



The role of pore diffusion in determining NH₃ SCR active sites over Cu/SAPO-34 catalysts



Xiaoqian Hu^a, Ming Yang^b, Dequan Fan^a, Gongshin Qi^b, Jun Wang^a, Jianqiang Wang^a, Tie Yu^a, Wei Li^{b,*}, Meiqing Shen^{a,c,d,*}

^a Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, People's Republic of China

^b General Motors Global Research and Development, Chemical and Materials Systems Lab, 30500 Mound Road, Warren, MI 48090, USA

^c State Key Laboratory of Engines, Tianjin University, Tianjin 300072, People's Republic of China

^d Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, People's Republic of China

ARTICLE INFO

Article history:

Received 7 February 2016

Revised 8 May 2016

Accepted 22 May 2016

Keywords:

Cu/SAPO-34

NH₃ SCR

Active sites

Diffusion limitation

Kinetics

Zeolite particle size

ABSTRACT

Cu/SAPO-34 catalysts have been extensively investigated recently for NO_x selective catalytic reduction (SCR) reactions. Due to the small pore size (4.3 Å) of the zeolites, it is a natural concern that the reaction rates might be dictated by the pore diffusion regime rather than the intrinsic kinetics. In this work, a series of Cu/SAPO-34 catalysts, with identical Cu ion active site loadings but varying zeolite particle sizes (1–9 μm), were evaluated. A variety of characterization techniques (XRD, BET, H₂ TPR, and NH₃ TPD) have confirmed that the same copper species and surface chemistry existed in these samples despite the different SAPO-34 particle sizes. While the Thiele modules governing the pore diffusion effects were vastly different, up to nine times, these samples shared a similar turnover frequency (TOF) and apparent activation energy (44.8 ± 3.0 kJ/mol) for the NH₃ SCR reaction. These results unequivocally conclude that under the representative SCR reaction conditions investigated in this work, the reaction rates on Cu/SAPO-34 powder catalysts are kinetically controlled and pore diffusion plays little role in disguising the intact intrinsic activity per single-site copper.

© 2016 Elsevier Inc. All rights reserved.

1. Introduction

Copper-zeolite materials with isolated copper ions as the catalytic centers are highly active catalysts for a variety of reactions [1–5]. These catalytic species have been studied extensively in order to understand the fundamentals of heterogeneous single-site catalysis. For nanoscale single-site heterogeneous powder catalyst particles using mesoporous oxide supports such as alumina, silica, ceria, and titania [6–9], the diffusion impact can easily be overcome by increasing the flow rate and decreasing the pellet size. This holds true for a variety of emission control reactions, including CO oxidation [7], DeNO_x reactions [8], and the water-gas shift [9]. However, in terms of zeolites, the microporous structure may lead to diffusion limitations inside the micropores and

hinder the unambiguous identification of the active sites and the precise measurement of intrinsic catalytic activity on those active sites.

For the NH₃ SCR reaction, NH₃ acts as a reducing agent to selectively react with NO_x (facilitated by O₂) to make nitrogen and water under lean-combustion operation conditions [10]. Ion-exchanged small-pore molecular sieves with a chabazite (CHA) structure (e.g., Cu/SSZ-13 and Cu/SAPO-34) have received widespread attention due to their exceptional catalytic performance and superior hydrothermal durability in SCR applications [11–13]. Several studies have attempted to understand the active sites and the intrinsic reaction kinetics [14–17]. Xue et al. [14] found that the number of isolated exchanged Cu(II) was proportional to the NH₃ SCR rate and these single-site species were the true active sites in the temperature range 100–200 °C, as indicated by the same TOF for the Cu/SAPO-34 with various copper loadings. The low-temperature reactions ensure that the kinetic measurements are performed in the differential region, and avoid side-reaction complications caused by the NH₃ oxidation reaction. Bates et al. [18] reported that the NH₃ SCR rate per gram of the Cu/SSZ-13 catalyst increased linearly with the Cu:Al ratio up to 0.2.

