

BiMnO₃ 钙钛石上低温 NH₃ 选择性催化还原 NO

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摘要: 首次将钙钛石 BiMnO₃ 用于低温条件下 NH₃ 选择性催化还原 NO 反应中. 结果表明, 该催化剂在 100~240 °C 范围内表现出较好的催化活性. 实验和理论计算显示, 相对于 LaMnO₃, BiMnO₃ 优异的低温催化活性归因于其较强的 Lewis 酸性和较多的表面吸附氧物种. 此外, BiMnO₃ 还具有较好的抗水、抗硫性能.

关键词: 钙钛石; 锰酸铋; 酸性; 选择催化还原; 低温

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BiMnO₃ Perovskite Catalyst for Selective Catalytic Reduction of NO with NH₃ at Low Temperature

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Abstract: A perovskite was used for selective catalytic reduction of NO with NH₃ (NH₃-SCR) at low temperature in the presence of excess oxygen. The BiMnO₃ perovskite catalyst showed high activity in NH₃-SCR at 100–240 °C. Experiment and DFT calculation showed that more Lewis acid sites and a high concentration of surface oxygen on BiMnO₃ as compared with LaMnO₃ were responsible for its better performance. In addition, BiMnO₃ was also resistant to water vapor and a mixture of H₂O and SO₂.

Key words: perovskite; bismuth manganite; acidity; selective catalytic reduction; low temperature

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氨气选择催化还原 (NH₃-SCR) NO_x (NO 和 NO₂) 是目前最有效的固定源 NO_x 消除技术. 实际应用中采用 V₂O₅-WO₃/TiO₂ 催化剂^[1]. 但该催化体系存在使用有毒 V₂O₅, 氧化能力较强和操作温度窗

口较窄等不足. 因此, 高效低温 (< 250 °C) SCR 催化剂成为新的研究热点^[2]. 近年来, 过渡金属氧化物 (Fe, V, Cr, Cu, Ce 和 Mn) 已用于低温 NH₃-SCR 反应, 其中, Mn 基催化剂因活性最好而被广泛研究.

Smirniotis 等^[3]报道了 20%Mn/TiO₂ 催化剂在 120 °C 下可有效转化 NO. Qi 等^[4]也发现铈锰复合氧化物催化剂在 120 °C 下可几乎完全消除 NO. 此外, 铬锰^[5]、铁锰^[6,7]和锡锰复合氧化物均表现出较好的催化活性^[8].

钙钛矿型氧化物 (通式 ABO₃) 具有结构明确、易于合成、价格低廉和高温稳定性好等优点^[9], 因而广泛应用于 CO 氧化^[10]、烃类氧化^[11]、NO_x 分解以及汽车尾气处理^[12~14]等领域中. 但到目前为止, 尚未见钙钛石用于低温 NH₃-SCR 反应的报道.

Mn 基钙钛石具有优异的氧化还原性能. Kim 等^[13]最近发现, LaMnO₃ 具有很高的氧化 NO 到 NO₂ 的催化活性. 但作为 NH₃-SCR 反应催化剂, 它还必须同时具有酸性位和氧化还原中心^[15~18], 而 LaMnO₃ 钙钛石的酸性较弱, 因此限制了其在 NH₃-SCR 反应的应用. 改变钙钛石的 A 位离子可调变 Mn 基钙钛石的酸碱性. 本文发现用 Bi 取代 La, 所得 BiMnO₃ 样品的酸性显著提高, 因而表现出较高的低温 NH₃-SCR 活性.

BiMnO₃, LaMnO₃ 以及 MnO₂ 催化剂制备及表征方法参照文献^[13,19~22]. Bi₂O₃ 由国药集团化学试剂有限公司提供. NH₃-SCR 催化剂活性评价在固定床石英反应器中进行. 反应采用 0.24 ml 催化剂 (40~80 目), 原料气组成为 0.1% NH₃, 0.1% NO 和 5% O₂, Ar 为平衡气, 空速 10000 h⁻¹, 反应稳定 0.5 h 后进行活性测试. 尾气各组分的含量采用四级杆质谱仪在线检测 (Hiden QIC-20), 从而算得 NO 转化率. 样品的 X 射线光电子能谱 (XPS) 分析在

ESCALAB MK II 型 X 射线光电子能谱仪上进行. 样品吸附吡啶红外 (FT-IR) 光谱在 Nicolet 410 型红外光谱仪上测定. CO₂ 程序升温脱附 (CO₂-TPD) 实验在配有质谱的自制装置上进行.

