

Electronic Supplementary Information (ESI)

Synthesis of highly dispersed cobalt catalyst for hydroformylation of 1-hexene

Bin Wang, Jian-Feng Chen and Yi Zhang*

State Key Laboratory of Organic-Inorganic Composites, Research Centre of the Ministry of Education for High Gravity Engineering and Technology, Beijing University of Chemical Technology, Beijing 100029, China.

* Authors to whom correspondence should be addressed:

Prof. Yi Zhang (Y. Zhang)

E-mail: yizhang@mail.buct.edu.cn;

Fax: +86 10 64423474;

Tel: +86 10 64447274

Contents

Item	Page
Experimental details	3
Table S1	8
Fig. S1	9

Experimental details

Typically, various Co/SiO₂ catalysts were prepared by the incipient wetness impregnation of aqueous cobalt nitrate onto SiO₂ support (pore volume: 1.061 mL/g, pore diameter: 6.7 nm, specific surface area: 451 m²·g⁻¹). The silica supports were pretreated with EG at room temperature for 1 h by incipient wetness impregnation method. And then, the samples were dried in air at 393 K for 12 h. A 10 wt% Co/SiO₂ catalyst was prepared as the following steps: a certain amount of Co(NO₃)₃·6H₂O was dissolved in water and then the cobalt nitrate aqueous solution was impregnated on the support. The obtained samples were dried in air at 393 K for 12 h and calcined at 673 K for 2 h with a heating rate of 2 K·min⁻¹. The noble metal Ru promoted Co/SiO₂ catalysts were prepared by co-impregnation of cobalt nitrate and ruthenium chloride aqueous solution on SiO₂ support while other preparing procedures were constant. The loading of Ru promoter was 1wt%. Before hydroformylation reaction, the catalysts were reduced by hydrogen at 673 K for 10 h and passivated by 1% oxygen diluted with nitrogen at room temperature. The prepared catalysts were denoted as Co/SiO₂, Co/SiO₂ (EG), Co-Ru/SiO₂ and Co-Ru/SiO₂ (EG), where EG indicated that the silicate supports were pretreated by EG.

X-ray diffraction (XRD) patterns of the passivated catalysts were recorded on D/max2500VB2+/PC X-ray diffractometer using graphite monochromatized Cu K α radiation ($\lambda = 0.15406$ nm). The samples were scanned in the 2θ range of 20-80° with a speed of 2 °/min.

The morphologies of the passivated catalysts were observed by transmission electron microscope (TEM, JEOL 2100F). The specimen was prepared by

ultrasonically suspending the catalyst powder in ethanol. A drop of the suspension was deposited on a carbon-enhanced copper grid and dried in air. The average size of the dispersed Co particles were determined by measuring the diameter of more than 100 cobalt particles. More than 100 metallic Co particles were randomly selected in TEM images and measured the diameter of them. The average particle size of metallic Co can be obtained from the following formula:

$$d = \frac{\sum_{i=1}^n d_i}{n}$$

Where d is the average particle size of metallic Co; d_i is the size of individual Co particle; n is the number of Co particles.

Temperature programmed reduction (TPR) experiments were carried out in a quartz U-tube reactor connected to a thermal conductivity detector (TCD), using 0.1 g unreduced catalysts. The gas stream, 10% H₂ diluted by Ar as reducing gas, was fed via a mass flow controller at 30 mL/min and the temperature was increased from 323 K to 1073 K at a rate of 8 K/min. The effluent of reactor passed through a 5A molecular sieve trap to remove produced water before reaching TCD. TPR of CuO in the same conditions was carried out and used to calibrate the TCD for quantitative evaluation of H₂ consumption. It is assumed that all noble metal atoms and CuO were completely reduced at the TPR conditions. And then, the H₂ consumption corresponding to reduction of cobalt oxide can be separated from TPR and the reduction degree of catalyst can be calculated according to the conversion of metallic Co₃O₄ to Co.

Oxygen titration was carried out on chemical adsorption instrument (Quantachrome, ChemBET) and used to characterize the reducibility of obtained catalysts. The

reduction degree of prepared catalysts was determined by oxygen titration at 673 K using pure O₂ pulse method. The passivated catalysts of about 0.1 g were re-reduced by hydrogen at 673 K for 1 h, and then the whole system was purged by helium stream of 20 mL/min for 1 h in order to remove physical and chemical adsorbed hydrogen on the catalyst surface. The oxygen pulses were introduced into the reactor by a six-pot valve to re-oxidize the catalysts at 673 K. The reduction degree was calculated by assuming stoichiometric conversion of metallic Co to Co₃O₄, from the consumed oxygen.

H₂ chemisorption experiments for passivated catalysts were performed in a static mode at 373 K using a conventional volumetric apparatus (FINESORB-3010, FINETEC). Research grade gases (H₂: 99.9995%) were used without further purification. Typically, 0.1 g of catalyst was used. Before adsorption of H₂, the catalysts, which were previously reduced by H₂ and passivated, were treated in H₂ at 673 K for 1 h, followed by evacuation. H₂ adsorption isotherms were measured at 373 K.

X-ray photoelectron spectrum (XPS) of the calcined catalyst was performed on VG Scientific ESCALAB 250 spectrometer to investigate the chemical state of surface cobalt species. The spectra were excited by the monochromatized Al K α source (1486.6 eV).

