

1 **Photochemical benzene to toluene methylation using methanol cata-**
2 **lyzed by gallium nitride nanowire**

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15 **ABSTRACT:** As a highly important functional group that is widely used throughout the whole chemical industry and
16 crucial to all living organisms, it is difficult to directly incorporate benzene into other molecules in synthesis due to the
17 chemical inertness rendered by benzene's highly symmetrical aromatic structure. Here we show a facile and clean pho-
18 tochemical approach to directly transform benzene into the more versatile and less toxic toluene using methanol as a
19 renewable material and gallium nitride as a powerful yet robust catalyst. In addition, we also demonstrated that by using
20 the gallium nitride nanowire catalyst, toluene can be directly synthesized from methane and methanol.

21 Since the first illustration of its highly symmetric structure in 1865¹, the benzene ring, also known as the phenyl func-
22 tional group, has been widely adapted into various important products including polyesters², nylons³, pharmaceuticals⁴,
23 etc., of which over 35 million metric tons are produced annually worldwide⁵. In addition, the phenyl group is crucial to
24 all living organisms, as three out of twenty amino acids contain phenyl groups. Benzene is one of the most readily
25 accessible sources used to synthesize phenyl-containing compounds; for example, it can be found abundantly in crude

1 oil⁶ and biomass⁷. However, benzene is inert to common chemical transformations⁸ unless subjected to harsh conditions,
2 e.g., highly pressurized oxygen plus flammable gas under 250 °C (cumene process)⁹. On the other hand, as one of the
3 closest benzene derivatives, toluene undergoes chemical transformations much easier¹⁰ thanks to the addition of the
4 methyl on the benzene ring. Therefore, toluene serves as a much more common precursor towards the synthesis of various
5 phenyl-containing products¹¹. In addition, the toxicity level drops dramatically from benzene, which is highly carcinogenic,
6 to toluene¹². It is thus highly desirable to enable a direct benzene to toluene conversion under ambient conditions
7 that uses sustainable and benign materials. Although preceding works have been seen in literature¹³⁻¹⁵, those are mostly
8 heat-driven reactions that require harsh temperatures (>200 °C). In addition, due to the elevated temperatures, these
9 reactions usually suffer from poor selectivity and give a mixture of different products (toluene, n- $\backslash m\backslash p$ -xylene, mesitylene,
10 etc.). Recently, we have shown that by using an easily accessible light source, a well-engineered gallium nitride
11 nanowire (GaN NW) can catalyze the direct photochemical conversion of methanol-to-ethanol via a methyl carbene
12 intermediate¹⁶. We therefore envision that the carbene intermediate can be highly useful in the methylation of the phenyl
13 C-H bond, enabling a direct, simple conversion of benzene to toluene. Herein, we would like to report a GaN NW-
14 catalyzed photochemical methylation of benzene to toluene using methanol (Figure 1).

15 GROWTH AND IDENTIFICATION OF CATALYST

16 The GaN NW described in our research was grown via plasma-assisted molecular beam epitaxy (PA-MBE, see Sup-
17 porting Information for detailed growth condition) (Figure 2). *n*-, *p*-type doping was applied to grow the corresponding
18 *n*-GaN NW and *p*-GaN NW, as significant near-surface energy band bending can be observed with doping. The undoped
19 GaN NW was also grown and will be mentioned as intrinsic(*i*)-GaN NW. The typical growth time for the NWs is 4 hours,
20 yielding a surface area of the top plane (polar plane, c-plane) and of the side plane (non-polar plane, m-plane) of 0.17
21 m²·g⁻¹ and 5.53 m²·g⁻¹ respectively. *p*-GaN NW grown for 2 h was also used in this study, showing a c-plane area of 0.17
22 m²·g⁻¹ and an m-plane area of 2.77 m²·g⁻¹.

23 CATALYST PERFORMANCE

24 A 3.5 cm² slice of a GaN NW grown for 4 h (equiv to 0.35 mg GaN) was then placed on the bottom of a 120 mL glass
25 flange equipped with a sealing O-ring and an evacuation seal. The flange was capped with a quartz window and evacuated
26 using a vacuum oil pump until the internal pressure dropped below 5 × 10⁻² mbar. 5 μL (equiv to 0.124 mmol) of HPLC
27 grade methanol and 10 μL (equiv to 0.112 mmol) of HPLC grade benzene was then introduced through the evacuation

1 seal to the flange before the flange was cooled to 4 °C in a chiller and irradiated with a 300 W full-arc xenon lamp for
2 12 h (Figure 3A). The gas phase inside the flange was analyzed using a valve syringe and gas chromatography mass
3 spectrometer (GC-MS). To our delight, by using *p*-doped GaN NW, 0.038 mmol of toluene was detected, which corre-
4 sponds to a 34% yield (Figure 3B). This yield is much higher than the methanol-to-ethanol conversion we published
5 earlier under similar reaction conditions¹⁶. In addition, no ethanol was detected throughout the investigation, indicating
6 the methyl carbene intermediate generated from methanol prefers to attack the benzene's *sp*²-C-H bond rather than the
7 methanol's *sp*³-C-H bond. We then examined the benzene to toluene conversion using *n*-GaN NW, which dramatically
8 reduced the toluene yield to 0.0069 mmol. *i*-GaN also gave a reduced yield of 0.0094 mmol. 0.35 mg of commercial
9 GaN powder gave 0.0023 mmol of toluene while no toluene was detected in the absence of either GaN or light. To
10 examine the robustness of the catalyst, six consecutive methylation experiments were conducted by recycling the same
11 catalyst; the catalyst showed no decrease in activity (Figure 3C). A 3.5 cm² slice of *p*-GaN NW grown for 2 h instead of
12 4 h (equiv to 0.17 mg of GaN) was also examined for catalytic benzene to toluene conversion; it gave a similar 0.038
13 mmol yield of toluene, resulting in a catalytic efficiency of 18100 μmol·g_{cat}⁻¹·h⁻¹ (Figure 3D). Considering the similar
14 yields granted by *p*-GaN grown for 2 h and 4 h, which possess identical c-plane areas but different m-plane areas, *p*-GaN
15 thin-film was then examined under the same reaction condition in order to determine the surface which was responsible
16 for the benzene to toluene conversion. The experiment gave 0.0092 mmol of toluene. This significant yield drop com-
17 pared to the optimized yield may indicate the participation of the m-plane since GaN thin-film is only composed of c-
18 plane. The absent m-plane may facilitate the conversion by promoting the adsorption of the benzene molecule and the
19 activation of its C-H bond¹⁷. This phenomenon is likely to occur in the benzene to toluene conversion despite our previous
20 study which indicates the methanol to carbene conversion was achieved solely on the c-plane¹⁶. We then used the *p*-GaN
21 grown for 2 h (0.17 mg GaN) to conduct a large-scale benzene to toluene conversion using 1 mL of methanol and 2 mL
22 of benzene under the optimized condition. 0.86 mmol of toluene was generated, giving an astonishing 422 mmol·g_{cat}⁻¹·h⁻¹
23 catalytic efficiency (Figure 3E). Isotope labeling experiment using ¹³CH₃OH also gave ¹³C labeled toluene (Figure 3F).
24 Xylene, Ethylbenzene, and Mesitylene, were not detected throughout the investigation.

25 MECHANISTIC STUDY

26 With the experimental result in hand, it is suggested that the benzene to toluene conversion might undergo via a carbene
27 intermediate similar to our previous discovery¹⁶. To further examine the mechanism, we periodically monitored the gen-
28 eration of toluene under the optimized reaction condition over the first two hours (Figure 4A). Then, the initial methanol

1 load was reduced by half (2.5 μL), and it was found that the reaction rate was significantly reduced to approximately 1/4
2 compared to the optimized reaction. As a benchmark, we also tried reducing the benzene amount (to 5 μL) and the
3 reaction rate was reduced to approximately 1/2. This indicates that the reaction rate equation is likely to be proportional
4 to the benzene activity coefficient and the methanol activity coefficient squared, suggesting a mechanism involving two
5 methanol molecules. A similar test was also conducted for our previous methanol-to-ethanol conversion and gave a sim-
6 ilar reaction rate decrease to 1/4 of the optimized yield (Figure 4B). Therefore, the initial carbene formation from meth-
7 anol is likely to involve two molecules. As indicated in Figure 4C, the negative-charged GaN c-plane under light illumina-
8 tion surface interacts with the methanol -OH first. The second methanol molecule attached to the first methanol mol-
9 ecule by hydrogen-bonding then undergoes elimination and gives the methyl carbene intermediate.

10 **DIRECT METHANE TO TOLUENE CONVERSION**

11 The GaN NW catalyst was previously shown by our group to also afford methane conversion to benzene under similar
12 light irradiation¹⁷. At this stage, we were very curious about the possibility to combine the methane aromatization with
13 benzene to toluene conversion: to directly synthesize toluene from methane (Figure 5A). We then introduced 0.1 mmol
14 UHP (> 99.999 %) methane and 2 μL methanol into the same reactor under the optimized condition using 3.5 cm^2 slice
15 of *p*-GaN NW as catalyst (0.35 mg). It was shown on GC-MS that 0.75 μmol toluene was generated, giving $179 \mu\text{mol} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$
16 catalyst efficiency (Figure 5B). Using the same condition, *n*-GaN NW and *i*-GaN NW gave 0.62 and 0.72 μmol
17 toluene, respectively. Considering *n*-GaN shows better activity than *i*- and *p*-GaN towards methane aromatization step,
18 the benzene to toluene conversion step seems to be rate-limiting as *p*-GaN, instead of *n*-GaN, gave the highest yield.

19 **CONCLUSION**

20 In conclusion, we have demonstrated that by using GaN as a robust catalyst, benzene methylation using methanol can
21 be achieved with high efficiency. In addition, it can be suggested by our experimental results that the photochemical
22 methanol transformation into methyl carbene involves two methanol molecules to facilitate the elimination. Furthermore,
23 we also showed that toluene can be directly accessible from methane using GaN as catalyst. Further applications regard-
24 ing GaN-catalyzed hydrocarbon conversions are already underway in our lab.

25 **ASSOCIATED CONTENT**

26 The Supporting Information is available free of charge on the ACS Publications website.
27

1 SI-pp13.pdf (Figure S1-S3, Figure S1-S3)
2

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7 **Author Contributions**

8 M. L. discovered the benzene to toluene conversion, designed (except for the kinetic study) and carried out (except for the
9 nanowire growth and identification) the experiments, and composed the manuscript. Z. Q. provided the original inspiration
10 and idea for this project. R. T. R. synthesized all the nanowire catalysts. L. L. inspired the methane to toluene conversion. L.
11 T. participated in crucial discussions. S. C. characterized the synthesized nanowire. Y.C. proofread the manuscript. R. K. per-
12 formed the computational study and provide important mechanistic insight. General guidance and project directing was pro-
13 vided by Z. M. and C.-J. L., who also designed the kinetic study experiment.

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15 No competing financial interests have been declared.