图 1 为不同催化剂上 NH₃-SCR 反应活性. 可以看出, 与 LaMnO₃ 和 MnO₂ 相比, BiMnO₃ 上 NO 转化率更高, 在 100 °C 时即高达 85%, 而 LaMnO₃ 在 180 °C 时 NO 转化率才达到 80%. 此外, Bi₂O₃ 几乎没有 NH₃-SCR 活性. 由此可见, Mn 基钙钛石的催化性能与其中 A 位阳离子的种类有关.

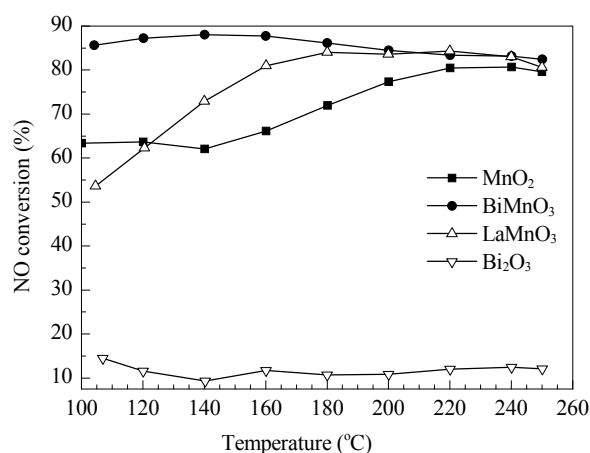


图 1 不同催化剂上 NH₃-SCR 反应活性

Fig. 1. Catalytic activities for NH₃-SCR over different catalysts. Reaction conditions: 0.24 ml catalyst, total flow rate = 40 ml/min, GHSV = 10000 h⁻¹, 0.1% NH₃, 0.1% NO, 5% O₂, Ar balance.

图 2(a) 为 LaMnO₃ 和 BiMnO₃ 的吡啶吸附 FT-IR 谱. 由图可见, BiMnO₃ 样品分别于 1450, 1490 和 1595 cm⁻¹ 处出现吸收峰, 其中 1450 和

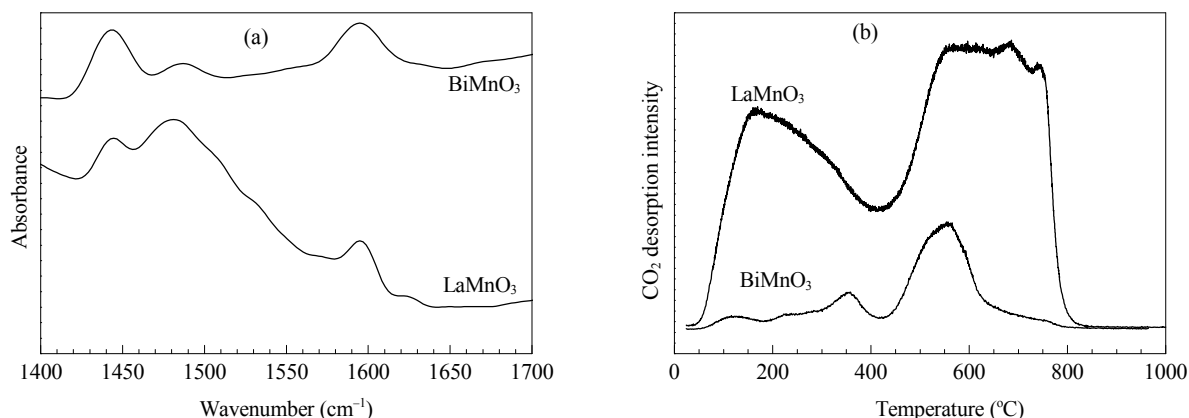


图 2 BiMnO₃ 和 LaMnO₃ 的吸附吡啶的 FT-IR 谱和 CO₂-TPD 谱

Fig. 2. FT-IR spectra of adsorbed pyridine (a) and CO₂-TPD spectra (b) of BiMnO₃ and LaMnO₃.

