Application of Pt/Al$_2$O$_3$ catalysts produced by sol-gel process to uranyl ion reduction

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Abstract Various kinds of active alumina supports were obtained by the Institute of Nuclear Chemistry and Technology (INCT) sol-gel process in the following steps: (1) preparation of alumina sols by extraction of nitrates with Primene JMT from aluminium nitrate solution; (2) gelation to spherical particles (with diameter < 100 μm) by extraction of water from sol emulsion in 2-ethyl-1-hexanol; (3) sometimes conversion of NO$_3^-$ stabilized gel to OH$^-$ form by reaction with ammonia; (4) calcination of gels to γ-Al$_2$O$_3$ with specific surface area > 100 m^2/g at 500°C. The powders were then impregnated with chloroplatinic acid and recalcined at 500°C. Catalysts were also prepared by direct gelation of alumina sol containing hydroplatinic acid followed by steps (3) and (4). Pt/Al$_2$O$_3$ catalysts were used for the reduction of 1 M UO$_2$(NO$_3$)$_2^-$ 0.5 M HCOOH solution with hydrogen at atmospheric pressure. The course of the reduction was controlled analytically and by measuring the U(VI)/U(IV) redox potential. It was concluded that the catalysts obtained by impregnation of the supports prepared from nitrate stabilized gels exhibit the best activity and stability.

Key words sol-gel • Pt/Al$_2$O$_3$ catalysts • uranyl ion reduction

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Introduction

The problem of reduction of uranyl ion in the solution is very interesting from the technological point of view. It is generally known but not fully explained why uranyl ion does not form concentrated colloidal solutions [3, 8]. These colloidal uranium solutions, formed readily by U^{4+} cation contrary to the uranyl ion, are indispensable in the various variants of the sol-gel process of production of spherical grains of reactor fuels containing uranium dioxide or carbides [3, 5, 8, 15].

The problem of reduction of uranyl nitrate solution did not require any special attention when the precipitation-peptization method of U^{4+} sol preparation had been used. In that method, uranium(IV) hydroxide was precipitated from the starting solutions and, therefore the composition of the feed solutions was not important except for the degree of uranium reduction. It was then possible to use stabilizers of U^{4+} ion (e.g. urea or hydrazine), uranyl solutions of low concentrations (< 0.5 M/l) and an excess of nitric acid. In these conditions – very favorable for the UO$_2^{2+}$ reduction – the kind of catalyst was not important. Generally, platinized alumina in the form of irregular grains suspended in the reducing solutions or a fixed catalyst bed were used [3, 8, 17]. Alumina is widely used as a catalyst support because of its favorable beneficial physicochemical properties e.g. thermal and chemical stability, high surface area [1].

The problem of the composition of uranyl solutions and catalysts used in reduction of UO$_2^{2+}$ became very

important when the method of solvent extraction of nitrates was adapted for the preparation of the concentrated (> 1 M) urania sols (CUSP process [5, 15]). First urea and hydrazine were eliminated because the formation of ammonia from those components at elevated temperatures (at which the aqueous phase was ageing between successive extraction stages) caused thickening of the sol. Instead of the above mentioned stabilizers, formic acid was used to protect of U(IV) from reoxidation. The mentioned authors used the PtO_2^- Adam's catalyst. It was convenient because of its great sedimentation rate after the reduction process in which the catalyst is reduced to platinum metal.

Recently, various types of metallic catalyst dispersed in an oxide matrix were prepared by the sol-gel method. Generally, two procedures are used: preparation of xerogels as supports for metallic element [3 (p. 88), 6, 7, 10, 13, 14, 18] or introduction of an active metal before gelation, followed by a thermal treatment [6, 9–13, 18]. In all the cited papers, except [3] where inorganic sol-gel process was used, hydrolysis and condensation of liquid alkoxides were employed for the gelation step.

At the beginning of the present work, we believed that in order to increase the sedimentation rate and mechanical resistance of the catalyst it is necessary to prepare a catalyst of spherical shape. We have selected a platinum catalyst on alumina support. It can be prepared using a continuous INCT sol-gel process described in our earlier work [2, 4].

Experimental

The alumina supports were obtained in the following steps: (1) preparation of alumina sols by extraction of nitrates with Primene JMT from aluminium nitrate solution [4]; (2) gelation to spherical particles (diameter < 100 μm) by extraction of water from sol emulsion in 2-ethyl-1-hexanol [4]; (3) sometimes conversion of NO_3^- stabilized gel to OH^- form by reaction with ammonia; (4) calcination of gels at 500°C. The powders were then impregnated with chloroplatinic acid (2 ml 3% solution/1 g Al_2O_3) and after filtration and washing with H_2O, recalcined at 500°C. Catalysts were also prepared by direct gelation of alumina sol containing hydroplatinic acid followed by steps (3) and (4). A detailed flow sheet of the above described procedures is shown in Fig. 1.

The specific surface area of the powders was determined by the BET method, using nitrogen. X-ray diffraction measurements (using $CoK_{\alpha1}$ radiation) were carried out using a positional sensitive detector (Ital Structure).

