Electronic Supplementary Information (ESI)

Modified extra-large mesoporous silica supported Au-Ni as a highly efficient catalyst for oxidative coupling of aldehydes with methanol

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Experimental

1. Catalyst preparation

Ordered, extra-large mesoporous FDU-12 was synthesized according to the reported method.[1-2] La-Mg composite oxides modified FDU-12 (LaMg-FDU-12) was prepared by the incipient wetness impregnation method with a required amount of $La(NO_3)_3$-$Mg(NO_3)_2$ mixed solution and FDU-12 powders. The resulting slurry was dried at 333 K for 12 h under vacuum and calcinated in air at 573 and 823 K for 3 h, respectively. The theoretical loadings of both La and Mg were 1 wt%.

AuNi/LaMg-FDU-12 catalyst was prepared by co-precipitation method.[3] A required amount of $Ni(NO_3)_2$ and $HAuCl_4$ mixed solution was heated to 363 K and the obtained LaMg-FDU-12 support was added. After stirring for 0.5 h, the mixture was filtered and washed with deionized water until no chloride ions could be detected. After drying under vacuum, the powder was calcined in air at 723 K for 6 h. The theoretical loadings of both Au and Ni were 1 wt%.

2. Characterization of prepared catalysts

Small-angel X-ray scattering (SAXS) patterns were acquired using an Anton Paar 'SAXSess' equipped with both CCD and image plate detection. X-ray diffraction (XRD) patterns were recorded on a Rigaku SmartLab diffractometer using Cu K_α radiation at 45 kV and 200 mA.

XPS spectra were obtained on an ESCALAB 250Xi electron spectrometer using 300 W Al K_α X-ray source and the binding energies were referenced with C 1s at 284.6 eV. TEM and HAADF-STEM images were taken on a FEI TECNAI F20 microscope operated at 200 kV. CO_2-TPD spectra were measured on AutochemII 2920. N_2-sorption experiments were carried out at 77 K on a Micromeritics ASAP 2020 adsorption analyzer.

3. Catalytic oxidative coupling of aldehydes with methanol

0.75 g AuNi/LaMg-FDU-12 catalyst, 0.04 mol MAL, 0.64 mol methanol and 0.05 g $Mg(OH)_2$ were added to a 100 mL autoclave sequentially. After filling the autoclave with 0.3 MPa of oxygen, the reaction was stirred at 90 ℃ for 2 h with the oxygen flow rate of 30 mL min^{-1}. After cooling to room temperature, 1 mL reaction mixture and 0.2 mL ethanol (the internal standard) were mixed together. The obtained sample was directly subjected to GC analysis. Conversion and yields were measured by GC-FID (Agilent 6890 equipped with DB-624 capillary column). Qualitative analysis of esters and byproducts was made by GC-MS and identified by comparison with authentic samples. Catalytic oxidative coupling of other aldehydes with methanol was carried out in a similar way. The reproducibility for each experiment was repeated for three times.

Table S1 Textural parameters of typical samples.

Sample	BET (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore size (nm)
FDU-12	621	0.68	18.1
LaMg-FDU-12	416	0.49	17.6
La-FDU-12	512	0.57	17.6
Mg-FDU-12	570	0.63	17.8
AuNi/LaMg-FDU-12	274	0.38	18.0
Au/LaMg-FDU-12	209	0.34	18.3
Ni/LaMg-FDU-12	253	0.40	14.9
AuNi/LaMg-SiO_2	273	0.61	7.14
AuNi/AlMg-FDU-12	292	0.43	17.8
AuNi/LaMg-FDU-12[a]	254	0.35	18.0

[a] The sample was used for six times.

