

SEPARATION OF PLATINUM(IV) AND RHENIUM(VII) IN THE PROCESS OF WORKING-UP OF DEACTIVATED REFORMING CATALYSTS

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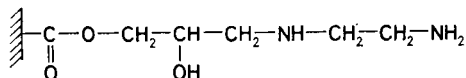
A procedure is suggested for the isolation of Pt(IV) and Re(VII) from solutions after the working-up of exhausted catalysts for the reforming of hydrocarbons, which in addition to the catalytically active Pt and Re contain Fe and Ti on Al_2O_3 as promoters. The solution is passed through a column packed with a glycidyl methacrylate chelating sorbent containing ethylenediamine functional groups; while Fe^{3+} , Ti^{4+} , and Al^{3+} cations pass freely, $[\text{PtCl}_6]^{2-}$ and ReO_4^- anions are retained by the column; they are subsequently separated by gradual elution, Re(VII) first with 1–3M- H_2SO_4 , then Pt(IV) with 2–5M- HNO_3 . Complexes of Pt(IV) with the polymeric ligands, forming during the separation, are identified by means of their infrared and electronic reflection spectra.

Reclamation of platinum and rhenium from deactivated catalysts for the reforming of hydrocarbons is gaining in importance as the consumption and rareness of these unreplaceable metals are steadily increasing. Although reclamation of precious metals has been often discussed in the literature^{1–3}, it is difficult to select a procedure which would be easily applicable and would meet all the particular process requirements.

In this paper, a procedure is suggested for the isolation of platinum(IV) and rhenium(VII) from solutions containing aluminium(III), iron(III), and titanium(IV) ions, emerging from the acid decomposition of exhausted reforming catalysts. The method consists of the use of a macroporous chelating sorbent. The elements reclaimed are obtained in separate substances, *viz.* chloroplatinic and perrhenic acids or their ammonium salts, as are used for fixing to the support and preparation of catalyst. Owing to its simplicity, the method can be conveniently used for practical purposes.

EXPERIMENTAL

The sorbent used was a glycidyl methacrylate–ethylene dimethacrylate copolymer chemically modified with ethylenediamine⁴, of the schematic formula



Spherical particles 0.1 mm in diameter, specific surface area $60 \text{ m}^2 \text{ g}^{-1}$, contained ethylenediamine (eda) functional groups in an amount of 2.3 mmol g^{-1} as found by elemental analysis for nitrogen (6.44%). The sorbent was prepared at the Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences in Prague.

Platinum and rhenium were isolated from extracts in *aqua regia* or 5M-HCl from deactivated reforming catalysts, containing 0.3% Pt, 0.3% Re, 0.1% Fe, and 0.2% Ti. The metals bonded to the sorbent were determined in the extracts spectrophotometrically: rhenium and platinum with the use of tin dichloride^{5,6}, titanium with ascorbic acid, aluminium with pyrocatechol violet, and iron with *o*-phenanthroline⁶. Nitric acid was evaporated from the solution before the analysis for platinum.

[PtCl₄(en)] as a model complex was prepared following ref.⁷; for C₂H₈N₂Cl₄Pt (397.0) calculated: 49.1% Pt, found: 48.4% Pt. Aquation of the complex was performed in 2M-HNO₃ in the presence of AgNO₃.

The electronic spectra of the model complex and complexes of Pt(IV) bonded to the sorbent were measured on a Perkin-Elmer 340 instrument, the infrared spectra of KBr disks, on a Perkin-Elmer 325 spectrophotometer.

RESULTS AND DISCUSSION

The isolation and separation of platinum and rhenium follow after a stage, where the deactivated reforming catalyst is freed from carbon residues by oxidation in an air stream. The rhenium heptoxide formed is isolated in a 80–90% yield by dissolving in aqueous ammonia, from which ammonium perrhenate is obtained by crystallization; the remaining oxides are transferred to solution by the action of *aqua regia*. The annealed catalyst can also be worked up directly by acid decomposition without prior isolation of rhenium⁸.

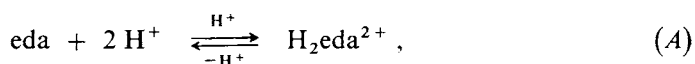
The acidic chloride extracts of the exhausted oxide catalyst contain [PtCl₆]²⁻ and ReO₄⁻ anionic species and Al³⁺, Fe³⁺, and Ti⁴⁺ cations. The polymeric sorbent bonds the anionic species from acid solutions (pH 0–1), thereby allowing for their separation because the unwanted cation impurities pass freely without being sorbed.

The method was tested on catalyst extracts containing rhenium and platinum in concentrations of 0.1–10 mmol l⁻¹. The amount of sorbent in the column was 1–100 g. Typical results are given in Table I. 500 ml of the sorption solution, which was extract in *aqua regia* diluted with one-half volume of water, was passed through the column which retained all platinum and rhenium. In the stage of desorption, the metals were released and mutually separated by elution with different agents (Table I). Perrhenate ions are displaced preferentially with 1–3M-H₂SO₄, the chloroplatinate anions are successively eluted with 2–5M-HNO₃.

