

## 钾对氧化铜催化活性炭还原 NO 反应的助催化作用

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**摘要:** 研究了活性炭负载的 Cu-K-O 复合氧化物催化剂上碳还原 NO 的反应. 结果表明, K 的加入可有效地提高 CuO 催化剂的活性和稳定性, 当 Cu/K 的质量比为 2 时催化性能最佳. X 射线衍射、X 射线光电子能谱和程序升温脱附-质谱等结果表明, K 与 Cu 间的协同作用可促进表面碳活化中心与表面氧化物生成 CO<sub>2</sub> 的反应, 保持表面 Cu<sup>2+</sup> 活性中心的数量, 从而有利于 Cu<sup>2+</sup>/Cu<sup>+</sup> 反应循环的进行.

**关键词:** 钾; 氧化铜; 活性炭; 一氧化氮; 选择性催化还原

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## Promoting Role of Potassium on the Catalytic Performance of Copper Oxide for the Reduction of NO by Activated Carbon

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**Abstract:** The reduction of NO by activated carbon over a Cu-K-O mixed oxide catalyst was investigated. We found that the addition of K to CuO obviously improved its catalytic performance and stability, and the optimum Cu/K weight ratio is 2. Characterization by X-ray photoelectron spectroscopy, X-ray diffraction, and temperature-programmed desorption shows that the presence of K can promote the reaction between the surface carbon active sites and the surface oxygen species to form CO<sub>2</sub> by a synergetic effect between Cu and K. Additionally, a higher surface concentration of Cu<sup>2+</sup> is retained, which favors the Cu<sup>2+</sup>/Cu<sup>+</sup> reduction cycle on the active sites.

**Key words:** potassium; copper oxide; activated carbon; nitrogen monoxide; selective catalytic reduction

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各种燃烧装置中产生的氮氧化物 (NO<sub>x</sub>) 是一种非常有害的大气污染物, 会造成酸雨和光化学烟雾, 同时对臭氧层造成严重的破坏<sup>[1]</sup>. 因此, NO<sub>x</sub> 的净化处理引起了全世界的广泛关注. 为了控制 NO<sub>x</sub> 的排放, 人们已经发展了多种高效的 NO<sub>x</sub> 净化技术<sup>[2]</sup>, 如负载型金属氧化物催化剂, 对以 NH<sub>3</sub> 为还原剂的

NO<sub>x</sub> 选择性催化还原 (SCR-NO<sub>x</sub>) 具有很高的活性和选择性, 是目前 NO<sub>x</sub> 脱除最有效和应用最广的方法, 但 NH<sub>3</sub> 的储运困难, 未反应的 NH<sub>3</sub> 会对大气环境造成二次污染<sup>[3]</sup>.

人们尝试用碳材料替代 NH<sub>3</sub> 用作还原剂, 进行 SCR-NO<sub>x</sub> 反应, 从而可以避免过量 NH<sub>3</sub> 的两次污染

及其储运问题. 在众多碳材料中, 活性炭 (AC) 因具有很高的比表面积、丰富的孔结构和易于调变的表面官能团等性质, 被广泛用作吸附剂和催化剂载体. 研究表明, K<sup>[4]</sup> 和一些过渡金属 (Fe, Cu, Co 和 Ni)<sup>[5–7]</sup> 可用作 AC 和焦炭还原 NO 反应的催化剂, 生成 N<sub>2</sub> 选择性可达 100%.

在碳还原 NO<sub>x</sub> 反应催化剂中, CuO 和 K<sub>2</sub>O 均有较高的催化活性, 但 CuO 稳定性较差<sup>[4,8]</sup>. 在同时消除柴油发动机尾气中 NO<sub>x</sub> 和碳微粒反应中, Cu-K-O 复合氧化物具有较高的催化活性<sup>[9]</sup>, 但 K 在催化剂中的作用还不清楚. 然而, 在针对发电厂等尾气中 NO<sub>x</sub> 的净化而提出的 AC 还原 NO<sub>x</sub> 的过程中, AC 作为一种还原剂不希望被 O<sub>2</sub> 氧化而消耗掉, 这与柴油发动机尾气中 NO<sub>x</sub> 和碳微粒需同时被消耗的净化过程不同. 将过渡金属 (如 Fe, Co 和 Cu) 负载在 AC 上用作碳和 NO 反应的催化剂已有报道<sup>[6,7,10,11]</sup>, 我们发现 CuO 对低温下 AC 还原 NO 的反应有较高催化活性<sup>[6]</sup>. 另外, 作为一种改性剂, K 的存在能提高 AC 表面吸附 NO<sub>x</sub> 的能力<sup>[12]</sup>. 因此, 以 AC 还原 NO<sub>x</sub> 为目标反应, 研究催化剂中 Cu 与 K 间协同作用, 以及通过 Cu 与 K 间协同作用来改善催化剂活性和稳定性, 抑制 CuO 催化剂的失活有重要意义.

因此, 本文考察了 K 的加入对 CuO 催化剂催化 AC 还原 NO<sub>x</sub> 反应性能的影响, 并讨论了催化剂中 Cu 与 K 间的协同效应.

## 1 实验部分

### 1.1 催化剂的制备

选用国产椰壳 AC 作为载体和还原剂 (上海活性炭有限公司, 比表面积为 620 m<sup>2</sup>/g), 使用前将其破碎并筛选出 20–40 目颗粒, 经去离子水洗涤后在 110 °C 干燥过夜.

采用等体积浸渍法制备催化剂. 按比例配制成 Cu(NO<sub>3</sub>)<sub>2</sub> 和 KNO<sub>3</sub> 的水溶液, 将 AC 在室温下浸泡 4 h, 然后在 40 °C 老化 4 h, 60 °C 老化 2 h, 80 °C 老化 0.5 h. 制备的样品经 120 °C 烘干过夜后, 在 300 °C 的 N<sub>2</sub> 气氛中焙烧 2 h. 经完全燃烧碳载体后测定 Cu 和 K 的含量为 10%. 2Cu-K-O/AC 催化剂由 6.67% Cu 和 3.33% K 构成, Cu/K 的质量比为 2.

