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Adsorption of Benzenesulfonic Acid; 3,3′,3″-Phosphinidynetris-, Trisodium Salt; and Di(μ-tertiobutylthiolato) Dicarbonyl, Bis(benzenesulfonic acid, 3,3′,3″-phosphinidynetris-, Trisodium Salt) Dirhodium from Aqueous Solutions on Silica

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Adsorption studies of benzenesulfonic acid; 3,3′,3″-phosphinidynetris-, trisodium salt (TPPTS); and di(μ-tertiobutylthiolato) dicarbonyl, bis(benzenesulfonic acid, 3,3′,3″-phosphinidynetris-, trisodium salt) dirhodium ($[\mathrm{Rh}(\mu\text{-S}^t\mathrm{Bu})(\mathrm{CO})(\mathrm{TPPTS})]_2$) from aqueous solutions on four different silica samples were carried out at 25 °C. The isotherms obtained were correlated by several models, among which Fowler's one was found to be the most satisfactory. The solubilities of TPPTS and $[\mathrm{Rh}(\mu\text{-S}^t\mathrm{Bu})(\mathrm{CO})(\mathrm{TPPTS})]_2$ in water at four temperatures in the range (25−80) °C were also studied.

Introduction

Heterogeneous catalysis allows us to keep the catalyst and the reactants and products of a catalytic reaction in different phases. Heterogeneous catalysis has found applications in the chemical industry for economical and ecological reasons, since it is possible to recover and recycle highly valuable catalysts. The recent development of supported aqueous-phase catalysis (SAPC)[1] has opened the way to hydroformylate very hydrophobic alkenes such as octene, dicyclopentadiene, or oleyl alcohol with water-soluble catalysts. But SAPC is still used with empirical rules, because the mechanisms governing the interactions between complex, water, and solid surface are not well elucidated. For this reason, it is necessary to study the adsorption of water-soluble ligands and catalytic complexes onto inorganic supports, as an important step in the preparation of a catalyst−support complex and the understanding of these catalytic properties.

On the other hand, the knowledge of catalyst solubility in water is important for determining the maximum catalyst/substrate ratio for the catalytic reaction in the presence of controlled small amounts of water.

This work presents the results of the adsorption of aqueous solutions of benzenesulfonic acid; 3,3′,3″-phosphinidynetris-, trisodium salt (TPPTS), the most used hydrosoluble ligand in biphasic catalysis; and di(μ-tertiobutylthiolato) dicarbonyl, bis(benzenesulfonic acid, 3,3′,3″-phosphinidynetris-, trisodium salt) dirhodium ($[\mathrm{Rh}(\mu\text{-S}^t\mathrm{Bu})(\mathrm{CO})(\mathrm{TPPTS})]_2$) on four different silica samples. The solubilities of TPPTS and $[\mathrm{Rh}(\mu\text{-S}^t\mathrm{Bu})(\mathrm{CO})(\mathrm{TPPTS})]_2$ in water at four temperatures in the range (25−80) °C were also studied. The solubility of TPPTS in water had been reported previously,[2] but the temperature of experimental determinations was not specified.

Table 1. Physical and Chemical Properties of the Silica Samples[a]

silica	DS22	DS50	sds60	sds200
BET surface area/$m^2\,g^{-1}$	173.16 (190)	488.27 (450)	438.66	316.59
total pore volume/$cm^3\,g^{-1}$	0.19	0.73	0.84	0.58
avg pore diameter/Å	44.9	59.44	76.5	73.5
mean size of the particles/μm	119	53	158	442

[a] Values in parentheses were given by the manufacturers.

Experimental Section

TPPTS was supplied by Rhône-Poulenc. The complex $[\mathrm{Rh}(\mu\text{-S}^t\mathrm{Bu})(\mathrm{CO})(\mathrm{TPPTS})]_2$ was synthesized as reported previously.[3,4] The chemical structures of the TPPTS and $[\mathrm{Rh}(\mu\text{-S}^t\mathrm{Bu})(\mathrm{CO})(\mathrm{TPPTS})]_2$ and their physicochemical properties are reported elsewhere.[3−5] The other chemicals, from commercial sources, were used as received. All the reactions and adsorption experiments were carried out in an inert atmosphere (argon or nitrogen) using standard methods.

