Supplementary information

Highly active and stable cobalt catalysts with tungsten carbide-activated carbon support for dry reforming methane: Effect of the different promoters

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Catalyst characterization

The crystal phases of catalyst were studied by XRD analysis using Ultima IV diffractometer equipped with Cu Kα radiation. The date was obtained in the range of 20-80 ° with 5 °/min. The crystal size was calculated according to Scheler equation (Eq. S1)

The loading of Co was quantitatively determined by inductively coupled plasma optical emission spectroscopy (ICP-OES Agilent 5110)

XPS analysis of the catalyst was performed using a Thermo Scientific K-Alpha X-ray photoelectronic spectrometer. Al Kα radiation（hv=1486.6 eV，pass energy=50 eV）was regard as the excitation source in an ultra-vacuum environment (8×l0-10 Pa). The spectral peaks of all samples were standardized with a C 1s peak at 284.8 eV.

H_2 temperature-programmed reduction (H_2-TPR), H_2 temperature-programmed desorption (H_2-TPD) were performed using a VDSorb-91x instrument equipped with a thermal conductivity detector (TCD). Before H_2-TPR experiment, 50 mg catalyst sample was pretreated in Ar atmosphere at 300 ℃ for 30 min. Then, the sample was cooled to 50 ℃. Then, the material was heated to 900 ℃ at a ramp rate 10 ℃/min under 10 vol.% H_2/Ar atmosphere. The H_2 emanative signal was tested online by TCD. The reduction degree of active metal Co is calculated by quantifying the consumption of H_2（Eq. S2）. Before H_2-TPD experiment, 50 mg catalyst sample was heated to 600 ℃ at a ramp rate 10 ℃/min under 5 vol.% H_2/Ar atmosphere（30 ml/min）, and maintain 60 min for prereduction. Then, the sample was cooled to 50 ℃. Subsequently, a 60 mL·min^{-1} H_2 chemisorption pulse was carried out at 10 vol.% H_2/Ar (30 mL·min^{-1}). Finally, the sample was heated to 900 ℃ at a ramp rate 10 ℃/min for H_2 desorption. The H_2 emanative signal was tested online by TCD. The dispersion, specific surface area and crystal size of active metal Co can be calculated by H_2 desorption. (Eq. S3-S5)

TG analysis of the catalyst was performed using a TGA 5500 instrument. 6 mg catalyst was placed in a ceramic crucible. Then, the sample was heated to 900 ℃ at a heating rate of 10 ℃/min in air atmosphere (100 ml/min), meanwhile, the quality variations of catalyst sample were recorded.

The particle size and morphology of catalyst was studied by TEM under a working voltage of 200Kv (Tecnai G2 F30, FEI). The test sample was first ground into fine powder then dispersed into an ethanol solution. The sample was ultrasound for 40 min. Then, adopting the drip tube, the solution was dropped onto the copper mesh.

Subsequently, the sample was dried naturally. Finally, the sample was analyzed.

Physical properties and structural characteristics of catalysts were analyzed by N_2 physical adsorption-desorption experiments using Beishide 3H-2000PS2 apparatus at liquid nitrogen temperature (-196 ℃). 0.1 g sample was degassed at 250 ℃ for 6 h under vacuum to remove water and impurities from the material surface. The specific surface areas were calculated using BET method based on N_2 adsorption curve. The full pore size distribution of the samples was obtained according to the Density Functional Theory (DFT) calculation method.

Infrared analysis of catalyst was performed using Thermo Fisher Is 5 infrared spectrometer. The scanning range was 4000-400 cm^{-1}, the resolution was 4 cm^{-1}, and the number of scanning samples was 32 times.

