Electronic Supplementary Material

On the monolayer dispersion behavior of Co_3O_4 on HZSM-5 support: designing applicable catalysts for selective catalytic reduction of nitrogen oxides by ammonia

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Supporting information:

1.Supplementary Experimental Information

1.1 Catalyst characterization

Powder X-ray diffraction (XRD) measurements of the prepared catalysts were recorded on Bruker AXSD8 Focus diffractometer instrument operating at 40 kV and 30 mA, with a Cu target and Kα-ray irradiation (λ= 1.54056 Å). Scans were taken from 5 to 70 ^{o} and with a step of 2 ^{o} min^{-1}. In order to maintain good comparability of the data, all the samples were tested continuously.

XPS tests were carried out on a Perkin-Elmer PHI1600 system using a single Mg-Kα-X-ray source operating at 300 W and 15 kV of voltage. The spectra were obtained at ambient temperature with an ultrahigh vacuum. The binding energies were calibrated using the C 1s peak of graphite at 284.8 eV as a reference.

Solid-state 1H MAS (Magic Angle Spinning), 27Al MAS and 29Si {1H} MAS NMR experiments were performed on a Bruker Avance III HD 400WB (9.4 T) spectrometer, operating at 400.2 MHz for 1H, 104.3 MHz for 27Al and 79.5 MHz for 29Si, at spinning speed (SS) of 10-20 kHz on a 3.2 mm CPMAS probe. 1H MAS NMR spectra were acquired under dry air with a 1H π/2 pulse of 3.0 μs, and recycle times of 0.1-5 s. 27Al MAS NMR spectra were acquired under dry air with a 1H π/6 pulse of 1.4 μs, and recycle times of 1-5 s. 29Si {1H} MAS NMR were acquired under dry air with a 1H π/2 pulse of 3.84 μs, and a recycle time of 2 s. High-power 1H decoupling was carried out using SPINAL64 with a typical field strength of 65 kHz. The 1H, 27Al and 29Si chemical shifts were referenced externally to adamantane CH at 38.48 ppm, 1 L Al (NO3)3 solution at 0 ppm and 3-(Trimthylsilyl)-1-propane sulfonic acid sodium salt at 0 ppm.

Chemical compositions of catalysts were ascertained *via* inductively coupled plasma optical emission spectrometry (ICP-OES) on the Agilent Technologies 5100 ICP-OES.

N2 adsorption-desorption measurements was used to examine the pore structure of the prepared samples. The measurements were carried out at 77 K on Micromeritics ASAP 2020 instrument. Before testing, all samples were pre-treated in vacuum at 200 °C for 6 hours. The Specific surface areas was calculated using the Brunauer-Emmett-Teller (BET) method in the relative pressure (p/p_0) range of 0.4~1.0. Mesopore size was calculated via the Barrett-Joyner-Halenda (BJH) method, while microporous volumes of the samples were calculated by the Horvath-Kawazoe method.

Hydrogen temperature programed reduction (H_2-TPR) experiments were carried out on the FINESORB-3010C-243 automatic temperature programmed chemical adsorption instrument. The catalyst amount used in the tests was 100 mg. First, the catalyst was pretreated in a 99.99% Ar flow of 30 mL min^{-1} at 120 °C for 60 min to remove any possible surface impurities and then cooled down to ambient temperature. Afterwards, the feed gas was switched to a 10% H_2/Ar mixture with a flow rate of 30 mL min^{-1} until the baseline was stabilized. The temperature was then increased from ambient temperature to 800 °C with a heating rate of 10 °C min^{-1}. A thermal conductivity detector (TCD) was employed to monitor the H_2 consumption, which was quantified by using a CuO (99.99%) calibration standard.

EPR technique was used to measure the surface oxygen property of Co_3O_4/ZSM-5 catalysts. 10 mg catalyst powder was dispersed in 5 mL of DDI water, and after ultrasonic vibration, 200 μL of mixed solution was taken out and 100 μL of dmpo solution with a concentration of 100 mM were added. Afterwards, the samples were put into a capillary tube, and transferred into liquid N_2 at 243 K and the

EPR spectra were recorded at 243 K with Bruker A300 EPR Spectrometer, operating with a field modulation of 100 kHz and microwave frequencies of 9067.558 MHz.

