Electronic Supplementary Information (ESI) for

Nano Beta Zeolites Catalytic-Cracking Effect on Hydrochlorofluorocarbon Molecule for Specific Detection of Freon

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Experimental Section

Chemicals

All chemicals used in this work including Zinc chloride ($ZnCl_2$), sodium dodecyl sulfate (SDS), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), hexadecyl trimethyl ammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$), tetraethyl ammonium hydroxide solution (TEAOH, 35wt.% in H_2O), ammonium nitrate (NH_4NO_3), methanol, ethanol, toluene and tert-butylamine are purchased from Sigma-Aldrich. The catalyst of γ-Al_2O_3 is purchased from Strem Chemicals, Inc. ZSM-5, NaY, Mordenite and beta zeolites are purchased from Nankai University Catalyst Co., Ltd.

Synthesis of mesoporous silica nanoparticles (MSNs)

The preparation process of MSNs is detailed as follows. Firstly, 0.8 g of NaOH is dissolved in 10 ml of deionized (DI) water to prepare a NaOH aqueous (2 M) solution. Then, 1.5 g of CTAB is added into a mixed solution that is composed of 720 ml of DI water and 5.25 ml of 2M NaOH (aq) solution. Under magnetic stirring, the mixture is heated at 80°C in an oil bath. After the CTAB is completely dissolved, 7.5 ml of TEOS is added dropwise to the above-mentioned solution. Then, the solution is continuously stirred at 80°C for 2 hours. After that, the precipitate is collected and dried. Finally, the sample is calcined at 550°C for 3 hours with a heating rate of 1°C/min under air.

Synthesis of n-BEAs with different Si/Al ratios

The Si/Al ratio of n-BEA sample can be adjusted by changing the addition amount of $Al_2(SO_4)_3 \cdot 18H_2O$. For convenience, n-BEAs prepared in this work are named as n-BEA-*x*, where *x* is taken as an integer close to the exact Si/Al ratio that is identified by both X-ray fluorescence

(XRF) and energy dispersive spectrometer (EDS). Taking n-BEA-10 as an example, the synthesis process is detailed as follows. 0.03 g of NaOH and 0.56 g of $Al_2(SO_4)_3 \cdot 18H_2O$ are dissolved in 3 g of TEAOH solution and stirred for 0.5 hours. After that, 1 g of MSNs is dispersed in the above-mentioned solution and continuously stirred until the mixture becomes an ivory gel. Subsequently, the gel is transferred into a 10 ml Teflon-lined stainless-steel autoclave and sealed. Then, the autoclave is heated at 170°C for 20 hours. After cooling down to room temperature, the gelatinous product is carefully collected and repeatedly washed at least 3 times with DI water. Subsequently, the product is dried at 60°C for 10 hours and calcined at 550°C for 6 hours. The heating rate for the calcination is 2°C/min. In order to achieve high catalytic performance, the calcined n-BEA-10 sample should be hydrogenated furtherly through an ion exchange process (i.e., the residual Na^+ ions are exchanged with NH_4^+) and the hydrogenation process is detailed as follows. 1.6 g of NH_4NO_3 is dissolved in 20 ml of DI water to obtain an aqueous NH_4NO_3 solution (1 M). The previously obtained n-BEA-10 sample is re-dispersed into 5 ml of NH_4NO_3 (aq) solution. The abovementioned mixture is stirred at 90°C for 6 hours to conduct the ion exchange process. The ion exchange process should be repeated at least two times. In the last ion exchange process, the collected n-BEA-10 sample needs to be washed with DI water three times and dried at 115°C for 12 hours. Finally, the dried product is calcined at 550°C for 4 hours with a heating rate of 1°C/min. With the similar methods but different $Al_2(SO_4)_3 \cdot 18H_2O$ amount, a serious of n-BEA samples with different Si/Al ratios can be obtained: 0.38 g for n-BEA-15, 0.28 g for n-BEA-20, 0.19 g for n-BEA-30 and 0.14 g for n-BEA-40.

Preparation of ZnO nanowires (ZnO NWs) *via* a hydrothermal method

Firstly, 0.2 g of $ZnCl_2$ and 1.8 g of SDS are ultrasonically dissolved in 35 ml of DI water to form a homogeneously solution. Then, 20 g of Na_2CO_3 is added into the abovementioned solution and stirred until the Na_2CO_3 is completely dissolved. After that, the precursor solution is transferred and sealed into a 50 ml Teflon-lined stainless-steel autoclave and heated at 140°C for 12 h. After the hydrothermal treatment, white precipitates are collected *via* high-speed centrifugation and washed repeatedly with DI water to remove the residual chemicals. Under vacuum, the obtained sample is dried at 60°C for 4 h.

