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APPENDICES

Appendix A Sample Preparation Calculations

In this work, several different adsorbents were used in this study, prepared by incipient wetness impregnation method with two different pore size aluminas including mesoporous and macroporous aluminas. The metal precursors deposited on the adsorbents were CuCl_2 and NiCl_2 . To modify the dispersion property, citric acid (CA) was used as a dispersing agent, with molar ratios of CuCl_2/CA by 5 and 10, respectively. The physical properties of those components are listed in Table A1. They were tabulated in order to be used in further calculations.

Table A1 Physical properties of chemical used in sample preparation step

Property	Chemical						
	m- Al_2O_3	M- Al_2O_3	CuCl_2	CuCl	NiCl_2	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	CA
BET surface area (m^2/g)	278	194	–	–	–	–	–
Pore volume (cm^3/g)	0.761	0.674	–	–	–	–	–
Molecular weight (g/mol)	–	–	134.45	99.00	129.62	237.62	192.12
Density (g/cm^3)	0.914	1.008	3.386	4.145	3.550	1.920	1.665

A1 Amount of Metal Precursor (in gram) Calculation

Example: Amount of CuCl_2 (in gram) to be impregnated on m- Al_2O_3 vary by the percentage of CuCl_2 monolayer coverage on the adsorbent.

Remark: Concentration of metal-containing solution corresponds to CuCl_2 monolayer coverage on alumina.

$$\text{From } \text{CuCl monolayer} = \left(\frac{0.095 \text{ g}_{\text{CuCl}}}{100 \text{ m}^2_{\text{Al}_2\text{O}_3}} \right), (\text{Gui } et al., 1984)$$

$$\therefore \text{CuCl monolayer on m-}\text{Al}_2\text{O}_3 = \left(\frac{0.095 \text{ g}_{\text{CuCl}}}{100 \text{ m}^2_{\text{Al}_2\text{O}_3}} \right) \times \left(278 \frac{\text{m}^2}{\text{g}_{\text{adsorbent}}} \right)$$

$$\begin{aligned}
 &= 0.2641 \frac{\text{g}_{\text{CuCl}}}{\text{g}_{\text{adsorbent}}} \\
 &= 0.2641 \frac{\text{g}_{\text{CuCl}}}{\text{g}_{\text{adsorbent}}} \times \frac{\text{mol}}{99.00 \text{ g}_{\text{CuCl}}} \\
 \therefore \text{CuCl monolayer} &= 2.668 \frac{\text{mmol}}{\text{g}_{\text{adsorbent}}} \\
 \text{From } \text{mol}_{\text{CuCl}_2} &= \text{mol}_{\text{CuCl}} \\
 \text{CuCl}_2 \text{ monolayer} &= 2.668 \frac{\text{mmol}_{\text{CuCl}_2}}{\text{g}_{\text{adsorbent}}} \\
 &= 2.668 \frac{\text{mmol}_{\text{CuCl}_2}}{\text{g}_{\text{adsorbent}}} \times 134.45 \frac{\text{g}_{\text{CuCl}_2}}{\text{mol}_{\text{CuCl}_2}} \\
 \therefore \text{CuCl}_2 \text{ monolayer} &= 0.359 \frac{\text{g}_{\text{CuCl}_2}}{\text{g}_{\text{adsorbent}}}
 \end{aligned}$$

For 10 g of m-Al₂O₃;

$$\text{Thus, amount of CuCl}_2 = 3.59 \text{ g}_{\text{CuCl}_2}$$

$$\text{Then, 10\% monolayer} = 0.359 \text{ g}_{\text{CuCl}_2}$$

$$20\% \text{ monolayer} = 0.718 \text{ g}_{\text{CuCl}_2}$$

$$\text{and 30\% monolayer} = 1.077 \text{ g}_{\text{CuCl}_2}$$

A2 Amount of Dispersing Agent (Citric Acid), in gram, Calculation

Example: Amount of CA (in gram) with the molar ratio (CuCl₂/CA) of 10 and 30% monolayer coverage of CuCl₂, impregnated on mAl₂O₃.

$$\text{From } \frac{\text{mol}_{\text{CuCl}_2}}{\text{mol}_{\text{CA}}} = 10$$

$$\therefore \text{mol}_{\text{CA}} = \frac{\text{mol}_{\text{CuCl}_2}}{10}$$

$$\frac{m_{\text{CA}}}{M_{\text{CA}}} = \frac{\text{mol}_{\text{CuCl}_2}}{10}$$

$$\begin{aligned}
 \therefore m_{CA} &= \frac{M_{CA} \times mol_{CuCl_2}}{10} \\
 &= 192.12 \frac{g_{CA}}{mol} \times \frac{1.077 g_{CuCl_2}}{10 \times (134.45 g_{CuCl_2}/mol)} \\
 &= 0.154 g_{CA}
 \end{aligned}$$

A3 Volume of Metal-Containing Solution (DI water) Calculation

Example: The volume of solvent (DI water, cm³) for 30% Cu/m-Al₂O₃ modified with dispersing agent (CA). The ratio of Cu/CA is 10 and the amount of adsorbent used is 10 g.

$$\text{From } V_{DI} = V_{\text{pore}} - V_{\text{solute}} \quad (1)$$

$$\text{where } V_{\text{solute}} = V_{\text{metal}} + V_{\text{dispersing agent}} \quad (2)$$

$$\begin{aligned}
 \text{From } V_{\text{metal}} &= \frac{m_{\text{metal}}}{\rho_{\text{metal}}} \\
 &= \frac{1.077 g_{CuCl_2}}{3.386 g_{CuCl_2}/cm^3} \\
 &= 0.32 \text{ cm}^3
 \end{aligned}$$

$$\begin{aligned}
 \text{and } V_{\text{dispersing agent}} &= \frac{m_{CA}}{\rho_{CA}} \\
 &= \frac{0.154 g_{CA}}{1.665 g_{CA}/cm^3} \\
 &= 0.09 \text{ cm}^3
 \end{aligned}$$

substitute all of the value in Equation (2):

$$\begin{aligned}
 \therefore V_{\text{solute}} &= 0.32 + 0.09 \text{ cm}^3 \\
 &= 0.41 \text{ cm}^3
 \end{aligned}$$

For 10 g of m-Al₂O₃;

$$V_{\text{pore}} = 7.61 \text{ cm}^3$$

substitute all of the value in Equation (1):

$$\begin{aligned}
 \therefore V_{DI} &= 7.61 - 0.41 \text{ cm}^3 \\
 &= 7.20 \text{ cm}^3
 \end{aligned}$$

As mentioned above, the adsorbents used in this work were prepared by incipient wetness impregnation method. The way of calculation to make an appropriate metal-containing solution to be impregnated on various types of adsorbents, namely mesoporous and macroporous alumina, in desired percentage of monolayer coverage is shown in Appendix A. The calculation of all the prepared adsorbents is summarized in Table A2.

