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APPENDIX A
CALCULATIONS

In this study, the following physical properties of Micro 850 graphite were to be measured and calculated:

the BET total surface area, BET (m^2/g)

the average diameter of graphite flakes, d (μm)

the average thickness of graphite flakes, h (μm)

the basal plane surface area, A_1 (m^2/g)

the edge plane surface area, A_1 (m^2/g).

The BET total surface area, BET and the average diameter of graphite sample, d were measured by manufacturer. For determining the thickness of graphite flakes, the basal plane surface area and edge plane surface area, they can be determined by the following assumption.

1. The graphite flakes are taken as a disk.
2. N_2 adsorption has no selectivity between the edge plane surface and basal plane surface.
3. The graphite sample is a graphitic carbon with no pores.

The thickness, h can be calculated from the geometry by the following equation.

$$h = 0.9091 \frac{1}{(BET - 1.8182/d)}$$

Knowing the average particle diameter, d and thickness, h and the density (2.2 g/cm^3) was used in this study) of the sample, the edge plane surface area, A_2 and basal plane surface area can be simply calculated from the geometry of the flakes.

The following method is the order of calculation.

1. Calculate the volume of a graphite flake by the equation as follows:

$$\text{volume per one flake} = \frac{\pi d^2 h}{4}$$

Knowing the density of the sample and volume of a graphite, the mass of a graphite flake can be determined.

2. Determine the total surface area of a graphite flake by the following equation:

The total surface area of a graphite flake

= (BET) x (the mass of a graphite flake)

3. Determine the ratio between the basal plane surface area of one graphite and the total surface area of a graphite flake and the ratio between the edge plane surface area of one graphite and the total surface area of a graphite flake.

$$\frac{\text{the basal plane surface area of one flake}}{\text{total surface area of one flake}} = \frac{2\pi(d/2)^2}{2\pi(d/2)^2 + 2\pi(d/2)h}$$

$$\frac{\text{the edge plane surface area of one flake}}{\text{total surface area of one flake}} = \frac{2\pi(d/2)h}{2\pi(d/2)^2 + 2\pi(d/2)h}$$

Knowing total surface area of a graphite flake and the ratio between the basal plane surface area of one graphite and the total surface area of a graphite flake or the ratio between the edge plane surface area of one graphite and the total surface area of a graphite flake, the basal plane surface area and the edge surface area of one flake can be determined.

4. Convert the basal plane surface area and edge plane surface area of one flake into the basal surface surface area and edge surface area per one gram of the graphite sample by dividing with the mass of a graphite flake.

For determining reaction rate on the different bases, the mass reduction data from TGA experiments between 10% to 20% burnoff and the initial surface of graphite were only used.

1. Reaction rate based on weight $= \dfrac{\text{the mass reduction data}}{\text{initial weight of graphite}}$

2. Reaction rate based on total surface area

$$= \left(\frac{\text{the mass reduction data}}{\text{initial weight of graphite}}\right)(\text{BET})$$

3. Reaction rate based on edge surface area

$$= \left(\frac{\text{the mass reduction data}}{\text{initial weight of graphite}}\right)(\text{edge surface area})$$

4. Turnover frequency

$$= \frac{\left(\dfrac{\text{the mass reduction data}}{\text{initial weight of graphite}}\right)(\text{edge surface area})(\text{Avogadro Number})}{(\text{Molecular weight of carbon})\left(0.120\ \dfrac{\text{edge carbon atoms}}{(\text{A}^{\circ})^{2}}\right)}$$

APPENDIX B

EXPERIMENTAL DATA

Table B-1 TOF for carbon-NO reaction at various temperature (6% NO concentration, Micro850 graphite).

