chlorine-free atmosphere, a redispersion of Pt particles occurs on the chlorinated surface of a transition alumina followed by sintering of supported Pt crystallites during the removal of chloride [14]. When dechlorination of Pt/Al₂O₃ proceeds further, chloride facilitates the sintering of Pt crystallites on alumina surface and in this way influences the extent of Pt dispersion in Pt/Al₂O₃ catalysts. The α-Al₂O₃ support contains significantly lower amounts of surface OH groups than γ-Al₂O₃ [20]. It appears that the formation of hydroxychloride complexes such as [Pt(IV)(OH)_xCl_y]_s was suppressed upon heating the Pt/α-Al₂O₃ sample. Thus the absence of chlorine in the Pt/α-Al₂O₃ catalyst improves the Pt dispersion.

On the other hand, the coordination of alumina atoms as well as the amount and the nature of surface OH group are different in the alumina supports of interest and accordingly different types of interaction between metal Pt and Al₂O₃ supports can be expected. It was reported that Pt crystallites are more tightly bound to the “dry” alumina surface than to the

Table 3. Composition of the unreduced Pt/Al₂O₃ catalysts as determined by XPS method

Sample	Oxidized Pt species*	Oxy- or hydroxychlorinated Pt species*	Pt species /Al**	Cl ⁻	
				BE, eV	Cl ⁻ /Al
Pt/γ-Al ₂ O ₃		73.2 (37.5), 75.4 (62.5)	0.08	278.6	0.15
Pt/δ-Al ₂ O ₃	73.9 (35.7)	75.6 (64.3)	0.14	278.8	0.11
Pt/α-Al ₂ O ₃	73.0 (43.7), 75.0 (56.3)		0.80	undetected	

* Numbers in parentheses are the percentage of Pt species.

** The ratio of peak areas including oxidized Pt species and oxy- or hydroxychlorinated Pt species.

hydroxylated alumina [21, 22]. The XPS results indicate that the Pt species with lower oxidation degree were formed in the Pt/ α -Al₂O₃ catalyst, and a stronger interaction with the α -Al₂O₃ support can be envisaged.

In this work, the catalytic activity of Pt catalysts in aqueous-phase reforming of ethylene glycol to hydrogen was studied. The catalysts were prepared by impregnation of γ -, δ -, and α -alumina with H₂PtCl₆. The Pt catalyst on α -Al₂O₃ showed the highest catalytic activity, even though the platinum loading and BET surface area of Pt/ α -Al₂O₃ are characterized by the lowest values. With this catalyst, the rate of hydrogen production reached a value of 452 $\mu\text{mol min}^{-1} \text{g}^{-1}$ at 225°C and 29.5 kPa (feed containing 10 wt % ethylene glycol, a feed flow rate of 6 ml/h). Compared to other catalysts Pt/ α -Al₂O₃ shows the highest dispersion of Pt on the surface. The TEM-EDX, TPR-H₂ and XPS measurements showed that the Pt/ α -Al₂O₃ catalyst contains no chlorine. The presence of chlorine would facilitate sintering of metal Pt on alumina surface during the further dechlorination of Pt/Al₂O₃ catalysts and in this way influences the metal Pt dispersion. Moreover, changes in the coordination of Al atoms as well as the variations in the amount and the nature of surface OH group in different alumina supports can affect the interaction between metallic Pt and alumina support. It was speculated that metal Pt is adsorbed more strongly on the α -Al₂O₃ surface than on the γ -Al₂O₃.

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