O_2-TPD was measured on Micromeritics Auto Chem 2920 chemical adsorption instrument with a TCD. Generally, 50 mg sample was placed in a quartz reactor, and pretreated at 550 ℃ for 1 hour in an ultra-high purity He flow of 30 mL min^{-1}. Afterwards, the sample was cooled down to 50 ℃ and saturated with a 10% O_2/He flow of 30 mL min^{-1} for 1 hour. Following this step, the sample was purged again in a 99.99% He gas stream of 30 mL min^{-1} for 30 min to remove any physically adsorbed O_2. Then, a test was performed from 100 °C to 800 °C with a heating rate of 10 °C min^{-1}.

NH_3-TPD and NO-TPD were carried out to determine the amount of surface acid sites and NO adsorption sites on Co_3O_4/ZSM-5 catalysts, which were measured on DAS-7000 chemical adsorption instrument with a TCD. Typically, 50 mg sample was placed in a quartz reactor and saturated with NH_3 or NO at room temperature. Afterwards, the sample was purged with a 30 mL min^{-1} 99.99% He flow for 60 min to remove any physically adsorbed molecules. TPD was then carried out from 50 ºC to 800 ºC with a heating rate of 10 ºC min^{-1} in a 30 mL min^{-1} He flow.

Pyridine-Infrared Radiation (Py-IR) was used to determine the types of acid on the catalyst surface. In this paper, Py-IR is performed on TENSOR 27 infrared spectrometer manufactured by Bruker, Germany. The catalyst samples were compressed into self-hold tablets and placed in the pyridine *in-situ* cell. After vacuum pretreatment for 60 min at 500 ºC, pyridine was adsorbed to saturation at ambient temperature. Afterwards, the in-situ cell was vacuumed again to get rid of the physically adsorbed pyridine. The pyridine infrared absorption spectra of the samples were measured at 50, 200 and 350 ºC, respectively. The scanning range is 4000 ~ 400 cm^{-1}, with the resolution of 4 cm^{-1}.

In situ diffuse reflectance infrared Fourier transform spectra (*In situ* DRIFTS) were conducted on a Bruker Vertex instrument (TENSOR II) equipped with an MCT detector chilled in liquid nitrogen. A micro-size in-situ FTIR furnace equipped with ZnSe windows was used. Prior to the experiments, the sample was pretreated at 400 °C for 1 h with an Ar flow, then cooled to 50 °C. *In situ* DRIFTS spectra were recorded from 4000 to 1000 cm^{-1} with a resolution of 2 cm^{-1}. OPUS 7.5 software was used to process data. For each experiment, the background spectra were collected before the sample was exposed to the adsorbates. Subsequently, the reaction gas was introduced into the *In situ* reactor, with the experiments carried out at desired temperatures.

1.2 Activity evaluation

The reaction performance of NO_x-SCR by NH_3 over the catalysts was tested in a fixed-bed horizontal straight quartz reactor containing 50 mg catalyst. The reaction feed consists of 5% O_2, 500 ppm NO, 500 ppm NH_3 with an Ar balance gas. The total flow rate is 50 mL min^{-1}, which is equivalent to a WHSV of 60,000 mL h^{-1} g_{cat}^{-1}. A thermocouple with its head point contacting the catalyst bed was used to control the reaction temperature. The kinetic data were obtained by raising the reaction temperature with a 50 °C gap. An online SHP8400 PMS gas mass spectrometry was used to analyze the products. In order to obtain steady-state kinetic data, the reaction was stabilized at a certain temperature for 30 min before the measurement.

NH_3 oxidation was performed with a feed consists of 5% O_2, 500 ppm NH_3 and balanced by Ar, and NO oxidation was performed with a feed consists of 5% O_2, 500 ppm NO and balanced by Ar. Generally, 50 mg catalyst was loaded into a fixed-bed horizontal straight quartz reactor, and the thermocouple touched the catalyst bed to accurately control the reaction temperature. The total flow rate is 25 mL min^{-1},

which is equivalent to a WHSV of 30,000 mL h^{-1} g_{cat}^{-1}. The products were also analyzed by an online SHP8400 PMS gas mass spectrometry. The test was conducted every 50℃ at a heating rate of 5℃ min^{-1}. Prior to each test, it was stabilized at a determined temperature for 30 minutes to obtain steady state kinetic data.

