Chemical Engineering Journal 335 (2018) 483–490

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Study on improving the SO_2 tolerance of low-temperature SCR catalysts using zeolite membranes: NO/SO_2 separation performance of aluminogermanate membranes

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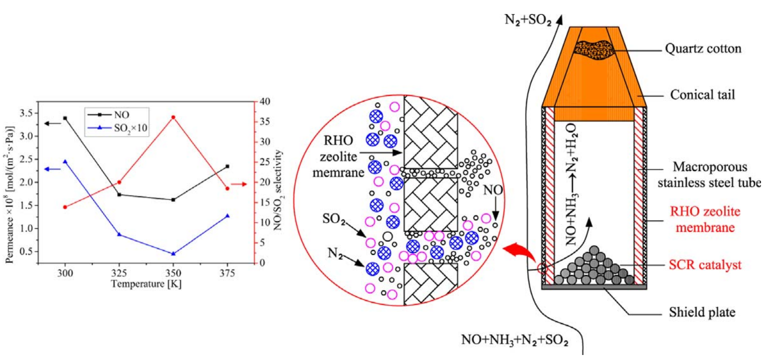
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Zeolite membrane
Separation
SO_2
SCR catalyst

ABSTRACT

A novel idea is proposed to improve the SO_2 tolerance of low-temperature selective catalytic reduction (SCR) catalysts by using a RHO zeolite membrane to separate NO from SO_2 to reduce the contact between SO_2 and the SCR catalysts. RHO zeolite membranes were prepared on a macroporous stainless steel tube. The results from XRD and SEM measurements indicated that the crystals on the surface were pure RHO zeolites and a uniform and continuous layer of RHO zeolite membrane covered the surface of the support. Permeation measurements using different feed gases indicated that the prepared RHO zeolite membrane could effectively separate NO from SO_2. A maximum NO/SO_2 selectivity of 36.14 was obtained when using $NO/SO_2/N_2$ mixtures. The SO_2 permeation decreased a lot in the present of water. Surface diffusion and activated diffusion were believed to be the main transport mechanisms of the RHO zeolite membrane.

1. Introduction

NOx induces many environmental problems, including photochemical smog and greenhouse effects; coal-fired power plants are one of the major emission sources of NOx [1]. The most effective technology for denitrification is currently selective catalytic reduction with ammonia (NH_3-SCR) in coal-fired power plants, and the catalysts which determine the denitrification efficiency are the key component of the SCR system [2].

The commercial vanadium-based catalysts have a few disadvantages, such as the biological toxicity of vanadium species, the narrow temperature operation window, and the high activity for the oxidation of SO_2 to SO_3 [3]. The development of low-temperature SCR catalyst that work downstream after electrostatic precipitator and

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http://dx.doi.org/10.1016/j.cej.2017.10.184
Received 15 September 2017; Received in revised form 30 October 2017; Accepted 31 October 2017
Available online 02 November 2017
1385-8947/

desulfurizer has attracted increasing attention. Many low-temperature SCR catalysts with high catalytic activities have been reported, including metal oxides and zeolite catalysts [4]. However, poisoning due to the residual SO_2 in the flue gas at low temperature has prohibited the commercial application of low-temperature SCR catalysts [5–7]. Therefore, it is important to improve the SO_2 tolerance of low-temperature SCR catalysts.

Zeolites are widely used in the field of gas separation, such as for air separation [8], natural gas upgrading [9], and carbon capture and storage [10–12], due to their excellent adsorption capacity, good flexibility and molecular sieving abilities. This paper presents a novel idea to improve the SO_2 tolerance of low-temperature SCR catalysts by using zeolite membranes to separate NO and NH_3 from SO_2 in the flue gas to reduce the contact between SO_2 and the low-temperature SCR catalysts.

In the last few decades, molecular sieves have been used as supports of the active components in SCR catalysts due to their good surface acidity and large intragranular surface area [13,14]. However, molecular sieves mainly act as carriers to disperse the active components, instead of improving the SO_2 tolerance of low-temperature SCR catalysts. Molecular sieves are also used to adsorb and remove NOx and NH_3 [15,16]. Clinoptilolite can absorb 6.255–14.155 mgN/g ammonia in a 0.17–15.7 mgN/L ammonia concentration [17]. The irreversible amount of NO adsorbed in LTA exchange with metal cations is in the range of ~1.5–2.7 mmol/g (1 atm), which is slightly greater than ~1.2–1.9 mmol/g that can be achieved using FAU molecular sieves [18]. Hence, the basic SCR reaction will not be influenced while using zeolite membranes to improve the SO_2 tolerance of low-temperature SCR catalysts. However, there have been reports that a few zeolites have a comparable or better SO_2 adsorption than NO adsorption [19]. Thus, in the presence of NO and SO_2 simultaneously, it is important to choose an appropriate molecular sieve that has a great NO/SO_2 separation selectivity.

