

Catalytic Activity Enhancement of Cu-Zn-based Catalyst for Methanol Steam Reforming with Magnetic Inducement

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S.1 Ce distribution in Al₂O₃ framework via support characterization

The XRD patterns of the CeO₂-doped Al₂O₃ supports with and without magnetic inducement were investigated to verify Ce insertion into Al₂O₃ framework. The characteristic peaks of Al₂O₃ from the highest diffraction planes of (4 0 0) and (4 4 0), corresponding to the diffraction angles at ~46 and ~67 degrees in the diffractogram, are analyzed to calculate the lattice constants of the support structures, which are shown in Table S1.

Table S1. Lattice constants of γ -Al₂O₃ and CeO₂-doped Al₂O₃ supports with and without magnetic inducement.

Support	Magnetic inducement	Lattice constant (Å)
γ -Al ₂ O ₃	No magnet	7.8721
	No magnet	7.8810
CeO ₂ -Al ₂ O ₃	N-N	7.8962
	N-S	7.8864

Larger lattice constant implies better Ce insertion into Al₂O₃ framework, thus a comparatively high lattice constant is achieved when the supports were prepared with N-N magnetic inducement. It implies that same pole magnetic inducement can enhance the partial doping of Ce into Al₂O₃ framework. In addition, the lattice constants of CeO₂-doped Al₂O₃ supports prepared with and without magnetic inducement have only small variations, which manifest that the magnetic inducement during support preparation has negligible influence on the crystal structure of γ -Al₂O₃.

In addition, SEM-EDS was used to determine the Ce distribution in Al₂O₃ framework by random sampling from 5 points on 5 particles of each CeO₂-doped Al₂O₃ support. Figure S1 shows the SEM images of Ce-doped Al₂O₃ supports prepared with and without magnetic inducement and also lists the sampling points. The Ce composition is represented in terms of molar ratio of Ce:Al, obtained from the ratio of the atomic percentage of each element determined by EDS, as listed in Table S2.

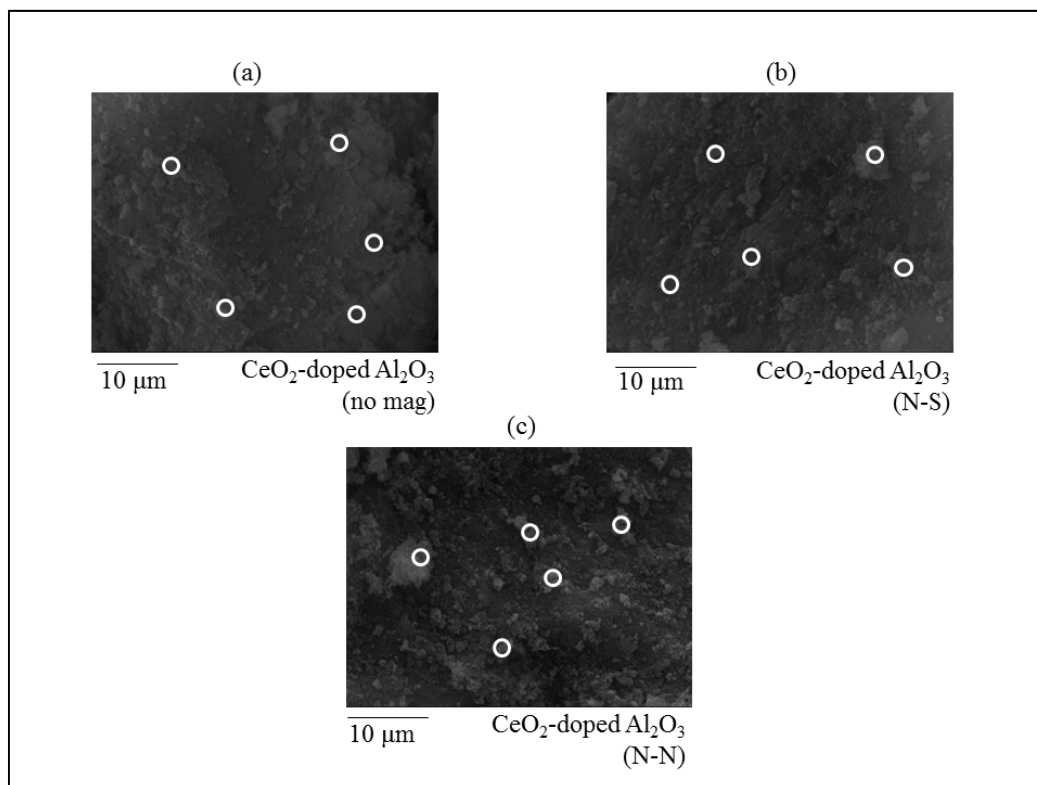


Figure S1. SEM-EDS images of CeO₂-doped Al₂O₃ supports with and without magnetic inducement: (a) CeO₂-doped Al₂O₃ (no mag), (b) CeO₂-doped Al₂O₃ (N-S), (c) CeO₂-doped Al₂O₃ (N-N). The considered 5 points are circled in each support.