Table A2 Summary of Adsorbent Preparation Calculations

No. IFP Cata Sepa	No.	Label	Adsorbent (Alumina)				Metal Impregnation					Dispersing Agent			Solution (cm ³)		Time (h)		
			m- Al ₂ O ₃	M- Al ₂ O ₃	Amt (g)	V _{pore}	CuCl ₂	NiCl ₂	Loading (%)	g _{metal}	g _{Cu/Ni}	V _{metal}	CA	Cu/CA	Amt (g)	V _{CA}		Solute	DI
94795	01	mCu1024	√		10	7.61	√		10	0.359	0.170	0.11					0.11	7.50	24
94796	02	mCu2024	√		10	7.61	√		20	0.718	0.339	0.21					0.21	7.40	24
94797	03	mCu3024	√		10	7.61	√		30	1.077	0.509	0.32					0.32	7.29	24
94798	04	MCu1024		√	10	6.74	√		10	0.250	0.118	0.07					0.07	6.67	24
94799	05	MCu2024		√	10	6.74	√		20	0.500	0.236	0.15					0.15	6.59	24
94800	06	MCu3024		√	10	6.74	√		30	0.750	0.354	0.22					0.22	6.52	24
94801	07	mNi1024	√		10	7.61		√	10	0.161	0.073	0.05					0.05	7.56	24
94802	08	mNi2024	√		10	7.61		√	20	0.322	0.146	0.09					0.09	7.52	24
94803	09	mNi3024	√		10	7.61		√	30	0.483	0.219	0.14					0.14	7.47	24
94804	10	MNi1024		√	10	6.74		√	10	0.112	0.051	0.03					0.03	6.71	24
94805	11	MNi2024		√	10	6.74		√	20	0.224	0.101	0.06					0.06	6.68	24
94806	12	MNi3024		√	10	6.74		√	30	0.336	0.152	0.09					0.09	6.65	24
94807	13	mCu1012	√		10	7.61	√		10	0.359	0.170	0.11					0.11	7.50	12
94808	14	mCu2012	√		10	7.61	√		20	0.718	0.339	0.21					0.21	7.40	12
94809	15	mCu3012	√		10	7.61	√		30	1.077	0.509	0.32					0.32	7.29	12
94810	16	MCu1012		√	10	6.74	√		10	0.250	0.118	0.07					0.07	6.67	12
94811	17	MCu2012		√	10	6.74	√		20	0.500	0.236	0.15					0.15	6.59	12
94812	18	MCu3012		√	10	6.74	√		30	0.750	0.354	0.22					0.22	6.52	12
94813	19	mNi1012	√		10	7.61		√	10	0.161	0.073	0.05					0.05	7.56	12
94814	20	mNi2012	√		10	7.61		√	20	0.322	0.146	0.09					0.09	7.52	12
94815	21	mNi3012	√		10	7.61		√	30	0.483	0.219	0.14					0.14	7.47	12
94816	22	MNi1012		√	10	6.74		√	10	0.112	0.051	0.03					0.03	6.71	12
94817	23	MNi2012		√	10	6.74		√	20	0.224	0.101	0.06					0.06	6.68	12
94818	24	MNi3012		√	10	6.74		√	30	0.336	0.152	0.09					0.09	6.65	12

Table A2 (Cont.) Summary of Adsorbent Preparation Calculations

No. IFP Cata Sepa	No.	Label	Adsorbent (Alumina)				Metal Impregnation					Dispersing Agent				Solution (cm ³)		Time (h)	
			m- Al ₂ O ₃	M- Al ₂ O ₃	Amt (g)	V _{pore}	CuCl ₂	NiCl ₂	Loading (%)	g _{metal}	g _{Cu/Ni}	V _{metal}	CA	Cu/CA	Amt (g)	V _{CA}	Solute		DI
94819	25	mCu1006	√		10	7.61	√		10	0.359	0.170	0.11					0.11	7.50	6
94820	26	mCu2006	√		10	7.61	√		20	0.718	0.339	0.21					0.21	7.40	6
94821	27	mCu3006			10	7.61	√		30	1.077	0.509	0.32					0.32	7.29	6
94822	28	MCu1006		√	10	6.74	√		10	0.250	0.118	0.07					0.07	6.67	6
94823	29	MCu2006		√	10	6.74	√		20	0.500	0.236	0.15					0.15	6.59	6
94824	30	MCu3006		√	10	6.74	√		30	0.750	0.354	0.22					0.22	6.52	6
94825	31	mNi1006	√		10	7.61		√	10	0.161	0.073	0.05					0.05	7.56	6
94826	32	mNi2006	√		10	7.61		√	20	0.322	0.146	0.09					0.09	7.52	6
94827	33	mNi3006	√		10	7.61		√	30	0.483	0.219	0.14					0.14	7.47	6
94828	34	MNi1006		√	10	6.74		√	10	0.112	0.051	0.03					0.03	6.71	6
94829	35	MNi2006		√	10	6.74		√	20	0.224	0.101	0.06					0.06	6.68	6
94830	36	MNi3006		√	10	6.74		√	30	0.336	0.152	0.09					0.09	6.65	6
94831	37	mCu1003	√		10	7.61	√		10	0.359	0.170	0.11					0.11	7.50	3
94832	38	mCu2003	√		10	7.61	√		20	0.718	0.339	0.21					0.21	7.40	3
94833	39	mCu3003	√		10	7.61	√		30	1.077	0.509	0.32					0.32	7.29	3
94834	40	MCu1003		√	10	6.74	√		10	0.250	0.118	0.07					0.07	6.67	3
94835	41	MCu2003		√	10	6.74	√		20	0.500	0.236	0.15					0.15	6.59	3
94836	42	MCu3003		√	10	6.74	√		30	0.750	0.354	0.22					0.22	6.52	3
94837	43	mNi1003	√		10	7.61		√	10	0.161	0.073	0.05					0.05	7.56	3
94838	44	mNi2003	√		10	7.61		√	20	0.322	0.146	0.09					0.09	7.52	3
94839	45	mNi3003	√		10	7.61		√	30	0.483	0.219	0.14					0.14	7.47	3
94840	46	MNi1003		√	10	6.74		√	10	0.112	0.051	0.03					0.03	6.71	3
94841	47	MNi2003		√	10	6.74		√	20	0.224	0.101	0.06					0.06	6.68	3
94842	48	MNi3003		√	10	6.74		√	30	0.336	0.152	0.09					0.09	6.65	3
94843	49	m-Al ₂ O ₃	√		10	7.61													
94844	50	M-Al ₂ O ₃		√	10	6.74													