Calculation equations

$$d = \frac{k\lambda}{\beta cos\theta} \quad \text{Eq. S1}$$

Where d is crystal size, k is shape factor (Spherical or spheroid, k=0.9), λ is the X-ray wavelength (λCu Kα= 0.15418 nm), β is the FWHM of the strongest diffraction peak, and θ is the corresponding diffraction angle.

$$R_{Co}(\%) = \frac{2 \times H_{2,consumption} \times 10^{-6} \times M_{Co}}{m_{Co}} \times 100 \quad \text{Eq. S2}$$

$$D_{Co}(\%) = \frac{2 \times H_{2Uptake} \times 10^{-6} \times M_{Co} \times \delta}{m_{Co}} \times 100 \quad \text{Eq. S3}$$

$$S_{Co}(m^2 \cdot g^{-1}) = \frac{2 \times H_{2uptake} \times 10^{-6} \times N_{AV}}{\sigma_{Co}} \times 100 \quad \text{Eq. S4}$$

$$d_{Co}(nm) = \frac{96}{D_{Co}} \quad \text{Eq. S5}$$

Where, H_2uptake is quantitatively measured by H_2-TPR (μmol·g^{-1}). δ is the stoichiometric factor of the Co/H molar ratio in chemical adsorption (1). N_{AV} is the Avogadro constant (6.02 ×10^{23} mol^{-1}). σ_{Co} is the average number of surface Co atoms (1.51 ×10^9 at·m^2).