* Corresponding authors at: General Motors Global Research and Development, Chemical and Materials Systems Lab, 30500 Mound Road, Warren, MI 48090, USA. Fax: +001 586 986 8697 (W. Li). Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering and Technology, Tianjin University, 92 Weijin Road, Nankai District, Tianjin 300072, People's Republic of China. Fax: +86 22 27407002 (M. Shen).

E-mail addresses: wei.1.li@gm.com (W. Li), mqshen@tju.edu.cn (M. Shen).

Table 1
Kinetic diameters of molecules relevant to NH₃ SCR over the typical Cu/SAPO-34 catalysts [27].

Molecule	Kinetic diameter (Å)	Molecule	Kinetic diameter (Å)
NH ₃	2.900	CO ₂	3.300
NO	3.492	H ₂ O	2.641
NO ₂	–	O ₂	3.467
N ₂ O	3.828	N ₂	3.640–3.800

Combining this result with UV–vis–NIR and XAS results, they confirmed that the isolated and stable Cu(II) species were the active sites. Yu et al. [17] examined the reaction orders of NH₃ SCR reactants over Cu/SAPO-34 catalysts and proposed a preliminary reaction mechanism from the perspective of adsorption strength on the isolated copper sites. Differently, Gao et al. [19] measured the NH₃ SCR kinetics on Cu/SSZ-13 catalysts with different Cu loadings (1.31–5.15 wt.%) and found that the reaction rate per total Cu decreased with increasing Cu loading. These authors speculated that all the copper species were equally active for the SCR reaction, and the reaction was controlled by intraparticle diffusion limitations, especially at higher Cu loadings. The latter assumption is against the reaction engineering principle that an obvious downshift of the apparent activation energy should be observed when intraparticle pore diffusion controls the reaction [20], as the report showed intact E_a for all the Cu/SSZ-13 catalysts in the temperature window of 403–433 K [19]. This in turn reinforces the fundamental importance of finding the exclusive true catalytic copper center and presenting the reliable intrinsic kinetics per active site in the shadow of potential intraparticle pore diffusion control problems.

Indeed, reaction engineering studies have been carried out on this specific reaction and material system to tackle mass transfer problems, but were mainly for purposes of improved understanding of wall-shape or monolith catalytic reactors [21–25]. For example, a pioneering work by Metkar et al. [21] compared the NH₃ SCR conversions obtained on Fe/ZSM-5 and Cu/ZSM-5 catalysts with the same washcoat volumes but different washcoat thicknesses. The clear influence of mass transfer limitations originating from washcoat interparticle diffusion and external gas film resistance in these monolithic catalysts was evaluated. Differently, targeting the Cu/SAPO-34 NH₃ SCR catalysts of particle forms in this work, we intend to specifically examine the role of intraparticle pore diffusion in determining the intrinsic kinetics per true active site.

In the present work, we synthesized Cu/SAPO-34 catalysts with different particle sizes while maintaining the same actual loading of the copper active sites (~1 wt.%) and total copper (~2 wt.%). These catalytic materials were probed by the NH₃ SCR reaction in order to evaluate the role of pore diffusion in NH₃ SCR reactions.

Cu/SAPO-34 catalysts have a large particle size (>1000 nm) but a narrow pore size (4.3 Å) [26], close to the kinetic diameters of the NH₃ SCR reactants (2.6–3.8 Å [27]; see Table 1). After ruling out the impact of external mass diffusion control during the reaction, we revisited the abovementioned kinetics problem (true kinetics vs. pore diffusion control) on these rather ideal platforms (only vastly different in dimensions), which had the same surface chemistry, as confirmed in this work.

2. Experimental

2.1. Catalyst preparation

Cu/SAPO-34 catalysts were synthesized using a modified one-pot method reported before [28–30]. Synthesis gel molar composition was as follows: 1 Al₂O₃:1 P₂O₅:0.5 SiO₂:0.05 CuO:2 morpholine (MOR):0.05 tetraethylenepentamine (TEPA):61.7 H₂O. The Si, P, Al, and Cu sources were silica sol (40 wt.% SiO₂, Qingdao

Table 2
The composition of the Cu/SAPO-34 catalysts.