1595 cm^{-1} 可以归属为 Lewis 酸性位的吸收峰; 1490 cm^{-1} 为 Lewis 和 Brönsted 酸性位总和^[9]. LaMnO_3 出现与 BiMnO_3 相似的吸收峰, 但其强度都较弱, 表明 BiMnO_3 的 Lewis 酸性位更多. 此外, 这两个样品在 1540 cm^{-1} 处均未出现 Brönsted 酸的特征峰^[9,23], 说明 Mn 基钙钛石上的 B 酸酸量和强度均较低. 图 2(b) 为 BiMnO_3 和 LaMnO_3 的 CO_2 -TPD 谱. 由图可见, 用 Bi 取代 La 后, BiMnO_3 的碱性明显减弱, 从侧面表明其酸性较强. 对于低温 NH_3 -SCR 催化剂, 一般认为 NH_3 吸附于 Lewis 酸性位上, 再脱氢形成 NH_2 类活性中间物种; NH_2 与气相中的 NO 或者表面亚硝基类物种结合形成 NH_2NO , 随后分解形成 N_2 和 H_2O ^[2,22,24]. 此外, Smirniotis 等^[3]认为, 对于低温 SCR 反应, 催化剂上 Lewis 酸性位比 Brönsted 酸性位更重要. 可见, BiMnO_3 具有较强 Lewis 酸性, 有利于 NH_3 吸附与活化, 因而表现出更高的低温 NH_3 -SCR 催化活性.

为了进一步说明 BiMnO_3 的酸性, 本文采用密度泛函理论进行了计算. 电负性是原子的重要特性, 反映其吸引电子的能力^[25]. Sanderson 提出的电负性标度和电负性均衡原理已成功地用于计算不同化合物的键能, 并阐明了沸石分子筛的酸碱性^[26,27]. 根据该原理, 化合物的酸强度与氧离子上的负电荷密度有关; 即氧离子上的负电荷密度越小, 其酸性越强. 而 Bader 和 Voronoi 电荷分析法广泛应用于原子电荷定量表征^[28,29]. 表 1 为由 Bader 和 Voronoi 法算得 BiMnO_3 和 LaMnO_3 上各原子电荷密度. 由表 1 可见, Bi, La 和 Mn 原子提供电子给 O 原子.

表 1 Bader 和 Voronoi 法计算的 LaMnO_3 和 BiMnO_3 原子电荷

Table 1 Calculated values of atomic charges of LaMnO_3 and BiMnO_3 by Bader and Voronoi methods

Sample	Atom	Bader charge	Voronoi charge
BiMnO_3	Mn ₁	11.2917	11.4299
	Mn ₂	11.2748	11.4069
	O ₁	-7.1764	-7.2729
	O ₂	-7.1772	-7.2986
	O ₃	-7.1833	-7.3057
	Bi	13.1798	12.7044
LaMnO_3	Mn ₁	11.2963	11.4238
	Mn ₂	11.2964	11.4238
	O ₁	-7.2392	-7.4002
	O ₂	-7.2541	-7.3955
	O ₃	-7.2541	-7.3613
	La	8.9563	8.4191

Each Mn or O is located in a different coordination environment.

BiMnO_3 上氧的平均 Bader 和 Voronoi 电荷密度明显小于 LaMnO_3 的, 此外, Bi 的 Sanderson 电负性远远高于 La^[25]. 可见, BiMnO_3 的酸性更强, 从而有利于 NH_3 的吸附和活化, 因此表现出更高的低温 NH_3 -SCR 活性, 与实验结果一致.