Fig.S1

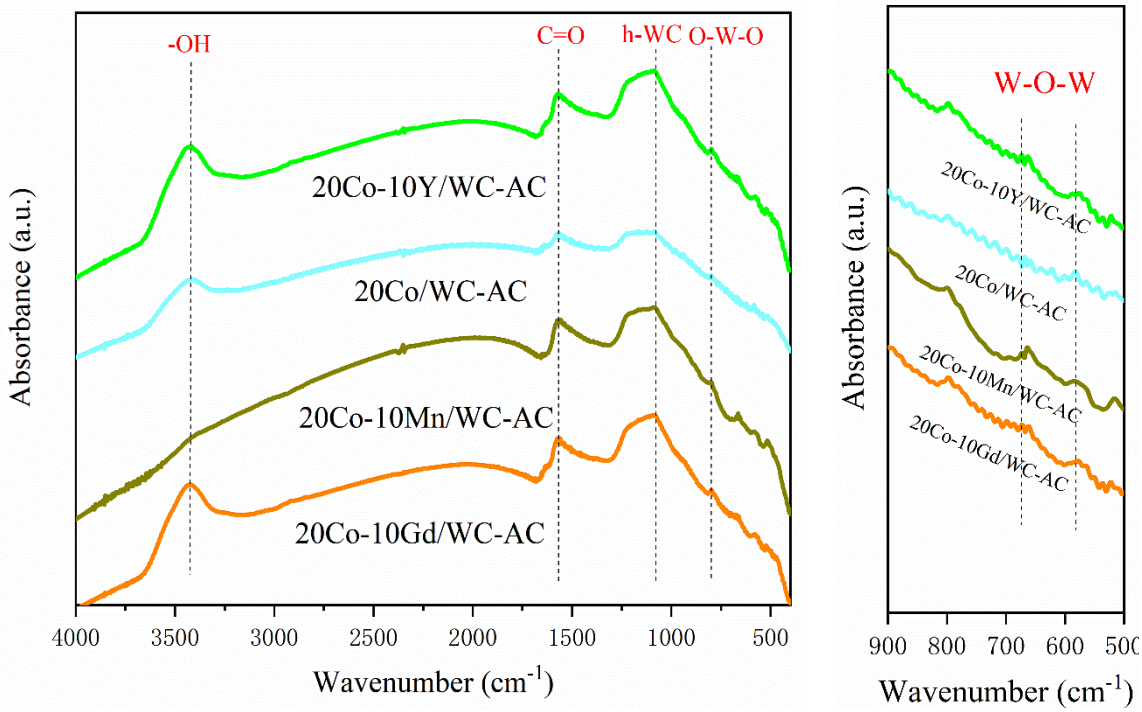

Fig. S1 FT-IR patterns of catalysts with different promoters

Fig.S2

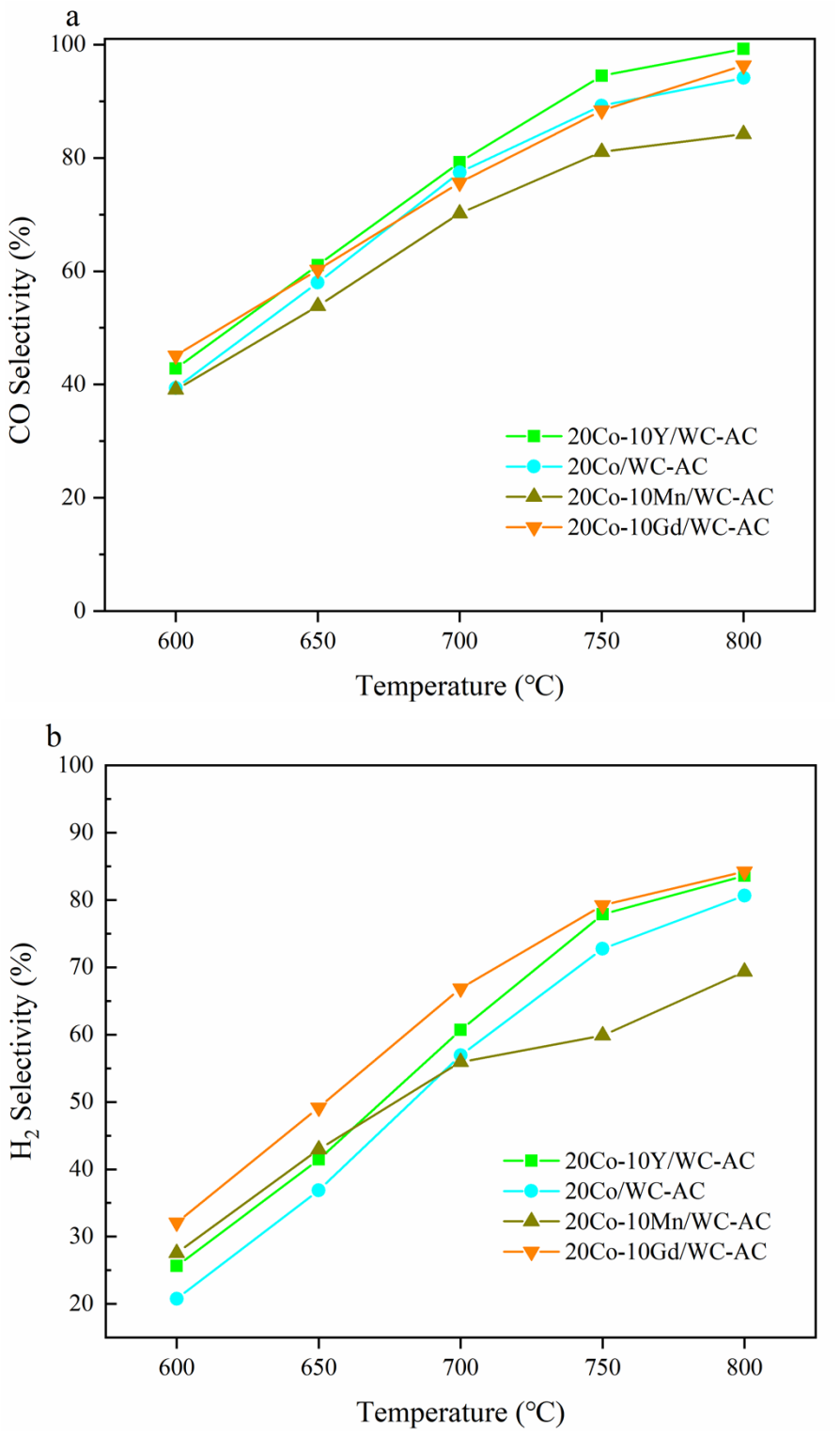

Fig.S2 The activity test of catalysts with different promoters (a) CO selectivity (b) H_2 selectivity