The conversion rate of NO_x and NH_3 was calculated by the following equation：

$$NO_x\text{Conversion} = \frac{[NO_x]_{in} - [NO_x]_{out}}{[NO_x]_{in}} \times 100\%$$

$$NH_3\text{Conversion} = \frac{[NH_3]_{in} - [NH_3]_{out}}{[NH_3]_{in}} \times 100\%$$

Where $[NO_x]_{in}$ and $[NO_x]_{out}$ represent the NO_x concentration (including NO and NO_2) in the inlet or outlet gas feed. The concentration of N_2 and N_2O in the outlet stream were determined by a mass spectrometry.

2 Supplementary Results

2.1 Supplementary Figures

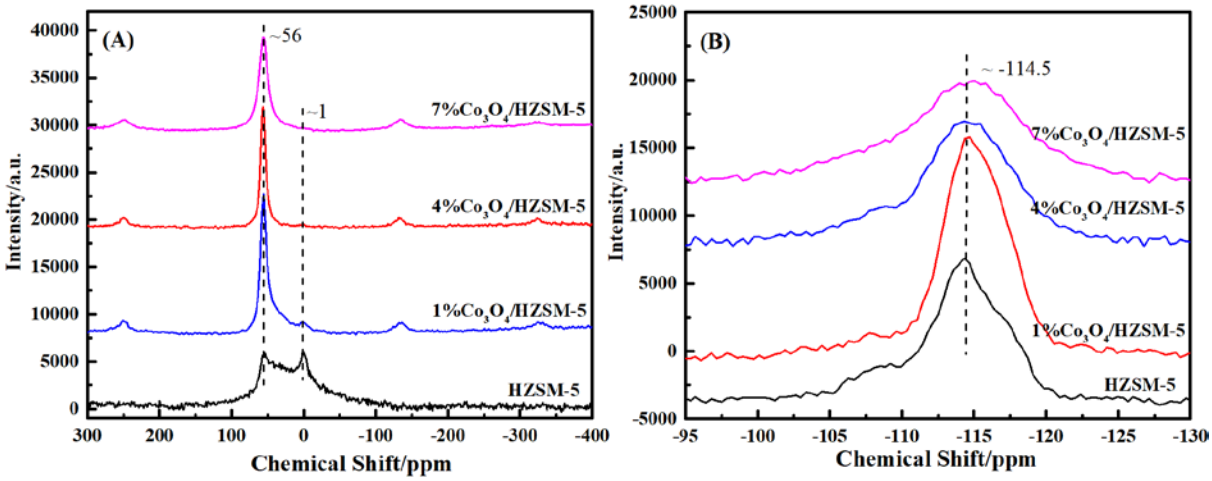

Fig. S1. Solid-state NMR investigation of the catalysts. (A) ^{27}Al MAS NMR spectra and (B) ^{29}Si MAS NMR spectra.