Fabrication of the ZnO/n-BEA bilayer sensor

In this work, a kind of lab made micro-hotplate is used to fabricate gas sensor. The fabrication process of the micro-hotplate is described in our previous works.[S1, S2] To fabricate the ZnO/n-BEA bilayer sensor, 2 mg of ZnO NWs is evenly dispersed in 1 ml of ethanol. Then, the ZnO dispersion is dropped onto the sensing area of the micro-hotplate and naturally dried to form the bottom sensing layer. This step should be repeated for 5 times, and the volume of each drop is 1 μl. For loading the catalyst, 1 mg of n-BEA catalyst is firstly mixed with 1 ml of ethanol ultrasonically. After that, 1 μl of the n-BEA dispersion is dropped onto the ZnO bottom layer. Finally, the micro-hotplate is *in situ* heated at 350°C for 2 hours to calcinate the bilayer sensor.

Characterization

FEI Tecnai G^2 F20 microscope with an accelerating voltage of 200 kV is used to obtain the transmission electron microscopy (TEM) images of MSN and n-BEAs. Quantitative energy dispersion spectra (EDS) analysis of n-BEAs is performed by using an Oxford X-Max[N] 80 system.

Crystal structures of the samples are analyzed by powder X-ray diffraction (XRD) with a Bruker model D8 focus diffractometer that equipped with a Cu anode to produce X-ray (40 kV, 40 mA). The XRD patterns of catalysts are collected in a continuous scan mode from 5° to 40°, with a 0.02° sampling interval. And the pattern of ZnO nanowires is collected from 30° to 80° with a 0.02° sampling interval. N_2 sorption isotherms are measured at 77 K with a Micromeritics ASAP2020 system. Applying a commercial-available TPD instrument (Xiamen High-End MEMS Technology Co., Ltd., model: LoC-TPD 1000), the NH_3-temperature programmed desorption (NH_3-TPD) curves are measured under He flow with a heating temperature from 50°C to 400°C at 10°C/min. Field scanning electron microscopy (FE-SEM, Hitachi S4800) is used to characterize the morphologies of zeolites and sensor. Atomic-resolution TEM image of the sample is obtained by spherical aberration-corrected FEI Titan Cubed Themis G2 300 S/TEM at 300 kV. On-line MS is implemented on a Pfeiffer ThermoStar mass spectrometer, the scan range is set from 15 to 120 amu. Besides the on-line MS analysis, Gas Chromatography-Mass Spectrometry (GC-MS, Agilent 7890A-5975C) is used to identify the components of the eluent solution.

Calculation of isosteric heat values *via* Grand canonical Monte Carlo (GCMC) simulation

The isosteric heat values are calculated by GCMC simulation with Sorption module of Materials Studio package (version 2017). The standard universal force field (UFF) is used for simulation and the centre of mass (COM) distribution contour is calculated under fixed pressure (0.1 kPa) and fixed temperature (723 K). The equilibration steps are set as 100,000 and the production steps are set as 10,000,000. All the data are collected for GCMC simulation.

***Operando* experimental setup for studying sensing mechanism**

Fig. S11 shows the schematic diagram of the experimental setup. Pure R22 gas is diluted by air to obtain 1000 ppm R22-contained gas. Then, the diluted R22 gas flows through a program-controlled furnace which contains n-BEA-20 catalyst. The temperature of the furnace is set according to the catalytic temperature. The exhausted gas is then spilled into two parts: a small amount of the gas is allowed to flow into the capillary tube for on-line MS analysis, and the rest is eluted with some organic absorbent (e.g. methanol, ethanol, and toluene/tert-butylamine) to adsorb the generated substances. Finally, the obtained eluent is analyzed by GC-MS.
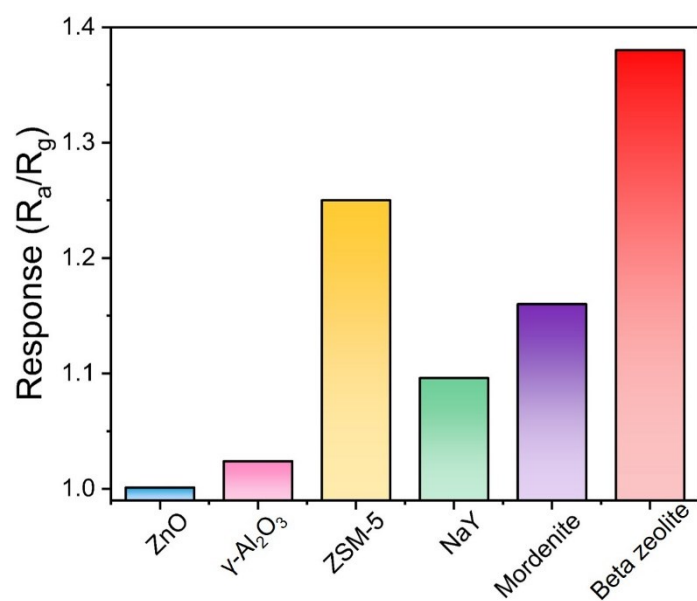
Supplementary Figures