### 1.2 催化剂的表征

样品的比表面积在 Micromeritics ASAP 2020

型比表面积仪上测定. 样品在 120 °C 和 1 × 10<sup>-4</sup> Pa 条件下脱气 10 h 后, 于 -196 °C 测定 N<sub>2</sub> (99.99%) 的吸附等温线, 使用 BET 方法计算比表面积. 催化剂的 X 射线衍射 (XRD) 谱在 Bruker/D8 Focus 型 X 射线衍射仪上测定, Cu K<sub>α</sub> 辐射源, 工作电压和电流分别为 40 kV 和 40 mA. X 射线光电子能谱 (XPS) 在 Thermo ESCALAB 250 型光谱仪上测定, 仪器的真空度为 1 × 10<sup>-7</sup>~2 × 10<sup>-8</sup> Pa, 用 150 W 单色 Al K<sub>α</sub> 射线 ( $h\nu=1486.6$  eV) 为激发源, 样品的结合能用表面污染碳 (C 1s 284.6 eV) 进行荷电校正.

样品的程序升温脱附 (TPD-MS) 实验在自制的反应装置上进行<sup>[13]</sup>, 采用石英管反应器 ( $\varphi$  10 mm × 300 mm), 管式电炉程序升温加热. 反应尾气利用四极质谱仪 (INFICON IPC400, 英国) 在线跟踪分析. 在 NO 程序升温脱附 (NO-TPD) 实验中, 200 mg 样品于 120 °C 用 He (50 ml/min) 吹扫 1 h 后降温至 50 °C, 在此温度下用 1% NO-99% Ar (50 ml/min) 吸附 30 min 后, 切换成纯 He 气吹扫样品至质谱仪跟踪信号稳定 (即无残留或物理吸附 NO 存在) 后, 进行程序升温脱附, He 气流量 50 ml/min, 升温速率 10 °C/min.

### 1.3 催化剂的性能评价

AC 还原 NO 反应在石英管固定床微型反应器 ( $\varphi$  10 mm × 300 mm) 中进行, 催化剂用量 500 mg, 反应空速 GHSV = 20000 h<sup>-1</sup>, 反应气中 NO 浓度为 0.2%, Ar 为稀释气, 常压. AC 还原 NO 反应在两种模式下进行, 以 3 °C/min 从 100 °C 程序升温至 500 °C; 400 °C 恒温反应. 反应产物主要为 N<sub>2</sub>, N<sub>2</sub>O 生成量可忽略不计. 反应原料气及产物由两台气相色谱仪 (福立 GC9790, 中国温岭; 科创 GC-8810, 中国上海) 进行在线分析, 其中 Poropak Q 分离柱用于分析 CO<sub>2</sub>, N<sub>2</sub>O 和 H<sub>2</sub>O; 5A 分子筛分离柱用于分析 O<sub>2</sub>, N<sub>2</sub>, NO 和 CO, TCD 检测器, Ar 作载气.

## 2 结果与讨论

### 2.1 催化剂上 AC 还原 NO 反应活性

图 1 为 K 含量对 Cu-K-O/AC 催化 AC 还原 NO 反应性能的影响. 由图可见, 当以 K<sub>2</sub>O 为催化剂时, NO 还原 50% 时的温度 ( $T_{50}$ ) 为 380 °C; 当以 CuO 为催化剂时,  $T_{50}$  为 330 °C, 表明 K<sub>2</sub>O 的催化活性远低于 CuO. 当 K 负载量为 3.33% 时, 即 Cu/K

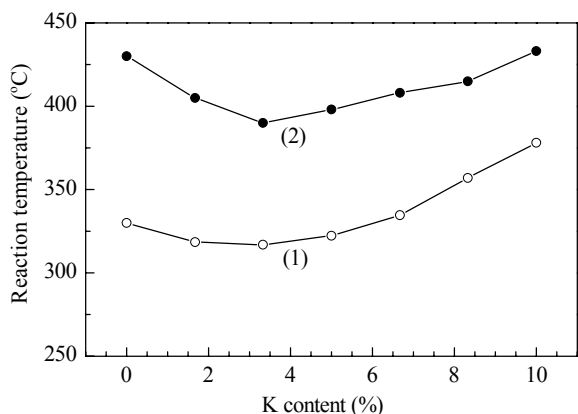


图1 K含量对Cu-K-O催化AC还原NO反应性能的影响

Fig. 1. Effect of K content on the reduction of NO by AC over the Cu-K-O catalyst for  $T_{50}$  (1) and  $T_{100}$  (2) are the temperatures at which 50% and 100% of the NO was reduced, respectively.

的质量比为2时, 2Cu-K-O/AC催化剂活性最高,  $T_{50}$ 仅为317 °C. 另外, 在 $K_2O$ 与CuO上NO还原反应的NO全部还原时的温度( $T_{100}$ )分别为433和430 °C, 两者活性比较接近. 当在CuO中加入K后,  $T_{100}$ 明显下降, 当K和Cu的负载量分别为3.33%和6.67%时,  $T_{100}$ 仅为390 °C.

图2为不同催化剂上AC还原NO反应活性随温度的变化. 由图可见, 在300 °C以下反应时, 2Cu-K-O/AC和CuO/AC的催化活性相近, 而 $K_2O$ /AC几乎没有催化活性; 当反应温度大于300 °C时, K的加入显著提高了CuO催化活性.