Temperature (^{o}C)	500	550	600	650	700	750
Rate of carbon removal (mg/min)	0.0013	0.0028	0.0069	0.0155	0.0397	0.0864
Initial graphite weight (mg)	5.0180	5.0820	5.0680	6.1590	5.1780	6.0760
Reaction rate based on weight (g carbon/gcarbon min)	0.0003	0.0006	0.0014	0.0025	0.0077	0.0142
Reaction rate based on total surface area (g carbon/BET m^2 hr)	0.0010	0.0021	0.0053	0.0097	0.0297	0.0550
Reaction rate based on edgesurface area (g carbon/edge m^2 hr)	0.0354	0.0740	0.1822	0.3356	1.0221	1.8949
TOF (sec^{-1})	0.0411	0.0859	0.2116	0.3897	1.1870	2.2005
1000/T (K^{-1})	1.2934	1.2148	1.1453	1.0832	1.0276	0.9774
lnTOF	-3.1919	-2.4540	-1.5530	-0.9425	0.1714	0.7887
NO pressure (atm)	0.0633	0.0609	0.0587	0.0617	0.0616	0.0614
ln NO pressure	-2.7598	-2.7985	-2.8355	-2.7860	-2.7864	-2.7901

Table B-2 TOF for carbon-NO reaction at various temperature (20% NO concentration, Micro850 graphite).

Temperature(°C)	500	550	600	650	700	750
Rate of carbon removal (mg/min)	0.0024	0.0056	0.0192	0.0536	0.1032	0.2223
Initial graphite weight (mg)	5.0590	5.0770	5.1450	5.1660	5.1720	6.1730
Reaction rate based on weight (g carbon/g carbon min)	0.0005	0.0011	0.0037	0.0104	0.0200	0.0360
Reaction rate based on total surface area (g carbon/BET m^2 hr)	0.0018	0.0043	0.0145	0.0401	0.0773	0.1394
Reaction rate based on edge surface area (g carbon/edge m^2 hr)	0.0630	0.1477	0.4985	1.3824	2.6613	4.8018
TOF (sec^{-1})	0.0732	0.2133	0.5789	1.6053	3.0905	5.5762
1000/T (K^{-1})	1.2934	1.2148	1.1453	1.0832	1.0276	0.9774
lnTOF	-2.6146	-1.5451	-0.5467	0.4733	1.1283	1.7185
NO Pressure (atm)	0.2100	0.2196	0.2194	0.2141	0.2256	0.2223
ln NO pressure	-1.5606	-1.516	-1.5167	-1.5412	-1.4889	-1.5039

Table B-3 TOF for carbon-NO reaction at various temperature (40% NO concentration, Micro850 graphite).

Temperature (°C)	500	550	600	650	700	750
Rate of carbon removal (mg/min)	0.0082	0.0221	0.0430	0.0904	0.2328	0.4153
Initial graphite weight (mg)	5.4220	5.0000	5.2330	6.1070	5.3000	5.8760
Reaction rate based on weight (g carbon/g carbon min)	0.0015	0.0044	0.0082	0.0148	0.0439	0.0707
Reaction rate based on total surface area (g carbon/BET m^2 hr)	0.0059	0.0171	0.0318	0.0573	0.1700	0.2736
Reaction rate based on edge surface area (g carbon/edge m^2 hr)	0.2019	0.5891	1.0948	1.9744	5.8562	9.4233
TOF (sec^{-1})	0.2345	0.6841	1.2714	2.2928	6.8006	10.9430
1000/T(K^{-1})	1.2934	1.2148	1.1453	1.0832	1.0276	0.9774
lnTOF	-1.4504	-0.3797	0.2401	0.8298	1.9170	2.3927
NO pressure (atm)	0.4074	0.4075	0.4119	0.4048	0.3915	0.4051
ln NO pressure	-0.8979	-0.8976	-0.8869	-0.9045	-0.9377	-0.9037

Table B-4 Comparison of TOF for Micro 850 graphite with SP-1 and Micro 450 graphite at various temperature in carbon-NO reaction (6% NO concentration).

Temperature (°C)	1000/T (K^{-1})	TOF (sec^{-1})			lnTOF		
		Micro 850 graphite	SP-1 graphite	Micro 450 graphite	Micro 850 graphite	SP-1 graphite	Micro 450 graphite
500	1.2934	0.0411	-	0.0308	-3.1919	-	-3.4794
550	1.2148	0.0859	0.7888	0.0708	-2.4540	-0.2373	-2.6472
600	1.1453	0.2116	1.8941	0.0999	-1.5530	0.6388	-2.3036
650	1.0832	0.3897	2.7979	0.2445	-0.9425	1.0289	-1.4084
700	1.0276	1.1870	5.9876	0.5955	0.1714	1.7897	-0.5183
750	0.9774	2.2005	16.5204	1.0887	0.7887	2.8046	0.0850

Table B-5 TOF for carbon-N_2O reaction at various temperature (6% N_2O concentration, Micro850 graphite).