图 3 为 BiMnO_3 和 LaMnO_3 的 Mn 2p 和 O 1s 的 XPS 谱. 可以看出, 两个样品在 639–660 eV 处均有两个峰, 可归属于 Mn 2p_{3/2} 和 Mn 2p_{1/2}^[5]. 通过分峰可将 Mn 2p_{3/2} 拟合为 641.7 和 624.2 eV 两个峰, 分别对应于 Mn⁴⁺ 和 Mn³⁺ 物种^[30]. 峰面积计算结果发现, BiMnO_3 和 LaMnO_3 催化剂表面层的 Mn⁴⁺/Mn³⁺ 比例非常接近. 图 3(b) 为 BiMnO_3 和 LaMnO_3 催化剂 O 1s XPS 谱. 由图可见, 该峰呈不对称分布, 表明催化剂表面存在多种氧物种. O 1s

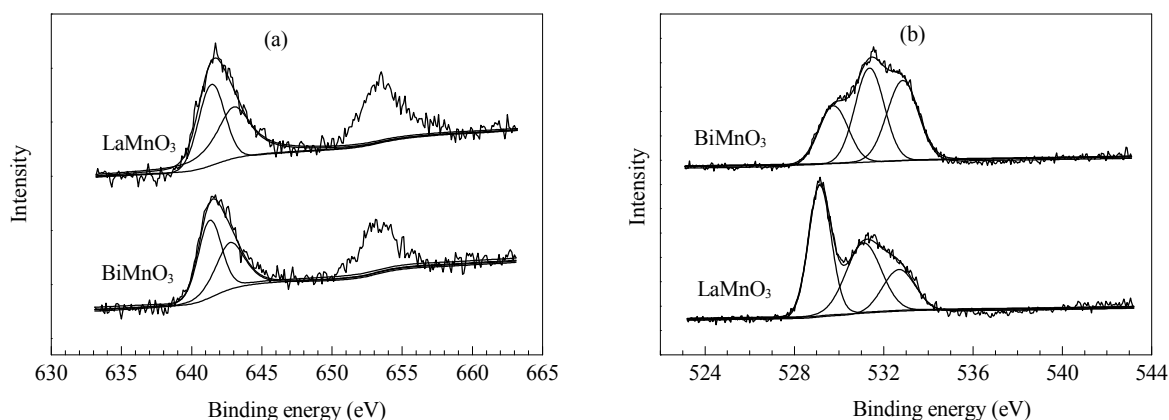


图 3 BiMnO_3 和 LaMnO_3 的 Mn 2p 和 O 1s XPS 谱

Fig. 3. Mn 2p (a) and O 1s (b) XPS spectra of BiMnO_3 and LaMnO_3 .

结合能越小,氧原子核周围电荷密度越大,而 LaMnO₃ 催化剂的 O 1s 结合能略小于 BiMnO₃,表明其碱性略强^[31],与理论计算结果一致。

将 O 1s 进行分峰拟合为三个峰:结合能在 529.6~530.0 eV 的为晶格氧 O_β (O²⁻); 531.3~531.7 eV 的可归属为表面吸附氧 O_α; 而结合能大于 533 eV 可能是吸附水^[30]。通过计算发现, BiMnO₃ 具有更高的表面吸附氧比例 (O_α/(O_α + O_β))。众所周知,表面吸附的氧物种最活泼。因此,高比例的表面吸附氧物种有利于 NO 的氧化以及 NH₃ 的活化。所以, BiMnO₃ 比 LaMnO₃ 更有利于以快速 SCR 方式消除 NO^[32]。

在固定源脱硝中,尾气即使经脱硫后,仍含有少量的水蒸气和 SO₂,从而引起催化剂失活。因此,需

要考察 H₂O 和 SO₂ 的存在对 BiMnO₃ 催化剂上 NH₃-SCR 反应性能的影响。催化剂先在 140 °C 连续稳定反应 1 h 后,再于 140 °C 分别考察 5% H₂O 的添加与 5% H₂O 和 0.01% SO₂ 同时添加对催化剂 SCR 活性的影响,结果见图 4。可以看出,通入 5% H₂O,反应 5 h 后 NO 转化率由初始的 85.5% 略降到 84.1%; 当停止通入 H₂O 后,催化剂活性又很快得到恢复。当同时通入 H₂O 和 SO₂ 时,反应 9 h 后 NO 转化率从 85.5% 下降至 82.7%,而停止后 BiMnO₃ 催化活性又迅速恢复到初始水平。可见, H₂O 和 SO₂ 对 BiMnO₃ 催化剂的毒化而造成的部分失活是可逆的,这主要是由 H₂O 和 SO₂ 与反应物之间的竞争吸附所致^[6,33]。因此, BiMnO₃ 具有较高的抗水和抗硫性能。