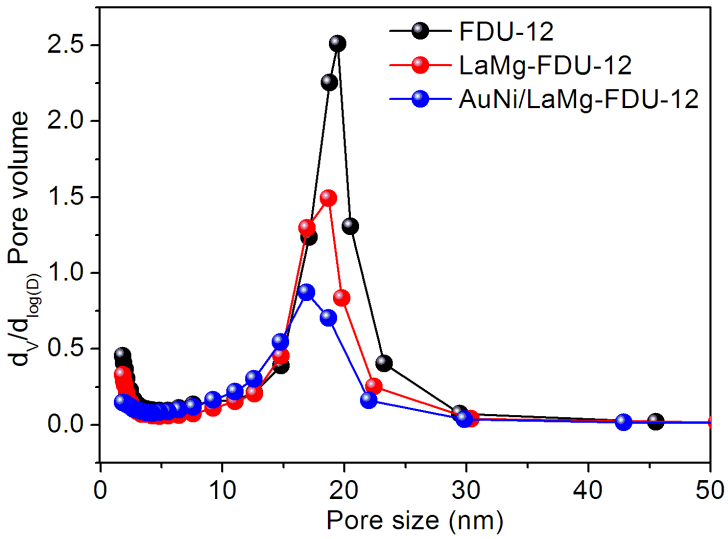

Fig. S1 BJH pore size distribution of FDU-12, LaMg-FDU-12 and AuNi/LaMg-FDU-12

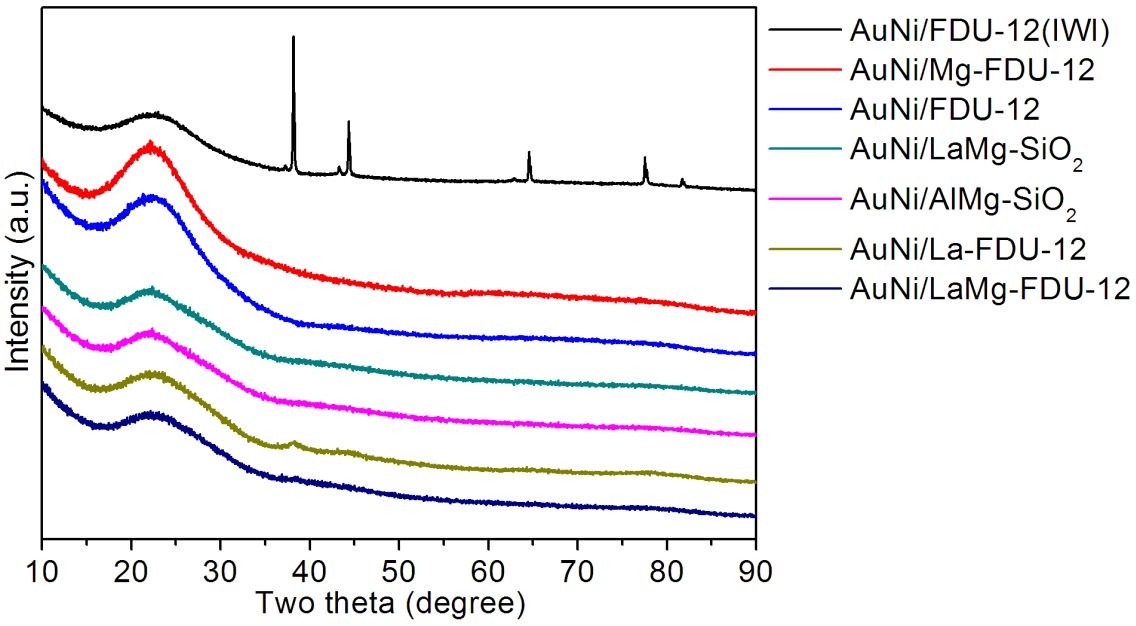

Fig. S2 XRD patterns of some typical catalysts.