Table S2. Ce distribution in CeO₂-doped Al₂O₃ supports with and without magnetic inducement.

Magnetic inducement	Ce:Al molar ratio × 10 ²		
	Range	Average	SD
No magnet	2.3-13.8	8.0	4.8
N-N	7.5-8.0	7.7	0.3
N-S	2.7-3.9	3.2	0.5

The result shows that applying magnetic field with different pole orientations during support preparation leads to the difference in composition and distribution of Ce. When no magnetic inducement is applied, the range of Ce:Al molar ratio widely varies from 2.3 to 13.8 with high standard deviation, implying that Ce is randomly inserted in the Al₂O₃ framework of the support during the sol-gel process. Applying magnetic inducement makes Ce distribution better, which is evident from the narrower range and lower standard deviation of Ce:Al molar ratio.

The data in Table S2 also imply that the application of same pole magnetic arrangement (N-N) obtains the highest Ce:Al molar ratio and the best Ce distribution in Al₂O₃ framework. In contrast, the application of N-S magnetic pole arrangement takes the lowest Ce:Al molar ratio. The results correspond with the results of the lattice constants of Table S1 and the surface area of the supports in Table 2 in the main text. The supports prepared with N-N magnetic inducement have higher lattice constant and lower surface area due to its relatively high Ce composition and uniform Ce distribution in the supports. Based on these points, it can be manifested that the application of

magnetic inducement during the sol-gel process can control Ce composition and distribution of CeO₂ in Al₂O₃ framework.

S.2 Effect of magnetic inducement on combination of support modification and metal loading

Table S3, S4, S5, and S6 show H₂ production rates from MSR over Cu-Zn catalysts supported on γ -Al₂O₃ and CeO₂-doped Al₂O₃ prepared with and without magnetic inducement between 200–300 °C. A graph comparing the data from Table S3, S4, and S6 is shown as Figure 1 in the main text for easier data visualization.

Table S3. H₂ production rate over Cu-Zn/ γ -Al₂O₃ catalysts loaded with and without magnetic inducement.

Magnetic inducement	H ₂ production rate (μmol/min)				
	200 °C	225 °C	250 °C	275 °C	300 °C
No magnet	60±2	95±13	193±21	320±20	523±46
N-N	67±2	155±10	347±17	615±37	830±70
N-S	72±2	170±20	392±22	667±32	854±88

Table S4. H₂ production rate of Cu-Zn catalyst prepared over CeO₂-doped Al₂O₃ (no magnet) support. Cu-Zn metal loading was carried out with and without magnetic inducement.

Magnetic inducement	H ₂ production rate (μmol/min)				
	200 °C	225 °C	250 °C	275 °C	300 °C
No magnet	150±30	371±43	619±61	850±80	1095±81
N-N	165±40	550±50	943±47	1565±81	1699±70
N-S	174±42	730±56	1306±62	1680±72	1782±81

Table S5. H₂ production rate of Cu-Zn catalyst prepared over CeO₂-doped Al₂O₃ (N-S) support. Cu-Zn metal loading was carried out with and without magnetic inducement.

Magnetic inducement	H ₂ production rate (μmol/min)				
	200 °C	225 °C	250 °C	275 °C	300 °C
No magnet	167±42	530±40	916±42	1388±72	2002±88
N-N	177±31	890±10	1615±31	2240±64	2403±43
N-S	184±20	923±25	1728±32	2345±50	2474±73

Table S6. H₂ production rate of Cu-Zn catalyst prepared over CeO₂-doped Al₂O₃ (N-N) support. Cu-Zn metal loading was carried out with and without magnetic inducement.

Magnetic inducement	H ₂ production rate (μmol/min)				
	200 °C	225 °C	250 °C	275 °C	300 °C
No magnet	175±50	754±60	1349±91	1800±95	2099±99
N-N	181±30	986±43	1865±53	2344±73	2400±58
N-S	195±22	1253±64	2146±82	2645±84	2796±76

S.3 Magnet setup for support preparation

The magnet setup that was used to create different magnetic environments during support preparation is composed of an aluminium frame attached with metal plates. 40 mm × 30 mm × 12.5 mm Neodymium magnets of 320 mT surface magnetic field were arranged in a 3 × 3 configuration. The distance between magnets from each side of the frame is 25 cm.