Fig. S1 Sensing responses of the ZnO-NWs based sensors with different catalysts. The concentration of Freon R22 is 50 ppm and the working temperature is 450°C.
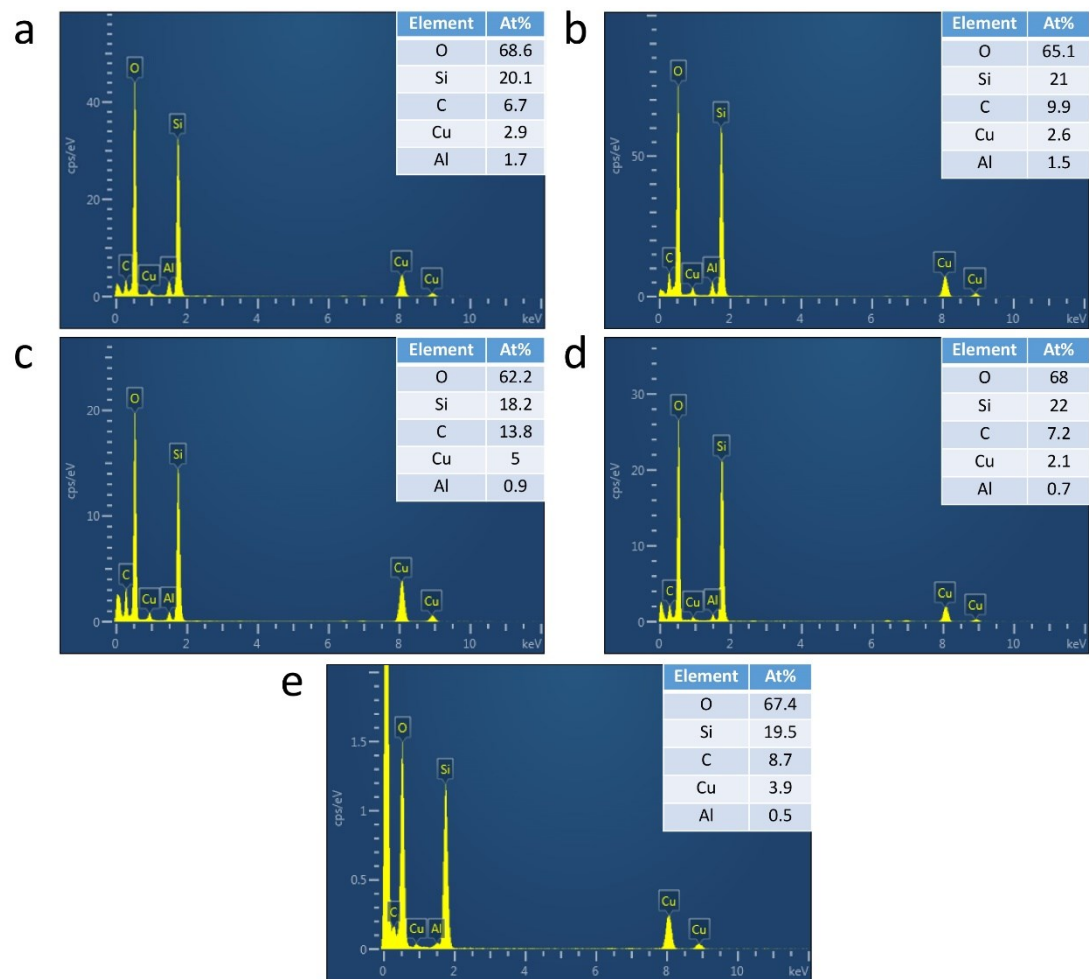
Fig. S2 EDS results of the prepared (a) n-BEA-10, (b) n-BEA-15, (c) n-BEA-20, (d) n-BEA-30 and (e) n-BEA-40.
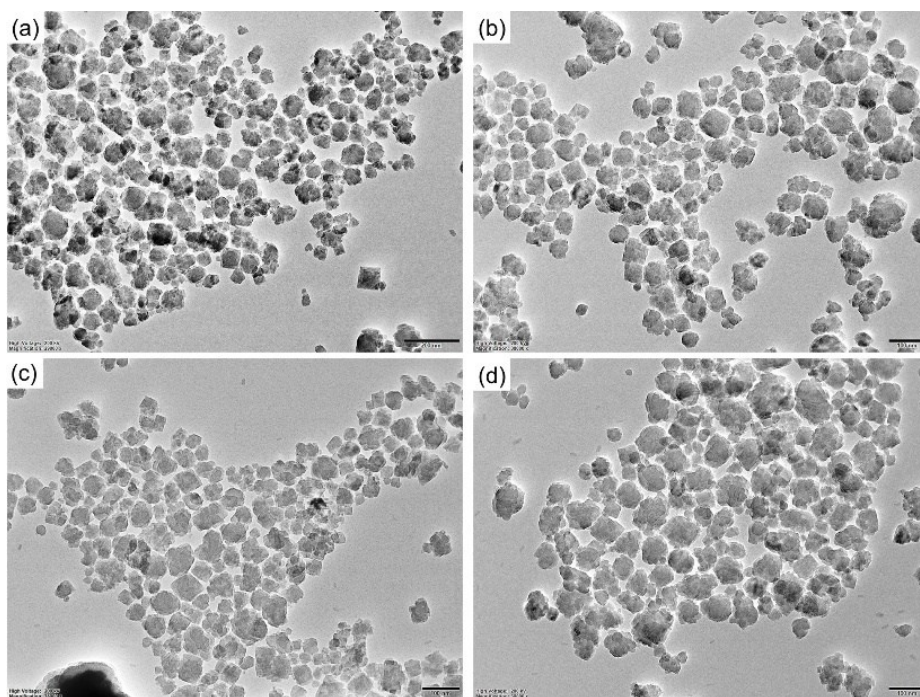
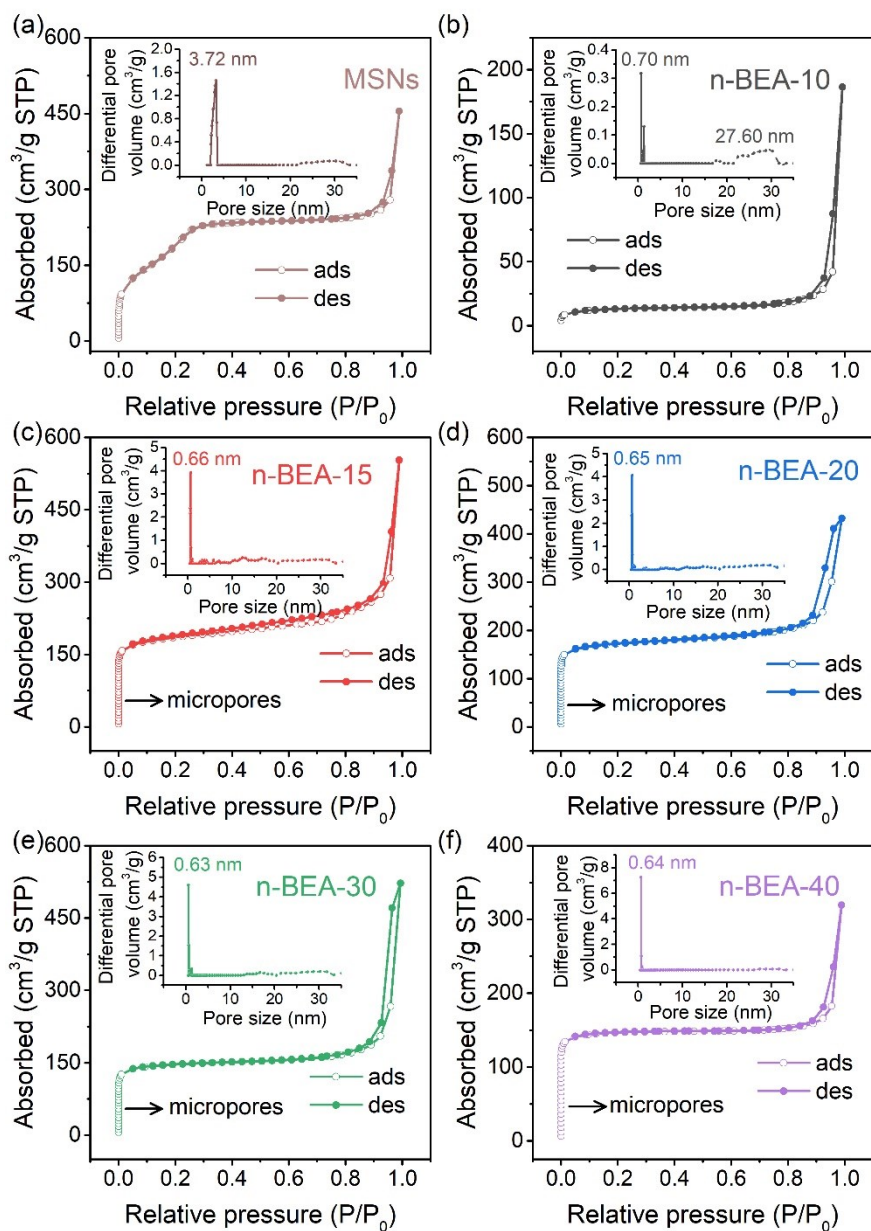**Fig. S3** Low-magnified TEM images of n-BEA-20 sample which show the nanoparticles are well-dispersed.