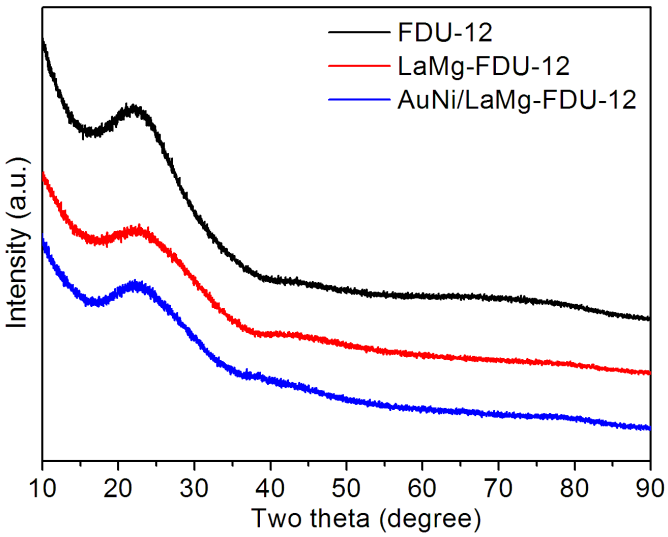

Fig. S3 XRD patterns of FDU-12, LaMg-FDU-12 and AuNi/LaMg-FDU-12.

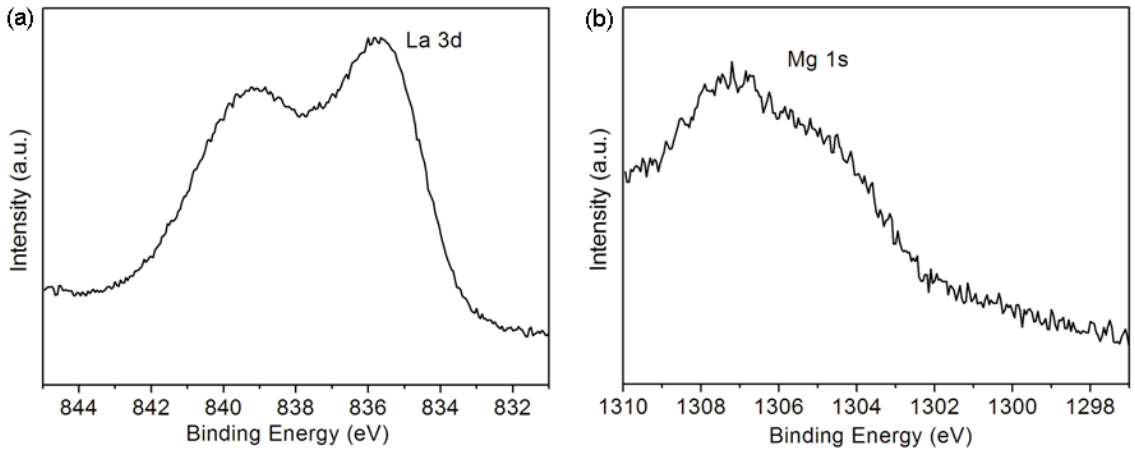

Fig. S4 XPS of La 3d (a) and Mg 1s (b) in AuNi/LaMg-FDU-12.

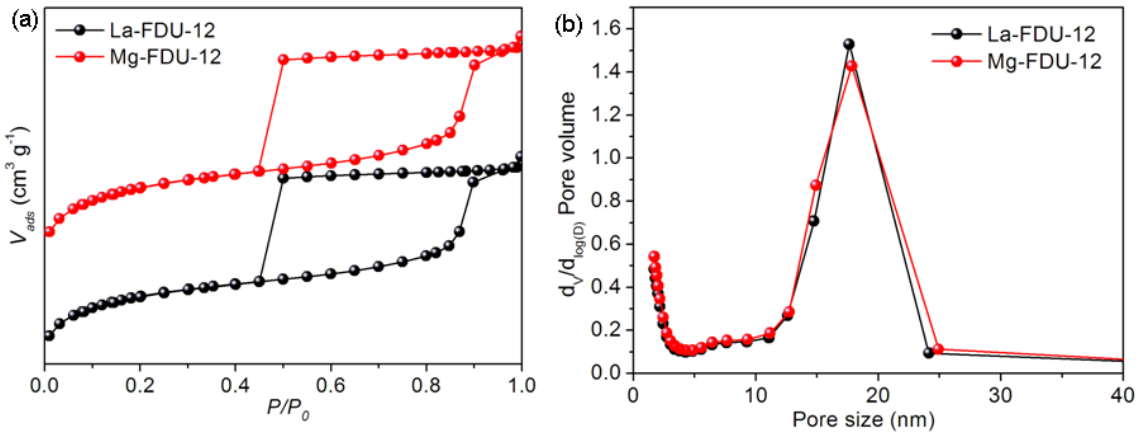

Fig. S5 N_2-sorption isomers (a) and BJH pore size distribution (b) of La-FDU-12 and Mg-FDU-12.

