Table S1.

CHClF2 hydrodechlorination on Pd-Pt/(acac)/Norit1600 catalysts precalcined at 320 oC for 1 h. Turnover frequencies, product selectivities and activation energies.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalysta,b | Reaction temperature  oC | TOFc  s-1 | Product selectivity, % | | | | Activation energy,  kJ/mol |
| CH4 | CH3F | CHF3 | CH2F2 |  |
| Pd*100*(acac)  H/Pd = 0.123 | 272 | 1.06E-3 | 26.7 | - | - | 73.3 | 97.3 ± 1.9 |
| 262 | 7.15E-4 | 23.2 | - | - | 76.8 |
| 252 | 4.7E-4 | 20.6 | - | - | 79.4 |
| Pd*80*Pt*20*(acac)  H/(Pd+Pt) = 0.191 | 271 | 1.41E-3 | 32.8 | 3.6 | - | 63.6 | 97.8 ± 5.2 |
| 262 | 1.02E-3 | 24.7 | 5.2 | - | 70.1 |
| 251 | 6.2E-4 | 24.9 | 6.0 | - | 69.1 |
| Pd*60*Pt*40*(acac)  H/(Pd+Pt) = 0.252 | 271 | 1.95E-3 | 43.0 | 9.5 | - | 47.5 | 91.1 ± 8.8 |
| 262 | 1.30E-3 | 40.8 | 9.3 | - | 48.9 |
| 251 | 9.0E-4 | 36.6 | 14.8 | - | 48.6 |
| Pd*40*Pt*60*(acac)  H/(Pd+Pt) = 0.331 | 271 | 1.64E-3 | 44.2 | 13.5 | - | 42.3 | 76.6 ±4.3 |
| 263 | 1.25E-3 | 40.9 | 14.6 | - | 44.5 |
| 252 | 8.7E-4 | 36.5 | 14.9 | - | 48.6 |
| Pt*100*(acac)  H/Pt = 0.465 | 271 | 6.0E-4 | 58.4 | 14.9 | 14.0 | 12.7 | 103.6 ± 2.7 |
| 262 | 4.0E-4 | 60.2 | 20.7 | 4.0 | 19.1 |
| 251 | 2.5E-4 | 74.0 | 9.4 | - | 16.6 |

a For the catalyst designation, see Methods (subsection 3.1).

b Metal dispersion data (from H2 chemisorption) located below catalyst designation.

c GHSV 5760 h-1, catalyst weight 0.20 g.

Table S2.

CHClF2 hydrodechlorination on Pd-Pt/(acac)/Norit1600 catalysts precalcined at 350 oC for 1 h. Turnover frequencies, product selectivities and activation energies.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalysta,b | Reaction temperature  oC | TOFc  s-1 | Product selectivity, % | | | | Activation energy,  kJ/mol |
| CH4 | CH3F | CHF3 | CH2F2 |  |
| Pd*100*(acac)  H/Pd = 0.161 | 272 | 2.30E-3 | 29.5 | - | - | 70.5 | 102.3 ±1.5 |
| 261 | 1.46E-3 | 25.0 | - | - | 75.0 |
| 251 | 9.25E-4 | 20.6 | - | - | 79.4 |
| Pd*80*Pt*20*(acac)  H/(Pd+Pt) = 0.223 | 272 | 2.30E-3 | 38.0 | 4.2 | - | 57.8 | 98.8 ± 2.8 |
| 261 | 1.50E-3 | 33.7 | 4.0 | - | 62.3 |
| 251 | 9.6E-4 | 30.0 | 4.0 | - | 66.0 |
| Pd*60*Pt*40*(acac)  H/(Pd+Pt) = 0.243 | 272 | 2.32E-3 | 43.6 | 7.9 | - | 48.5 | 97.7 ± 4.8 |
| 261 | 1.61E-3 | 39.4 | 8.5 | - | 52.1 |
| 251 | 1.02E-3 | 35.0 | 8.5 | - | 56.5 |
| Pd*40*Pt*60*(acac)  H/(Pd+Pt) = 0.321 | 272 | 2.25E-3 | 47.2 | 13.2 | - | 39.6 | 92.9 ±1.3 |
| 262 | 1.55E-3 | 41.5 | 14.9 | - | 43.6 |
| 251 | 9.9E-4 | 38.4 | 15.6 | - | 46.0 |
| Pt*100*(acac)  H/Pt = 0.348 | 272 | 7.5E-4 | 52.8 | 13.8 | 22.0 | 11.4 | 107.5 ±0.4 |
| 262 | 4.8E-4 | 60.2 | 20.6 | - | 19.2 |
| 251 | 2.9E-4 | 66.3 | 18.7 | - | 15.0 |

a,b,c As in Table 1.

Table S3.