Two different silica samples from Degussa, Sipernat 22 (DS22) and Sipernat 50 (DS50), and two from SDS with particle sizes of (60−200) μm (sds60) and (200−500) μm (sds200) were used as supports. Their BET surface area, pore volume, and average pore sizes were measured by nitrogen sorptometry, using a NOVA-1000 version 3.70 analyzer. Particle size measurements were obtained on a Mastersizer MALVERN S. Table 1 shows the physicochemical properties of the adsorbents determined in this work, together with some information provided by the manufacturers.

The solubility studies were carried out as described elsewhere.[6,7] The mass of solid was chosen to be in small excess relative to the highest estimated solubility in the

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Table 2. Solubility of TPPTS and [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$ in Water

	C_s/(g/100 g H$_2$O)			
	t/°C = 25	t/°C = 40	t/°C = 60	t/°C = 80
TPPTS	98.2	105.9	117.7	130.6
[Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$	102.7	108. 9	119.1	132.5

Table 3. Van't Hoff α and β Parameters and Correlation Coefficients (r) for Eq 1

solute	α	β/K	r
TPPTS	6.4121	−545.6624	0.997
[Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$	6.2502	−485.3274	0.987

chosen amount of water. The content of the vessel was stirred at 100 rpm. The dissolution process was studied as a function of the time at 25 °C. It was determined that, after 30 min, the concentration remained constant for both TPPTS and [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$. At each temperature, after 2 h, samples of the supernatant (1 cm^3) were withdrawn from the stirred vessel and filtered through a 0.2 μm membrane (Sartorius) to exclude solid particles. The filtered sample is diluted for measuring the concentration of TPPTS or [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$. Each value of the solubility is an average of three measurements.

In adsorption experiments, a fixed amount of silica (0.5 g) and 6 cm^3 of an aqueous solution of TPPTS or [Rh(μ-S-^{t}Bu)(CO)(TPPTS)]$_2$ were placed in a 50 cm^3 glass-stoppered flask and shaken at 100 rpm for 24 h in a thermostated oscillating bath (JULABO-SW-20C). The aqueous solutions of TPPTS and [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$ were prepared in deaerated water. The initial concentrations of solutions were in the ranges (0.0001−0.64) g/g of solution for TPPTS and (0.0001−0.68) g/g of solution for [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$, which cover the concentration range reported in the works on SAPC and biphasic catalysis.[1−3,8−13] Preliminary experiments had shown that these adsorption processes reached equilibrium within 12 h. Each experiment was duplicated under identical conditions.

The concentration of TPPTS in the aqueous phase was determined by UV spectrophotometry (262.7 nm) with a Hitachi U-2000 apparatus. The concentration of Rh in the aqueous phase was determined by atomic absorption spectrometry (328.1 or 343.5 nm) with a VARIAN AA275 spectrometer.

Results and Discussion

Table 2 shows the average values of the solubilities of TPPTS and [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$ in water. The relative uncertainties were less than 3%. Both compounds are extremely soluble in water. For TPPTS, the values obtained are higher than those reported before.[2] For both compounds, the solubility increases with temperature. The solubility was correlated according to the Van't Hoff equation:

$$\ln C_S/(\mathrm{g}/100\ \mathrm{g\ H_2O}) = \alpha + \beta/(T/\mathrm{K}) \qquad (1)$$

where C_S is the solubility of TPPTS or [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$ and T is the absolute temperature. Table 3 shows the values of the α and β parameters and the correlation coefficients. The slope β of the Van't Hoff equation yields the standard enthalpy of dissolution.

Experimental results of equilibrium adsorption of TPPTS and [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$ on silica are given in Tables 4 and 5. The average relative error of measured concentration in the liquid phase was 3.78% (with a higher value of 7.45%) for TPPTS and 3.31% (with a higher value of 7.52%) for [Rh(μ-S^{t}Bu)(CO)(TPPTS)]$_2$.