图3为不同催化剂上AC还原NO反应活性随

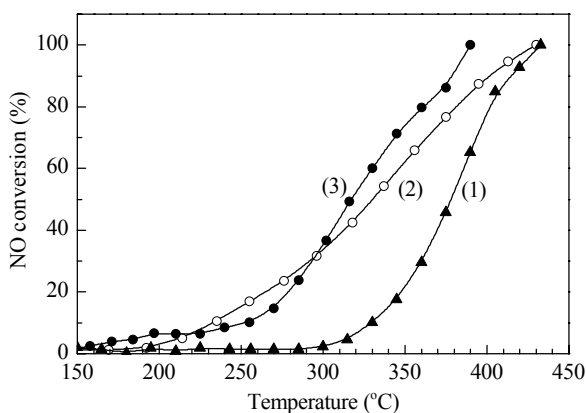


图2 反应温度对不同催化剂上AC还原NO反应性能的影响

Fig. 2. Effect of reaction temperature on the catalytic performance of the  $K_2O$ /AC (1), CuO/AC (2), and 2Cu-K-O/AC (3) catalysts for the reduction of NO by AC.

反应时间的变化. 由图可见, 在 $K_2O$ /AC催化剂上NO转化率保持在74%左右, 而在CuO/AC催化剂上, 随着反应时间的延长而急剧下降, NO转化率从起始时的90%降至300 min时的50%. 当以2Cu-K-O/AC为催化剂时, 反应300 min内NO转化率始终保持在95%以上. 由此可见, 2Cu-K-O/AC催化剂性能明显优于CuO和 $K_2O$ 催化剂. 3个催化剂的比表面积(CuO/AC为492 m<sup>2</sup>/g, 2Cu-K-O/AC为430 m<sup>2</sup>/g和 $K_2O$ /AC为465 m<sup>2</sup>/g)比较接近, 说明K对CuO的助催化作用主要得益于CuO和 $K_2O$ 间协同效应.

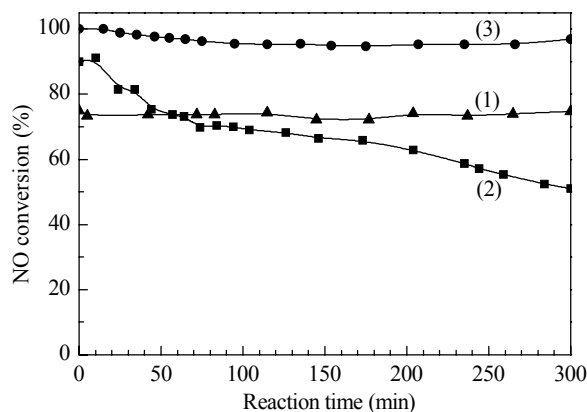


图3 反应时间对不同催化剂上AC还原NO反应性能的影响

Fig. 3. Effect of reaction time on the catalytic performance of the  $K_2O$ /AC (1), CuO/AC (2), and 2Cu-K-O/AC (3) catalysts for the reduction of NO by AC.

## 2.2 XPS 结果

表1为反应前后CuO/AC和2Cu-K-O/AC催化剂的Cu 2p<sub>3/2</sub>数据. 研究表明, 只有Cu<sup>2+</sup> (3d<sup>9</sup>)的Cu 2p<sub>3/2</sub>具有(2p→3d)卫星峰, 且两者相差约10 eV, 因此可以通过是否存在卫星峰来区分Cu<sup>2+</sup>是否为低价态的Cu<sup>0</sup>[14,15]. 由于Cu<sup>0</sup> (932.7 eV)和Cu<sup>+</sup> (932.6

表1 反应前后CuO/AC和2Cu-K-O/AC的Cu 2p<sub>3/2</sub>结合能

Table 1 Cu 2p<sub>3/2</sub> binding energies ( $E_b$ ) for CuO/AC and 2Cu-K-O/AC before and after the reaction

Catalyst	$E_b$ before reaction (eV)		$E_b$ after reaction (eV)	
	Cu <sup>0</sup> , Cu <sup>+</sup>	Cu <sup>2+</sup>	Cu <sup>0</sup> , Cu <sup>+</sup>	Cu <sup>2+</sup>
CuO/AC	932.7 (81.5%)	934.5 (18.5%)	932.6 (92.6%)	934.9 (7.4%)
2Cu-K-O/AC	932.6 (86.9%)	934.2 (13.1%)	932.7 (87.5%)	934.2 (12.5%)

eV)<sup>[16]</sup>结合能差别较小,因此可同归为低价 Cu 物种.

由样品的 Cu 2p<sub>3/2</sub> XPS 谱(未给出)可见,由于反应过程中 Cu<sup>2+</sup>被 AC 还原至较低价态(Cu<sup>+</sup>和 Cu<sup>0</sup>),使得较低结合能的峰增强和 Cu<sup>2+</sup>卫星峰减弱.在 400 °C 反应后,催化剂中 Cu<sup>2+</sup>的 Cu 2p<sub>3/2</sub>峰明显减弱,表明 Cu<sup>2+</sup>的数量减少,这是由于在反应中一些 Cu<sup>2+</sup>被 AC 还原所致<sup>[17,18]</sup>.由表 1 可见,使用后的 CuO/AC 催化剂中 Cu<sup>2+</sup>所占比例由 18.5% 降至 7.4%;而 2Cu-K-O/AC 催化剂在反应前后的 Cu<sup>2+</sup>数量变化较小, Cu<sup>2+</sup>所特有的卫星峰也变化不大.可见, K 的存在能明显提高 CuO/AC 催化剂的稳定性.在反应过程中 CuO/AC 的 Cu<sup>2+</sup>被 AC 还原至低价态,难以再氧化至 Cu<sup>2+</sup>,因而稳定性较差;而该催化剂具有较高初活性则是由于在催化剂表面具有较多的 Cu<sup>2+</sup>所致. K 的加入促进了 2Cu-K-O/AC 催化剂中低价 Cu 再氧化至 Cu<sup>2+</sup>,有利于 Cu 活性物种的氧化还原循环,因而 2Cu-K-O/AC 催化剂稳定性提高.