Fig. S4 N$_2$ sorption isotherms of the prepared samples. The inset of each figure exhibits the corresponding pore size distribution.
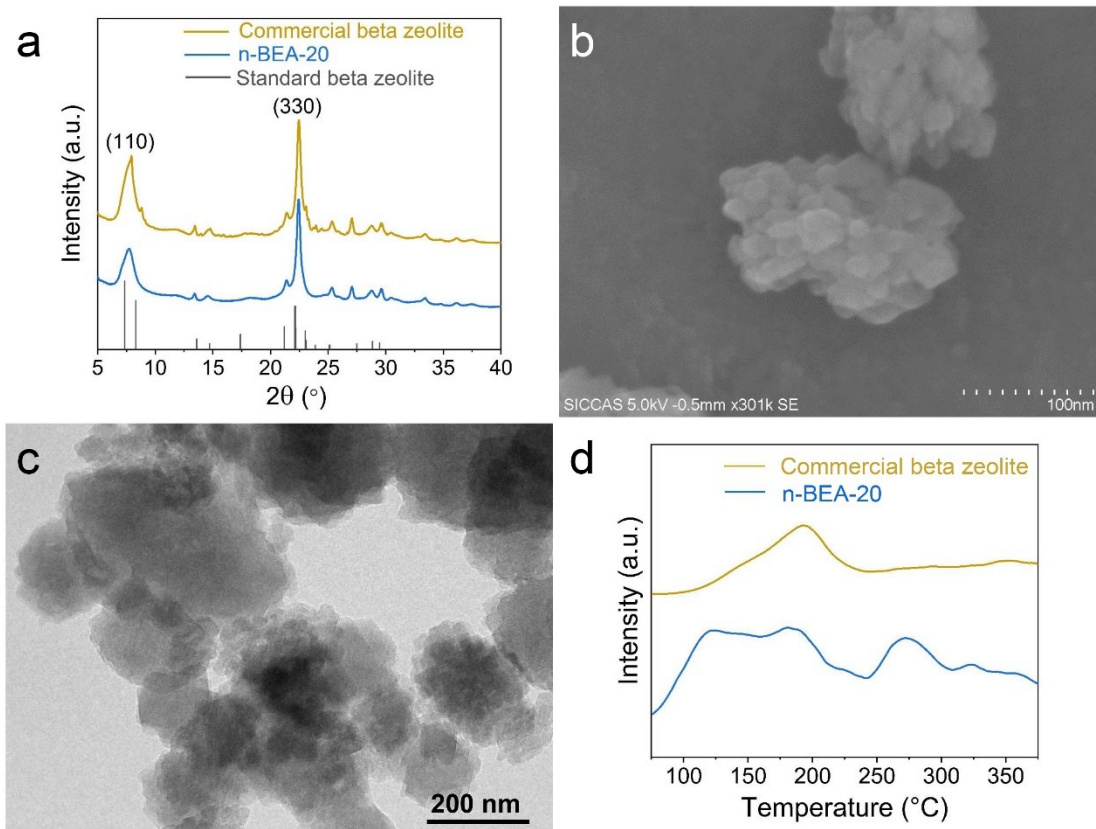
Fig. S5 Structural and acidic characterization of commercial beta zeolite. (a) XRD results indicate that the commercial beta zeolite has the same crystalline structure with n-BEA-20 catalyst. (b) SEM and (c) TEM image of the commercial beta zeolite. (d) NH_3-TPD curves of the commercial beta zeolite and n-BEA-20 for comparison.
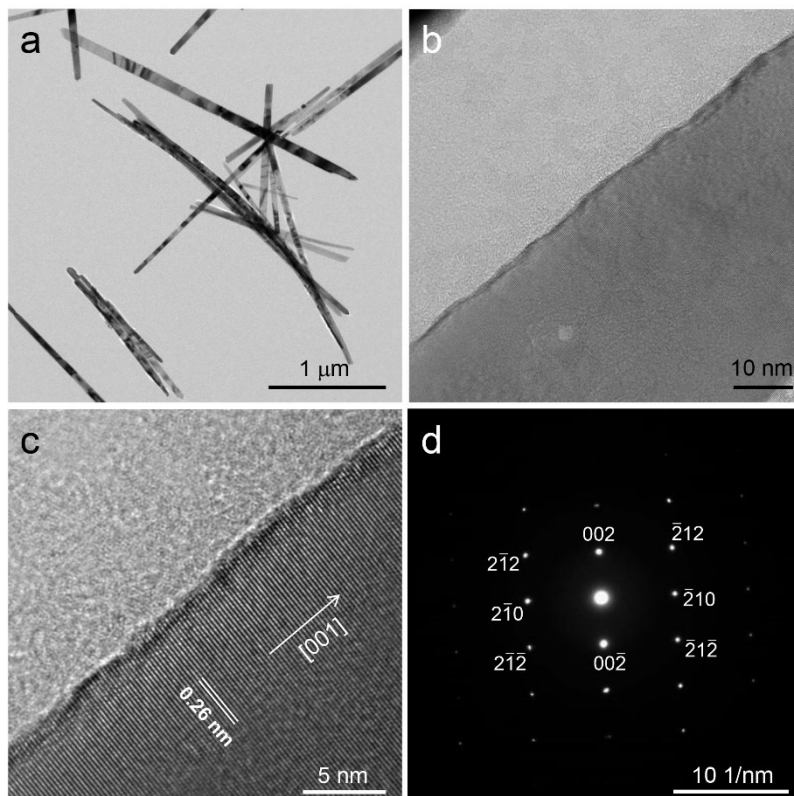