RHO zeolites, firstly reported and named by Harry E. Robson et al. in 1973 [20], were used in this work to separate NO from NO/SO_2 mixtures. NH_3, NO and SO_2 have molecular dynamics diameters of 0.26 nm, 0.317 nm and 0.36 nm, respectively. And the RHO zeolite has a three-dimensional channel of 0.36 nm size. It is expected that NH_3 and NO can pass through the RHO zeolite membrane while SO_2 cannot. Therefore, no contact between SO_2 and the low-temperature SCR catalysts occurs due to the molecular size limitation, and SO_2 will not poison the low-temperature SCR catalysts. Additionally, without contacting the SCR catalysts, SO_2 will not be oxidized to SO_3, which can reduce the flue gas acidity to decrease the chimney corrosion, acid rain and haze generation.

In this paper, RHO zeolite membranes were synthesized on the surface of a macroporous stainless steel tube. XRD and SEM were used to characterize the membranes, and the permeability of NO and SO_2 was detected using a permeation separation setup at three inlet concentrations. The NO/SO_2 separation performance using NO/SO_2/N_2 mixtures was further studied, and the feasibility of the idea proposed above was verified. Due to the limitations of the testing equipment, NH_3 permeation experiments were not performed. Since NH_3 has a much smaller molecular dynamics diameter and stronger polarity, it can be expected that NH_3 would permeate well through the RHO zeolite membrane.

2. Experimental

2.1. A protective device for SCR catalysts

Molecular sieves are used in core-shell structures to prevent contact between toxic and active components and to improve the anti-toxicity properties of the catalyst [21]. Since the molecular dynamics diameter of N_2 produced from the SCR reaction is 0.364 nm, which is slightly larger than that of SO_2, it is necessary to synthesis a zeolite membrane with excellent N_2/SO_2 separation selectivity if a core-shell structure is

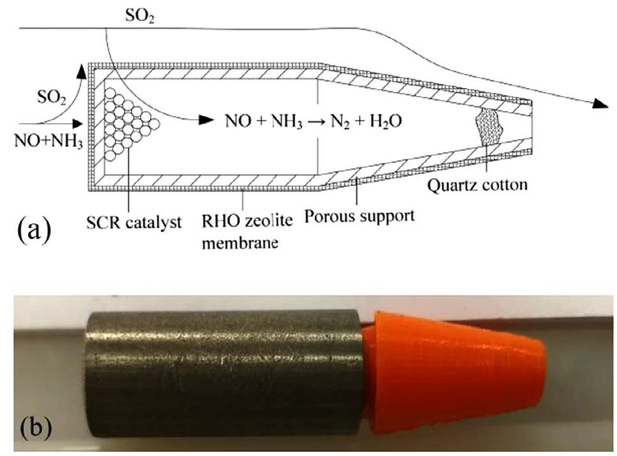

Fig. 1. Schematic of the protective device for SCR catalysts (a) and a picture of the actual object (b).

used. As shown in Fig. 1(a), an appropriate device is proposed to solve this problem. The RHO zeolite membrane was prepared on the surface of a porous support that has a tapered structure at the tail to avoid the backflow of the flue gas. The permeating NO and NH_3 react in the presence of the SCR catalysts, and the reaction product N_2 outflows from the tail.

In order to reduce the difficulty of the membrane preparation, a macroporous stainless steel tube (Mingtai Filter Material Co. Tiantai, China), instead of the complex structure in Fig. 1(a), was used as the support of the RHO zeolite membrane. The tapered structure at the tail, manufactured using 3D printing, was dense and nonporous to avoid the entrance of SO_2. Fig. 1(b) presents a picture of the actual object. The membrane on the support tube was characterized, and NO/SO_2 separation measurements were carried out in the following experiments.

2.2. Membrane preparation

RHO zeolite membranes were prepared using a secondary growth method. A stainless steel porous tube (5.5 mm i.d. and 8 mm o.d.) with 20–40 μm pore diameters was polished with 1000 grit sand papers and cleaned for 30 min using an ultrasonic cleaner before being used as the support for the membranes. The seeds were synthesized according to the procedure reported by Johnson and coworkers [22]. The outer surface of the treated support tube was simply rubbed with some seeds powder. After the zeolite gel (0.7 Cs_2O:2.3 Na_2O:2 GeO_2:Al_2O_3:70 H_2O) was transferred to the Teflon-lined autoclave, the rubbed support was vertically positioned at the bottom of the vessel. Then it was aged at room temperature for 4 days, followed by crystallization at 333 K for 6 h. The resultant RHO zeolite membrane was first placed into an ultrasonic cleaner for 10 min to remove the unstable film and then dried overnight at 313 K. It is worth mentioning that Na,Cs-AlGe-RHO zeolite membranes could be prepared under normal pressure, which enables their application.

2.3. Characterization

The crystalline structures of the membrane on the stainless steel porous tube were characterized by X-ray Diffraction (XRD) measurements using an X'Pert[3] powder (PANalytical B.V. Corp., Netherlands) with Cu Kα radiation (λ = 1.5425 Å). The sample was scanned from 5 to 50 degrees in the 2θ range. The surface morphologies of the seeds and the RHO zeolite membrane were described by scanning electron microscopy (SEM) images taken with a Sirion 200 SEM (FEI Corp., Netherlands). The samples were covered with gold on the surface to increase the resolution before the SEM measurements were conducted.