In general, high capacities are obtained for both compounds for all supports. The adsorption capacity is higher for TPPTS, which could be explained by its smaller molecular size. For both compounds, the adsorption capacity of silica increases with the total pore volume (DS22 < sds200 < DS50 < sds60), with the total surface area being the second key factor in the adsorption process. With respect to their adsorption capacity and their physical properties, the DS50 and sds60 samples appear to be the most efficient supports being used in supported catalysis among those studied.

Table 4. Adsorption Isotherms of TPPTS on Different Silica Samples at 25 °C[a]

DS22		DS50		sds60		sds200	
c_e/(g/g sol)	q_e/(g/g Si)	c_e/(g/g sol)	q_e/(g/g Si)	c_e/(g/g sol)	q_e/(g/g Si)	c_e/(g/g sol)	q_e/(g/g Si)
0.000 082	0.000 069	0.000 081	0.000 096	0.000 089	0.000 115	0.000 089	0.000 093
0.000 164	0.000 137	0.000 163	0.000 188	0.000 178	0.000 228	0.000 179	0.000 177
0.000 247	0.000 206	0.000 257	0.000 296	0.000 268	0.000 337	0.000 269	0.000 266
0.000 429	0.000 358	0.000 435	0.000 499	0.000 448	0.000 562	0.000 450	0.000 443
0.000 858	0.000 715	0.000 855	0.000 979	0.000 891	0.001 115	0.000 894	0.000 882
0.001 228	0.001 022	0.001 225	0.001 398	0.001 336	0.001 668	0.001 342	0.001 324
0.002 053	0.001 689	0.002 048	0.002 338	0.002 236	0.002 787	0.002 243	0.002 202
0.004 097	0.003 346	0.004 081	0.004 658	0.004 463	0.005 556	0.004 475	0.004 393
0.008 474	0.006 682	0.008 183	0.009 324	0.008 951	0.011 111	0.008 951	0.008 782
0.016 380	0.013 322	0.016 337	0.018 575	0.017 874	0.022 176	0.017 896	0.017 550
0.024 535	0.019 847	0.024 492	0.027 588	0.026 755	0.033 186	0.026 840	0.026 268
0.042 737	0.032 689	0.040 806	0.045 718	0.044 648	0.055 304	0.044 755	0.043 319
0.061 406	0.049 048	0.061 193	0.068 219	0.066 957	0.082 639	0.067 170	0.064 708
0.081 900	0.064 970	0.081 580	0.090 944	0.089 265	0.109 712	0.089 479	0.085 645
0.106 450	0.083 596	0.106 237	0.115 476	0.115 843	0.142 241	0.116 484	0.111 242
0.130 893	0.101 326	0.130 573	0.140 200	0.142 741	0.173 721	0.143 062	0.135 853
0.171 936	0.129 545	0.171 300	0.175 229	0.185 066	0.214 583	0.187 096	0.169 625
0.273 806	0.168 183	0.273 415	0.250 032	0.286 308	0.298 761	0.288 146	0.220 312
0.382 156	0.195 638	0.383 561	0.303 571	0.389 126	0.358 336	0.391 304	0.260 678
0.488 083	0.212 507	0.487 632	0.337 506	0.490 057	0.403 338	0.493 088	0.290 303
0.589 716	0.227 28	0.589 046	0.364 286	0.597 046	0.443 756	0.598 712	0.314 037

[a] q_e is the amount of adsorbate adsorbed at equilibrium per unit amount of adsorbent. c_e is the concentration of adsorbate in the aqueous phase at equilibrium.