### 2.3 XRD 结果

图 4 为在反应前后 CuO/AC 和 2Cu-K-O/AC 催化剂的 XRD 谱.由图可见,在新鲜催化剂上均有两个宽化的石墨化结构的峰,表明 AC 的石墨化程度较低,并在 35.5° 和 38.7° 处出现 CuO 衍射峰. K 的存在使得 2Cu-K-O/AC 样品上 CuO 的衍射峰变弱,

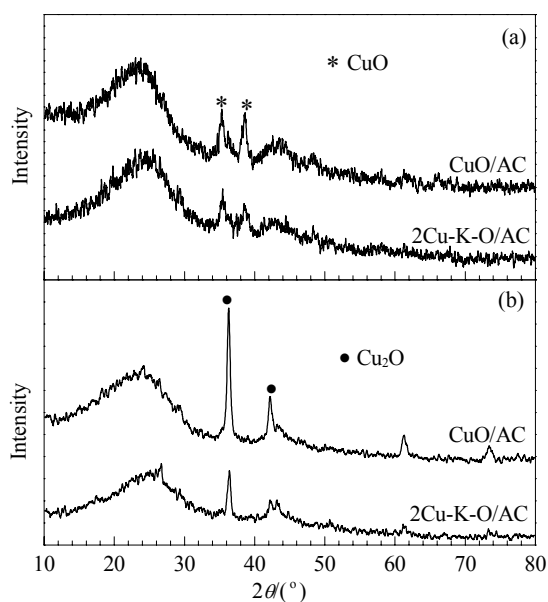


图 4 反应前后 CuO/AC 和 2Cu-K-O/AC 催化剂的 XRD 谱

Fig. 4. XRD patterns for CuO/AC and 2Cu-K-O/AC before (a) and after the reduction (b) of NO at 400 °C for 300 min.

这是由于 K 的加入使得 Cu 负载量从 10% 降至 6.67%. 在 400 °C 反应 300 min 后, CuO/AC 和 2Cu-K-O/AC 催化剂在 36.4° 和 42.3° 处出现 Cu<sub>2</sub>O 的衍射峰.另外,由于生成的 Cu<sup>0</sup>较少或高度分散于 AC 上,没有观察到 Cu<sup>0</sup>的衍射峰.由此可见,反应过程中 CuO 被 AC 还原至低价态的 Cu 物种,而 K 的加入抑制了 Cu<sub>2</sub>O 的产生,这是由于 K 的存在使得表面 Cu<sup>2+</sup>浓度增加,并使得 CuO 负载量相对降低.

### 2.4 TPD 结果

图 5 为不同催化剂样品的 NO-TPD 谱.由图可见, K<sub>2</sub>O/AC 上 NO 的脱附峰最大,其次是 2Cu-K-O/AC 和 CuO/AC,而 AC 上的最小;另外在 4 个催化剂上 NO 脱附峰顶温度分别为 ~400, ~250, ~210 和 ~135 °C. NO 脱附峰的位置和强度取决于催化剂样品对 NO 的吸附强度和吸附量.作为一种酸性气体, NO 可以很强烈地吸附在碱性的 K<sub>2</sub>O/AC 上,因此其吸附 NO 的强度和数量最多,而 K 的加入有助于提高 CuO/AC 样品吸附 NO 的能力.

另外,由以上各样品在 NO-TPD 中产生的 N<sub>2</sub>-TPD 谱可见,在 K<sub>2</sub>O/AC 样品上 N<sub>2</sub>脱附峰最强,峰顶温度为 420 °C; 2Cu-K-O/AC 有两个 N<sub>2</sub>的脱附

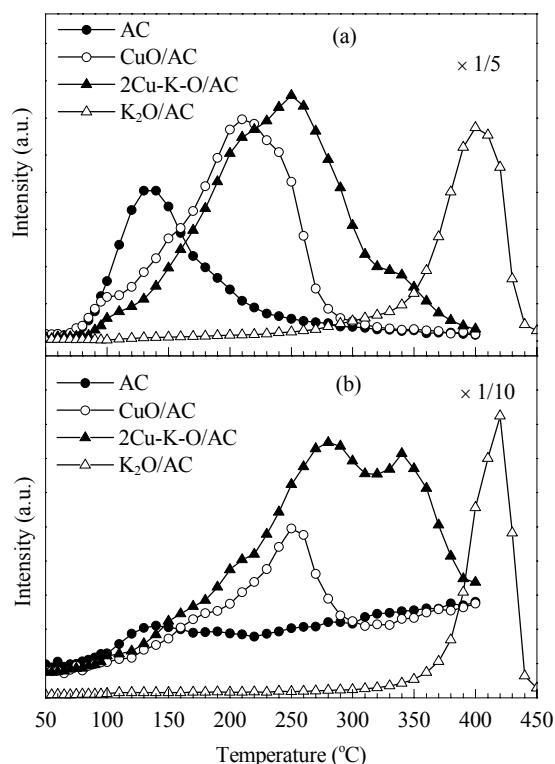


图 5 不同催化剂在 NO-TPD 过程中 NO 和 N<sub>2</sub> 脱附曲线  
Fig. 5. Desorption curves of NO (a) and N<sub>2</sub> (b) during NO-TPD.

峰, 分别位于 280 和 340 °C; CuO/AC 在 250 °C 有一个小的脱附峰; 由于 AC 很难还原 NO, 所以其上 N<sub>2</sub> 脱附峰最小, 峰顶温度在 135 °C. 由此可见, K 的加入有利于提高 CuO/AC 对 NO 的吸附能力, 因而 AC 还原 NO 反应活性增加.

图 6 为不同催化剂在 He-TPD 过程中 CO<sub>2</sub> 和 CO 脱附曲线, CO<sub>2</sub> 和 CO 是表面碳活性中心和含氧官能团反应的产物<sup>[7]</sup>. 由图可见, 在 K<sub>2</sub>O/AC 样品上有一大一小两个 CO<sub>2</sub> 脱附峰, 分别位于 200 和 420 °C; CuO/AC 样品的两个 CO<sub>2</sub> 脱附峰分别位于 255 和 450 °C; K 的加入使得 CuO/AC 的 CO<sub>2</sub> 脱附峰强度明显增加, 也就是说, K-Cu 间协同效应促进了表面碳活性中心与表面氧物种的反应. AC 样品在 150~500 °C 处有一个较大的 CO<sub>2</sub> 脱附峰, 归因于表面羧酸官能团与 C 反应生成 CO<sub>2</sub><sup>[6]</sup>, 负载 CuO 和/或 K<sub>2</sub>O 后, AC 表面上该 CO<sub>2</sub> 脱附峰明显减小.