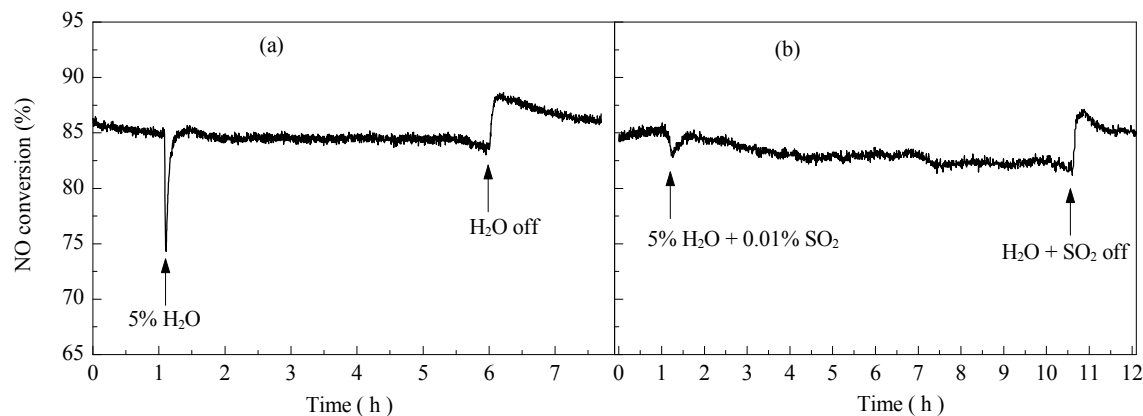


图 4 H₂O 及 SO₂ 对 BiMnO₃ 催化剂上 NH₃-SCR 活性的影响

Fig. 4. Effect of H₂O and SO₂ on SCR activity over BiMnO₃ catalyst. Reaction conditions: 0.24 ml catalyst (40–80 mesh), total flow rate = 40 ml/min, GHSV= 10000 h⁻¹, 140 °C, 0.1% NO, 0.1% NH₃, 0.01% SO₂, 5% H₂O, Ar balance.

综上所述, BiMnO₃ 钙钛石催化剂具有较高的低温 NH₃-SCR 催化活性,可归因于其较高的 Lewis 酸性以及表面吸附氧物种浓度。此外,该催化剂还具有较好的抗水和抗硫性能。

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英 译 文

English Text

Selective catalytic reduction of NO_x (NO and NO₂) by ammonia (NH₃-SCR) is currently regarded as the most effective technology for removing NO_x from stationary combustion processes. A commercial catalyst for NH₃-SCR is V₂O₅-WO₃/TiO₂ [1]. However, the problems of the toxicity of vanadia, high activity for the oxidation of SO₂ to SO₃, and relatively narrow temperature window have motivated continuing effects to develop a catalyst for low temperature SCR (below 250 °C) that can be used downstream of the electrostatic precipitator and desulfurization [2]. Transition metal (Fe, V, Cr, Cu, Ce, and Mn) oxide based catalysts have been explored intensively for NH₃-SCR at low temperature. Manganese based catalysts have received much attention because of their excellent performance. Smirniotis et al. [3] reported that 20 wt% Mn/TiO₂ was extremely active at 120

°C. Qi et al. [4] showed that a Mn-Ce mixed oxide catalyst yielded nearly 100% NO conversion at 120 °C at a high space velocity of 42000 h⁻¹. Cr-Mn mixed oxide [5], Fe-Mn based oxides [6,7], and MnO_x-SnO₂ catalysts have all displayed good performance [8].

Perovskite oxides with a general formula of ABO₃ have long been studied because of their well defined structure, ease of synthesis, low cost, and high thermal stability [9]. Previous studies have focused on CO oxidation [10], oxidation of hydrocarbons [11], and NO_x decomposition, and exhaust treatment [12–14]. No report on the application of perovskite oxides for NH₃-SCR at low temperature has been published. Mn-based perovskite oxides are of particular interest because of their excellent redox properties. LaMnO₃ was found to be active for NO oxidation [13]. Although NO oxidation to NO₂ is an important step in lean NO_x reduction, and NO₂ enhances the activities of NH₃-SCR, the poor acidity of the oxide has limited its use for NH₃-SCR because both redox and acidity properties are necessary for the SCR reaction [15–18]. However, it may be possible to develop a suitable perovskite catalyst by the substitution of the cations in positions A or B with others with different charge/radius ratios, which could generate acid sites. Here we report that the BiMnO₃ perovskite displayed a stronger acidity and good activity for NH₃-SCR at low temperature in comparison with LaMnO₃.