Fig. S6 (a-c) TEM images and (d) electron diffraction (ED) pattern of the ZnO nanowires.
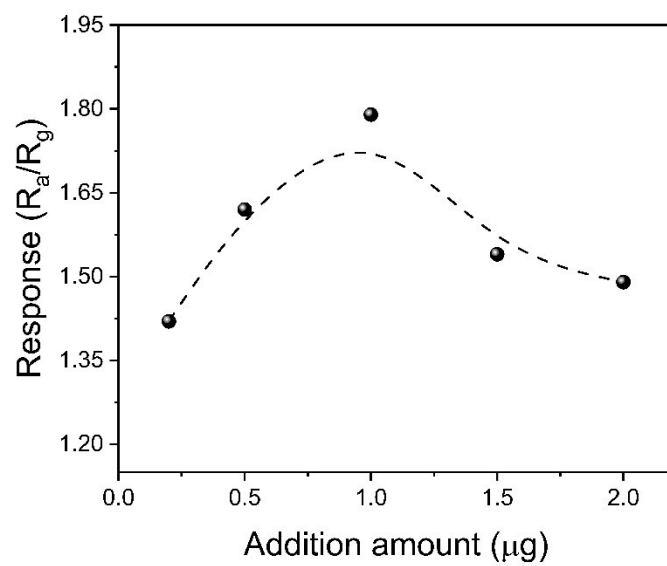
Fig. S7 Relationship between the addition amount of n-BEA-20 catalyst and sensing response. The concentration of R22 gas is 50 ppm and the working temperature is 450°C.
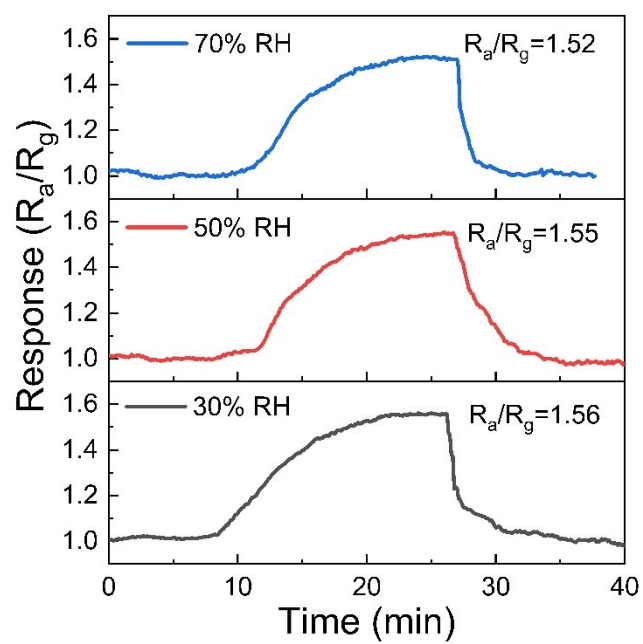
Fig. S8 Sensing response of the ZnO/n-BEA-20 sensor to 10 ppm R22 gas under different ambient humidity.
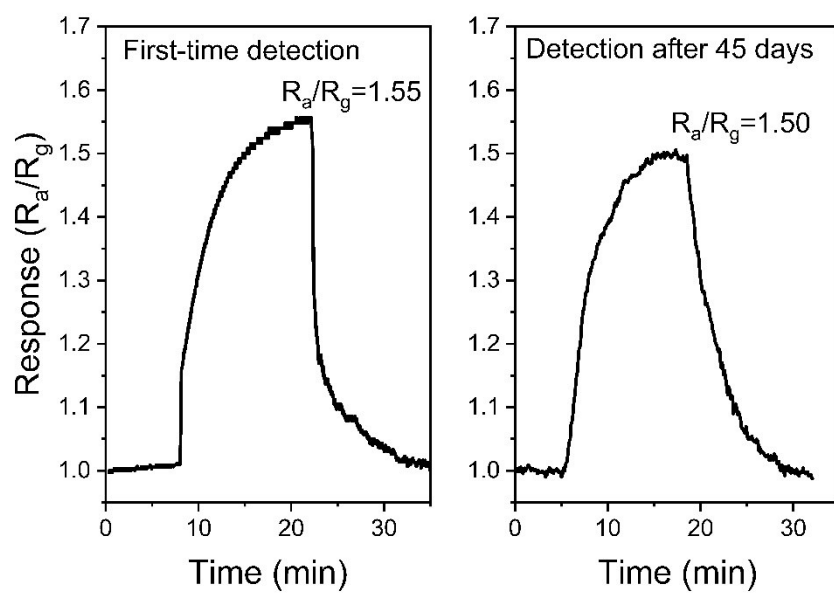
Fig. S9 Long-term stability of the ZnO/n-BEA-20 sensor. The concentration of R22 gas is 10 ppm and the working temperature is 450°C.