Fig.S3

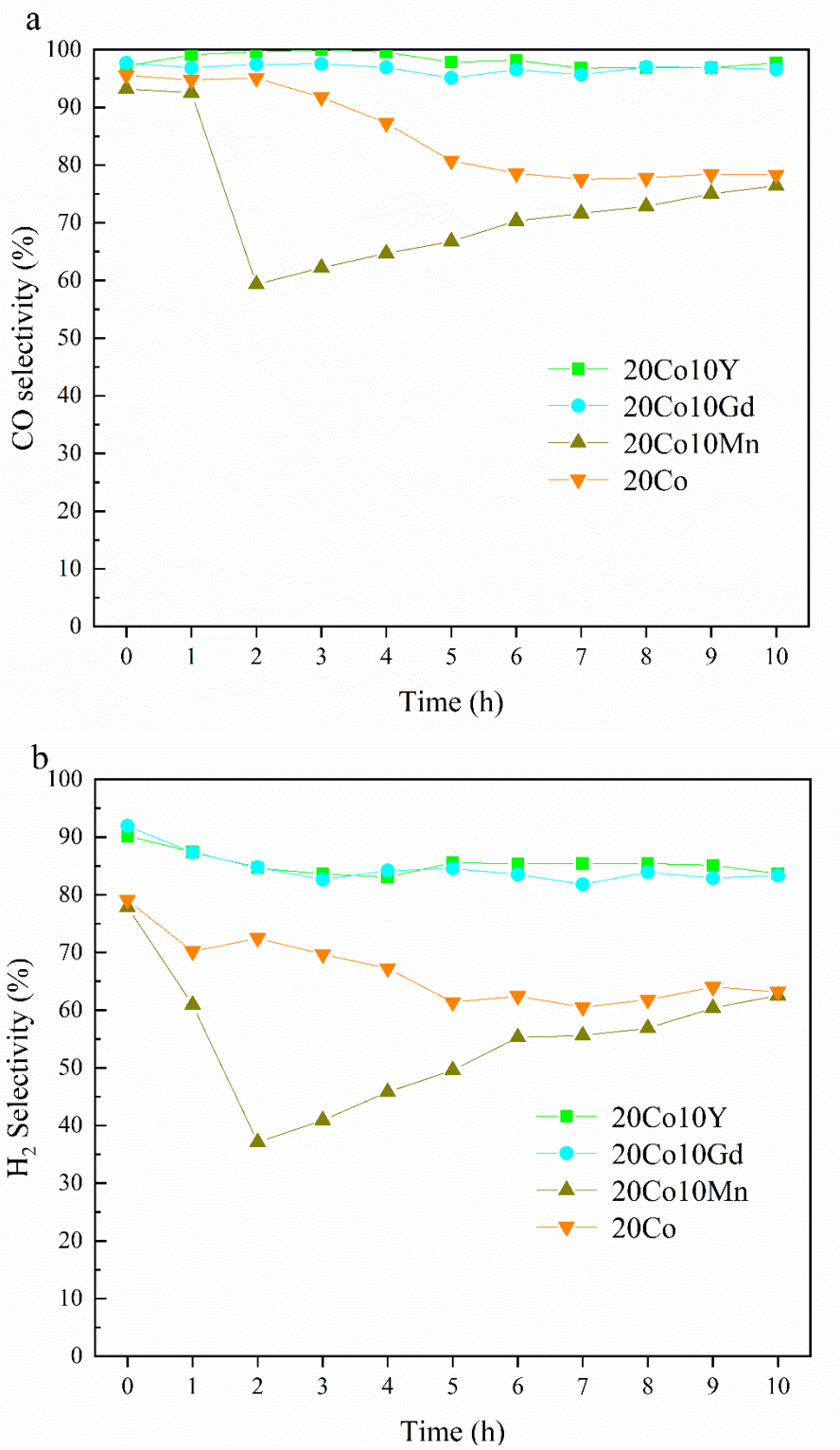

Fig.S3 The stability test of catalyst modified different promoter (a) CO selectivity (b) H_2 selectivity