CHClF2 hydrodechlorination on Pd-Pt/(acac)(/Nortit1600 catalysts precalcined at 400 oC for 15 min. Turnover frequencies, product selectivities and activation energies.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalysta,b | Reaction temperature  oC | TOFc  s-1 | Product selectivityc, % | | | | Activation energy,  kJ/mol |
| CH4 | CH3F | CHF3 | CH2F2 |
| Pd*100*(acac)  H/Pd = 0.105 | 272 | 2.63E-3 | 33.7 | - | - | 66.3 | 98.5± 3.7 |
| 262 | 1.80E-3 | 30.1 | - | - | 69.9 |
| 252 | 1.15E-3 | 24.4 | - | - | 75.6 |
| Pd*80*Pt*20*(acac)  H/(Pd+Pt) = 0.198 | 272 | 2.50E-3 | 37.5 | 4.0 | - | 58.5 | 92.6 ± 8.3 |
| 262 | 1.60E-3 | 33.2 | 4.0 | - | 62.8 |
| 251 | 1.1E-4 | 28.9 | 3.9 | - | 67.2 |
| Pd*60*Pt*40*(acac)  H/(Pd+Pt) = 0.212 0.229 | 272 | 2.52E-3 | 42.6 | 7.8 | - | 49.5 | 94.4 ± 6.4 |
| 261 | 1.72E-3 | 38.4 | 8.4 | - | 53.2 |
| 251 | 1.09E-3 | 34.0 | 8.5 | - | 57.5 |
| Pd*40*Pt*60*(acac)  H/(Pd+Pt) = 0.317 | 272 | 2.10E-3 | 44.2 | 14.0 | - | 41.8 | 88.3 ± 2.8 |
| 262 | 1.43E-3 | 40.5 | 14.9 | - | 44.6 |
| 252 | 1.0E-4 | 36.4 | 15.7 | - | 47.9 |
| Pt*100*(acac)  H/Pt = 0.273 | 271 | 9.2E-4 | 53.1 | 13.8 | 21.5 | 11.5 | 97.9 ± 12.8 |
| 262 | 5.8E-4 | 60.4 | 19.2 | - | 20.4 |
| 251 | 4.0E-4 | 70.2 | 19.3 | - | 10.5 |

a,b,c As in Table 1.

Table S4.

CHClF2 hydrodechlorination on Pd-Pt/Norit catalysts prepared from metal chlorides. Turnover frequencies, product selectivities and activation energies.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Catalysta,b | Reaction temperature  oC | TOFc  s-1 | Product selectivityc, % | | | | Activation energy,  kJ/mol |
| CH4 | CH3F | CHF3 | CH2F2 |
| Supported on Norit1600, after calcination at 400 oC (0.25 h), and reduction at 400 oC (3 h) | | | | | | | |
| Pd*100*(Cl)  H/Pd = 0.266 | 271 | 2.80E-3 | 36.8 | 1.2 | - | 62.0 | 95.9 ± 1.3 |
| 261 | 1.90E-3 | 33.6 | 1.2 | - | 65.2 |
| 252 | 1.30E-3 | 30.1 | - | - | 69.9 |
| Pd*60*Pt*40*(Cl)  H/(Pd+Pt) = 0.277 0.287 | 271 | 2.80 E-3 | 53.4 | 5.6 | - | 41.0 | 91.1 ± 1.4 |
| 261 | 1,90 E-3 | 50.9 | 5.9 | - | 43.2 |
| 252 | 1.35E-3 | 47.4 | 6.3 | - | 46.2 |
| Pt*100*(Cl)  H/Pt = 0.62 | 271 | 1.0E-3 | 70.9 | 12.9 | 0.3 | 15.8 | 97.0 ± 4.4 |
| 261 | 6.9E-4 | 68.7 | 12.7 | - | 18.5 |
| 252 | 4.6E-4 | 66.9 | 13.5 | - | 19.6 |
| Supported on Norit1800, after reduction at 400 oC for 3 h | | | | | | | |
| 3 wt.% Pd  H/Pd = 0.215 | 272 | 2.90E-3 | 34.8 | - | - | 65.2 |  |
| 261 | 2.10E-3 | 31.0 | - | - | 69.0 | 86.4 ± 9.1 |
| 251 | 1.35E-3 | 25.7 | - | - | 74.3 |  |

a,b,c As in Table 1.

SET S1. Characteristics of 3 wt.% Pd/Norit1800 catalyst.

Taken from M. Bonarowska, B. Burda, W. Juszczyk J. Pielaszek, Z. Kowalczyk, Z. Karpiński, Appl. Catal. B 35 (2001) 13-20 .

Support: Norit RO 08 activated by helium pretreatment at 1800 oC.

Preparation: ex-PdCl2,aq acidified with HCl, incipient wetness

Metal dispersion after reduction at 400 oC: H/Pd = 0.20; CO/Pd = 0.21 (previous data);

H/Pd = 0.215 (recent measurement).

Pd crystallite size (from XRD line broadening): -~3 nm.

adapted from Bonarowska et al., cited above.

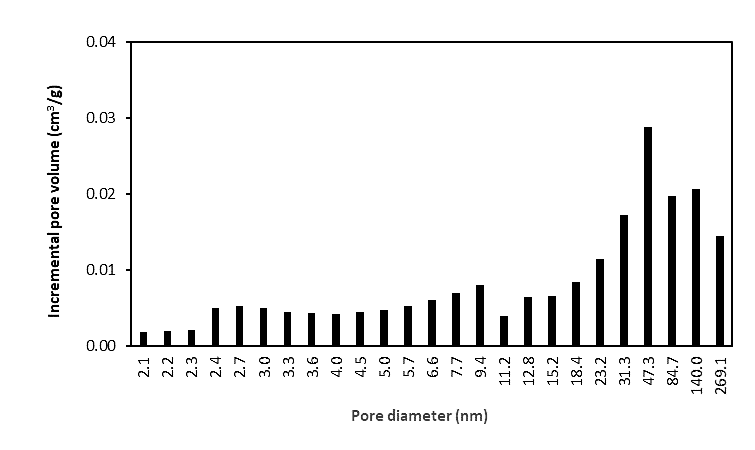
Characteristics based on determination of N2 adsorption isotherm.

BET surface area 85.2 m2/g

Tplot micropore volume = 0.0010 cm3/g

BJH pore volume (adsorption) 0.2082 cm3/g

BJH pore volume (desorption) 0.2065 cm3/g.



Pore size distribution