The reduction was accomplished in a glass-batch slurry reactor (Sovirel) to which 1 liter of 1 M $UO_2(NO_3)_2^-$ ("nuclear grade" purity) – 0.5 M HCOOH solution and 14 g of catalyst had been added. Purified hydrogen was introduced through a pore filter in the bottom of the reactor. Solutions were vigorously agitated by means of a turbine stirrer. The course of reduction was controlled analytically and by measuring the U(VI)/U(IV) redox potential. The plateau after the sharp inflection point on the curve potential mv vs. time indicates completion of the uranium reduction.
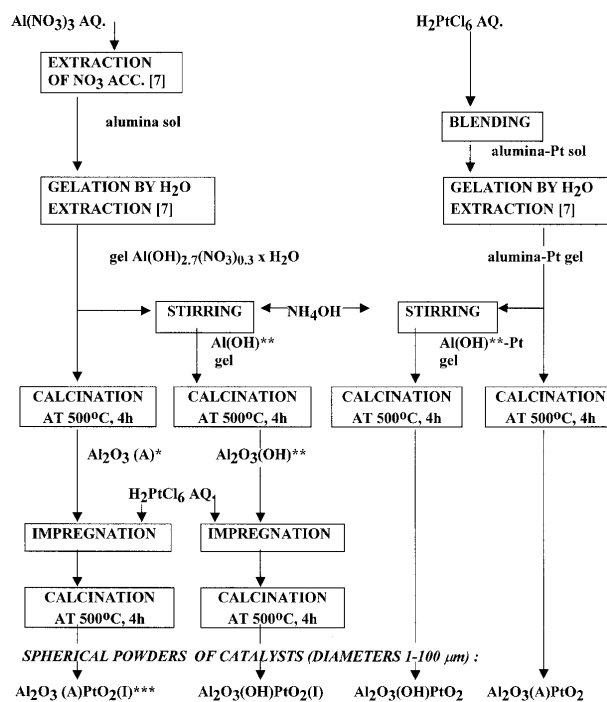

Fig. 1. Flow sheet of the sol-gel process for preparation of Pt/Al_2O_3 catalysts. * – (A) precursors derived from anion-containing gels; ** – (OH) precursors derived from OH^--containing gels; *** – (I) catalysts prepared by impregnation. It was found by XRD studies that all alumina oxides calcined at 500°C had γ-structure.

The desired end point of the process was estimated by calculating first derivatives of the curve. When the value of the derivative, immediately after reaching a maximum at the inflection point, became approximately 0, the hydrogen flow was stopped.

Results and discussion

Physicochemical characterization of the prepared catalysts as well as the results of reduction reactions carried out using these catalysts are shown in Table 1.

The Pt content in all samples prepared by impregnation varied from 2.0 to 2.6%. This indicates that the supports have an excellent adsorption ability because according to [1] the maximum amount of Pt adsorbed on alumina carriers corresponds to 2.1%. The Pt contents in the samples prepared by gelation of alumina-Pt sols were 3%.

On the basis of the results presented in Table 1, the order of catalytic activities is as follows

$$Al_2O_3(A)PtO_2(I) > Al_2O_3(OH)PtO_2(I) >>$$
$$>> Al_2O_3(OH)PtO_2 > Al_2O_3(A)PtO_2$$
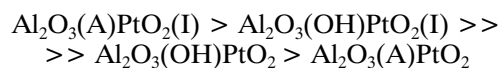
The activity of catalysts depends first of all on the way of preparation. In our process, samples (I) obtained by impregnation of the earlier prepared γ-Al_2O_3 powders exhibit a better activity than that prepared by the addition of Pt solution before gelation, followed by a similar thermal treatment. These observations, contradictory to the data of [13], can be interpreted as

Table 1. Characterization of the catalysts and UO$_2^{2+}$ reduction process. SSA – specific surface area , * – the same catalysts as in experiment No. 1b, after 10 consecutive runs, ** – the support was prepared in fluidal gelation column ORNL type [3, 8], *** – commercial alumina in α form.

No.	Type of catalyst	[%]			Particle diameter [μm]	SSA [m^2/g]	Reduction			Final molar ratio NH$_4^+$/ΣU
		Pt	N(NO$_3$)	Cl			t [°C]	time [min]	final % of U^{4+} in ΣU	
1	Al$_2$O$_3$(A)PtO$_2$(I)	2.6	0.15	0.35	<100	140	20	40	100	0.04
1a	"	"			<49	160	20	45	99	0.04
1b	"	"			40–100		40	40	100	0.06
1c	"	"			"		20	40	100	0.04
1d*	after 10 " runs				"		20	50	96	0.03
1F***	"	"			200–400		20	360	89	0.04
2	Al$_2$O$_3$(OH)PtO$_2$(I)	2.3	0.0	0.0	<100	145	20	80	96	0.05
2F***	"	"			200–400		20	600	0	
3	Al$_2$O$_3$(OH)PtO$_2$	3.0	0.0	0.0	<100	220	20	160	100	
4	Al$_2$O$_3$(A)PtO$_2$	3.0	0.1	0.3	<100	110	20	340	95	
5	Al$_2$O$_3$***(I)	2.0	0.0	0.0	<49	15	20	900	0	

the results of Pt poisoning during calcination of alumina-Pt gel containing several percent of organic substances (surfactants, solvents) adsorbed in the process or/and by trapping the dispersed metals in the closed pores in microspheres. The last interpretation seems to be less likely, because of a similar or higher specific surface area. The first version is also more probable because organics are absent if microspheres are calcined at 500°C before impregnation.