The BiMnO₃, LaMnO₃, and MnO₂ catalysts were synthesized and characterized using the methods described in the references [13,19–22]. Bi₂O₃ (analytical reagent) was obtained from Sinopharm Chemical Reagent Co, Ltd. China.

NH₃-SCR activity measurements were performed in a fixed bed quartz flow reactor at atmospheric pressure. The reaction conditions were 0.24 ml catalyst (40–80 mesh), GHSV = 10000 h⁻¹, 0.1% NO, 0.1% NH₃, 5% O₂, Ar balance. The activity data were collected after half an hour at each temperature after the catalytic reaction had reached steady state. The gas concentrations in the outlet stream were monitored by an online quadrupole mass spectrometer (QIC-20, Hiden, UK). NO conversion (X_{NO}) was calculated by $X_{\text{NO}} = (1 - [\text{NO}]_{\text{out}}/[\text{NO}]_{\text{in}}) \times 100\%$.

IR spectra of adsorbed pyridine were recorded on a Nicolet 410 FT-IR spectrometer. CO₂ temperature-programmed reduction (CO₂-TPD) was performed using a quadrupole mass spectrometer to record the CO₂ signals. X-ray photoelectron spectroscopy (XPS) was carried out on an ESCALAB MK II X-ray photoelectron spectrometer (VG Scientific, UK).

NO conversions over the BiMnO₃ and LaMnO₃ catalysts at reaction temperatures from 100 to 250 °C are shown in Fig. 1. BiMnO₃ showed a much higher NO conversion than those of LaMnO₃ and MnO₂. At 100 °C, 85% NO conversion was obtained and there was more than 85% NO conversion at

100–180 °C over BiMnO₃, while LaMnO₃ had the 80% NO conversion at above 160 °C. Bi₂O₃ displayed very low activity. This result clearly implied that the catalytic activity was associated with the kind of A cations in the Mn based perovskite.

The IR spectra of adsorbed pyridine were used to determine the acidic properties of the Mn-based perovskite catalysts. As shown in Fig. 2(a), the infrared spectra of pyridine adsorbed on BiMnO₃ exhibited bands at 1450, 1490, and 1595 cm⁻¹ due to the vibration modes of pyridine bonded to Lewis acidic sites [9]. Pyridine adsorbed on LaMnO₃ showed similar bands but with a lower intensity, suggesting a lower concentration of Lewis acid sites. The bands at 1540–1545 cm⁻¹, ascribed to Brønsted acid sites, were very small on the two samples, which indicated their very weak Brønsted acidic sites [9,23].

The basic properties of the metal oxide catalysts were measured by CO₂-TPD. Figure 2(b) shows typical CO₂ TPD-MS profiles obtained from the BiMnO₃ and LaMnO₃ catalysts, which demonstrated that both the strength and amount of basic sites were decreased by the substitution of Bi for La in the Mn based perovskite catalyst. It is generally accepted that the adsorption of NH₃ is the first step in NH₃ activation. For Mn-based catalysts, most researchers [2,22,24] believed that NH₃ is adsorbed on a Lewis acid center, and it is subsequently transformed into NH₂. NH₂ would react with gas phase NO or nitrite intermediates on the surface to give N₂ and H₂O. Smirniotis et al. [3] proposed that Lewis acidity was more important than Brønsted acidity for low temperature SCR catalysts. Hence, BiMnO₃ with a stronger Lewis acidity and a higher ratio of Lewis to Brønsted acidic site was better for the adsorption and activation of NH₃ and it displayed a higher activity for NH₃-SCR at low temperature as compared with LaMnO₃.

