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10

Pt particle size/nm

TEM data

Influence of a precursor solution on the characteristics of platinum on alumina catalysts

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The precursor solution aging does not influence the characteristics of platinum on alumina catalysts prepared by the impregnation of a support with platinum nitrate solutions. The precursor solution interaction with an oxide support and the annealing treatment following the impregnation determine the size of active component particles in the final catalysts.

The platinum-based catalysts and, particularly, platinum on alumina catalysts are of great practical importance.^{1–3} A number of studies have been devoted to the investigation of the influence of catalyst preparation conditions and precursor solution composition on the characteristics of prepared catalysts.^{4–7} At the same time, the mechanisms of the formation of supported active component particles remain unclear. In the context of particle size effects in catalysis,^{6,8–10} the controlled preparation of catalysts with particular parameters is a problem of considerable current interest. It is well known that platinum nitrate solutions, which are widely used for catalyst preparation, are very complicated compositions.^{4,5} Only the solutions in nitric acid are stable. Platinum nitrate solution is prone to hydrolysis upon dilution.⁴ This leads to the formation of a hydrated platinum oxide precipitate with the lapse of time.⁴ This work considers the influence of the composition of platinum(IV) nitrate solutions and the solution aging on the characteristics of Pt on alumina catalysts. The platinum nitrate solutions were studied by small angle X-ray scattering (SAXS), and the catalyst samples were characterized by high-resolution transmission electron microscopy (HRTEM).

The platinum on alumina catalysts were prepared using a method described elsewhere.^{8,11} Commercial platinum(IV) nitrate solution (Delphi; Pt content, 24.77 wt%) and γ -Al₂O₃ alumina (Sasol, $S_{\text{BET}} = 198 \text{ m}^2 \text{ g}^{-1}$) were used. To investigate the influence of solution aging on the characteristics of the final catalyst, a 1% aqueous solution of platinum nitrate (pH ~ 1) was prepared and its aliquot portions were taken 0.5, 6, 12, 18 and 24 h after the mixing of the commercial platinum nitrate solution with water. Both SAXS measurement and catalyst sample preparation were started simultaneously for each time of aging. y-Al₂O₃ was dried at 120 °C for 8 h before impregnation. The 1 wt% Pt/γ -Al₂O₃ catalysts were prepared by the wet impregnation of alumina. The samples were dried at 120 °C for 4 h and then calcinated at 400 °C for 4 h in air.

Based on the SAXS data (Figure 1), the radius of gyration of the polynuclear species existing in platinum nitrate solution was determined for each time (Table 1).¹² It is evident that the size of the species is growing significantly with time upon solution aging due to hydrolysis. After a while a precipitate forms.



Pt^{IV} nitrate

precursor solutions

10

Pt particle size

Sample no.	nitrate solution aging/h	<i>R</i> _G (solution)/nm (SAXS)	(catalyst)/nm (HRTEM)	
1	0.5	3.2±0.2	1.3±0.3	
2	6	5.4±0.2	1.2±0.3	
3	12	7.9±0.2	1.4±0.3	
4	18	9.4±0.2	1.4±0.3	
5	24	10.3±0.3	1.5±0.4	



Figure 1 Small angle X-ray scattering curves depending on solution aging

The results of HRTEM indicate that the mean size of platinum particles on the surface of alumina does not depend on the aging of precursor solution. The mean particle size of platinum particles is similar for all prepared samples (Table 1 and Figure 2). The set of experiments on solution aging was repeated and the result was reproduced. No dependence of the particle size of platinum on the surface of alumina on the platinum nitrate solution aging was found.