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18 FRQNT

19 CFI

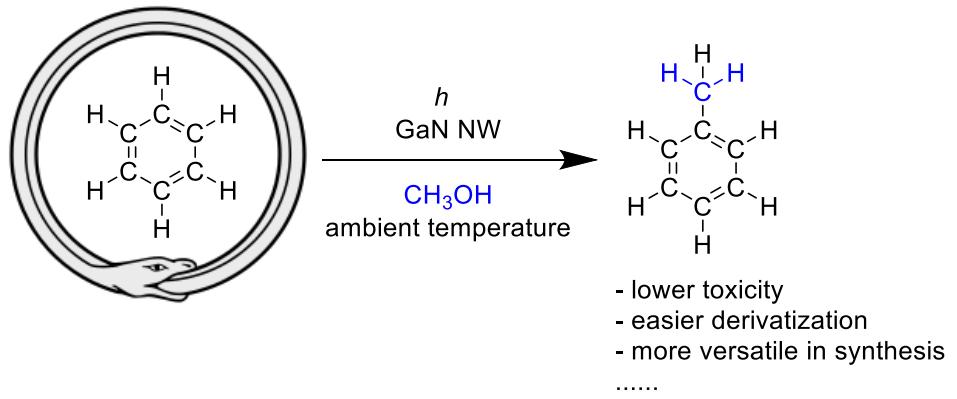
20 Emission Reduction Alberta

21 **ACKNOWLEDGMENT**

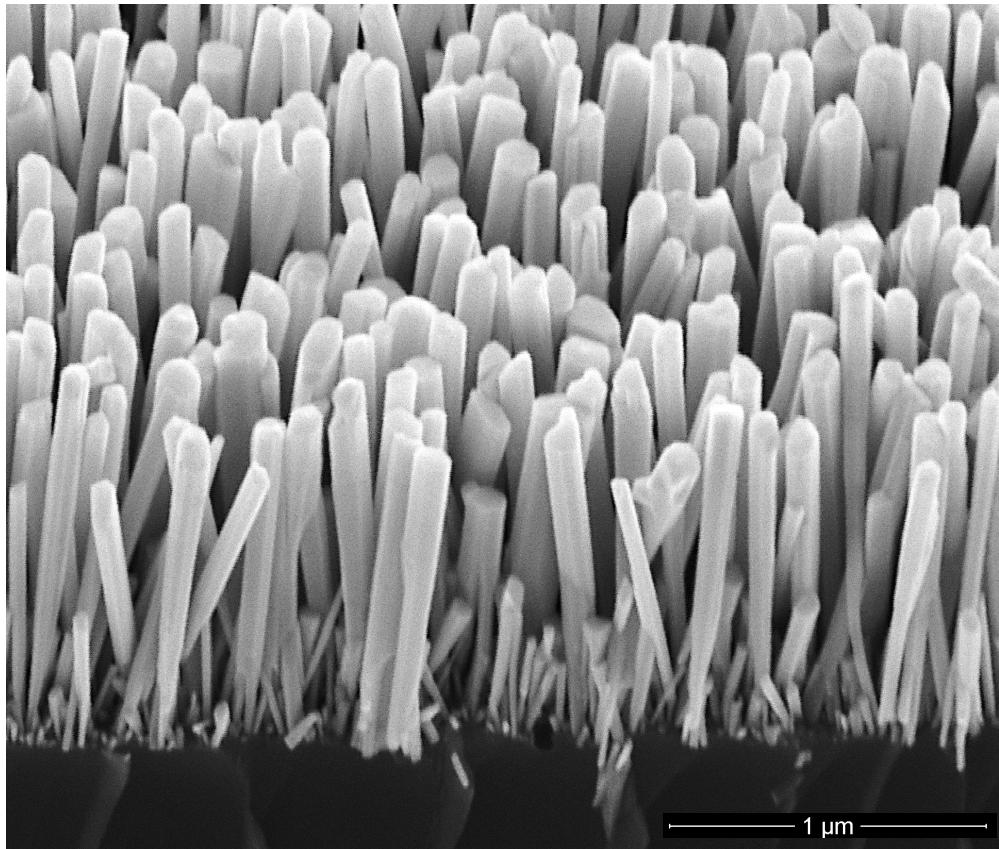
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23 **REFERENCES**

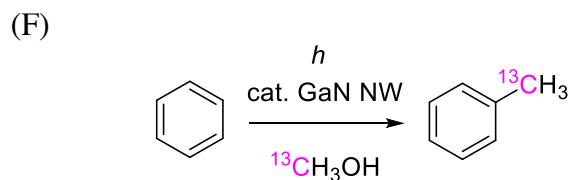
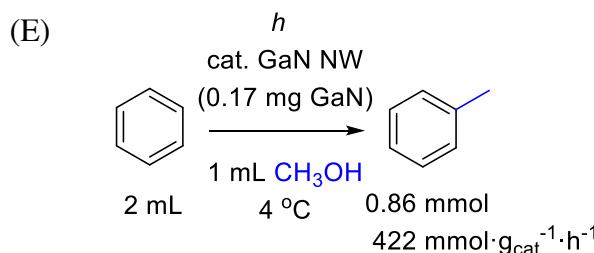
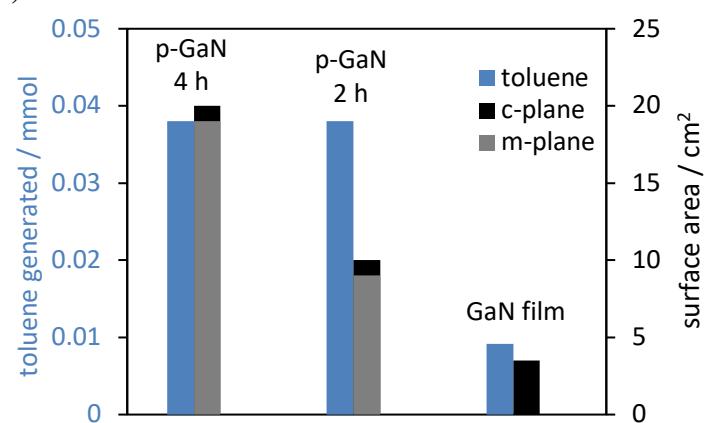
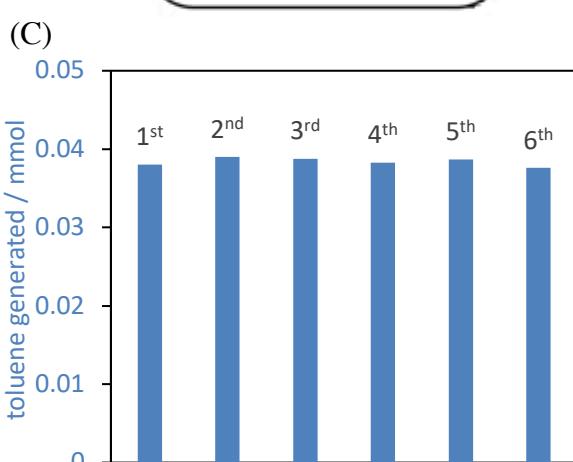
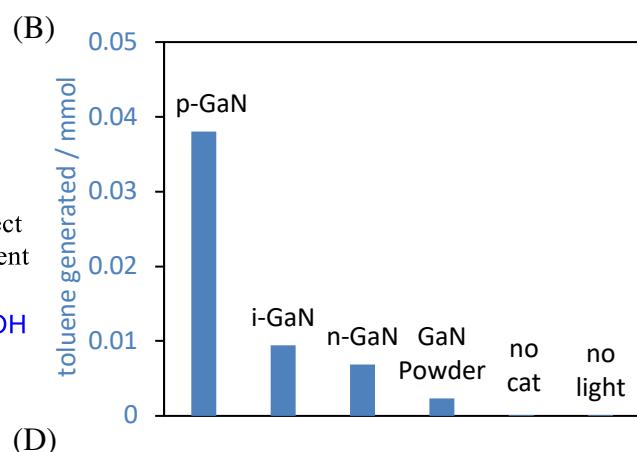
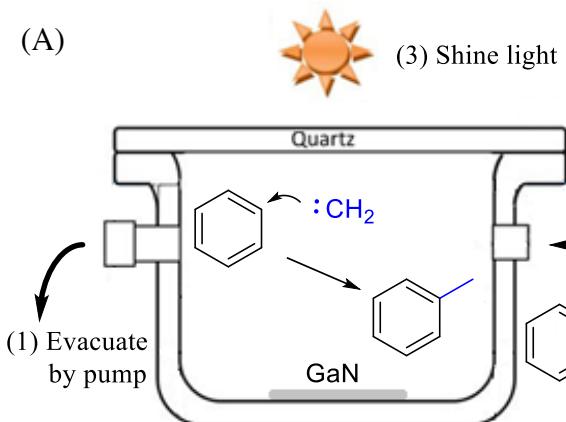
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1
 2 Figure 1. Photo-driven benzene methylation into toluene using methanol.
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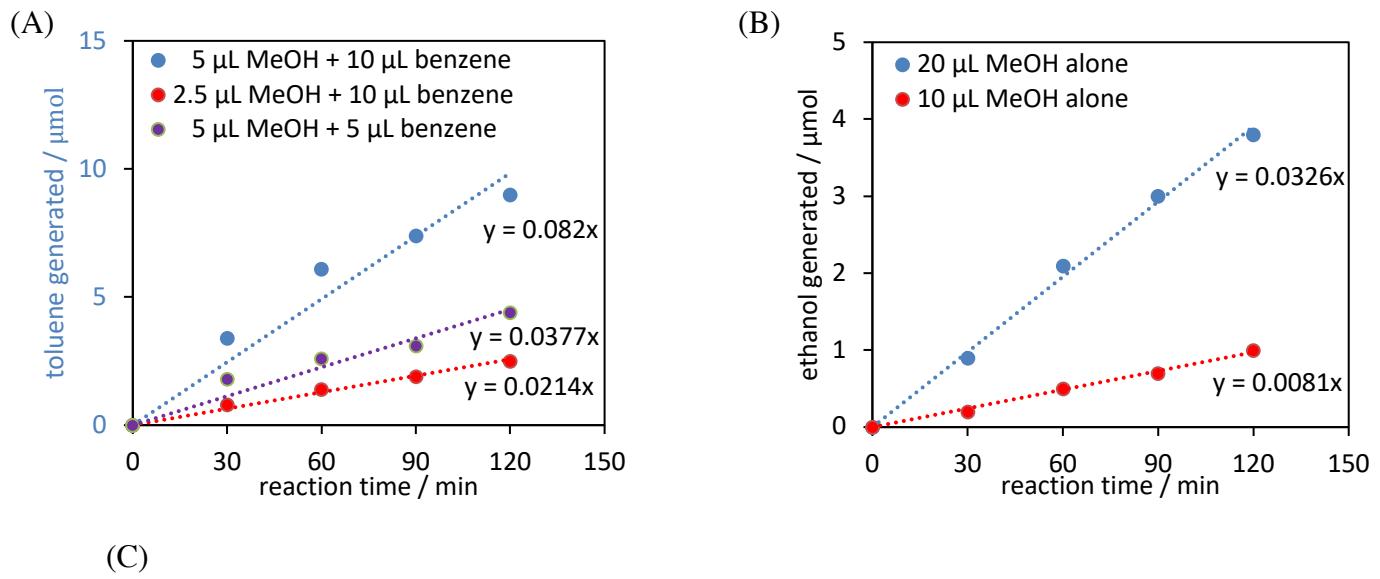


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 5 Figure 2. Scanning Electron Microscopy (SEM) of GaN NW grown from MBE.
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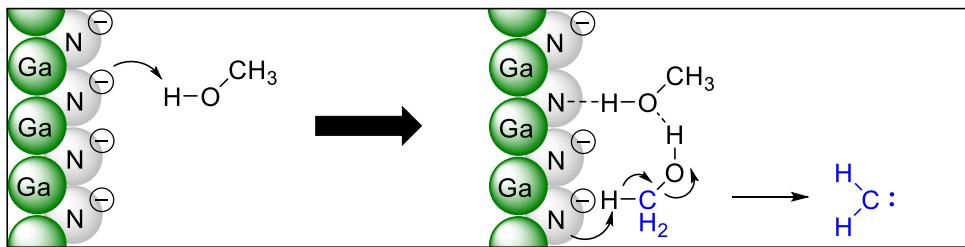
4 Figure 3. Catalyst performance examination. (A) Reaction setup and procedures. (B) Performance of cat-
5 alyst with different doping. (C) Catalyst recyclability test. (D) Catalysts performance with quantification
6 of surface area. (E) Large-scale benzene to toluene conversion. (F) Isotope labeling experiment.

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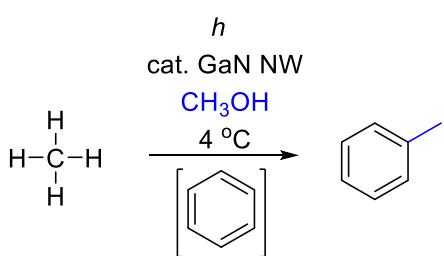
(C)



3

4 Figure 4. Reaction kinetic study and the proposed mechanism. (A) Kinetic study of benzene to toluene
5 conversion. (B) Kinetic study of methanol-to-ethanol conversion. (C) Proposed mechanism involving
6 two methanol molecules.

1 (A)



(B)

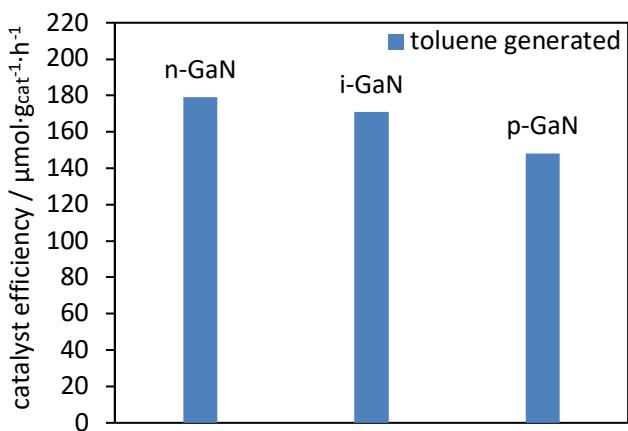


Figure 5. Direct methane to toluene conversion. (A) Reaction equation. (B) Catalyst efficiency with different doping.