Table 5. Adsorption Isotherms of $[Rh(\mu\text{-}S^tBu)(CO)(TPPTS)]_2$ on Different Silica Samples at 25 °C[a]

DS22		DS50		sds60		sds200	
c_e/(g/g sol)	q_e/(g/g Si)	c_e/(g/g sol)	q_e/(g/g Si)	c_e/(g/g sol)	q_e/(g/g Si)	c_e/(g/g sol)	q_e/(g/g Si)
0.000 088	0.000 065	0.000 086	0.000 099	0.000 097	0.000 109	0.000 096	0.000 088
0.000 217	0.000 156	0.000 215	0.000 239	0.000 231	0.000 265	0.000 235	0.000 212
0.000 431	0.000 314	0.000 430	0.000 477	0.000 471	0.000 523	0.000 470	0.000 424
0.000 626	0.000 447	0.000 623	0.000 688	0.000 683	0.000 756	0.000 681	0.000 613
0.000 835	0.000 594	0.000 831	0.000 919	0.000 915	0.001 008	0.000 913	0.000 822
0.004 146	0.002 938	0.004 138	0.004 523	0.004 528	0.004 974	0.004 536	0.003 992
0.008 342	0.005 858	0.008 316	0.009 085	0.009 113	0.009 977	0.009 097	0.008 015
0.041 164	0.028 541	0.041 012	0.044 789	0.045 152	0.049 149	0.045 068	0.039 702
0.082 418	0.057 125	0.082 252	0.088 994	0.090 286	0.097 701	0.090 227	0.078 784
0.123 525	0.085 329	0.123 455	0.131 296	0.135 416	0.144 119	0.135 084	0.115 974
0.177 641	0.115 746	0.177 832	0.177 143	0.189 112	0.189 028	0.188 941	0.155 036
0.332 043	0.169 546	0.332 81	0.267 857	0.345 612	0.282 830	0.344 906	0.218 125
0.487 012	0.199 386	0.487 321	0.322 034	0.497 383	0.328 683	0.497 127	0.262 574
0.640 186	0.212 738	0.640 032	0.354 286	0.648 816	0.361 507	0.648 321	0.295 006

[a] q_e is the amount of adsorbate adsorbed at equilibrium per unit amount of adsorbent. c_e is the concentration of adsorbate in the aqueous phase at equilibrium.

Table 6. Adsorption Isotherm Models for $\theta = q_e/q_s$, Where θ Is the Fractional Coverage, q_e Is the Amount of Adsorbate Adsorbed at Equilibrium per Unit Amount of Adsorbent, q_s is the Monolayer Capacity, c_e Is the Concentration of Adsorbate in the Aqueous Phase at Equilibrium, χ Is the Adsorbate−Adsorbate Interaction Parameter, ν Is the Heterogeneity Parameter, and K and a Are Other Parameters

model	equation	
Langmuir	$\theta = Kc_e/(1 + Kc_e)$	(2)
Fowler	$\theta = Kc_e/(e^{-\chi\theta} + Kc_e)$	(3)
Jovanovic−Freundlich	$\theta = 1 - e^{-(ac_e)^{\nu}}$	(4)
Fowler−Guggenheim/ Jovanovic−Freundlich	$\theta = 1 - e^{-(ac_e e^{\chi\theta})^{\nu}}$	(5)

Adsorption isotherms are important to understand how adsorbates interact with the support. In this regard, the correlation of adsorption data using either a theoretical or empirical equation is essential for practical proposes. Different isotherm models have been used to correlate single-component isotherm data. The majority of those models were proposed originally for the treatment of gas mixtures; however, their application to liquid mixtures is supported by theoretical and practical reasons.[14] Among them several types are found: (i) simple isotherm models for homogeneous surfaces without lateral interactions, like the Langmuir model;[15] (ii) isotherm models for homogeneous surfaces with lateral interactions, like the Fowler model;[16] (iii) isotherm equations for heterogeneous surfaces without lateral interactions, like the Jovanovic−Freundlich model;[17] and (iv) isotherm equations for heterogeneous surfaces with lateral interactions, like the Fowler−Guggenheim/Jovanovic−Freundlich model.[18] The four above-mentioned isotherm models (Table 6) were checked in the present study for correlating the equilibrium data.