Table A2 (Cont.) Summary of Adsorbent Preparation Calculations

No. IFP Cata Sepa	No.	Label	Adsorbent (Alumina)				Metal Impregnation					Dispersing Agent			Solution (cm ³)		Time (h)		
			m- Al ₂ O ₃	M- Al ₂ O ₃	Amt (g)	V _{pore}	CuCl ₂	NiCl ₂	Loading (%)	g _{metal}	g Cu/Ni	V _{metal}	CA	Cu/CA	Amt (g)	V _{CA}		Solute	DI
94845	51	mCA1024	√		10	7.61							√	10	0.051	0.03	0.031	7.58	24
94846	52	MCA1024		√	10	6.74							√	10	0.036	0.02	0.021	6.72	24
94847	53	mCA10Cu1024	√		10	7.61	√		10	0.359	0.170	0.11	√	10	0.051	0.03	0.137	7.58	24
94848	54	MCA10Cu1024		√	10	6.74	√		10	0.250	0.118	0.07	√	10	0.036	0.02	0.095	6.72	24
94849	55	mCA10Cu3024	√		10	7.61	√		30	1.077	0.509	0.32	√	10	0.154	0.09	0.411	7.52	24
94850	56	MCA10Cu3024		√	10	6.74	√		30	0.750	0.354	0.22	√	10	0.107	0.06	0.286	6.68	24
94851	57	mCA10Cu10024	√		10	7.61	√		100	3.590	1.697	1.06	√	10	0.513	0.31	1.368	7.30	24
94852	58	MCA10Cu10024		√	10	6.74	√		100	2.500	1.182	0.74	√	10	0.357	0.21	0.953	6.53	24
94853	59	mCA05Cu1024	√		10	7.61	√		10	0.359	0.170	0.11	√	5	0.103	0.06	0.168	7.55	24
94854	60	MCA05Cu1024		√	10	6.74	√		10	0.250	0.118	0.07	√	5	0.071	0.04	0.117	6.70	24
94855	61	mCA05Cu3024	√		10	7.61	√		30	1.077	0.509	0.32	√	5	0.308	0.18	0.503	7.43	24
94856	62	MCA05Cu3024		√	10	6.74	√		30	0.750	0.354	0.22	√	5	0.214	0.13	0.350	6.61	24

Appendix B Topological Index (χ_T) Calculations

Brenlé and Papirer (1997) have proposed the method to determine the topological index by using Wiener's index. The idea of their work is to use relative scales, centered around C, which is based on the weighing of the elements of the distance matrix D starting with atomic numbers of the elements that built the molecules, to adapt Wiener's (W) index to molecules other than hydrocarbons.

B1 Computation of the Elements of the Diagonal of Matrix D

Initially all the elements of the diagonal are equal since they correspond solely to carbon atoms and their value is fixed equal to zero ($d_{ii} = 0$). The new procedure suggests one to determine the diagonal coefficients of the matrix by taking into account the total number of electrons (Z_i) of atom i according to the following relationship:

$$d_{ii} = 1 - \left(\frac{6}{Z_i} \right). \quad (1)$$

B2 Computation of the Elements that do not Belong to the Diagonal of Matrix D

For alkanes, the sole bonds are C–C bonds whose length is arbitrarily taken as equal to 1. Hence for calculating d_{ij} , one simply has to count the number of bonds joining i and j . Now, when the molecule contains heteroatoms, all bonds will not have the same lengths. The d_{ij} terms that do not belong to the diagonal are then computed as the sum of the lengths r of the bonds between i and j , using

$$d_{ij} = \sum_r k_r \quad (2)$$

(this sum is made on all r bonds existing between i and j with $i' = 1, 2, \dots$, number of bonds between i and j). k_r is the length of the r th bond and is determined for each of them through

$$k_r = \frac{1}{b_r} \times \frac{36}{Z_i \cdot Z_{i'}} \quad (3)$$

where Z_i and $Z_{j'}$ are the (total) numbers of electrons of atoms i' and j' entering in the r th bond; b_r takes values equal to 1, 2, or 3 according to the type of bond (simple bond $b_r = 1$, double $b_r = 2$, or triple $b_r = 3$). Table B2 gives some values of parameter k_r .

Table B1 k_r values for different types of bonds

Type of bond	k_r
C—C	1
C=C	0.5
C≡C	0.333
C—C aromatic	0.67
C—N	0.857
C=N	0.429
C—N aromatic	0.571
C—O	0.75
C=O	0.375
N—N	0.735
N=N	0.368
C—F	0.667
C—Cl	0.353

B3 Extension of Parameter χ_T to Polar Molecules

There are three steps to calculate for χ_T : determination of the graph and the matrix distance of the molecule, calculation of the corresponding Wiener index, and finally evaluation of χ_T . This procedure is best illustrated on the hand of an example (CHCl_3). Figure B1 illustrates the graph of chloroform from which matrix D is computed.

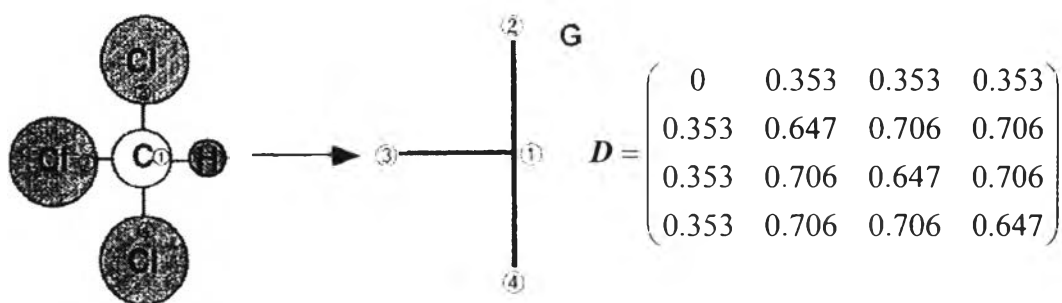


Figure B1 Graph and matrix D of chloroform.

The following step is the determination of the Wiener index according to

$$W = \frac{1}{2} \sum_{i=1}^n d_{ii} + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n d_{ij} \quad (4)$$

Finally, parameter χ_T is obtained by application of the relation

$$\chi_T(W) = 1.8789 \times W^{0.3271} \quad (5)$$

Example: The χ_T of thiophene.

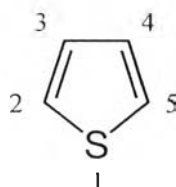


Figure B2 Thiophene structure.