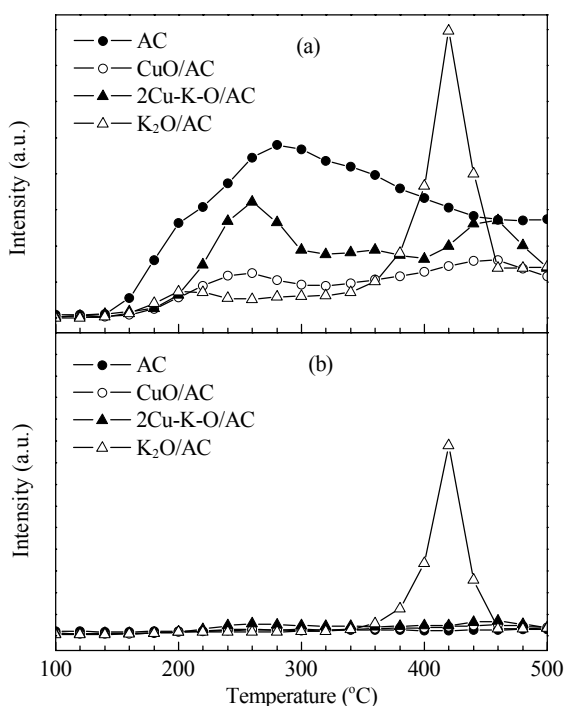


图 6 不同催化剂在 He-TPD 过程中 CO<sub>2</sub> 和 CO 的脱附曲线

Fig. 6. Desorption curves of CO<sub>2</sub> (a) and CO (b) during He-TPD.

同时, 由图 6(b) 可见, AC, CuO/AC 和 2Cu-K-O/AC 上几乎检测不到脱附的 CO, 而在 K<sub>2</sub>O/AC 上于 420 °C 附近出现一个较大的 CO 脱附峰, 同时伴随着 CO<sub>2</sub> 的脱附, 这表明 K 的存在促进了表面碳活性中心与表面氧物种反应生成 CO<sub>2</sub> 和 CO.

K 的存在可以弱化 AC 表面 C-C 键, 有助于在碳表面形成表面碳活性中心 (或者说是活性的碳物种)<sup>[19,20]</sup>, 从而促进了碳物种与表面氧物种的反应. 这与在氧化铁中加入 K 相类似, 即 K 的加入有利于电子向 Fe 转移, 使铁离子更易被碳还原<sup>[9]</sup>. 当 NO 吸附在 AC 表面时, K 的存在有助于 CuO/AC 表面形成活化的碳物种和 NO 的吸附, 从而促进了 NO 还原反应的进行.

### 3 结论

K 是 CuO 催化 AC 还原 NO 反应高效的助催化剂, 当 Cu/K 的质量比达 2/1 时, Cu-K-O/AC 催化剂具有较高的活性和稳定性. K 的加入提高了 CuO 吸附 NO 的能力, 使得催化剂表面 Cu<sup>2+</sup> 含量较高, 促进了 Cu<sup>2+</sup>/Cu<sup>+</sup>(Cu<sup>0</sup>) 间氧化还原循环的进行, 从而改善了 CuO 催化剂性能. 同时 K 的存在能有效地促进表面碳活性中心与表面氧物种反应生成 CO<sub>2</sub> 和 CO. 当以 Cu-K-O/AC 为催化剂, NO 完全转化温度仅为 390 °C, 运行 300 min, 其保持活性.

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### 英 译 文 *English Text*

The removal of NO<sub>x</sub> from the exhaust gases of various combustion sources is still a problem for the pollution control of waste gas, and it has gained worldwide attention in recent years. Intense research effort has been devoted to the control of NO<sub>x</sub> emissions [2] and to the development of highly effective technologies for NO<sub>x</sub> removal because NO<sub>x</sub> has been identified as a component in acid rain and photochemical smog, and it has been implicated in the destruction of ozone [1]. Using ammonia as a reducing agent, supported metal oxide catalysts exhibit high activity and selectivity for the selective catalytic reduction (SCR) of NO, which is the most widely used technology for NO<sub>x</sub> elimination. However, the emission of unreacted ammonia may also pollute the environment, and the storage and transportation of ammonia is not desirable [3].

The use of carbon materials as reducing agents instead of ammonia has been proposed as a possible way to reduce NO<sub>x</sub> and thus the re-pollution effect of unreacted ammonia and its storage and transportation can be avoided. Among the various carbon materials, activated carbon (AC) with its high surface area, bulk porosity, and various surface chemical properties has been recognized as a good adsorbent and support. Potassium [4] and some transition metals (Fe, Cu, Co, and Ni) [5–7] have been used as catalysts for NO reduction by activated carbon and other chars. One of the advantages of this process is the high selectivity to N<sub>2</sub> of almost 100%.

Copper oxide, as a conventional oxidation catalyst, has high activity but low stability and potassium oxide has good stability and good activity for the oxidation of carbon by NO<sub>x</sub> [4,8]. Simultaneous removal of NO<sub>x</sub> and carbon soot from a simulated diesel engine exhaust, the Cu-K-O mixed oxide exhibits a better catalytic activity [9]. The role of K in this catalyst for the simultaneous removal of NO<sub>x</sub> and soot is still unclear while carbon soot is mainly combusted by oxygen.

However, the process of NO<sub>x</sub> removal by AC reduction during deNO<sub>x</sub> at the exhausts of coal-fired power plants is different from that of the simultaneous removal of NO<sub>x</sub> and soot in diesel engine exhausts. This is because AC as a reducing agent in the deNO<sub>x</sub> process for power plant exhaust gas cannot be oxidized by oxygen.