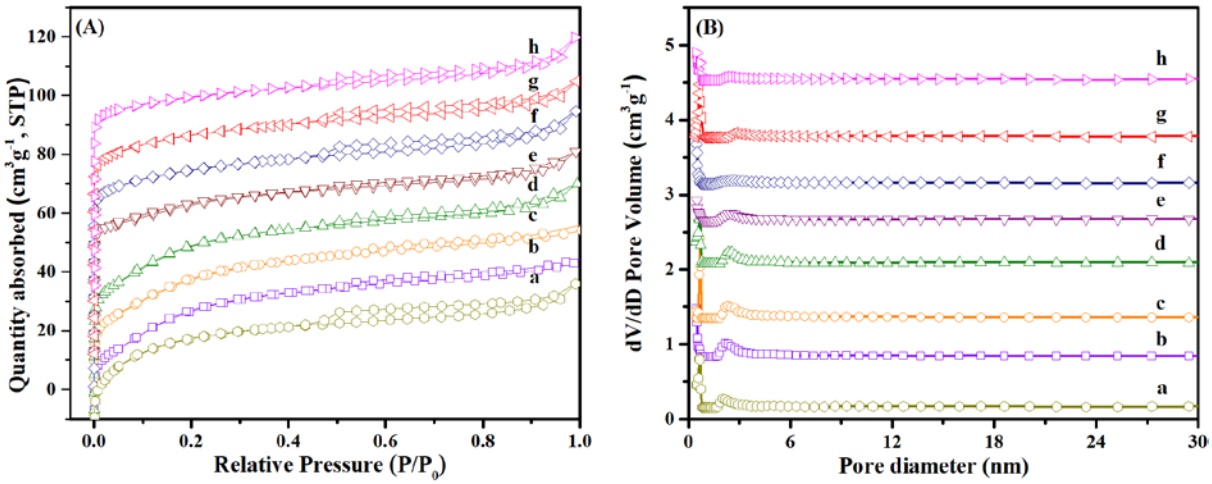

Fig. S2 N_2 adsorption-desorption profiles of the Co_3O_4/ZSM-5 catalysts. (A) Isotherms; (B) Pore size distribution profiles.

a. ZSM-5, b. 1% Co_3O_4/ZSM-5, c. 2% Co_3O_4/ZSM-5, d. 3% Co_3O_4/ZSM-5, e. 4% Co_3O_4/ZSM-5, f. 5% Co_3O_4/ZSM-5, g. 6% Co_3O_4/ZSM-5, h. 7% Co_3O_4/ZSM-5

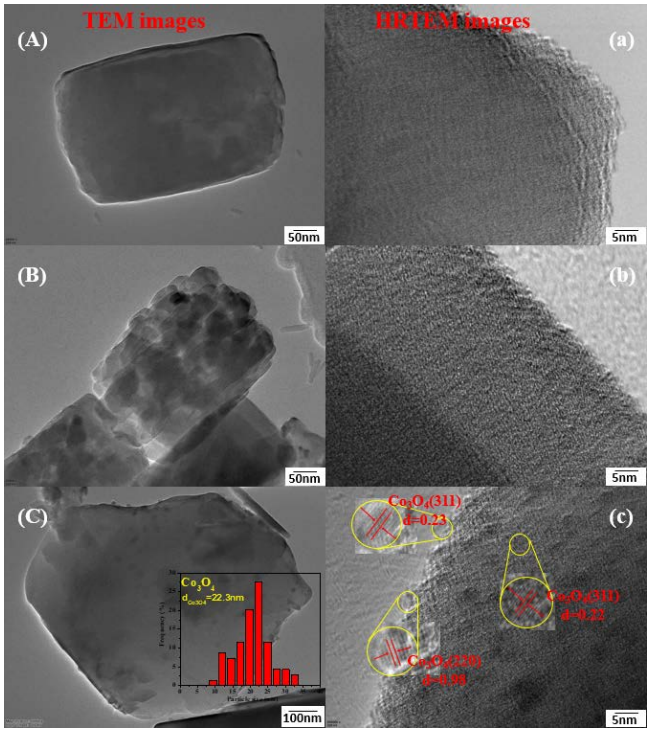

Fig. S3 TEM and HRTEM images of the catalysts. (A) and (a) 1% Co_3O_4/ZSM-5, (B) and (b) 4% Co_3O_4/ZSM-5, (C) and (c) 7% Co_3O_4/ZSM-5.