Calculating d_{ii} value by performing Equation (1) gives

$$d_{ii} : \quad d_{11} = 0.625$$

$$d_{22} = 0$$

$$d_{33} = 0$$

$$d_{44} = 0$$

$$d_{55} = 0$$

$$\therefore \sum_{i=1}^5 d_{ii} = 0.625$$

Calculating k_r value by performing Equation (3) gives

$$\begin{aligned} k_r: \quad \text{C—C} &= 1 \\ \text{C=C} &= 0.5 \\ \text{C—S} &= 0.375 \end{aligned}$$

Calculating d_{ij} by performing Equation (2) (the shortest path calculations) gives

$$\begin{aligned} \therefore \sum_{i=1}^5 \sum_{j=1}^5 d_{ij} &= \sum_{i=1}^5 \sum_{j=1}^5 \left(\sum_r k_r \right) \\ &= \begin{bmatrix} 0.625 & 0.375 & 0.875 & 0.875 & 0.375 \\ 0.375 & 0 & 0.5 & 1.5 & 0.75 \\ 0.875 & 0.5 & 0 & 1 & 1.5 \\ 0.875 & 1.5 & 1 & 0 & 0.5 \\ 0.375 & 0.75 & 1.5 & 0.5 & 0 \end{bmatrix} \\ &= 17.125 \end{aligned}$$

From Equation (4), it becomes

$$\begin{aligned} W &= \frac{1}{2} \sum_{i=1}^5 d_{ii} + \frac{1}{2} \sum_{i=1}^5 \sum_{j=1}^5 d_{ij} \\ &= \frac{1}{2} (0.625 + 17.125) \\ &= 8.875 \end{aligned}$$

Then, χ_T value is obtained by performing Equation (5)

$$\begin{aligned} \chi_T &= 1.8789 \times W^{0.3271} \\ &= 1.8789 \times (8.875)^{0.3271} \\ &= 3.84 \end{aligned}$$

\therefore The topological index (χ_T) of thiophene is 3.84.

Appendix C IGC Characterization Calculations

The IGC experiments were carried out at different temperatures ranging between 200–250 °C. Injection of normal alkanes (Hexane–Decane, namely C₆–C₁₀) as probe molecules (reference) and toluene ($\chi_T = 6.26$) and thiophene ($\chi_T = 3.84$) as polar probe molecules to the stationary phases (different adsorbents to be studied) were performed and the retention time (t_R) measured. The experimental data were averaged as shown in Table C1.

For further calculations, the reduced 30% Cu/m-Al₂O₃ adsorbent was selected as an example. The conditions used in the experiments with 30% Cu/m-Al₂O₃ adsorbent as stationary phase are summarized in Table C2.

Table C1 Summary of IGC data (an average of retention time, min)

Temperature	Probe Molecules	Average Retention Time (min)											
		mAA	MAA	mCu10 24H2	mCu20 24H2	mCu30 24H2	mCA05 Cu3024 H2	mNi10 24H2	mNi20 24H2	mNi30 24H2	MCu10 24H2	MCu20 24H2	MCu30 24H2
200	Hexane	0.72	0.65	0.77	0.74	0.74	0.72	0.57	0.78	0.76	0.6	0.51	0.56
	Heptane	1.42	1.23	1.51	1.45	1.21	1.38	1.09	1.58	1.55	1.15	0.90	1.11
	Octane	2.87	2.50	3.00	2.84	2.24	2.79	2.07	3.19	3.10	2.29	1.78	2.27
	Nonane	5.82	5.16	6.24	5.82	4.41	5.71	3.96	6.61	6.34	4.67	3.60	4.5
	Decane	11.86	10.34	12.68	11.84	8.50	11.44	7.52	13.23	12.74	9.45	7.24	9.01
	Toluene	4.80	4.31	5.72	5.91	3.97	5.42	4.02	6.20	7.12	4.78	4.03	4.99
	Thiophene	2.04	1.87	2.28	4.25	2.14	4.14	1.72	2.49	2.82	1.91	2.00	3.42
225	Hexane	0.47	0.41	x	x	0.49	0.44	x	x	x	x	x	x
	Heptane	0.82	0.69	x	x	0.75	0.77	x	x	x	x	x	x
	Octane	1.52	1.33	x	x	1.27	1.44	x	x	x	x	x	x
	Nonane	2.90	2.50	x	x	2.35	2.78	x	x	x	x	x	x
	Decane	5.51	4.58	x	x	3.97	5.04	x	x	x	x	x	
	Toluene	2.38	2.10	x	x	2.01	2.52	x	x	x	x	x	
	Thiophene	1.08	0.99	x	x	1.22	2.01	x	x	x	x	x	x

Table C1 (Cont.) The summary of IGC data (an average of retention time, min)

Temperature	Probe Molecules	Average Retention Time (min)											
		mAA	MAA	mCu10 24H2	mCu20 24H2	mCu30 24H2	mCA05 Cu3024 H2	mNi10 24H2	mNi20 24H2	mNi30 24H2	MCu10 24H2	MCu20 24H2	MCu30 24H2
250	Hexane	0.30	0.28	x	x	0.34	0.28	x	x	x	x	x	x
	Heptane	0.50	0.45	x	x	0.49	0.42	x	x	x	x	x	x
	Octane	0.87	0.75	x	x	0.74	0.70	x	x	x	x	x	x
	Nonane	1.49	1.35	x	x	1.30	1.27	x	x	x	x	x	x
	Decane	2.70	2.44	x	x	2.10	2.19	x	x	x	x	x	x
	Toluene	1.27	1.11	x	x	1.16	1.19	x	x	x	x	x	x
	Thiophene	0.62	0.54	x	x	0.74	0.92	x	x	x	x	x	x

Table C2 Parameters used in calculations (exclusively for reduced 30% Cu/m-Al₂O₃ adsorbent)

Parameters	Value
He flowrate, F (cm ³ /min)	33.33
Ambient temperature, T_{amb} (K)	298.15
Solid mass, m_{solid} (g)	4.10
Density of mesoporous alumina, $\rho_{\text{m-Al}_2\text{O}_3}$ (g/cm ³)	0.914
Solid density, ρ_{solid} (g/cm ³)	0.986 ^a
Ideal Gas constant, R (J/mol K)	8.314
Column diameter, D (cm)	1
Column length, L (cm)	10

^a The calculation was shown in Appendix C2.