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded with a Vertex 70V spectrometer (Bruker) equipped with a liquid nitrogen-cooled MCT detector (resolution 2 cm⁻¹), using an in situ cell with CaF₂ windows. About 15 mg of

the sample, which was previously reduced by H₂ and passivated, was loaded into the cell. Prior to CO adsorption, the sample was in situ treated with a H₂ (30 mL/min) gas flow at 673 K for 1 h, followed by purging with a N₂ (30 mL/min) gas flow at the same temperature for 0.5 h, and then was cooled to 303 K. CO (30 mL/min) was introduced into the cell at room temperature for 0.5 h. After the catalysts were purged by a N₂ (30 mL/min) gas flow for 0.5 h to remove the physical adsorption CO, the spectra of adsorbed CO were collected. The results given herein are difference spectra between the spectra before and after CO adsorption.

The BET surface areas of the passivated and spent catalysts were obtained via nitrogen physisorption at 77 K using a Micrometrics ASAP 2010 analyzer. All the catalysts were degassed at 473 K for 6 h prior to measurement.

Hydroformylation of 1-hexene was carried out in a mechanical stirring reactor with inner volume of 85 mL. The detailed procedure was conducted as follows. 13.5 mmol of 1-hexene was mixed with 20 mL of toluene in the autoclave and then 0.1 g of the obtained catalyst was loaded into reactor. The autoclave was then firmly sealed and purged with feed gas to replace the air inside it by means of pressuring-depressurizing. Firstly the autoclave was pressured to 3 MPa with syngas (H₂/CO=1) at room temperature, and then the gas was slowly vented. This step was repeated for 3 times to ensure that there was no oxygen in the autoclave. After that, the syngas was injected to 5 MPa and the autoclave was heated to 403 K. The reaction was started and lasted for 1 h; meanwhile the autoclave was mechanically stirred at 1600 rpm.

At the end of the reaction, the reactor was cooled in ice bath to lower than 283 K

rapidly and the pressure was released. The liquid product was separated from the solid catalyst by natural sedimentation. The resulting mixture was analyzed quantitatively by a gas chromatograph (GC, Beifen) equipped with a KB-1 capillary column (0.32 mm \times 0.25 μ m \times 30 m) and a flame ionization detector (FID).

The 1-hexene conversion (C, %), heptanal selectivity (S, %) and ratio of normal heptanal and isomeric heptanal (n/iso) were defined as:

$$Con. = \frac{n_1 - n_2}{n_1} \times 100\%$$

$$Sel. = \frac{n_a}{n_1 - n_2} \times 100\%$$

$$n / iso = \frac{n_{normal}}{n_{isomer}}$$

Where n_1 is the mole number of 1-hexene into the reactor (mol); n_2 is the mole number of unreacted 1-hexene after reaction (mol); n_{normal} and n_{iso} are the mole number of normal heptanal (n-heptanal) and isomeric heptanal (iso-heptanal) produced during reaction (mol), respectively.

The used catalysts were washed by toluene for several times and then used for 1-hexene hydroformylation under the same reaction conditions to test stability of catalyst.

Table S1 BET surface areas of the various catalysts

Catalyst	Surface area (m ² /g)	
	Passivated	Spent ^a
Co/SiO ₂	316.2	314.2
Co/SiO ₂ (EG)	331.5	327.9
Co-Ru/SiO ₂	315.7	311.8
Co-Ru/SiO ₂ (EG)	329.6	330.7

^a After one reaction entry.

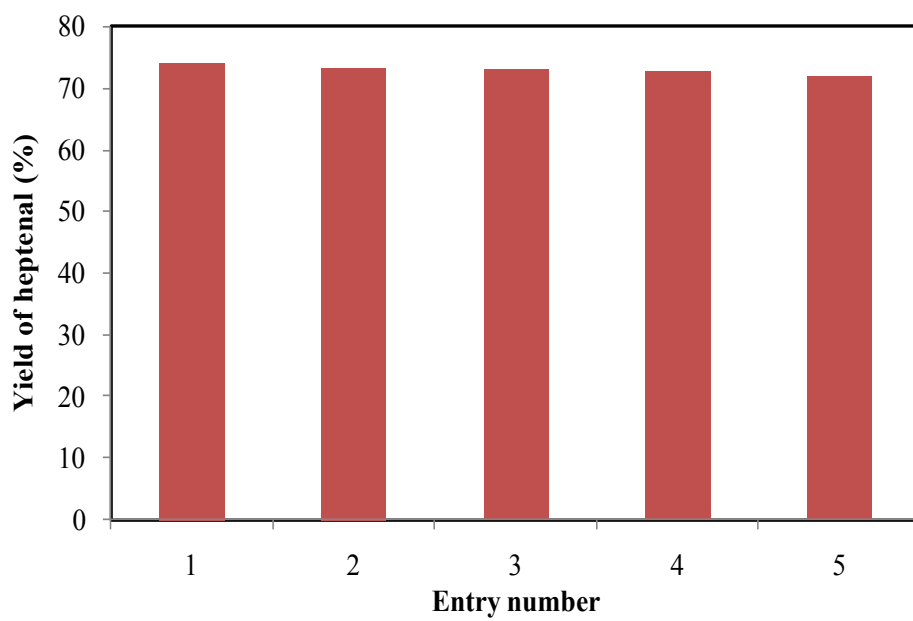


Fig. S1 The heptanal yield of Co-Ru/SiO₂ (EG) catalyst with different reaction entry.