Transition metals (Fe, Co, and Cu) supported on AC have been studied as catalysts for the reaction of carbon and NO [6,7,10,11]. We have previously found that Cu is highly active for the reduction of NO by AC at low temperature [6]. As a modifier, the presence of K on the surface of AC can improve its ability to adsorb NO<sub>x</sub> [12]. Therefore, an investigation on the synergetic effect between Cu and K for the improvement of the catalytic activity and stability of NO reduction by AC and the inhibition of CuO deactivation during the reduction of NO by AC is warranted.

In this paper, the effect of K addition to CuO on the catalytic performance of Cu-K-O for NO reduction by AC was studied and factors affecting the activity as well as the stability of the CuO catalyst for NO reduction by AC were also investigated. Based on the surface reaction of the oxygen species and the carbon active sites, the synergetic effect between copper oxide and potassium oxide for the improvement of the catalytic activity and the stability are discussed.

## 1 Experimental

### 1.1 Catalyst preparation

The original activated carbon (AC, Shanghai Activated Carbon Co., Ltd.) was prepared by the carbonization of coconut shells under nitrogen and further activation with steam. Its BET surface area was 620 m<sup>2</sup>/g. The AC sample was then sieved to 20–40 mesh, washed with deionized water and dried at 110 °C overnight.

The Cu-K-O/AC catalyst was prepared by impregnating AC with an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub> at room temperature for 4 h, and then aged at 40 °C for 4 h, at 60 °C for 2 h, and at 80 °C for 0.5 h, respectively. After being dried in air overnight at 120 °C, the catalyst sample was calcined in N<sub>2</sub> at 300 °C for 2 h. The loading of Cu and K in the Cu-K-O/AC catalyst was about 10%, which was determined by burning off the carbon supports and excluding the ash content of AC. 2Cu-K-O/AC consisted of 6.67% Cu and 3.33% K on AC, in which the weight ratio of Cu/K was 2.

### 1.2 Catalyst characterization

The BET surface areas of the samples were measured on a Micromeritics ASAP 2020 instrument by N<sub>2</sub> adsorption at

-196 °C and the BET method. The samples were degassed at 120 °C and  $1 \times 10^{-4}$  Pa for 10 h before the measurements. The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker/D8 Focus X-ray powder diffractometer with Cu  $K_{\alpha}$  radiation and with a working voltage of 40 kV and a current of 40 mA. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 with Al  $K_{\alpha}$  radiation ( $h\nu = 1486.6$  eV). The pressure of the analyzer chamber was  $1 \times 10^{-7}$  to  $2 \times 10^{-8}$  Pa. All the binding energies ( $E_b$ ) were calibrated using the C 1s line (284.6 eV) of adventitious carbon. The Cu  $2p_{3/2}$  peaks were deconvoluted using the Shirley-type baseline and an iterative least-squares optimization algorithm.

Temperature-programmed desorption (TPD-MS) [13] was carried out in a quartz flow reactor ( $\Phi$  10 mm  $\times$  300 mm) system coupled to a quadrupole mass spectrometer (IPC400, INFICON Co. Ltd.). In the NO-TPD experiments, 200 mg sample was used after being pretreated 120 °C in a He flow of 50 ml/min for 1 h, and then cooled to 50 °C. After 1% NO-99% Ar (50 ml/min) was passed through the sample for 30 min, the sample was flushed with He at the same temperature until no NO was detected. The NO-TPD of the sample was performed in 50 ml/min He and the heating rate of 10 °C/min. In the direct TPD testing of the sample the He flow was also 50 ml/min.

### 1.3 Catalytic performance

The catalytic reduction of NO by AC was carried out at atmospheric pressure in a fixed bed microreactor ( $\Phi$ 10 mm  $\times$  300 mm). The outlet gases were analyzed by two gas chromatographs (Fuli 9790, KeChuang 8810) with two thermal conductivity detectors and two separation columns. A Poropak Q column was used for the separation of CO<sub>2</sub>, N<sub>2</sub>O, and H<sub>2</sub>O, and a 5 A zeolite column was used for the separation of NO, N<sub>2</sub> and CO. A 500 mg catalyst was used and the space velocity (GHSV) was 20000 h<sup>-1</sup> while the concentration of NO in Ar was 0.2%. The NO reduction reaction was evaluated using a temperature-programmed reaction (TPR) at a heating rate of 3 °C/min from 100 to 500 °C, and the temperature of the isothermal reaction was 400 °C. In the reduction of NO, N<sub>2</sub> was the intended product and N<sub>2</sub>O was also formed but its concentration was too low for detection.

## 2 Results and discussion

### 2.1 Catalytic activity for the reduction of NO by AC

The effect of catalyst composition or K content on the catalytic performance  $T_{50}$  (the reaction temperature for 50% NO conversion) and  $T_{100}$  (the reaction temperature for 100%

NO conversion) for the reduction of NO by AC are shown in Fig. 1.  $T_{50}$  data shows that the catalytic activity of K<sub>2</sub>O is much lower than that of CuO.  $T_{50}$  over K<sub>2</sub>O is ~380 °C and  $T_{50}$  over CuO is ~330 °C. At a K loading of 3.33%, that is, a Cu/K weight ratio of 2/1 the catalyst was found to have the highest activity.  $T_{50}$  is 317 °C. The  $T_{100}$  curve shows that the catalytic activity of K<sub>2</sub>O was similar to that of CuO and  $T_{100}$  over K<sub>2</sub>O is 433 °C while  $T_{100}$  over CuO is 430 °C. After K was added to the CuO catalyst,  $T_{100}$  declined obviously and at a Cu content of 6.67% and a K content of 3.33%,  $T_{100}$  is only 390 °C.