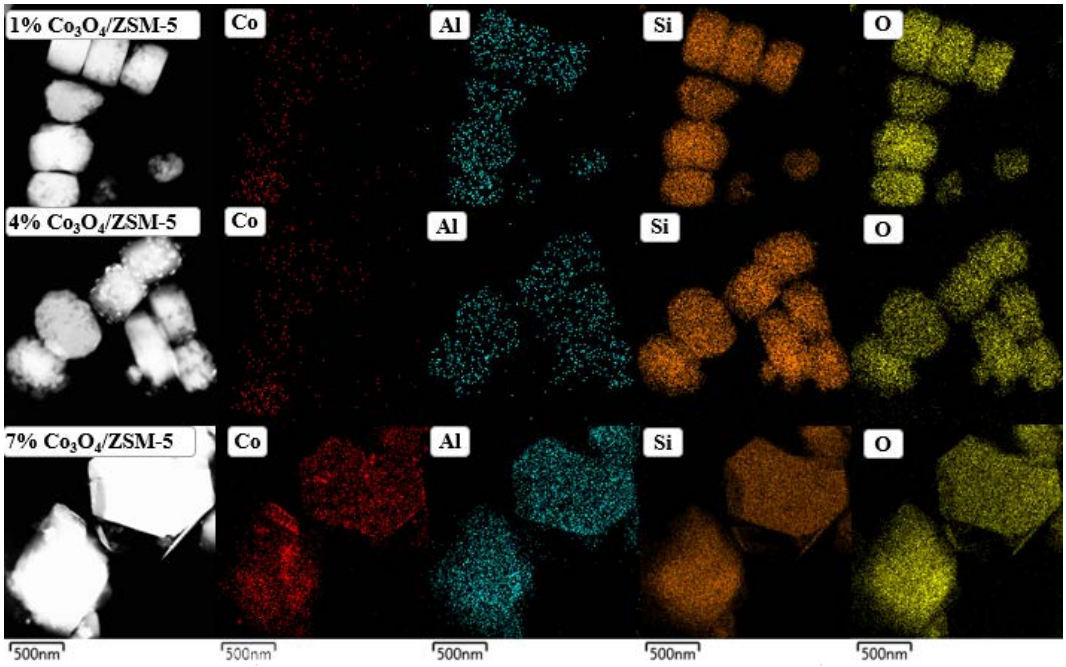

Fig. S4 EDX-mapping images of 1% Co_3O_4/ZSM-5, 4% Co_3O_4/ZSM-5 and 7% Co_3O_4/ZSM-5 catalysts.