Table 7. Comparison of Model Correlations for TPPTS Where q_s Is the Monolayer Capacity, χ Is the Adsorbate−Adsorbate Interaction Parameter, ν Is the Heterogeneity Parameter, K and a Are Other Parameters, SEE Is the Average Standard Error of Estimation, and F_{cal} Is the Calculated Fisher Parameter

model and parameters	silica			
	DS22	DS50	sds60	sds200
1. Langmuir				
q_s/(g/g Si)	0.4579	0.8516	1.1813	0.7182
K/(g sol/g)	1.8850	1.3905	1.0964	1.4331
SEE	5.06	3.30	3.41	4.13
F_{cal}	136.0	299.9	285.6	207.4
2. Fowler				
q_s/(g/g Si)	0.2893	0.5051	0.6068	0.4161
K/(g sol/g)	2.8448	2.2614	2.0570	2.3653
χ	0.9947	0.9183	1.0172	0.9785
SEE	1.04	0.47	0.70	0.86
F_{cal}	3645.0	75057.1	7918.1	4298.8
3. Jovanovic−Freundlich				
q_s/(g/g Si)	0.2953	0.5218	0.6750	0.4185
a/(g sol/g)	2.8423	2.2719	1.9483	2.4930
ν	1.0008	1.0046	1.0066	1.0085
SEE	3.17	2.03	2.38	2.54
F_{cal}	162.1	348.5	403.3	361.6
4. Fowler−Guggenheim/Jovanovic−Freundlich				
q_s/(g/g Si)	0.2250	0.3885	0.4690	0.3208
a/(g sol/g)	3.5179	2.9170	2.6332	3.0268
χ	0.5610	0.4116	0.4912	0.5052
ν	0.9924	0.9980	0.9980	0.9974
SEE	1.05	0.50	0.78	0.91
F_{cal}	976.0	4655.4	1671.1	1141.6

Regressions of the experimental data to the adsorption isotherm models were performed using a corrected Newton algorithm. The procedure calculates the values of the isotherm parameters which minimize the average standard error of estimation (SEE):

$$\mathrm{SEE} = 100\sum_{i=1}^{n}\frac{|q_{e,i}^{exp} - q_{e,i}^{t}|}{q_{e,i}^{exp}} \tag{6}$$

where $q_{e,i}^{exp}$ are the elements of the vector q_e^{exp} containing the given experimental adsorbed phase concentrations at equilibrium, $q_{e,i}^{t}$ are those corresponding to theoretical values calculated by the model being studied, and n is the number of data points.

The selection of the most adequate model was performed using Fisher's test. The model selected exhibited the highest value of the Fisher parameter F_{calc}:[19]

$$F_{calc} = \frac{(n - l)\sum_{i=1}^{n}(q_{e,i}^{exp} - \overline{q_e^{exp}})^2}{(n - 1)\sum_{i=1}^{n}(q_{e,i}^{exp} - q_{e,i}^{t})^2} \tag{7}$$

where $\overline{q_e^{exp}}$ is the mean value of the vector q_e^{exp} and l is the number of adjusted parameters of the model.

Tables 7 and 8 summarize the results of the nonlinear regression analysis of the models evaluated in this work. In general, the agreement of the models with the data is

Table 8. Comparison of Model Correlations for $[Rh(\mu\text{-}S^tBu)(CO)(TPPTS)]_2$ Where q_s Is the Monolayer Capacity, χ Is the Adsorbate−Adsorbate Interaction Parameter, ν Is the Heterogeneity Parameter, K and a Are Other Parameters, SEE Is the Average Standard Error of Estimation, and F_{cal} Is the Calculated Fisher Parameter