Figure 2 shows the catalytic activities of different catalysts for the reduction of NO by AC. The results show that for the catalytic reduction of NO by AC at lower than 300 °C, K<sub>2</sub>O/AC is hardly active and CuO/AC has a similar activity to 2Cu-K-O/AC. At higher than 300 °C, the presence of K in CuO can obviously improve its catalytic activity.

Figure 3 shows the variation in NO conversion for reaction times from 10 to 300 min at 400 °C. Over the K<sub>2</sub>O/AC catalyst, ~74% NO was reduced in a stable manner by AC. Over the CuO/AC catalyst, the NO conversion gradually decreased from 90% to 50% with an increase of the reaction time from 10 to 300 min. For the 2Cu-K-O/AC catalyst, a stable NO conversion of higher than 95% was obtained. These results indicate that the 2Cu-K-O/AC catalyst has remarkably superior performance compared with that of the CuO or K<sub>2</sub>O catalysts for the catalytic reduction of NO by AC. Based on the BET surface area data for CuO/AC (492 m<sup>2</sup>/g), 2Cu-K-O/AC (430 m<sup>2</sup>/g) and K<sub>2</sub>O/AC (465 m<sup>2</sup>/g), the promotional effect of K on the CuO catalyst may be considered to be a chemical synergetic effect between CuO and K<sub>2</sub>O rather than an improvement of the textural properties such as the surface area of the CuO catalyst.

### 2.2 XPS result

Cu  $2p_{3/2}$  XPS spectra of CuO/AC and 2Cu-K-O/AC before and after the reduction of NO at 400 °C for 300 min were obtained (spectra not shown), and the Cu  $2p_{3/2}$  XPS data are listed in Table 1. It has been reported that the Cu<sup>2+</sup> species ( $3d^9$ ) has a shake-up satellite peak ( $2p \rightarrow 3d$ ) at about 10 eV higher than the Cu  $2p_{3/2}$  transition [14,15], which is often used to differentiate between Cu<sup>2+</sup> and reduced copper. Distinguishing between Cu<sup>0</sup> and Cu<sup>+</sup> using XPS data is difficult because the  $E_b$  of Cu<sup>0</sup> (932.7 eV) is very close to the  $E_b$  of Cu<sup>+</sup> (932.6 eV) [16].

The Cu  $2p_{3/2}$  XPS spectra of the catalysts show that the intensities of the peaks at relatively low binding energies increase because of Cu<sup>2+</sup> reduction by AC to Cu<sup>+</sup> or Cu<sup>0</sup>, and a decrease in the peak intensity of the oxidized species (Cu<sup>2+</sup>) with very few shake-up satellite peaks is apparent. After the catalyst was used in the reaction, the Cu  $2p_{3/2}$  peak area of

$\text{Cu}^{2+}$  was reduced obviously indicating a decrease in the amount of  $\text{Cu}^{2+}$  after use, because some  $\text{Cu}^{2+}$  are reduced by AC [17,18]. The Cu  $2p_{3/2}$  XPS data in Table 1 show that the amount of  $\text{Cu}^{2+}$  species in the fresh CuO/AC catalyst decreased from 18.5% to 7.4% after the reaction, and that for the 2Cu-K-O/AC catalyst the amount of  $\text{Cu}^{2+}$  species after use hardly changed while the shake-up satellite peaks were also unchanged. These results show that the presence of K can remarkably improve the stability of CuO/AC. The lower stability of CuO/AC (Fig. 2) is due to the reduction of the  $\text{Cu}^{2+}$  species during NO reduction, and the high initial activity of CuO/AC in the reduction of NO can be attributed to the higher amount of surface  $\text{Cu}^{2+}$ . Because  $\text{Cu}^+$  (or  $\text{Cu}^0$ ) are re-oxidized difficultly by NO at 400 °C, the amount of surface  $\text{Cu}^{2+}$  cations is lower resulting in the deactivation of CuO/AC. 2Cu-K-O/AC is more stable than CuO/AC since the addition of K promotes the re-oxidation of  $\text{Cu}^+$  (or  $\text{Cu}^0$ ) to  $\text{Cu}^{2+}$  and the oxidation/reduction cycle of the active species.

### 2.3 XRD result

The XRD patterns of CuO/AC and 2Cu-K-O/AC before and after the reduction of NO are shown in Fig. 4. For the fresh catalysts, two broad diffraction peaks are apparent for the graphitic structure, which indicates that this AC has a low degree of graphitization. The peaks observed at  $2\theta = 35.5^\circ$  and  $38.7^\circ$  are the CuO diffraction peaks. The presence of K in the sample weakens the CuO diffraction peaks because of the decrease in Cu content (6.67%). In the XRD patterns (Fig. 4(b)) of the samples used in the reduction of NO at 400 °C for 300 min,  $\text{Cu}_2\text{O}$  diffraction peaks were observed at  $2\theta = 36.4^\circ$  and  $42.3^\circ$ , and the  $\text{Cu}^0$  diffraction peaks expected at  $2\theta = 43.3^\circ$  and  $50.4^\circ$  were too weak to be detected, which shows that small amounts of  $\text{Cu}^0$  were produced or that the  $\text{Cu}^0$  cations were highly dispersed on AC. These results show that CuO is reduced by the carbon substrate to lower oxidation states ( $\text{Cu}_2\text{O}$ ) during the reaction, and the presence of K weakens the  $\text{Cu}_2\text{O}$  diffraction peaks, which corresponds to the higher surface concentration of  $\text{Cu}^{2+}$  and its lower loading in the sample.