If the sorbent with bonded [PtCl₆]²⁻ ions is washed with water or dilute ($c < 0.1 \text{ mol l}^{-1}$) acids, the acidity of the system is lowered. This has an unfavourable

consequence, *viz.*, the occurrence of a substitution reaction of the chloro complexes giving rise to platinum(IV) chelates with the ethylenediamine functional groups. In contrast to platinum(IV) complexes with non-chelating amine polymeric ligands, the chelates cannot be desorbed readily and consequently, platinum remains irreversibly bonded to the resin (this gives evidence of chelation taking place during the separation).

Platinum(IV) sorbs even from highly acid chloride solutions, where it is present in the form of the $[\text{PtCl}_6]^{2-}$ chloro complex. The basic functional groups of the sorbent, $-\text{NH}(\text{CH}_2)_2\text{NH}_2$ (eda), are neutralized in such conditions ($\text{pH} < 2$) and the protonated amino groups, $\text{H}_2\text{eda}^{2+}$, then can react with the anionic chloroplatinate species by electrostatic interaction. The sorbent behaves as an anion exchanger. The amount of protonated groups of the sorbent decreases with decreasing concentration of hydrogen ions,



and at the same time, the $[\text{PtCl}_6]^{2-}$ ions are subject to hydrolysis,



TABLE I

Isolation and separation of platinum(IV) and rhenium(VII) using a 30×100 mm column containing 20 g of sorbent

Composition of solution	Volume ml	Amount of metal, mg				
		Re	Pt	Fe	Ti	Al
Sorption solution	500	25.2	22.0	15.4	11.4	340
Passed solution, 0.2M- H_2SO_4 (column washing)	650	0.0	0.0	15.4	11.4	340
Bonded to sorbent		25.2	22.0	—	—	—
Desorption with						
1M- H_2SO_4	100	7.4	0.0			
3M- H_2SO_4	200	17.8	0.0			
2M- HNO_3	500	—	18.3			
5M- HNO_3	100	—	3.5			

so that complexing reactions between the platinum(IV) ions and the free ethylenediamine functional groups of the sorbent also start to take place. Which of the two reaction predominates on the sorbent, and in which manner then the platinum(IV) is bonded to the functional groups of the polymeric matrix, depends on the pH of the sorbent-sorbate (eluate) system. The various types of compound are different in colour and they can be discerned on the initially colourless sorbent. It was found

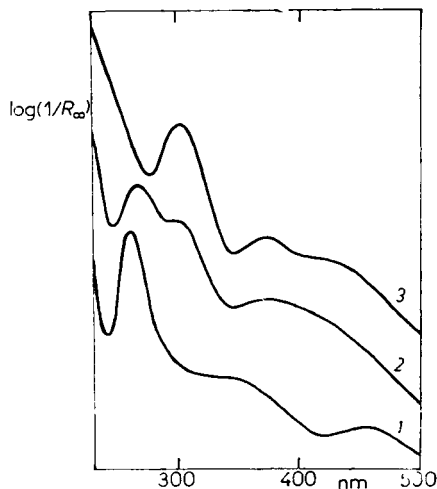


FIG. 1

Electronic reflection spectra of platinum(IV) complexes on sorbent. 1 $[\text{PtCl}_6]^{2-}$, Pt(IV) sorbed from chloride solutions at pH 0.5 (sample No 1), 2 sorbent with bonded $[\text{PtCl}_6]^{2-}$ ions after washing with 0.01M HCl (sample No 2), 3 $[\text{Pt}(\text{H}_2\text{O})_4\text{eda}]^{4+}$, sample No 2 eluted with 5M- HNO_3 (sample No 3)

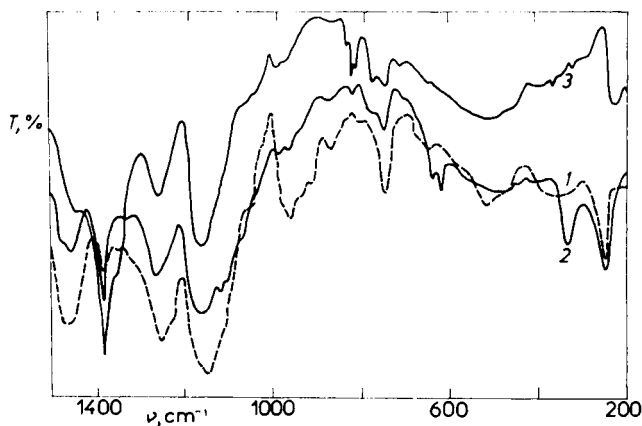


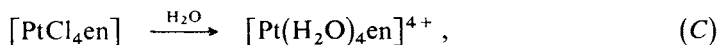
FIG. 2

Infrared spectra of sorbent samples. 1 sorbent washed with HCl, 2 sorbent with bonded $[\text{PtCl}_6]^{2-}$ ions, 3 sorbent with $[\text{Pt}(\text{H}_2\text{O})_4\text{eda}]^{4+}$ complex

experimentally that sorbed from chloride solutions at pH 3.5, platinum(IV) remains bonded to the polymer. Elution with 5M-HNO₃ leads to a recovery as low as 40%.