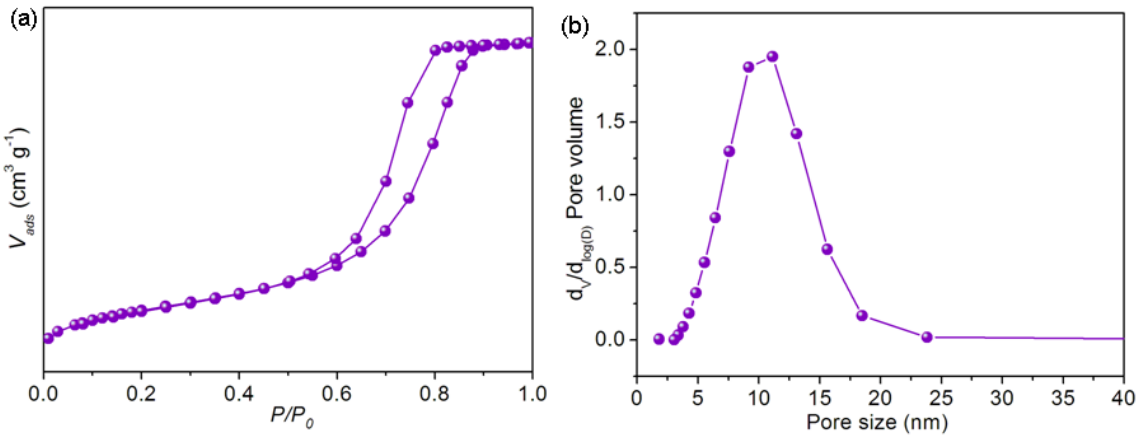

Fig. S6 N_2-sorption isomers (a) and BJH pore size distribution (b) of LaMg-SiO_2.

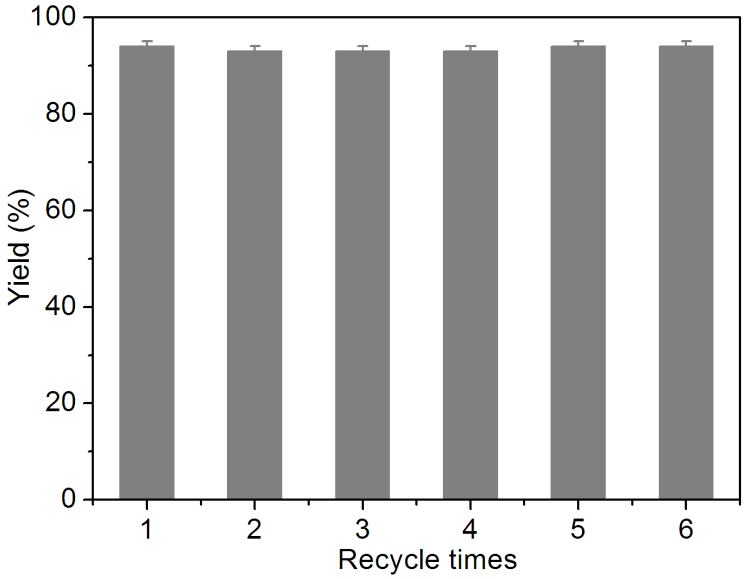

Fig. S7 Recycling tests of AuNi/LaMg-FDU-12 for the oxidative coupling of MAL with methanol.