model and	silica			
parameters	DS22	DS50	sds60	sds200
1. Langmuir				
q_s/(g/g Si)	0.4299	0.7497	0.7756	0.6220
K/(g sol/g)	1.7483	1.5411	1.4954	1.5020
SEE	5.33	4.28	4.65	4.45
F_{cal}	129.3	231.4	173.0	227.6
2. Fowler				
q_s/(g/g Si)	0.2625	0.4586	0.4678	0.3716
K/(g sol/g)	2.7196	2.4120	2.3634	2.4215
χ	1.1077	0.9916	1.0304	0.9818
SEE	1.05	0.76	0.81	0.88
F_{cal}	16728.9	19458.7	24281.9	1552.0
3. Jovanovic−Freundlich				
q_s/(g/g Si)	0.2568	0.4302	0.4378	0.3563
a/(g sol/g)	3.0642	2.8207	2.7862	2.6983
ν	1.0118	1.0134	1.0143	1.0103
SEE	3.18	2.51	2.91	2.44
F_{cal}	364.1	1015.3	557.9	512.7
4. Fowler−Guggenheim/Jovanovic−Freundlich				
q_s/(g/g Si)	0.2148	0.3654	0.3675	0.2849
a/(g sol/g)	3.1688	2.9384	2.9501	3.0408
χ	0.5836	0.4877	0.4997	0.5726
ν	0.9921	0.9951	0.9967	0.9941
SEE	1.70	1.01	0.89	0.98
F_{cal}	1852.2	1552.5	1599.1	273.9

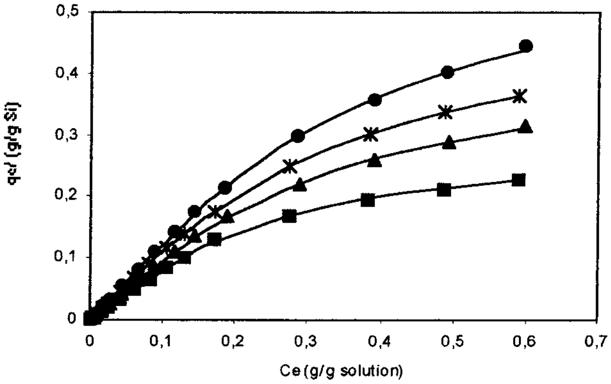

Figure 1. Comparison between experimental adsorption data of TPPTS (symbols) and values calculated using the Fowler model (lines) for different silica samples: sds60 (●); DS50 (∗); sds200 (▲); DS22 (■).

good, as SEE (eq 6) and F_{calc} (eq 7) values show. The F_{calc} values obtained are larger for the regression of the Fowler isotherm model than for the others studied. Figures 1 and 2 show the comparison between experimental adsorption data and values calculated using Fowler's isotherm.

It seems that, in terms of possible lateral interactions, in both Fowler and Fowler−Guggenheim/Jovanovic−Freundlich equations, TPPTS and $[Rh(\mu\text{-}S^tBu)(CO)(TPPTS)]_2$ behave rather similarly. The high absolute values of χ show the importance of adsorbate−adsorbate interactions in the sorption process. Regarding the surface heterogeneity, we can observe that the parameter ν in the Jovanovic−Freundlich and Fowler−Guggenheim/Jovanovic−Freundlich models is close to unity for all supports. When the heterogeneity parameter is equal to unity, as for the systems studied, adsorption takes place on a homogeneous surface. In this case, the Jovanovich−Freundlich isotherm model reduces to the Jovanovic isotherm for homogeneous surfaces.[17]

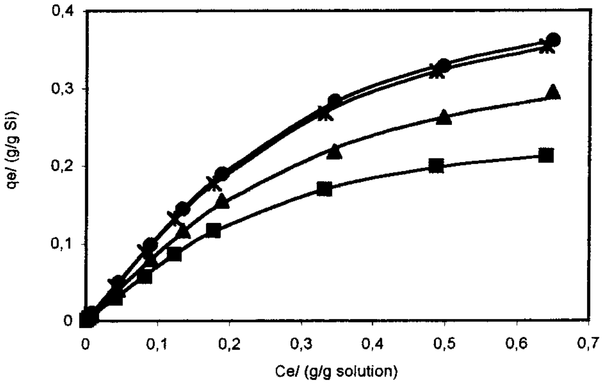

Figure 2. Comparison between experimental adsorption data of $[Rh(\mu\text{-}S^tBu)(CO)(TPPTS)]_2$ (symbols) and values calculated using the Fowler model (lines) for different silica samples: sds60 (●), DS50 (∗), sds200 (▲); DS22 (■).

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