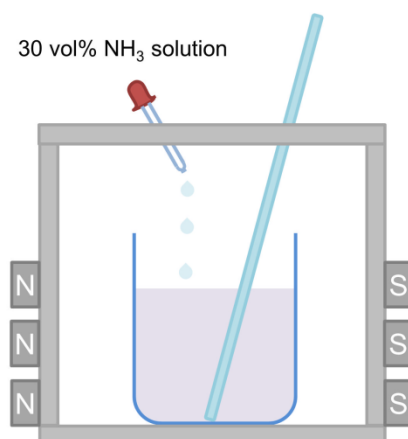


Figure S2. Magnet setup for support preparation

S.4 Stability of catalysts loaded under magnetic inducement

To determine the stability of the prepared catalysts, Cu-Zn (N-S)/CeO₂-Al₂O₃ (N-N) and Cu-Zn (no magnet)/CeO₂-Al₂O₃ (no magnet) catalysts underwent 24-h stability tests at 300 °C with pretreatment and reaction conditions similar to those used in the catalytic activity testing. The hydrogen production rate was determined using GC-TCD and reported in mmol/(s·kg_{cat}).

In Figure S3 and S4, a slight drop in activity was observed in both catalysts. Toward the end of the 24-h stability test, the decrease in catalytic activity becomes almost negligible. From this observation, it can be deduced that these Cu-Zn catalysts are reasonably stable, and a long-term stability test or a stability simulation will be required to determine the lifetime of these catalysts.

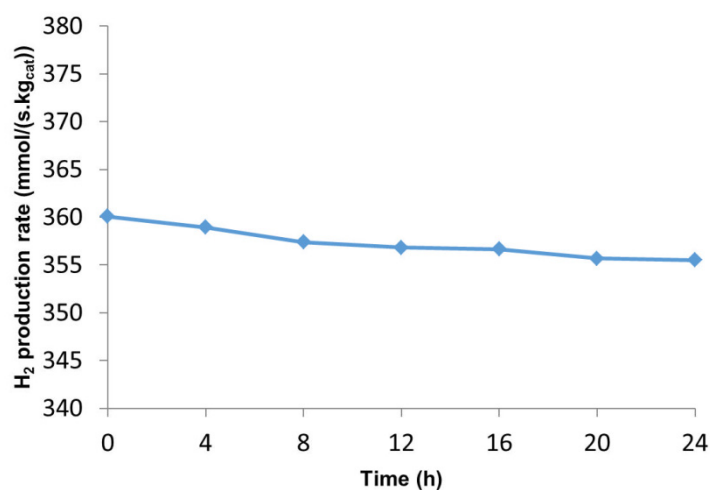


Figure S3. Stability test of Cu-Zn (N-S)/CeO₂-Al₂O₃ (N-N) at 300 °C for 24 h

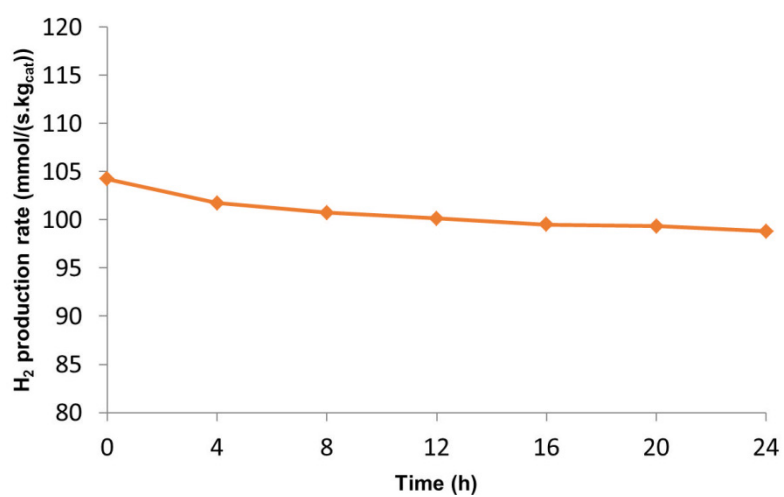


Figure S4. Stability test of Cu-Zn (no magnet)/CeO₂-Al₂O₃ (no magnet) at 300 °C for 24 h