Electronic Supplementary Information (ESI)

## Selective sorption of palladium by thiocarbamoyl–substituted thiacalix[*n*]arene derivatives immobilized in amberlite resin: Application to leach liquors of automotive catalysts

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| Constituents                     |                          |  |  |
|----------------------------------|--------------------------|--|--|
| Matrix structure                 | Acrylic                  |  |  |
| Classification                   | Nonionic<br>Spherical    |  |  |
| Specific surface area (m²/g)     | 500                      |  |  |
| Pore volume (cm <sup>3</sup> /g) | 0.6                      |  |  |
| Pore diameter (Å)                | 100                      |  |  |
| Apparent density (g/L)           | ~655                     |  |  |
| Moisture holding capacity (%)    | 61-69                    |  |  |
| Harmonic mean diameter<br>(mm)   | 0.43 - 0.69              |  |  |
| Uniformity coefficient           | ≦ 2.0                    |  |  |
| Effective pH range               | 0-14                     |  |  |
| Polarity                         | Intermediate<br>polarity |  |  |

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Fig. S2 FT-IR spectra of XAD, 8 and Pd(II) sorbed 8.



Fig. S3 XRD patterns of XAD, 8, and Pd(II) sorbed 8.



Fig. S4 (a-b) WDXRF spectra of C Kα for 8 before and after Pd(II) sorption



Fig. S5 (a-b) WDXRF spectra of N Kα for 8 resin before and after Pd(II) sorption.



Fig. S6 (a-b) WDXRF spectra of O Kα for 8 resin before and after Pd(II) sorption.



Fig. S7 (a-b) WDXRF spectra of S K $\alpha$  for 8 resin before and after Pd(II) sorption.



Fig. S8 Van't Hoff plot relating In K against 1/T (a) 7 (b) 8.

Table S2 Thermodynamic parameters of 7 and 8.

| Thermodyn  | amic  | 7      | 8      |
|--|-------|--------|--------|
| ∆Gº (kJ mol <sup>-1</sup> )                                | 303 K | -10.07 | -10.43 |
|  | 313 K | -9.96  | -9.98  |
|  | 323 K | -9.59  | -9.21  |
| $\Delta H^{o}$ (kJ mol <sup>-1</sup> )                     |       | -16.96 | -28.25 |
| $\Delta S^{\circ}$ (kJ mol <sup>-1</sup> K <sup>-1</sup> ) |       | -0.023 | -0.060 |



**Fig. S9** Effect of automotive catalyst volume. Bed height = 0.5 cm; flow rate = 0.1 mL/min; [Pd(II)] in automotive catalyst solution = 9.2 mg/L.

| S.     | Polymeric adsorbents                                       | Sorption capacity   | Ref.             |
|--------|--|---------------------|------------------|
| No     |  | (mg/g)              | 160              |
| 1<br>2 | Dialon WAZIJ<br>Melamine formaldehyde thiourea (MET) resin | ວ. <i>1</i><br>15 2 | 10a<br>16b       |
| 2      | Dualita CT 72  | 1J.Z<br>27 7        | 160              |
| с<br>л | Duolite G1-75  | 21.1                |                  |
| 4      | Thiourea-Formaldenyde Chelating Resin (PTFT)               | 30.7                | 160              |
| 5      | Thiourea-Formaldehyde Chelating Resin (PTF2)               | 49.8                | 16d              |
| 6      | Phosphine sulphide-chelating polymer (Polymer 3)           | 53.0                | 16e              |
| 7      | Duolite GT-73  | 21.2                | 17a              |
| 8      | Calix[4]pyrrole[2]thiophene immobilized polymer            | 65.0                | 17b              |
| 9      | POLYORGS V   | 18.4                | 17c              |
| 10     | POLYORGS VI  | 48.0                | 17c              |
| 11     | Polythioether resin with aminoisopropyl-mercaptan          | 64.8                | 17d              |
| 12     | Spheron Oxine 1000   | 57.0                | 17e              |
| 13     | Spheron Salicyl 1000                                       | 10.0                | 17e              |
| 14     | Spheron 1000   | 1.6                 | 17e              |
| 15     | Dithizone modified chloromethylated polystyrene            | 72.1                | 18a              |
| 16     | Amidinothioureido-silica gel                               | 14.9                | 18b              |
| 17     | Benzimidazolylazo resin                                    | 65.7                | 18c              |
| 18     | Lewatit MP-500   | 9.9                 | 18d              |
| 19     | Lewatit MP-500A  | 9.4                 | 18d              |
| 20     | TUF resin  | 31.8                | 18e              |
| 21     | Purolite S-940   | 53.2                | 19a              |
| 22     | Amberlite XAD-7 impregnated Cyphos IL-101                  | 71.0                | 9b               |
| 23     | Triisobutyl phosphine sulfide resin (Polymer A)            | 54.0                | 19b              |
| 24     | Triisobutyl phosphine sulfide resin (Polymer A)            | 76.3                | 19b              |
| 25     | IRA 910  | 81.6                | 19b              |
| 26     | Macroporous poly(vinyl-aminoacetone)                       | 66.8                | 19c              |
| 27     | Pyrazolone immobilized styrene-divinylbenzene              | 59.4                | 19d              |
| 28     | 7  | 51.55               | Present<br>study |
| 29     | 8  | 91.74               | Present study    |

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