Temperature (°C)	500	550	600	650	700	750
Rate of carbon removal (mg/min)	-	0.0007	0.0031	0.0125	0.0683	0.2172
Initial graphite weight (mg)	-	7.0300	7.1500	7.0310	7.0780	6.8580
Reaction rate based on weight (g carbon/g carbon min)	-	0.0001	0.0004	0.0018	0.0096	0.0317
Reaction rate based on total surface area (g carbon/BET m^2 hr)	-	0.0004	0.0017	0.0069	0.0374	0.1226
Reaction rate based on edge surface area (g carbon/edge m^2 hr)	-	0.0134	0.0570	0.2372	1.2866	4.2229
TOF(sec^{-1})	-	0.0156	0.0662	0.2755	1.4941	4.9039
1000/T(K^{-1})	-	1.2148	1.1453	1.0832	1.0276	0.9774
lnTOF	-	-4.1620	-2.7150	-1.2892	0.4015	1.5900
N_2O pressure (atm)	-	0.0604	0.0610	0.0603	0.0595	0.0602
ln N_2O pressure	-	-2.8070	-2.7975	-2.8092	-2.8225	-2.8095

Table B-6 TOF for carbon-N_2O reaction at various temperature (12% N_2O concentration, Micro850 graphite).

Temperature (°C)	500	550	600	650	700	750
Rate of carbon removal (mg/min)	0.0002	0.0021	0.0060	0.0308	0.1258	0.4262
Iinitial graphite weight (mg)	7.1760	7.0500	6.8990	7.0610	6.6030	6.6820
Reaction rate based on weight (g carbon/g carbon min)	3.2938E-05	0.0003	0.0009	0.0041	0.0191	0.0638
Reaction rate based on total surface area (g carbon/BET m^2 hr)	0.0001	0.0011	0.0034	0.0157	0.0738	0.2469
Reaction rate based on edge surface area (g carbon/edge m^2 hr)	0.0044	0.0389	0.1154	0.5408	2.5403	8.5045
TOF (sec^{-1})	0.0051	0.0452	0.1340	0.6280	2.950	9.8760
1000/T (K^{-1})	1.2934	1.2148	1.1453	1.0832	1.0276	0.9774
lnTOF	-5.2785	-3.0967	-2.0099	-0.4652	1.0818	2.2901
N_2O pressure (atm)	0.1222	0.1182	0.1190	0.1194	0.1210	0.1184
ln N_2O pressure	-2.1019	-2.1357	-2.1283	-2.1250	-2.1123	-2.1340

Table B-7 TOF for carbon-N_2O reaction at various temperature (20% N_2O concentration, Micro850 graphite).

Temperature (°C)	500	550	600	650	700	750
Rate of carbon removal (mg/min)	0.0004	0.0028	0.0130	0.0389	0.2001	0.5656
Initial graphite weight (mg)	7.1220	6.9330	6.9280	6.7600	6.9470	6.7010
Reaction rate based on weight (g carbon/g carbon min)	0.0001	0.0004	0.0019	0.0057	0.0288	0.0844
Reaction rate based on total surface area (g carbon/BET m^2 hr)	0.0002	0.0016	0.0073	0.0222	0.1115	0.3267
Reaction rate based on edge surface area (g carbon/edge m^2 hr)	0.0068	0.0534	0.2510	0.7663	3.8414	11.2547
TOF (sec^{-1})	0.0079	0.0620	0.2914	0.8898	4.4609	13.0697
1000/T (K^{-1})	1.2934	1.2148	1.1453	1.0832	1.0276	0.9774
lnTOF	-4.8462	-2.7803	-1.2329	-0.1167	1.4953	2.5703
N_2O pressure (atm)	0.1993	0.2035	0.2009	0.2007	0.1957	0.2010
ln N_2O pressure	-1.6127	-1.5921	-1.6048	-1.6058	-1.6311	-1.6045

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