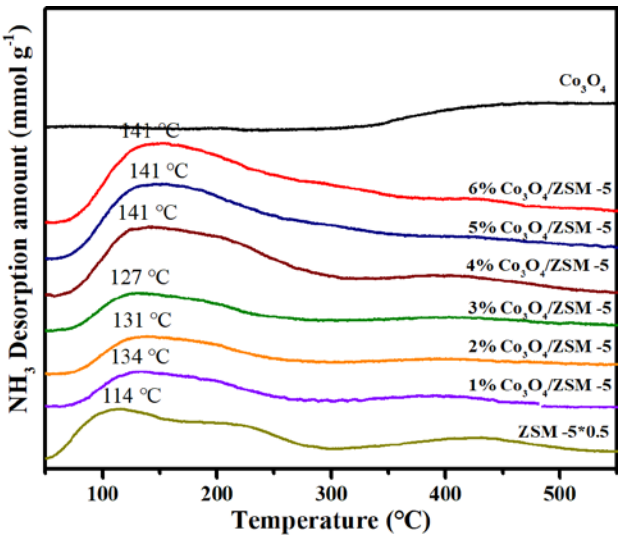

Fig. S5 NH_3-TPD profiles of the catalysts

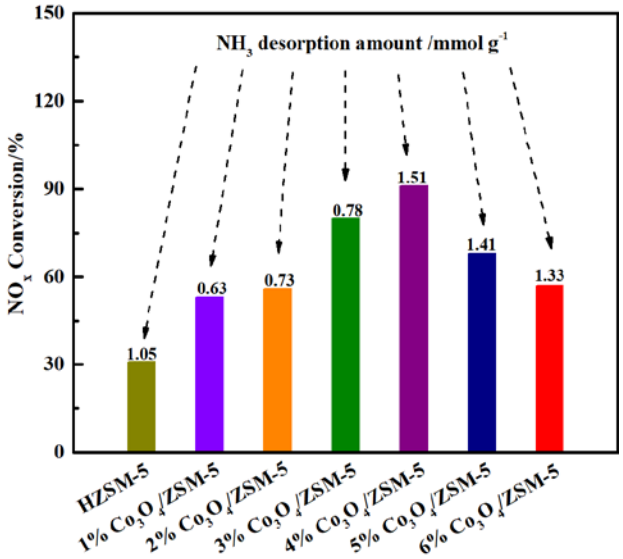

Fig. S6. Diagram of the relationship between catalyst activity and acid amount

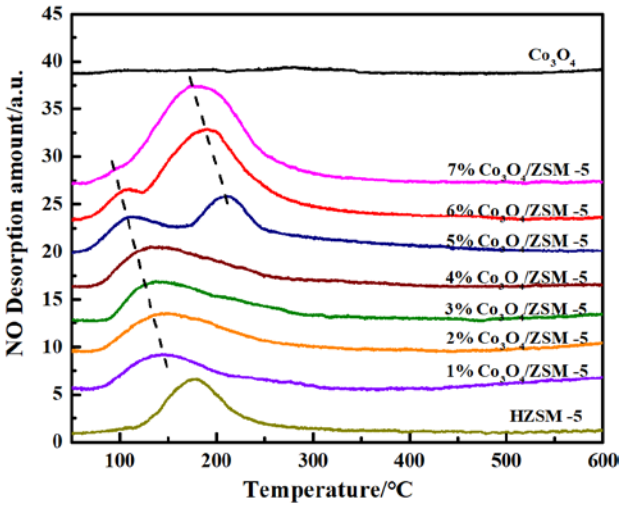

Fig. S7. NO-TPD profiles of the catalysts

2.2. Supplementary Tables

Table S1 The chemical compositions and texture properties of Co_3O_4/ZSM-5 catalysts.

Sample	Weight percentage Identified by ICP/%	$S_{BET}/m^2 \cdot g^{-1}$	D_{micro}/nm	$V_{micro}/cm^3 \cdot g^{-1}$	D_{meso}/nm	$V_{meso}/cm^3 \cdot g^{-1}$
HZSM-5	--	328	0.69	0.12	3.05	0.07
1% Co_3O_4/ZSM-5	1.0	324	0.66	0.10	2.55	0.09
2% Co_3O_4/ZSM-5	2.0	316	0.65	0.09	2.55	0.08
3% Co_3O_4/ZSM-5	3.1	309	0.63	0.10	2.83	0.09
4% Co_3O_4/ZSM-5	4.2	278	0.68	0.10	3.01	0.06
5% Co_3O_4/ZSM-5	4.8	257	0.66	0.10	3.44	0.06
6% Co_3O_4/ZSM-5	5.8	230	0.73	0.10	3.77	0.06
7% Co_3O_4/ZSM-5	6.8	218	0.67	0.09	4.07	0.06
Co_3O_4	--	4.06	--	--	37.06	0.014

Table S2 The deconvolution and integration results of the ^1H MAS NMR peaks

Sample	^1H signal of Co-OH species		^1H signal of acid sites	
	Chemical shift/ppm	Integrated area/a.u.	Chemical shift/ppm	Integrated area/a.u.
HZSM-5	--	--	6.8	1.00
1% Co_3O_4/ZSM-5	19.8	1.00	6.8	0.26
4% Co_3O_4/ZSM-5	32.2	1.49	6.8	0.21
7% Co_3O_4/ZSM-5	47.5	1.50	6.8	0.16

Table S3 NH_3-TPD quantification results of the catalysts.

Sample	NH_3 Desorption	
	Temperature/^oC	Acidic sites amount/mmol g^{-1}
1% Co_3O_4/ZSM-5	134	0.63
2% Co_3O_4/ZSM-5	131	0.73
3% Co_3O_4/ZSM-5	127	0.78
4% Co_3O_4/ZSM-5	141	1.51
5% Co_3O_4/ZSM-5	141	1.41
6% Co_3O_4/ZSM-5	141	1.33
HZSM-5	114	2.09

Table S4 NO-TPD quantification results of Co_3O_4/ZSM-5.

Sample	NO Desorption		
	$T_1/^oC$	$T_2/^oC$	Amount/a.u.
1% Co_3O_4/ZSM-5	143	--	34
2% Co_3O_4/ZSM-5	142	--	43
3% Co_3O_4/ZSM-5	136	--	46
4% Co_3O_4/ZSM-5	132	--	48
5% Co_3O_4/ZSM-5	113	212	70
6% Co_3O_4/ZSM-5	107	189	96
7% Co_3O_4/ZSM-5	--	180	100
ZSM-5	--	175	42