C1 Retention Volume (V_g) Calculation

Example: The retention volume (V_g) of thiophene injected on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C.

$$\text{From } V_g = Fj \frac{(t_R - t_M)}{m} \left(\frac{T}{T_{\text{amb}}} \right), \quad (1)$$

where t_R is the retention time (min), t_M the retention time of non-adsorbing marker (hold up time), p_0 the outlet column pressure, p_i the inlet pressure, T the column temperature, T_{amb} the ambient temperature (K), and j the James–Martin compressibility factor defined as:

$$j = \frac{3}{2} \left[\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \right]. \quad (2)$$

As there was no pressure drop along the column within the experiment, so the term j (James–Martin compressibility factor) can be neglected. So Equation (1) becomes;

$$V_g = \frac{Ft_R - Ft_M}{m} \left(\frac{T}{T_{\text{amb}}} \right)$$

$$V_g = \frac{Ft_R - V_1}{m} \left(\frac{T}{T_{amb}} \right) \quad (3)$$

$$\text{From } V_1 = V_C \times \epsilon_B, \quad (4)$$

$$\text{and } V_C = S \times L, \quad (5)$$

$$\begin{aligned} \text{substitute in Equation (5): } V_C &= \frac{\pi D^2 L}{4} \\ &= \frac{\pi (1 \text{ cm})^2 (10 \text{ cm})}{4} \\ &= 7.85 \text{ cm}^3, \end{aligned}$$

$$\text{and } \epsilon_B = 1 - \frac{\rho_B}{\rho_G}, \quad (6)$$

$$\left(\frac{\rho_B}{\rho_G} \right) = \frac{m_{solid} / V_C}{m_{solid} / V_{solid}} = \frac{V_{solid}}{V_C}, \quad (7)$$

$$\text{substitute (7) in (6): } \epsilon_B = 1 - \frac{V_{solid}}{V_C} = \frac{V_C - V_{solid}}{V_C}, \quad (8)$$

$$\begin{aligned} \text{substitute (8) in (4): } V_1 &= V_C - V_{solid}, \quad (9) \\ &= 7.85 - \frac{m_{solid}}{\rho_{solid}} \end{aligned}$$

$$\begin{aligned} &= 7.85 \text{ cm}^3 - \frac{4.10 \text{ g}_{\text{mCu3024H2}}}{1.047 \text{ g}_{\text{mCu3024H2}} / \text{cm}^3} \\ \therefore V_1 &= 3.93 \text{ cm}^3. \end{aligned}$$

The experiment was carried out at 225 °C, the retention volume of thiophene was 1.10 min, substitute all the parameters and Equation (9) in (3) then

$$\begin{aligned} V_g &= \frac{(33.33 \text{ cm}^3/\text{min})(1.10 \text{ min}) - 3.93 \text{ cm}^3}{4.10 \text{ g}} \left(\frac{225 + 273.15 \text{ K}}{298.15 \text{ K}} \right) \\ &= 13.34 \text{ cm}^3/\text{g}. \end{aligned}$$

\therefore The retention volume of thiophene injected on reduced 30% Cu/m- Al_2O_3 adsorbent at 225 °C is 13.34 cm^3/g .

C2 Particle Density Calculation

Example: Particle density (ρ_{mAA}^I) of reduced 30% Cu/m-Al₂O₃ adsorbent.

$$\text{From} \quad \rho_{mAA} = \frac{m_{mAA}}{V_{mAA}}, \quad (1)$$

$$\text{and} \quad \rho_{mAA}^I = \frac{m_{mAA}^I}{V_{mAA}}, \quad (2)$$

where ρ_{mAA} is the density of mesoporous alumina, ρ_{mAA}^I is the density of impregnated mesoporous alumina, then divide Equation (2) by Equation (1):

$$\begin{aligned} \frac{\rho_{mAA}^I}{\rho_{mAA}} &= \frac{m_{mAA}^I}{m_{mAA}} = \frac{m_{mAA}^I + m^I}{m_{mAA}} \\ &= 1 + \frac{m^I}{m_{mAA}}, \end{aligned} \quad (3)$$

from Table A2: $m_{mAA} = 10 \text{ g}$, and $m_{CuCl_2} = 1.077 \text{ g}$,

$$\begin{aligned} \text{from} \quad mol_{CuCl_2} &= mol_{CuCl} \\ \frac{m_{CuCl}}{M_{CuCl}} &= \frac{m_{CuCl_2}}{M_{CuCl_2}} \\ m_{CuCl} &= \frac{m_{CuCl_2} \times M_{CuCl}}{M_{CuCl_2}}, \end{aligned} \quad (4)$$

substitute the data from Table A1 and Table A2 in Equation (4);

$$\begin{aligned} \therefore m_{CuCl} &= \frac{1.077 \text{ g}_{CuCl} \times 99.00 \text{ g}_{CuCl}/\text{mol}}{134.45 \text{ g}_{CuCl_2}/\text{mol}} \\ &= 0.793 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{from Equation (3):} \quad \rho_{mAA}^I &= \rho_{mAA} \left(1 + \frac{m^I}{m_{mAA}} \right) \\ &= 0.914 \frac{\text{g}}{\text{cm}^3} \left(1 + \frac{0.793 \text{ g}}{10 \text{ g}} \right) \\ &= 0.986 \text{ g/cm}^3 \end{aligned}$$

\therefore The particle density of reduced 30% Cu/m-Al₂O₃ is 0.986 g/cm³.

The particle density of the adsorbents that were used for IGC characterization was summarized as shown in Table C3.

Table C3 Summary of particle density of the adsorbents

Adsorbents	Particle density ^a (g/cm ³)
Support: Mesoporous Alumina	
m-Al ₂ O ₃	0.914
Reduced 10% Cu/m-Al ₂ O ₃	0.938
Reduced 20% Cu/m-Al ₂ O ₃	0.962
Reduced 30% Cu/m-Al ₂ O ₃	0.986
Reduced 30% Cu/m-Al ₂ O ₃ modified with CA (Cu/CA=5)	0.986 ^b
10% Ni/m-Al ₂ O ₃	0.943
20% Ni/m-Al ₂ O ₃	0.973
30% Ni/m-Al ₂ O ₃	1.002
Support: Macroporous Alumina	
M-Al ₂ O ₃	1.008
Reduced 10% Cu/M-Al ₂ O ₃	1.027
Reduced 20% Cu/M-Al ₂ O ₃	1.045
Reduced 30% Cu/M-Al ₂ O ₃	1.064

^a Corresponding to the parameter value stated in Table A2.

^b CA mixed with metal-containing solution in impregnation step was decomposed by the reduction temperature at which 300 °C before using as an stationary phase in IGC. Thus, the amount of CA does not take into account for the particle density calculation.