Density functional theory (DFT) calculations were performed to analyze the higher acidity of BiMnO₃ in comparison with LaMnO₃. Electronegativity is an important fundamental property of an atom, which represents the power of an atom in a compound to attract electrons to itself [25]. Sanderson's scale and the associated electronegativity equalization principle can be used for calculating the bond energies of various compounds [26] and for elucidating the acidic and basic properties of zeolites [27]. According to this principle, there is an increase in acid strength when there is a decrease in the negative charge on the oxygen. For the quantitative characterization of the charges at each atomic site, Bader and Voronoi charge analyses are widely used [28,29]. Table 1 presents the atomic charges for the atoms in BiMnO₃ and LaMnO₃ calculated with the Bader and Voronoi schemes. As expected, the Bi, La, and Mn atoms donated electrons, while the O atoms accepted them. The average Bader charges for the oxygen in BiMnO₃ was slightly less

than that in LaMnO₃, which was also true of the Voronoi charges. The Sanderson's electronegativity value of Bi (2.342) was significantly larger than that of La (0.154) [25]. The smaller oxygen charge and higher Sanderson's electronegativity for BiMnO₃ explain the stronger acidity of the catalyst, which will facilitate the adsorption and activation of NH₃. Therefore, the BiMnO₃ catalyst has the better NH₃-SCR activity at low temperature.

Figure 3 shows the Mn 2*p* and O 1*s* XPS spectra of BiMnO₃ and LaMnO₃. For the two samples, two main peaks due to Mn 2*p*_{3/2} and Mn 2*p*_{1/2} were observed from 639 eV to 660 eV [5]. By performing a peak-fitting deconvolution, the Mn 2*p*_{3/2} spectra were separated into two peaks at 642.7 eV (Mn⁴⁺) and 641.2 eV (Mn³⁺) [30]. The value of the Mn⁴⁺/Mn³⁺ ratio in the surface layer of BiMnO₃ (1.07) was basically the same as that of LaMnO₃ (1.17).

As shown in Fig. 3(b), an asymmetric peak was observed in the XPS spectra of O 1*s* for the two catalysts. The binding energy of O 1*s* in LaMnO₃ was slightly lower than that of BiMnO₃. A decrease of the O 1*s* binding energy indicated an increase of the electron density around the O nucleus, which indicated an increased basicity of LaMnO₃ in comparison with BiMnO₃ [31]. This was consistent with the above DFT calculations.

The peak at 529.6–530.0 eV corresponded to lattice oxygen O_β (O²⁻) and the peak at 531.3–531.7 eV was assigned to chemisorbed oxygen (denoted as O_α). The peak at above 533 eV was associated with adsorbed molecular water [30]. The value of O_α/(O_α + O_β) in the surface layer of BiMnO₃ (0.62) was much higher than that of LaMnO₃ (0.44). It is commonly accepted that surface chemisorbed oxygen is the most active oxygen and highly active in oxidation reactions such as the oxidation of NO to NO₂, which benefits the adsorption of NH₃. So, BiMnO₃ with more O_α was better for the reduction of NO in the SCR process due to the occurrence of “fast SCR” [32].

Flue gases always contain small amounts of SO₂ and H₂O even after desulfurization. So it is necessary to investigate the influence of H₂O and SO₂ on the low temperature SCR reaction. The effect of H₂O or SO₂ + H₂O on the NO conversion over the BiMnO₃ catalyst was monitored as a function of time on stream at 140 °C. Before introducing H₂O or H₂O + SO₂, the SCR reaction was stabilized for 1 h at 140 °C. As indicated in Fig. 4, when only 5% H₂O was introduced into the feed gas mixture, the NO removal efficiency showed a negligible decrease from 85.5% to 84.1% after 5 h. After the removal of H₂O from the feed gas mixture, the NO removal was efficiency recovered to the original level. When 5% H₂O and 0.01% SO₂ were simultaneously added to the reactants, the NO conversion was decreased from 85.5% to 82.7% during the following 9 h and then returned quickly to 85.5% at which point it stabilized. These results suggested

that the poisoning effect of H₂O or H₂O and SO₂ on BiMnO₃ catalyst was reversible, and was mainly caused by the competitive adsorption of H₂O, SO₂, and reaction gases on the catalyst [6,33].

In summary, the BiMnO₃ perovskite catalyst showed good activity in NH₃-SCR at low temperature. The higher Lewis

acidity and high concentration of surface chemisorbed oxygen were responsible for the better activity. In addition, BiMnO₃ was resistant to poisoning by H₂O and SO₂.

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