

Enhanced Low-Temperature CO₂ Methanation over Ni-based Catalyst Supported on La₂O₃-Al₂O₃ Composite Supports

Longhao Xu, Wenhao Zhang, Liang Shen, Minghui Zhu * and Yi-Fan Han *

¹State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, School of Chemical Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China

*Correspondence: minghuizhu@ecust.edu.cn, yifanhan@ecust.edu.cn

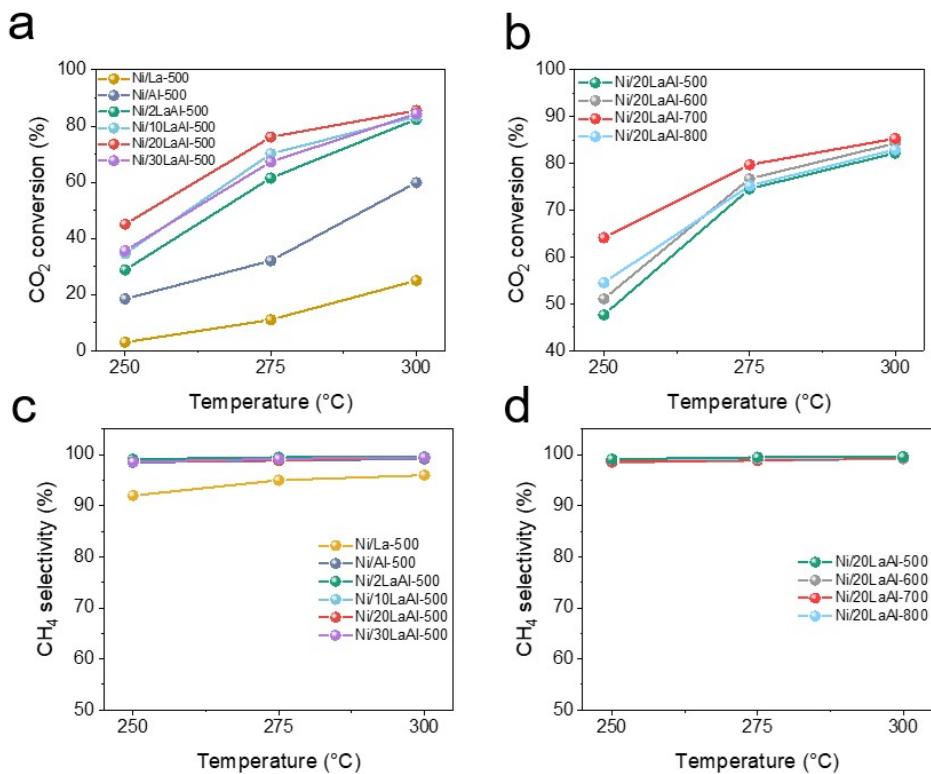


Fig. S1 CO_2 conversion and CH_4 selectivity of (a and c) Ni/30LaAl-500, Ni/20LaAl-500, Ni/10LaAl-500, Ni/2LaAl-500, Ni/Al-500 and Ni/La-500 catalysts, (b and d) Ni/20LaAl-500, Ni/20LaAl-600, Ni/20LaAl-700 and Ni/20LaAl-800 catalysts. (reaction conditions: 50 mg of catalyst, $\text{CO}_2/\text{H}_2/\text{N}_2 = 15:60:25$, 1 bar, WHSV = $30 \text{ L}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$).

Table S1. Apparent activation energies for investigated Ni/Al-X and Ni/20LaAl-X catalysts.

| Catalysts | Ea (kJ·mol ⁻¹) | |
|---------------|----------------------------|-------|
| | CH ₄ | CO |
| Ni/Al-500 | 121.13 | 91.64 |
| Ni/20LaAl-500 | 100.78 | 60.11 |
| Ni/Al-700 | 92.60 | 84.86 |
| Ni/20LaAl-700 | 80.44 | 52.88 |

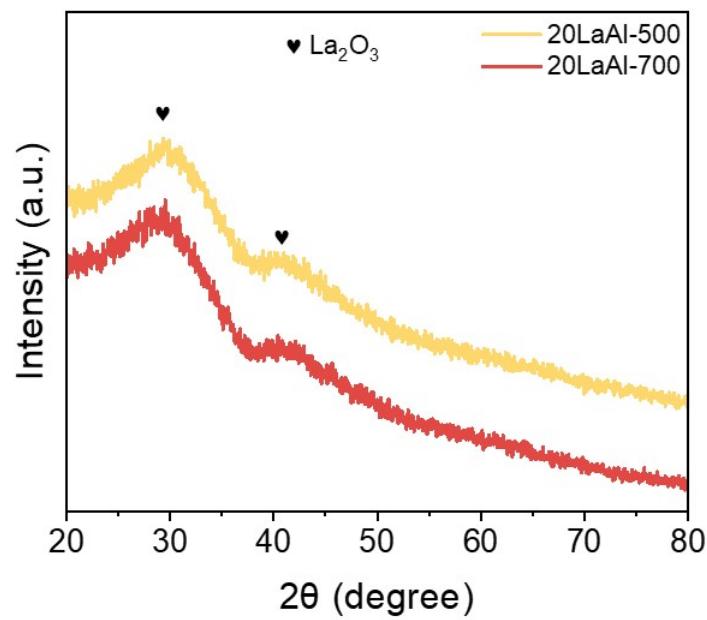


Figure S2. XRD patterns of 20LaAl-500 and 20LaAl-700 supports.

Table S2. Ni average size of the reduced Ni/Al-500, Ni/Al-700, Ni/20LaAl-500, Ni/20LaAl-700

catalysts obtained from 1. the Debye-Scherrer equation and 2. the TEM results.

| Catalysts | Ni crystal size ¹ (nm) | Ni average size ² (nm) |
|---------------|--------------------------------------|--------------------------------------|
| Ni/Al-500 | 12.8 | 7.39 |
| Ni/Al-700 | 15.1 | 7.96 |
| Ni/20LaAl-500 | 6.5 | 6.11 |
| Ni/20LaAl-700 | 8.3 | 4.71 |

Table S3. Surface atomic ratio of $\text{Ni}^0/(\text{Ni}^0+\text{Ni}^{2+})$ obtained from the XPS results.

| Catalysts | $\text{Ni}^0/(\text{Ni}^0+\text{Ni}^{2+})$ |
|---------------|--|
| Ni/Al-500 | 0.10 |
| Ni/Al-700 | 0.13 |
| Ni/20LaAl-500 | 0.19 |
| Ni/20LaAl-700 | 0.21 |

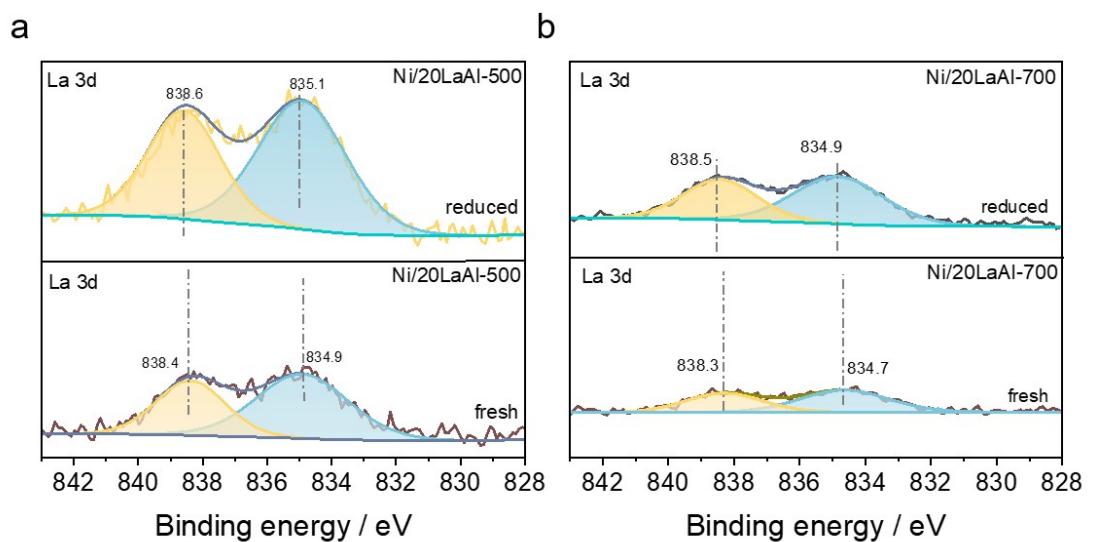


Fig. S3 Quasi *in-situ* XPS spectra of La 3d over (a) Ni/20LaAl-500 and (b) Ni/20LaAl-700 catalysts after calcination and H₂ reduction.

Table S4. Apparent reaction orders and for Ni/Al-700 and Ni/20LaAl-700 catalysts.

| Catalysts | Reaction order of CH ₄ formation | | Reaction order of CO formation | |
|---------------|---|----------------|--------------------------------|----------------|
| | CO ₂ | H ₂ | CO ₂ | H ₂ |
| Ni/Al-700 | 0.91 | 0.48 | 1.71 | -0.22 |
| Ni/20LaAl-700 | 0.73 | 0.43 | 1.54 | -0.11 |

Table S5. The basicity of the reduced catalysts (CO₂-TPD).

| Catalysts | Total basicity [μmol/g] |
|---------------|----------------------------|
| Ni/Al-500 | 82 |
| Ni/Al-700 | 129 |
| Ni/20LaAl-500 | 249 |
| Ni/20LaAl-700 | 256 |