C3 Enthalpy of Adsorption Calculation

Example: Heat of adsorption (ΔH_{ads}) of thiophene injected as polar probe molecule on reduced 30% Cu/m-Al₂O₃ adsorbent at different temperature ranging between 200–250 °C.

At low surface coverage, the heat of adsorption is obtained by plotting $\ln V_g$ against $1/T$, according to Equation (1):

$$\Delta H_{\text{ads}} = -R \frac{\partial(\ln V_g)}{\partial(1/T)} \quad (1)$$

The experimental data plotted in the graph was shown in Figure C1.

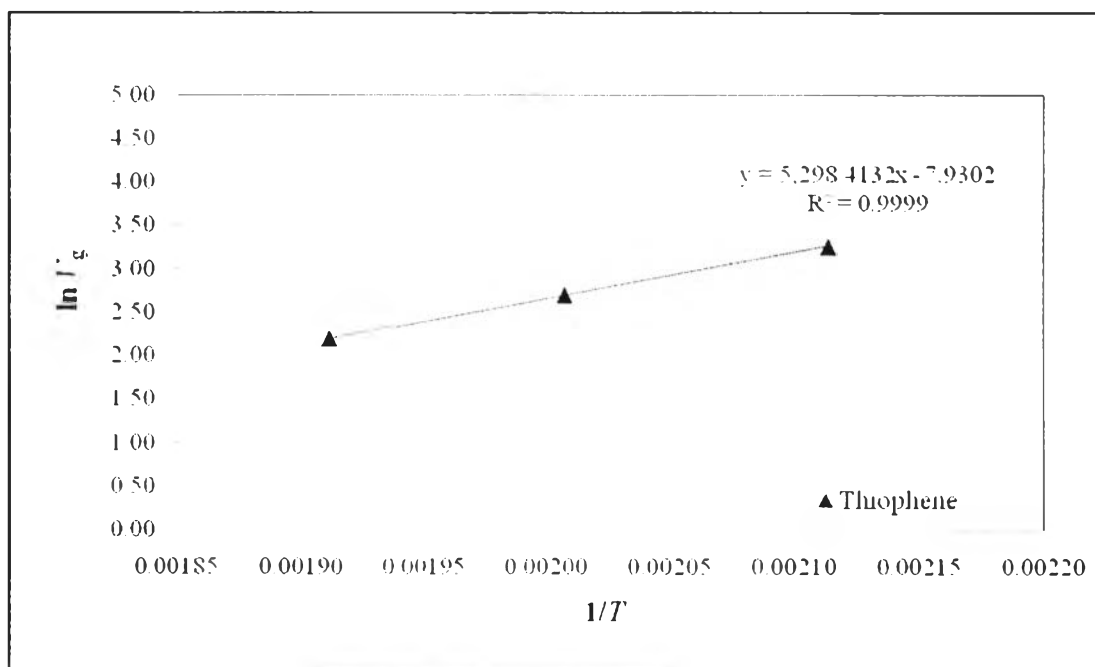


Figure C1 $\ln V_g$ against $1/T$ graph of thiophene injected on reduced 30% Cu/m-Al₂O₃ adsorbent at different temperature ranging between 200–250 °C.

According to the Figure C1, the equation of linear line was obtained by using the Microsoft Office Excel software, as shown in Equation (2):

$$y = 5298.4132x - 7.9302 \quad (2)$$

From Equation (1) is consistent with Figure C1 and Equation (2), the slope of the graph, $\frac{\partial(\ln V_g)}{\partial(1/T)}$, is 5298.41 K.

Substitute the value in Equation (1) gives

$$\begin{aligned}\Delta H_{\text{ads}} &= -(8.314 \text{ J/mol} \cdot \text{K})(5298.41 \text{ K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right) \\ &= -44.1 \text{ kJ/mol.}\end{aligned}$$

\therefore The heat of adsorption (ΔH_{ads}) of thiophene injected as polar probe molecule on reduced 30% Cu/m- Al_2O_3 adsorbent is -44.1 kJ/mol .

C4 Free energy of Adsorption of a Methylene Group Calculation

Example: The free energy of adsorption of a methylene group (ΔG_{CH_2}) as *n*-alkanes (C₆–C₁₀) were injected as probe molecules on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C.

The term, ΔG_{CH_2} , corresponds to the free energy of adsorption of a methylene group and is defined as the energy difference for the adsorption of two successive alkanes, and may be calculated from:

$$\Delta G_{\text{CH}_2} = -RT \ln \frac{V_{g(n)}}{V_{g(n+1)}}, \quad (1)$$

where $V_{g(n)}$ and $V_{g(n+1)}$ are the specific retention volumes of two consecutive *n*-alkanes having *n* and (*n* + 1) carbon atoms, respectively. ΔG_{CH_2} is independent of the reference state of the adsorbed molecule. The slope of the linear functions given in Figure D2 represent the increment in ΔG_{CH_2} .

The value of ΔG_{CH_2} is obtained by plotting $-RT \ln V_g$ against χ_T (shown in Figure C2) according to Equation (1). The slope of this curve is ΔG_{CH_2} .

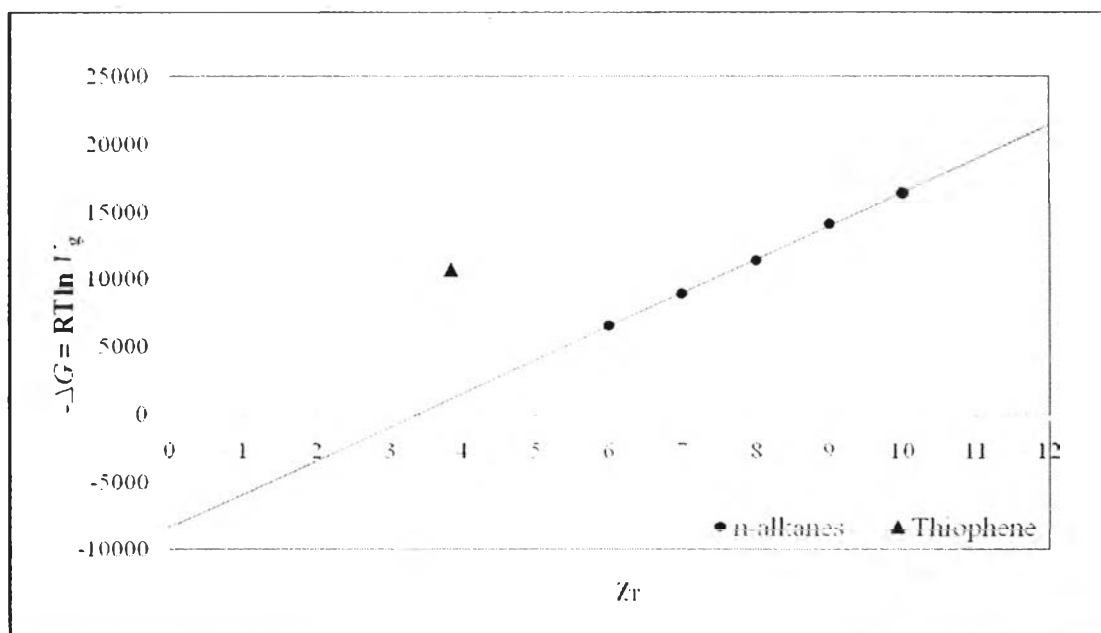


Figure C2 Free energy of adsorption of a methylene group based on *n*-alkanes, 30% Cu/m-Al₂O₃ adsorbent at 225 °C.