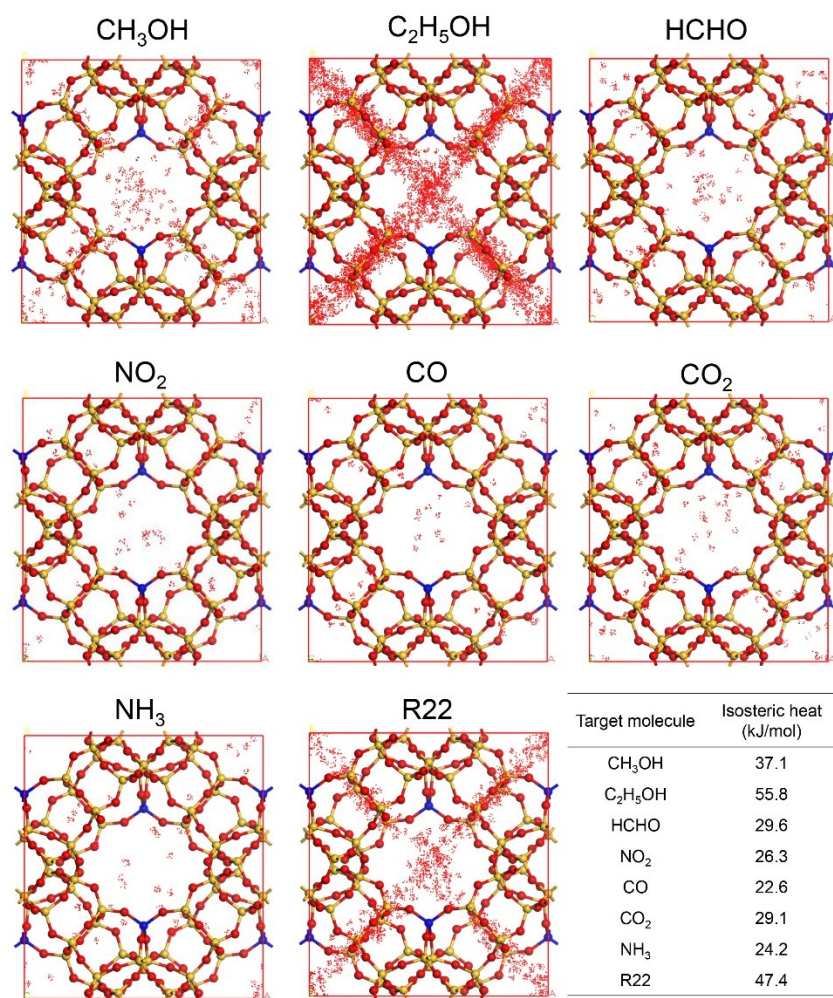| Target molecule	Isosteric heat (kJ/mol)
CH_3OH	37.1
C_2H_5OH	55.8
HCHO	29.6
NO_2	26.3
CO	22.6
CO_2	29.1
NH_3	24.2
R22	47.4