Soaking of samples in NH$_4$OH has a positive effect only for non-impregnated samples. This conclusion is in agreement with the data of paper [16] where an increase in the surface parameter of alumina after soaking was observed.

Soaking of samples before impregnation does not change the specific surface area, however this process has a negative effect on the catalyst activity. If the hypothesis that burning off organics from the supports exerts a positive effect is correct, then it can be suggested that the presence of strongly oxidising nitrates in the non-soaked powders facilitates the removal of organics during calcination.

The particle size distribution for powders with the grain diameters < 100 μm has no effect on the catalyst activity. However, spherical powders of catalysts with grain diameters > 300 μm exhibit a significantly lower activity.

As can be seen in Table 1 (experiments No. 1b and 1d), the stability of catalytic activity and mechanical resistance (preservation of spherical shape, Fig. 2) of the catalysts after 10 consecutive runs, were acceptable.

For gel derived samples, the specific surface area (SSA) in the region higher than 100 m^2/g has no effect on the catalyst activity. However, the catalyst prepared from the commercial α-alumina (No. 5) with low SSA (15 m^2/g) does not reveal any activity in the studied process.

The degree of reduction is generally higher for better quality catalysts. Temperature (in the range 20–40°C) does not affect the reduction process, however

higher temperature results in a slightly higher NH$_4^+$/ΣU molar ratio. The NH$_4^+$ content (derived from NO$_3^-$ reduction) is important if the reduced solution is used for the preparation of uranium sol by nitrate extraction [5, 15]. High content can cause thickening of the sol. In the present work, a value 0.01 recommended in the ORNL papers [5, 15], was always exceeded. According to the cited works, the hydrogen flow in the absence of UO$_2^{2+}$ i.e. immediately after the inflection point, results in the production of ammonia from NO$_3^-$. In the experiment No. 1b, we analyzed the molar ratio of NH$_4^+$/ΣU and the reduction degree in various steps of the process. The results are shown in Table 2.

It follows from the presented data that in our experiments ammonia is formed just before the reduction has been completed. It seems that application of the ORNL [5, 15] type batch reactor with a more uniform agitation of the solution and a more uniform distribution of the gaseous hydrogen will permit to decrease the amounts of ammonium ions.
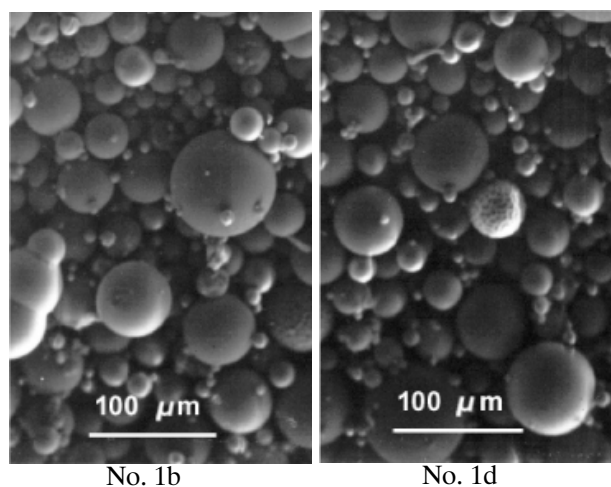

No. 1b   No. 1d

Fig. 2. Scanning electron micrograph of a freshly prepared Pt/Al$_2$O$_3$ catalyst (No. 1b), and the catalyst after 10 consecutive runs (No. 1d).

Table 2. Ammonia formation during uranyl ion reduction process

Time of sampling [min]	Reduction degree % U^{4+} in ΣU	$NH_4^+/\Sigma U$ molar ratio
0 – starting solution	0.0	0.00
10	30.0	0.00
35	80.0	0.02
40 – inflection point	100.0	0.04
45	100.0	0.08

Conclusions

A sol-gel method for the preparation of Pt/Al_2O_3 catalyst in the form of spherical powders (with diameter < 100 μm) has been elaborated. The activity of the catalysts to uranyl ion reduction depends, first of all, on the way of preparation. In our process, the samples obtained by impregnation of the sol-gel derived γ-Al_2O_3 powders exhibit a better activity than those prepared by the addition of Pt solution before gelation, followed by a similar thermal treatment.

The stability of catalytic activity and the mechanical resistance and of the catalysts are acceptable. The sedimentation rate of the prepared catalyst microspheres was more that 20 times higher than those prepared using irregularly shaped powders of similar particles size distribution.

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