According to the Figure C2, the equation of linear line was obtained by using the Microsoft Office Excel software, as shown in Equation (2):

$$y = -2453.3x + 8600. \quad (2)$$

From Equation (1) is consistent with Figure C1 and Equation (2), the slope of the graph, $-RT \ln \frac{V_{g(n)}}{V_{g(n+1)}}$, is -2453.3 J/mol.

Substitute the value in Equation (1) gives

$$\Delta G_{\text{CH}_2} = -2.45 \text{ kJ/mol.}$$

\therefore The free energy of adsorption of n -alkanes on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C is -2.45 kJ/mol.

C5 Surface Free Energy: Specific and Dispersive Component Calculations

As in the case of the free energy of adsorption, the surface free energy of the adsorbent, γ_s (J/m²), may be split into dispersion, γ_s^d , and specific, γ_s^s , contributions, corresponding to the dispersion and specific interactions, respectively:

$$\gamma_s = \gamma_s^s + \gamma_s^d \quad (1)$$

The dispersive component, intrinsic and unspecific for all molecules, is due to London forces and is given by:

$$\gamma_s^d = \frac{1}{4} \frac{\Delta G_{\text{CH}_2}^2}{\gamma_{\text{CH}_2} N^2 a_{\text{CH}_2}^2} \quad (2)$$

where N is the Avogadro number, a_{CH_2} is the area occupied by a $-\text{CH}_2$ group (0.06 nm²), and γ_{CH_2} (mJ/m²) is the surface tension of a surface consisting of CH_2 groups, which is a function of temperature:

$$\gamma_{\text{CH}_2} = 35.6 + 0.058(20 - T) \quad (3)$$

where T is the column temperature in °C.

The specific component (γ_s^s) of the surface free energy is closely related with the parameter of specific interaction of polar solutes (I^{sp}). This parameter involves the surface properties in terms of potential and acid–base interactions and may be determined from the difference of free energy of adsorption, $\Delta(\Delta G)$, between a polar solute and the real or hypothetical n -alkanes with the same surface area:

$$\gamma_s^s = I^{\text{sp}} = \frac{|\Delta(\Delta G)|}{Na_p} \quad (4)$$

where a_p is the polar solute surface area. In this work, a_p is calculated from the liquid density, ρ , and the molar weight of the solute, M , assuming spherical molecular shape in a hexagonal close-packed configuration:

$$a_p = 1.09 \times 10^{14} \left(\frac{M}{\rho N} \right)^{2/3} \quad (5)$$

where 10^{14} is the conversion factor (convert cm² to nm²).

C5.1 Dispersive Component Calculation

Example: The dispersive component (γ_s^d) of *n*-alkanes injected as probe molecules on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C.

$$\text{From Eq. (2)} \quad \gamma_s^d = \frac{1}{4} \frac{\Delta G_{\text{CH}_2}^2}{\gamma_{\text{CH}_2} N^2 a_{\text{CH}_2}^2},$$

calculate for γ_{CH_2} , as the experiment was carried out at $T = 225$ °C, by substituting the value of T in Equation (3) gives

$$\begin{aligned} \gamma_{\text{CH}_2} &= 35.6 + 0.058(20 - 225) \\ &= 23.71 \text{ mJ/m}^2. \end{aligned}$$

From ΔG_{CH_2} calculation in Appendix C4,

$$\Delta G_{\text{CH}_2} = -2453.3 \text{ J/mol}$$

Substitute all of the value in Equation (2):

$$\begin{aligned} \therefore \gamma_s^d &= \frac{1}{4} \left[\frac{(-2453.3)^2 \left(\frac{\text{J}}{\text{mol}} \right)^2}{(23.71) \frac{\text{mJ}}{\text{m}^2} (6.02 \times 10^{23})^2 (\text{mol}^{-1})^2 (0.06 \times 10^{-18})^2 (\text{m}^2)^2} \right] \\ &= \frac{1}{4} \left[\frac{(-2453.3)^2 \left(\frac{\text{J}}{\text{mol}} \right)^2 \cdot \left(10^3 \frac{\text{mJ}}{\text{J}} \right)^2}{(23.71) \frac{\text{mJ}}{\text{m}^2} (6.02^2 \times 10^{46}) (\text{mol}^{-1})^2 (0.06^2 \times 10^{-36}) (\text{m}^2)^2} \right] \\ &= \frac{1}{4} \left[\frac{(-2453.3)^2 \left(\frac{\text{J}}{\text{mol}} \right)^2 \cdot 10^{-4} \left(\frac{\text{mJ}}{\text{J}} \right)^2}{(23.71) \frac{\text{mJ}}{\text{m}^2} \cdot 6.02^2 (\text{mol}^{-1})^2 \cdot 0.06^2 (\text{m}^2)^2} \right] \\ &= 48.6 \text{ mJ/m}^2 \end{aligned}$$

\therefore The dispersive component (γ_s^d) of *n*-alkanes injected as probe molecules on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C is 48.6 mJ/m².

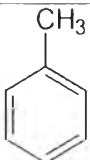

C5.2 Specific Component Calculation

Example: The specific component (γ_s^s) of thiophene injected as polar probe molecules on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C.

$$\text{From Eq. (4)} \quad \gamma_s^s = I^{sp} = \frac{\Delta(\Delta G)}{Na_p},$$

calculate for a_p , by using the parameters those are shown in Table C4.

