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# Correlation between Chemical structure and reactivity for GO regarding oxidative amine coupling reaction

Graphene oxide (GO) having oxygen-containing groups is expected as metal-free and environment-compatible catalyst. The research on GO catalyst progressed [1 - 3], although the detail mechanism for GO catalytic activity is not clear yet. Investigating Graphene Oxide (GO) properties before / after the catalytic reaction is a promising strategy for clarification of the mechanism for GO catalytic activity. Additionally, it is known that removing oxidative debris on GO by base-treatment is important factor to get the higher yield for the following catalytic reaction [1]. In this study, the principle for reactivity is investigated by conducting the oxidative amine coupling reaction of benzylamine (**1**) to N-benzylidenebenzylamine (**2**) using baGO and thermally reduced one (rbaGO) (**Scheme 1**).

baGO-Pristine was obtained by washing GO, synthesized by Hummers method, with NaOH. rbaGO was prepared by reducing baGO at 450˚C. After **Scheme 1**, the reaction media filtered for removing the catalyst was characterized by GC-MS. After the 1st cycle reaction, the recovered catalyst was used as that for the 2nd cycle (baGO-1st cycle, rbaGO-1st cycle). The chemical structure of each catalyst after the reaction was evaluated by XPS (Al K□), where it was washed with ethanol after the reaction.

The GC-MS yields of (**2**) for each catalyst is summarized in **Table 1**. The atomic ratio O/C of catalyst much decreases after the reduction or 1st cycle reaction and rbaGO shows poor yield, suggesting roles of baGO / rbaGO not as catalyst but as oxidant (**Fig.1**). However, baGO-1st cycle exhibits the highest yield in spite of C1s spectrum and O/C similar to that of rbaGO and rbaGO-1st cycle, which also indicates no more reduction for rbaGO in the 1st cycle reaction. Taking these results and appearance of nitrogen content after the 1st cycle reaction into consideration, a different mechanism in the 2nd cycle reaction is suggested, where nitrogen incorporated into rbaGO / baGO in the 1st cycle reaction plays an important role for the reactivity.

To clarify the most responsible functional groups in rbaGO / baGO for the higher catalytic reactivity in the 2nd cycle reaction, we have derived the amount of nitrogen-containing functional group per 100 mg in each GO sample for the 2nd cycle reaction. By plotting the amount of nitrogen-containing functional group and the GC-yield of the product, the correlation coefficient $r$ is calculated for each functional groups. In particular, the GC-yield tends to increase as Graphitic N (correlation coefficient $r$ = 0.94) and Oxidized N (correlation coefficient $r$ = 0.87) increase. The important roles of those functional groups in the oxidation amine coupling reaction could be explained by the enhancement in the oxygen adsorption ability, which is important to produce $O_2^{\cdot -}$ species from ambient oxygen molecules for proceeding the oxidative coupling reaction.

## References

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[2] A. Shaabani, M. Mahyari, and F. Hajishaabanha, Res. Chem. Intermed., 40, 8, 2799–2810 (2014).
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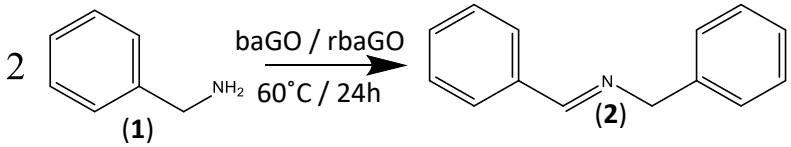
## Figures




**Scheme 1:** Oxidative amine coupling reaction of benzylamine (**1**) to N-benzylidenebenzylamine (**2**)

**Table 1:** GC Yield for (**2**) using each baGO

| Catalyst sample | Yield (%) |
|---|---|
| **baGO-Pristine** | 13 |
| **baGO-1st cycle** | 39 |
| **rbaGO** | 6 |
| **rbaGO-1st cycle** | 6 |

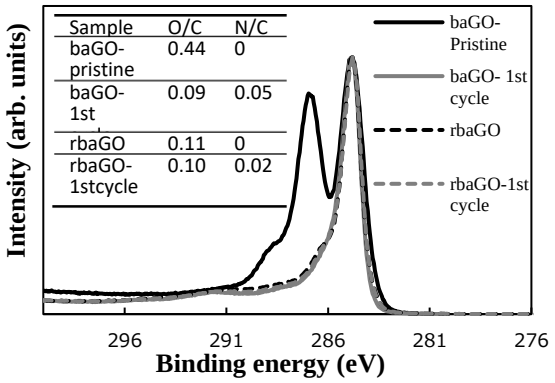



**Figure 2:** XPS C1s peak for each baGO after the reaction