Catalyst samples were tested in the total oxidation of propane in a flow-circulation reactor at 300 °C. The turnover frequencies (TOF) for samples nos. 1 and 5 are similar, namely, 0.36 and 0.39 s^{-1} , respectively. In comparison, TOF is 2.72 s⁻¹ for the reference sample with a mean Pt particle size of 7.9 nm, which was prepared as described elsewhere.¹¹ The direct size effect is



Figure 2 HRTEM image for Pt/γ -Al₂O₃ sample no. 5 (24 h aging).

well described^{6,8} for the total propane oxidation over platinum on alumina catalysts. This effect is much stronger than TOF difference found for samples nos. 1 and 5. Thus, the precursor solution aging does not influence the behavior of the final catalysts, pointing that there is no marked difference between catalysts prepared using fresh and aged precursor solutions.

To study the influence of the precursor solution on supported platinum particle size, two catalyst samples were prepared using a Pt^{IV} nitrate solution (pH \sim 1) and a Pt^{IV} nitrate solution with tetramethylammonium hydroxide (TMA) (pH ~ 6.5).¹¹ TMA was used to change the pH of the precursor solution.⁵ After impregnation and drying the samples of catalysts were divided into portions, which were treated under conditions described in Table 2. For reduced samples, CO-chemisorption experiments were performed using a published method.¹³ Table 2 summarizes platinum particle sizes calculated from the chemisorption and TEM data. According to the SAXS data,¹¹ the species in Pt^{IV} nitrate solution have a larger size as compared with the Pt^{IV} nitrate + TMA solution. After gentle reduction, very small Pt particles were found on the surface of both catalysts. At the same time, the samples behaved differently upon further annealing both in hydrogen and in air (Table 2). For the sample prepared with the solutions modified with TMA, the particle size increased more intensely under annealing conditions regardless of the treatment medium.

According to published data, varying the H₂[Pt(OH)₆]/HNO₃ ratio made it possible to control the colloidal platinum particle size in the precursor solution in wide ranges and, finally, the degree of dispersion of platinum in the resulting catalysts.^{8,10} Thus, the size of the colloidal particles is determinative for the supported particle size.^{8,10} The above data indicate that the size of the polynuclear species existing in platinum nitrate solution and formed due to solution aging or solution modification by TMA is not so principal for the control of platinum particle size. The observations can be explained by the assumption¹¹ that the interaction of platinum nitrate solution with the oxide support leads to the destruction of polynuclear species existing in precursor solution forming smaller particles of active component on the support surface. Precursor solution composition influences the interaction of an active component with the alumina support, particularly, due to alumina surface modification. Possibility of

Table 2 Chemisorption and TEM data.

Sample no.	Precursor solution	Treatment tempera- ture/°C	Medium	Treatment duration/h	Pt particle size (catalyst)/nm	
					Chemi- sorption	TEM
6	Pt ^{IV} nitrate	100	H ₂	1.5	1.3	1.7±0.4
		150	H_2	1	1.6	$1.7{\pm}0.4$
		200	H_2	1	1.9	1.4±0.3
		400	air	4	n/a	1.2 ± 0.3
7	Pt ^{IV} nitrate + TMA	100	H ₂	1.5	1.2	1.4±0.4
		150	H_2	1	2.4	1.6 ± 0.5
		200	H_2	1	n/a	$2.0{\pm}1.2$
		400	air	4	n/a	1.7±0.6

such a modification was shown previously.^{11,14} The formation of final particles is a result of the sintering of the active component on the support surface upon precursor decomposition treatments (such as reduction/air annealing *etc.*). The interaction of nitric acid or TMA with alumina can affect the destruction of the polynuclear species and the stabilization of the supported active component particles towards sintering. Note that the destruction of the polynuclear species in precursor solution as a stage of supported particle formation can promote a nonuniform distribution of the active component over the support grains (so-called shell distribution) observed in the prepared catalysts.

Therefore, the precursor solution interaction with oxide support in combination with annealing treatment following the impregnation determines the size of the active component particles of the final catalyst. The composition of the precursor solution influences this process. At the same time, under the experimental conditions, the size of the polynuclear species formed in the precursor solution is not critical for the characteristics of the catalysts. The modification of the chemical composition of the oxide support is a key to control catalyst properties in the course of preparation.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.01.022.

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