Table C4 Physical properties of polar probe molecules (toluene and thiophene) for IGC calculations

Chemicals	Chemical Formula	Structure	Molecular Weight (g/mol)	Boiling Point (°C)	Melting Point (°C)	Density (g/cm ³)
Toluene	C ₇ H ₈		92.14	110.6	-93	0.865
Thiophene	C ₄ H ₄ S		84.14	84	-38	1.051

Substitute the value in Equation (5) gives

$$\begin{aligned} a_p &= 1.09 \times 10^{14} \left(\frac{84.14 \frac{\text{g}}{\text{mol}}}{1.051 \frac{\text{g}}{\text{cm}^3} \cdot 6.02 \times 10^{23} \text{ mol}^{-1}} \right)^{2/3} \\ &= 1.09 \times \left(10^{14} \frac{\text{nm}^2}{\text{cm}^2} \right) \left(\frac{84.14}{1.051 \cdot 6.02 \times 10^{23}} \text{cm}^3 \right)^{2/3} \\ &= 1.09 \times \left(10^{14} \frac{\text{nm}^2}{\text{cm}^2} \right) \left(\frac{84.14}{1.051 \cdot 6.02 \times 10^{23}} \right)^{2/3} \text{cm}^2 \\ &= 0.2839 \text{ nm}^2 \end{aligned}$$

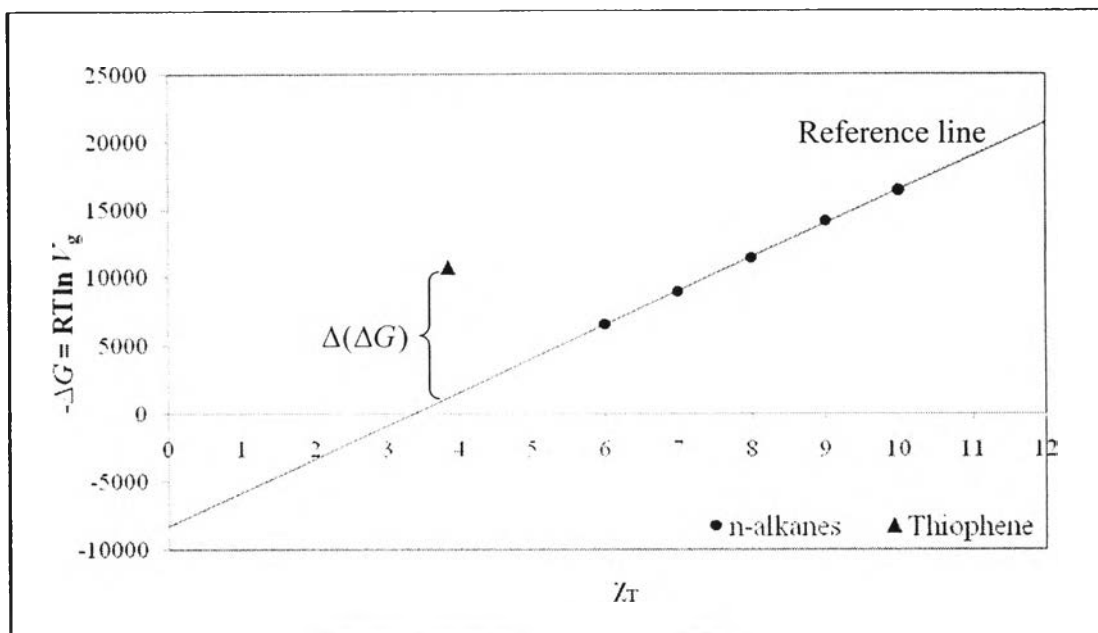


Figure C3 Specific interaction parameter, reduced 30% Cu/m-Al₂O₃ at 225 °C: *n*-alkanes (continuous line), thiophene (•).

According to the Figure C3, the equation of reference line was obtained by using the Microsoft Office Excel software, as shown in Equation (6):

$$y = -2453.3x + 8600$$

or

$$\Delta G_{\text{Ref}} = -2453.3 \chi_T + 8600 \quad (6)$$

For thiophene: $\chi_T = 3.84$

Note: the calculation of equivalent carbon number was shown in Appendix B.

Substitute the value of χ_T in Equation (6) gives

$$\begin{aligned} \Delta G_{\text{Ref}} &= -2453.3 (3.84) + 8600 \\ &= -821 \text{ J/mol.} \end{aligned}$$

From the experiment, the retention time for the thiophene on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C is 1.10 min. Calculation of V_g was shown in Appendix C1. The value of V_g is 13.34 cm³/g.

Calculate for the ΔG_{Polar} according to Equation (6):

$$\Delta G_{\text{Polar}} = -RT \ln V_g + C \quad (6)$$

$$\begin{aligned}
 \Delta G_{\text{Polar}} &= -8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot (225 + 373.15) \text{K} \cdot \ln(13.34) \\
 &= -10759 \text{ J/mol} \\
 \therefore |\Delta(\Delta G)| &= |\Delta G_{\text{Polar}} - \Delta G_{\text{Ref}}| \\
 &= |-10759 - (-821)| \\
 &= 9939 \text{ J/mol}
 \end{aligned}$$

Substitute all of the value in Equation (4):

$$\begin{aligned}
 \therefore \gamma_s^s &= \frac{9939 \frac{\text{J}}{\text{mol}}}{6.02 \times 10^{23} \text{ mol}^{-1} \cdot 0.2839 \text{ nm}^2} \cdot \left(\frac{10^3 \text{ mJ}}{\text{J}} \right) \cdot \left(\frac{10^{18} \text{ nm}^2}{\text{m}^2} \right) \\
 &= 58.1 \text{ mJ/m}^2.
 \end{aligned}$$

\therefore The specific component (γ_s^s) of thiophene injected as polar probe molecules on reduced 30% Cu/m- Al_2O_3 adsorbent at 225 °C is 58.1 mJ/m².

C5.3 Surface Free Energy Calculation

Example: The surface free energy (γ_s) of thiophene injected as polar probe molecules on reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C.

The surface free energy of thiophene on reduced 30% Cu/m-Al₂O₃ was obtained according to Equation (7):

$$\gamma_s = \gamma_s^d + \gamma_s^s, \quad (7)$$

from Appendix C5.1: $\gamma_s^d = 48.6 \text{ mJ/m}^2$

and from Appendix C5.2: $\gamma_s^s = 58.1 \text{ mJ/m}^2$

substitute all of the value in Equation (7) gives

$$\begin{aligned} \gamma_s &= 48.6 + 58.1 \\ &= 106.7 \text{ mJ/m}^2. \end{aligned}$$

\therefore The surface free energy (γ_s) of reduced 30% Cu/m-Al₂O₃ adsorbent at 225 °C is 106.7 mJ/m².

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Proceeding:

1. Aryusanil, T.; Malakul. P.; and Thomas, M. (2011, April 26) Desulfurization of hydrocarbon feeds by π -complexation adsorption: Characterization of copper halides impregnated on mesoporous and macroporous aluminas. The 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers. Bangkok. Thailand.