Fig. S10 Models and the calculated isosteric heat values of the target gaseous molecules adsorbed by beta zeolite. Silicon, aluminum and oxygen atoms are represented by red, blue and yellow balls respectively. The red dots between the framework of beta zeolite indicate the spatial distribution of the target molecules.
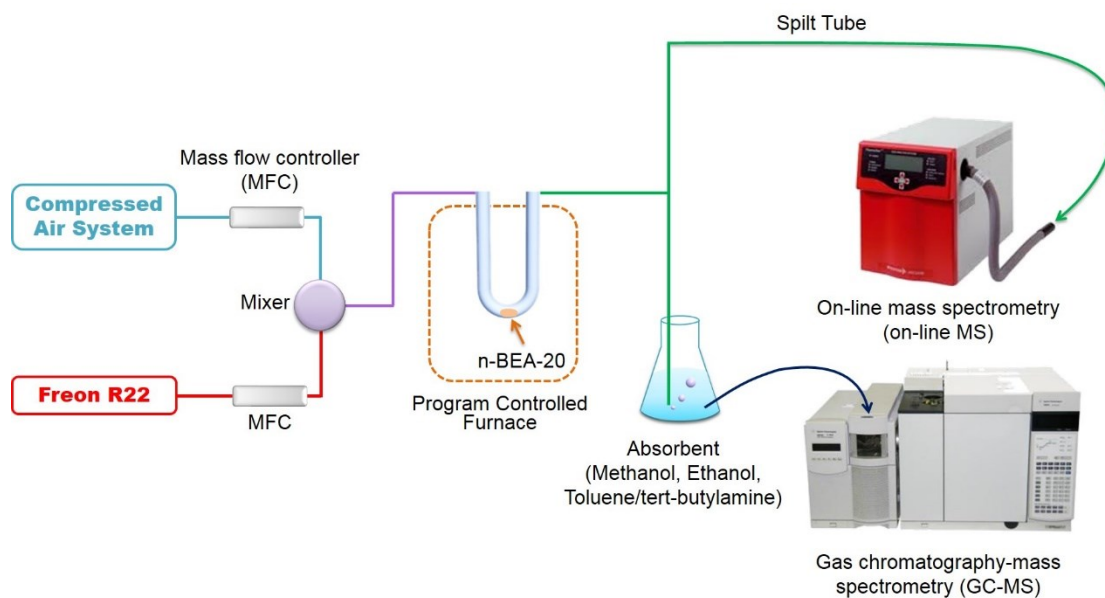
Fig. S11 *Operando* experiment setup for revealing the sensing mechanism. The exhausted R22 gas is identified by on-line mass spectrometry and gas chromatography-mass spectrometry.
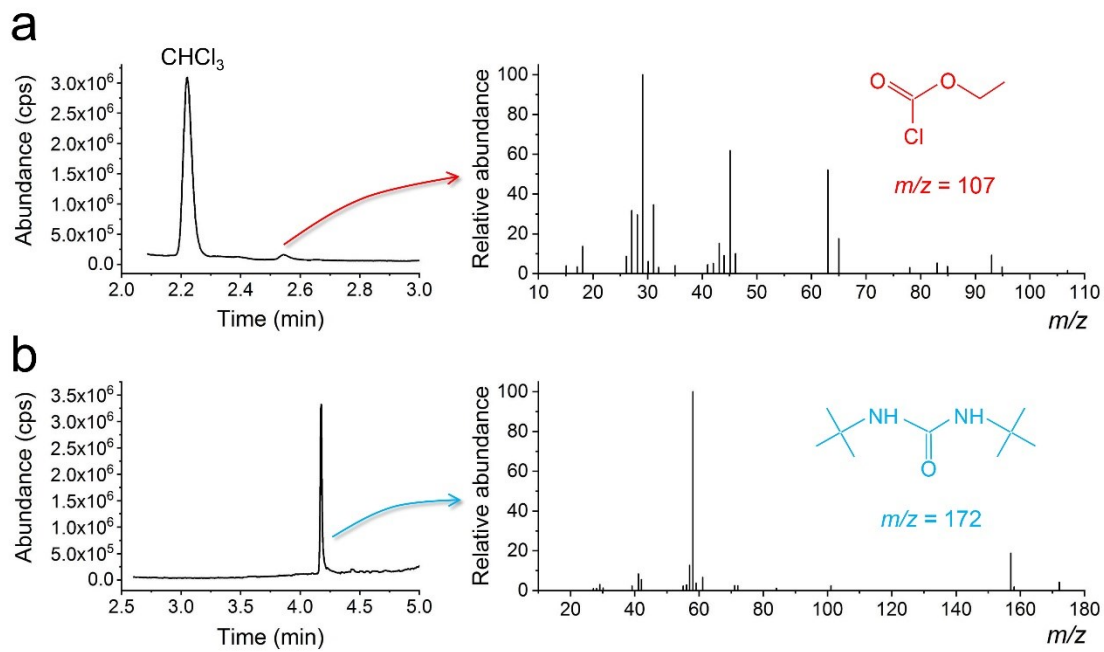
Fig. S12 GC-MS data of (a) ethanol and (b) toluene/tert-butylamine eluent which has absorbed the exhausted R22 gas.

References

S1. D. Xu, P. Xu, X. Wang, Y. Chen, H. Yu, D. Zheng and X. Li, *ACS Appl. Mater. Inter.*, 2020, **12**, 8091-8097.

S2. Y. Chen, P. Xu, X. Li, Y. Ren and Y. Deng, *Sensors and Actuat. B-Chem.*, 2018, **267**, 83-92.