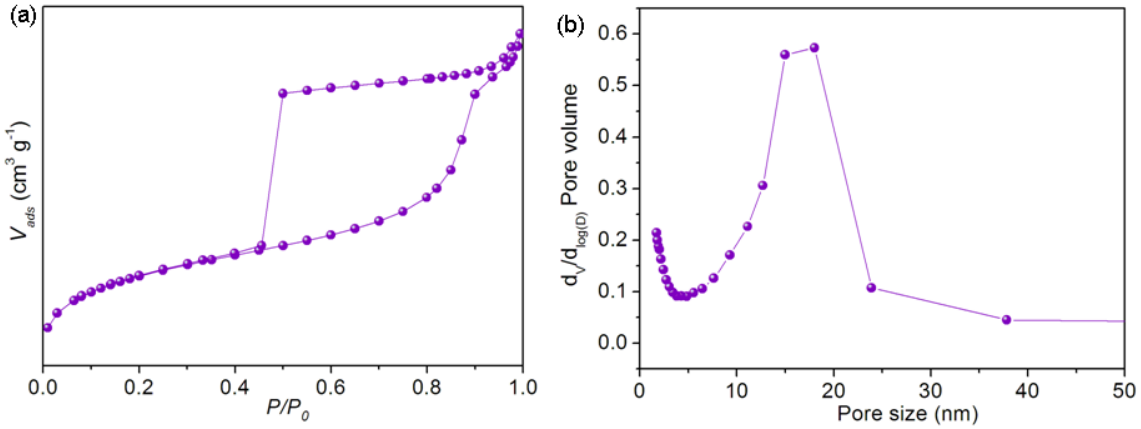

Fig. S8 N_2-sorption isomers (a) and BJH pore size distribution (b) of AuNi/LaMg-FDU-12 used for six times.

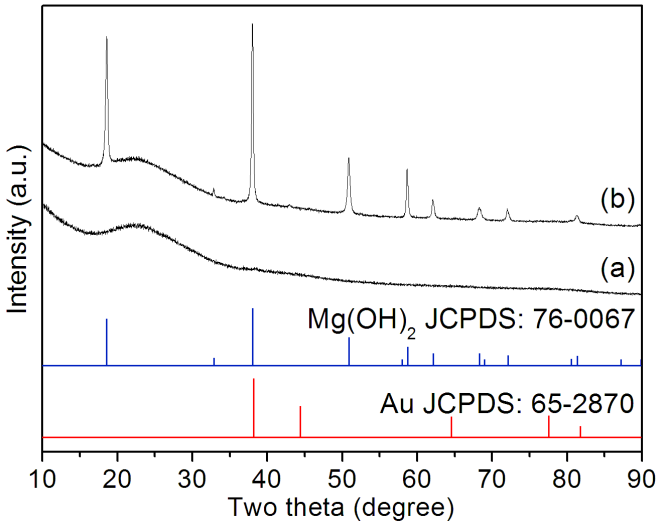

Fig. S9 XRD patterns of fresh AuNi/LaMg-FDU-12 (a) and AuNi/LaMg-FDU-12 used for six times (b).

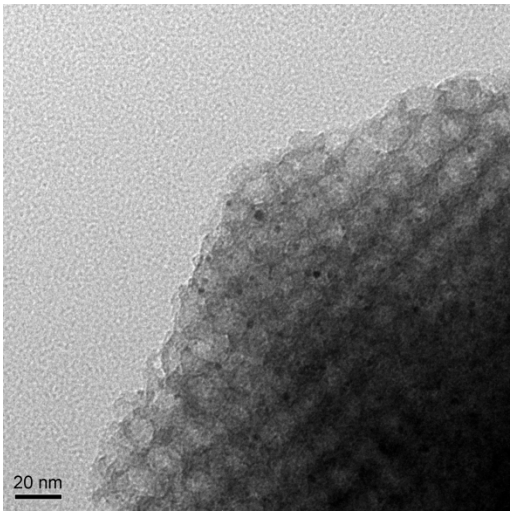

Fig. S10 TEM image of AuNi/LaMg-FDU-12 used for six times.

References

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3 K. Suzuki, T. Yamaguchi, K. Matsushita, C. Iitsuka, J. Miuya, T. Akaogi and H. Ishida, *ACS Catal.*, 2013, **3**, 1845-1849.