Fig.S4

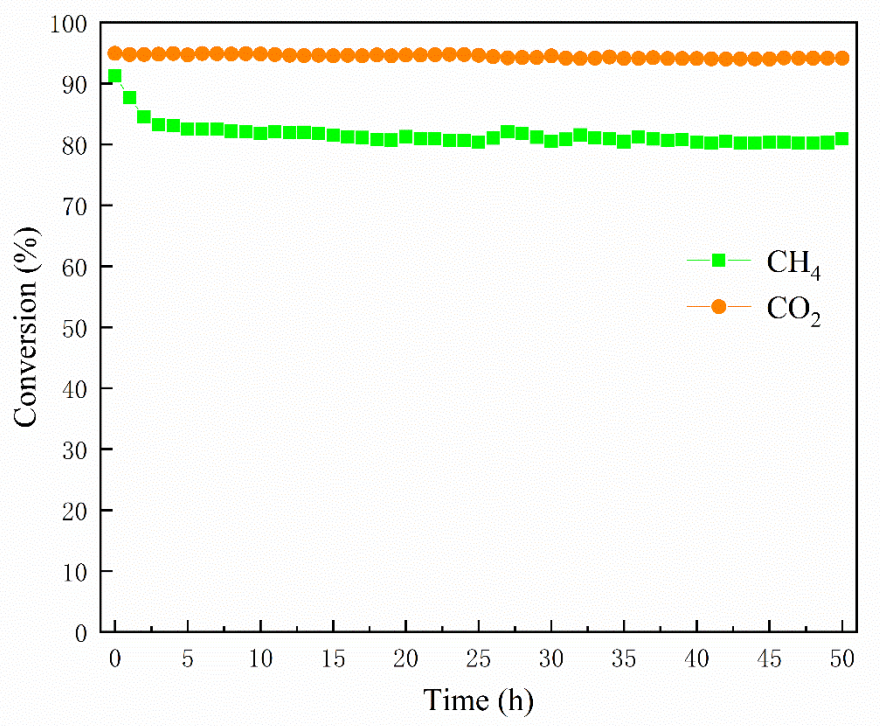

Fig.S4 The long stability test of Y-modification catalyst

Fig.S5

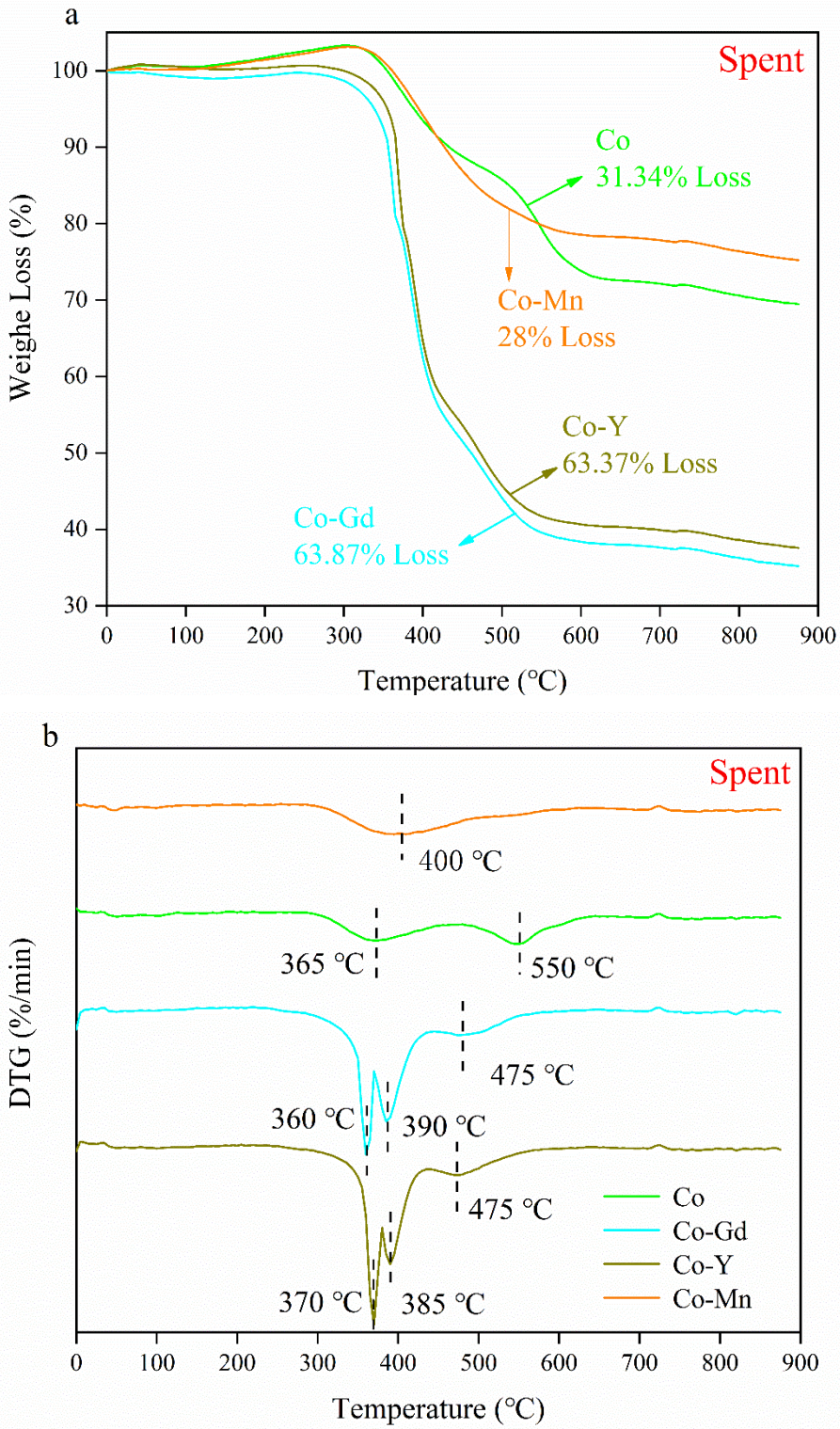

Fig.S5 (a) TG and (b) DTG profiles of spent catalyst modified different promoter

Fig.S6

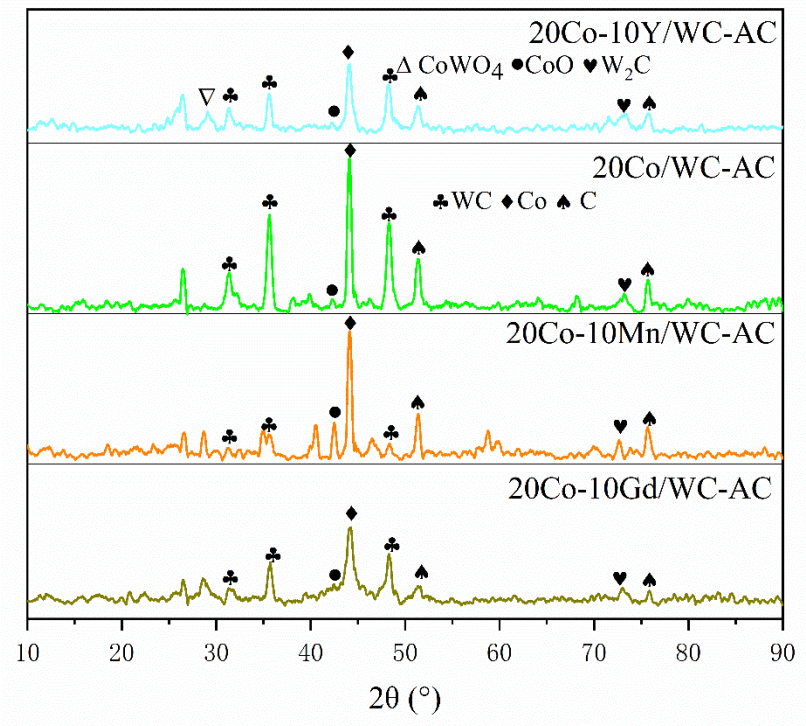

Fig.S6 XRD pattern of spent catalysts modified different promoters

Table S1

Table S1 Crystal size of Co of the fresh and the spend catalyst with different promoter

catalyst	Co Crystal size（nm）	
	fresh	spent
20Co-10Y/WC-AC	27	30
20Co/WC-AC	47	71
20Co-10Mn/WC-AC	54	80
20Co-10Gd/WC-AC	30	45