### 2.4 TPD result

The NO ( $m/z = 30$ ) and  $\text{N}_2$  ( $m/z = 28$ ) desorption curves from TPD-MS of NO adsorbed on AC, CuO/AC,  $\text{K}_2\text{O}/\text{AC}$ , and 2Cu-K-O/AC samples are shown in Fig. 5. In the desorption spectra of NO (Fig. 5(a)), the peak area for NO desorption over  $\text{K}_2\text{O}/\text{AC}$  was found to be higher than that over 2Cu-K-O/AC and CuO/AC, while AC gave the lowest value. The peak temperatures of NO desorption over  $\text{K}_2\text{O}/\text{AC}$ , 2Cu-K-O/AC, CuO/AC and AC were  $\sim 400$ ,  $\sim 250$ ,  $\sim 210$ , and  $\sim 135$  °C, respectively. The desorption peak be-

havior depends on the strength and amount of NO adsorption. NO, as an acidic gas, can adsorb strongly onto the basic  $\text{K}_2\text{O}/\text{AC}$  resulting in the highest adsorption strength and highest amount of adsorption among the four studied samples. AC can also adsorb NO but its adsorption strength and adsorption amount is the lowest among the studied samples. The presence of K improves the ability of CuO/AC to adsorb NO.

Figure 5(b) gives desorption curves for  $\text{N}_2$  in TPD of NO adsorbed over the four samples.  $\text{K}_2\text{O}/\text{AC}$  gave the highest amount of  $\text{N}_2$  desorption as shown by the peak at  $\sim 420$  °C but the reduction temperature was too high. 2Cu-K-O/AC has two peaks at  $\sim 280$  and  $\sim 340$  °C and CuO/AC has a small peak at  $\sim 250$  °C. AC has a very small  $\text{N}_2$  desorption peak at  $\sim 135$  °C, which shows that AC hardly reduces uncatalyzed NO. The results in Fig. 5 show that  $\text{K}_2\text{O}$  is a good intermediate for  $\text{NO}_x$  storage and the addition of K to the CuO catalyst can obviously enhance the adsorption strength and the amount of adsorbed NO while increasing its catalytic activity for the reduction of NO by AC.

Figure 6 shows the  $\text{CO}_2$  and CO desorption curves during the direct TPD (in a He flow) of 2Cu-K-O/AC, CuO/AC,  $\text{K}_2\text{O}/\text{AC}$ , and AC.  $\text{CO}_2$  and CO are the products of the surface carbon active sites reacting with surface oxygen groups [7]. For the  $\text{K}_2\text{O}/\text{AC}$  sample, two  $\text{CO}_2$  desorption peaks (a very small peak at 200 °C and a larger peak at 420 °C) are present. In the  $\text{CO}_2$  desorption profile of CuO/AC, two main peaks are present at 255 and 450 °C. Adding K to CuO can obviously increase the intensities of the  $\text{CO}_2$  desorption peaks, that is, the presence of K promotes the catalytic reaction between the surface carbon active sites and the surface oxygen species over CuO by a synergetic effect between Cu and K. For the AC sample, a large  $\text{CO}_2$  desorption peak is present at 150–500 °C, which is attributed to the reaction between the carboxylic acid groups and C to form  $\text{CO}_2$  [6] and this reaction is mostly prevented by supporting the CuO and/or  $\text{K}_2\text{O}$  catalyst components.

For the desorption curves of CO in the direct TPD of AC, CuO/AC and 2Cu-K-O/AC (Fig. 6(b)), CO was hardly detected at below 500 °C. For  $\text{K}_2\text{O}/\text{AC}$ , a large CO desorption peak is present at  $\sim 420$  °C with much more  $\text{CO}_2$  desorption having occurred (Fig. 6(a)). This indicates that K plays an important role in the reaction between surface carbon active sites and the surface oxygen groups leading to the formation of CO and  $\text{CO}_2$ .

The promotion role of  $\text{K}_2\text{O}$  for the formation of  $\text{CO}_2$  on the surface of AC is attributed to the weakening of the C–C bonds by K, which helps in the formation of active sites on the surface of carbon [19,20] and this leads to the activation of the surface oxygen species to enable a reaction with surface carbon active sites. This situation is similar to that of adding K (as  $\text{K}_2\text{CO}_3$ ) to iron oxide as an electron source for



iron, which results in the easier reduction of iron cations by carbon [9]. If the oxidant NO exists on the carbon surface, K in 2Cu-K-O/AC can promote the formation of carbon surface active sites and activate the adsorbed NO, resulting in an improvement of the reduction of NO by AC.

### 3 Conclusions

In summary, we found that K is a highly effective promoter of the CuO catalyst for the catalytic reduction of NO by AC. The Cu-K-O/AC catalyst with a Cu/K weight ratio of 2/1 shows higher activity and better stability for the catalytic reduction of NO by AC. The presence of K in CuO can ob-

viously increase the adsorption of NO on the surface of catalyst and maintain the higher surface concentration of  $\text{Cu}^{2+}$  to improve the  $\text{Cu}^{2+}/\text{Cu}^{1+}(\text{Cu}^0)$  redox cycle and the catalytic activity of CuO. In the Cu-K-O/AC catalyst, K plays an important role as it allows the surface carbon active sites to react with surface oxygen groups to form CO and  $\text{CO}_2$ . Over Cu-K-O/AC (Cu/K = 2, weight ratio) catalyst, the complete conversion temperature of NO was found to be 390 °C and the catalytic performance hardly changed after 300 min.

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## 第十二届全国均相催化学术会议通知

中国化学会第十二届全国均相催化学术讨论会定于2011年10月中旬在成都召开. 会议由中国催化学会均相催化专业委员会主办, 四川大学化学学院承办, 中国科学院成都有机化学研究所协办. 本届会议将全面展示两年来我国在均相催化和相关领域取得的研究成果, 交流和讨论均相催化发展的新趋势和所面临的机遇与挑战, 以促进我国均相催化学科和相关产业的发展. 会议主题包括均相催化及其工业应用、不对称催化、小分子催化、仿生催化胶束催化及纳米催化等. 大会组委会诚邀各位同行和相关仪器专家代表前来参会交流.

### 论文征集及奖励

投稿截止日期: 2011年6月30日.

论文必须未公开发表. 会议将设立全国均相催化基础研究和应用研究两个奖项, 分别奖励在均相催化基础研究和应用研究方面做出重要贡献的科学家各一名, 同时拟设立“第12届全国均相催化学术讨论会优秀墙报奖”奖项.

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