Platinum(IV) sorbed from acid chloride solutions at pH 0.5 and bonded to the resin in the [PtCl₆]²⁻ form (Fig. 1, sample No 1) starts to be coordinated by the sorption-active eda groups only during the washing of the column with 0.01M-HCl, owing to the pH increase (Fig. 1, sample No 2). Subsequent elution with 2–5M-HNO₃ brings about displacement of the remaining anionic complex species of Pt(IV), which are bonded by electrostatic forces, while the thermodynamically stable [Pt(H₂O)₄eda]⁴⁺ chelates remain on the sorbent (Fig. 1, sample No 3). Determination of chloride in this sorbent sample by elemental analysis was negative. The electronic spectrum of the complex with the [Pt(H₂O)₄eda]⁴⁺ polymeric ligand is identical with that of the sample with platinum(IV) bonded from solution at pH 3.5 and eluted with nitric acid. It was inferred from the electronic spectra in conjunction with published data^{7,9,10} that the species is neither *trans*-[Pt(H₂O)₂(en)₂]⁴⁺ type nor a complex with coordinated primary amine or ammonia ([Pt(H₂O)₄(NH₃)₂]⁴⁺).

The infrared spectrum of the sorbent sample with platinum bonded in the [Pt(H₂O)₄eda]⁴⁺ complex does not exhibit the band of the ν(Pt–Cl) stretching vibration at 345 cm⁻¹, which is very marked in the spectrum of the sorbent with [PtCl₆]²⁻ chloro complexes (Fig. 2). Of the metal–ligand bonding vibrations occurring in the low-frequency region¹¹, ν(Pt–N) at 500 cm⁻¹ and ν(Pt–O) at 380 cm⁻¹ were observed. Coordinated molecules of water give rise to bands at 820 and 778 cm⁻¹ and in the 520–450 cm⁻¹ range. The infrared spectrum of the glycidyl methacrylate sorbent with ethylenediamine functional groups and coordination-bonded platinum(IV) also displays absorption bands belonging to the polymeric matrix¹² and to the ionically bonded ONO₂⁻ species: a marked band of the ν₃ stretching vibration at 1385 cm⁻¹ and bands of the ν₁, ν₂, and ν₄ vibrations at 1048, 825, and 720 cm⁻¹, respectively. From the spectra it can be inferred that around Pt(IV) are bonded oxygen and nitrogen atoms; this is also borne out by the electronic spectra in the visible region. The electronic reflection spectrum of the aquated complex of Pt(IV) bonded to the sorbent *via* the eda functional groups displays maxima at 450(sh), 366, and 305 nm (Fig. 1). The absorption bands in the spectrum of the model complex formed by hydrolysis,



lie at 460, 370(sh), 309, and 208 nm.

REFERENCES

1. Kluksdahl H. E., Hopkins J. R.: U.S. 3578395; Chem. Abstr. 75, 25973 (1971).
2. Wiley Ch. L.: Ger. 2156109; Chem. Abstr. 77, 52839 (1972).

3. Kurbatov V. F., Yaksimova Z. P., Alikberova L. Yu., Galitskaya N. B., Ivanova N. I., Kryshchenko K. I., Novikov P. D.: U.S.S.R. 973483; Chem. Abstr. 98, 128682 (1983).
4. Švec F., Horák D., Kálal J.: Angew. Makromol. Chem. 63, 37 (1977).
5. Ojeda M. W., Romero J. W., Rivarola J. B. P.: Lat. Am. J. Chem. Eng. Appl. Chem. 13, 281 (1983).
6. Malát M.: *Absorpční anorganická fotometrie*, pp. 770, 286, 380, 684. Academia, Prague 1973.
7. Basolo F., Bailar J. C. jr, Tarr B. R.: J. Am. Chem. Soc. 72, 2433 (1950).
8. Mastný L., Bumbová M., Kálalová E., Švajgl O., Pražák V.: Chem. Prum. 36 61, 243 (1986).
9. Henegham L. F., Bailar J. C. jr: J. Am. Chem. Soc. 75, 1840 (1953).
10. Cox L. E., Peters D. G.: Inorg. Chem. 9, 1927 (1970).
11. Nakamoto K., McCarthy P. J.: *Spectroscopy and Structure of Metal Chelate Compounds*, p. 246. New York 1968.
12. Kálalová E., Radová Z., Kálal J., Švec F.: Eur. Polym. J. 13, 287 (1977).

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