Samples	Molar composition	Cu loading (wt.%)
Cu/SAPO-34-1	Si _{0.13} P _{0.38} Al _{0.49} O ₂	2.05
Cu/SAPO-34-4	Si _{0.13} P _{0.37} Al _{0.50} O ₂	2.02
Cu/SAPO-34-6	Si _{0.13} P _{0.39} Al _{0.48} O ₂	2.10
Cu/SAPO-34-9	Si _{0.12} P _{0.37} Al _{0.51} O ₂	2.16

Jiyida Silica Reagent Factory, China), orthophosphoric acid (85 wt.% H₃PO₄, Tianjin Kemiou Chemical Reagent Co., Ltd., China), pseudoboehmite (68 wt.% Al₂O₃, Shandong Aluminium Industry Co., Ltd., China), and copper (II) sulfate pentahydrate (Purity above 99 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd., China), respectively. MOR (Purity above 99 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd., China) was used as the template agent and TEPA (Purity above 99 wt.%, Tianjin Kemiou Chemical Reagent Co., Ltd., China) as the complexing agent of copper (II). First, the orthophosphoric acid and the pseudoboehmite were mixed with water, and the mixture was stirred for 1 h. Then the silica sol, MOR, TEPA, CuSO₄·5H₂O, and water were added and blended well. The next step of the synthesis was to add a controlled amount of SAPO-34 crystal seeds, obtained by mill grinding of the SAPO-34 powder for 1 h, into the mixture of precursors. To generate Cu/SAPO-34 catalyst samples with zeolite particle sizes 1, 4, 6, and 9 μm (to be discussed in the Results section), corresponding amounts of SAPO-34 crystal seeds were added as 0.5, 0.05, 0.01, and 0.005 wt.% of the theoretical final product (Cu/SAPO-34 catalyst), respectively. The particle size decreased with increasing amount of crystal seeds added. The mixture was sealed in an autoclave at 200 °C for 48 h. After this crystallization process, the sediment was separated from the liquid via centrifugation, washed with distilled water, and filtered. Finally, the zeolite powder was dried at 120 °C in an oven for 12 h and was calcined in a muffle furnace with air at 650 °C for 6 h.

These samples are named “Cu/SAPO-34-X”, where X stands for the average particle size measured by scanning electron microscopy (SEM). The Cu loadings in the catalysts were measured by inductively coupled plasma (ICP) and the Al, Si, and P content was determined by X-ray fluorescence (XRF), in Table 2.

2.2. Characterizations

The SEM experiment was carried out on a HITACHI S4800 field emission microscope. Before the scan imaging, the samples were immobilized on a carbon tape and covered with Au spray in order to become conductive.

X-ray diffraction (XRD, Bruker D8 Advance TXS, Cu K α radiation, $\lambda = 1.5418$ Å) was used to determine the structures and phase compositions. The XRD patterns were collected with a step size of 0.02° in the 2 θ range from 5° to 50°.

The surface area was measured by an F-Sorb 3400 volumetric adsorption–desorption apparatus down to 77 K and was calculated from the linear portion of the BET plot by measuring the N₂ isotherm. The Cu/SAPO-34 catalysts were pre-treated at 150 °C under vacuum for 3 h.

NH₃ temperature-programmed desorption (TPD) experiments were performed to evaluate the surface acidity of samples. A Nicolet IS10 FT-IR equipped with a 2 m gas cell was used to monitor the reactor outlet concentration of NH₃ at 5 s intervals. Prior to the TPD tests, the Cu/SAPO-34 catalysts were purged at 500 °C for 30 min using 500 mL/min 5% O₂/N₂, and then cooled down to 100 °C under N₂. NH₃ adsorption was performed at the same temperature using 500 mL/min 500 ppm NH₃/N₂ to saturate the samples. The samples were purged afterward with 500 mL/min N₂ to remove the weakly absorbed NH₃ at 100 °C. Finally, the catalysts were heated from 100 to 550 °C at a ramping rate of 10 °C/min.

دانلود مقاله



<http://daneshyari.com/article/60486>



- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات