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Research Article

Determination of Mechanism for Soot Oxidation with NO on Potassium Supported Mg-Al Hydrotalcite Mixed Oxides

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Soot oxidation with NO (in the absence of gas phase O₂) on potassium-supported Mg-Al hydrotalcite mixed oxides (K/MgAlO) was studied using a temperature-programmed reaction and in situ FTIR techniques. Nitrite and the ketene group were identified as the reaction intermediates and thus a nitrite-ketene mechanism was proposed in which surface active oxygen on K sites of K/MgAlO is transferred to soot by NO through nitrites. In the absence of gas phase O₂, soot oxidation with NO at lower temperatures (below 450 °C) is limited by the amount of active oxygen on the K sites. This kind of active oxygen is not reusable but can be replenished in the presence of gas phase O₂.

Keywords: Soot oxidation, Nitric oxide, Potassium, Hydrotalcite, Ketene group, Nitrite

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1 Introduction

Catalytic oxidation is an effective way to remove soot particulates emitted from diesel engines [1, 2]. To accomplish soot oxidation at lower temperatures, various catalysts were developed [3–9]. Therein, potassium-containing materials show considerable activity and the relevant mechanisms have been suggested in many studies [10–18]. Besides, catalytic soot oxidation is affected by the composition of the reaction gas (O₂ and/or NO_x). When NO coexists with O₂ in the reaction gas, soot can be readily oxidized due to the formation of NO₂ being more reactive than O₂ or NO [2]. If only NO exists in the reaction gas, soot oxidation is weak [19–21]. Although the mechanism for soot oxidation with NO + O₂ on potassium-supported Mg-Al hydrotalcite mixed oxides (K/MgAlO) has been determined [22], the details for soot oxidation with NO on K/MgAlO have not been clear. Illán-Gómez et al. [23] found that the presence of potassium facilitates the dissociative chemisorptions of NO and the subsequent transfer of active oxygen to carbon results in oxidation. However, the intermediates have not been exactly specified. In the present work, soot oxidation with NO (in the absence of gas phase O₂) on K/MgAlO was examined by temperature-programmed reaction (TPR). Furthermore, the reaction intermediates were identified using the in situ FTIR technique developed by [22]. Finally, a nitrite-ketene mechanism was proposed.

2 Experimental

The K/MgAlO sample with 5 wt-% of potassium and the MgAlO sample without potassium loading were prepared as described in [18]. For reference, the 5 wt-% K-supported ZrO₂ (Sinopharm Chemical Reagent Co. Ltd., China), denoted as K/ZrO₂, was also prepared using the same procedure.

The TPR reactions were conducted in a fixed bed microreactor consisting of a quartz tube (6 mm i.d.). Printex-U from Degussa was used as model soot. The soot was mixed with the sample in a weight ratio of 1:9 in an agate mortar for 30 min, resulting in a tight contact condition between soot and sample. For the noncatalytic soot oxidation, the sample was replaced with silica (blank). 50 mg of the mixture was pretreated in a flow of He (50 mL min⁻¹) at 200 °C for 1 h to remove surface-adsorbed species. After cooling down to room temperature, a gas flow with 1050 ppm NO in He (100 mL min⁻¹) was introduced and then TPR was started at a heating rate of 5 °C min⁻¹ until 700 °C. NO_x (NO and NO₂) and CO_x (CO and CO₂) in the effluent were analyzed online by a chemiluminescence NO_x analyzer (42i-HL, Thermo Environmental) and a gas chromatograph (GC) (SP-6890, Shandong Lunan Ruihong Chemical Instrument Corporation, China), respectively. N₂O, one of the possible products of NO reduction, was detected by a FTIR spectrometer (Tensor 27, Bruker) with a 2.4 m optical length gas cell.

The in situ FTIR spectra were recorded on the FTIR spectrometer over 400–4000 cm⁻¹ after 32 scans at a resolution of 4 cm⁻¹. Prior to the experiments, the background spectra were obtained in a He flow at room temperature. The mixture of soot and sample in a weight ratio of 1:9 in tight contact condition was pressed into a thin self-supporting wafer with a thickness of 7.5 mm.

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The wafer was loaded into an in situ infrared transmission cell capable of operating up to 500 °C and equipped with a gas flow system. All experiments were performed in the flow of 100 mL min⁻¹ with the heating rate of 5 °C min⁻¹.

3 Results and Discussion

Figs. 1a–c show the TPR patterns of K/MgAlO, MgAlO and the blank sample. For comparison, the TPR patterns without soot are also given. It was found that little NO₂ was detected in the TPR tests with or without soot. Thus, the participation of NO₂ in soot oxidation can be excluded. Furthermore, the negligible CO₂ observed during the tests without soot was due to the decomposition of remaining carbonates on the samples.

For the TPR test with soot on K/MgAlO, an evident CO₂ peak is formed below 450 °C, while the NO concentration remains almost constant. A similar situation is observed on MgAlO but the CO₂ peak is much weaker. This suggests that the presence of potassium promotes soot oxidation with NO. However, the amount of the produced CO₂ with NO on K/MgAlO is much less than that in the TPR test with NO + O₂ on the same sample [22], in which soot oxidation is almost completed at 450 °C.

From 450 to 700 °C, the reduction of NO and the corresponding production of CO_x are negligible on the blank and MgAlO samples. By contrast, NO concentrations greatly decrease on K/MgAlO and approach zero at ~700 °C, accom-

panied by the prevailing of CO₂ production and the gradual formation of CO. This is in agreement with the finding of Kapteijn et al. that NO can be effectively reduced on alkali metal-carbon systems [24]. Since no N₂O was detected in the TPR tests, the only product of NO reduction is N₂, i.e., the selectivity to N₂ is 100 %.

It is interesting that NO does not seem to participate in soot oxidation below 450 °C because no NO consumption is observed at the same time. Therefore the question arises, which oxidant is responsible for soot oxidation at lower temperatures. In fact, in inert atmosphere without any gaseous oxidant, the surface oxygen on K sites can oxidize soot into CO₂, which was observed in the experiments of carbothermic reduction of soot in previous work [18]. In the present work, however, the amount of the produced CO₂ on K/MgAlO (4552.0 μmol g⁻¹) is much more than that in the carbothermic reduction on the same sample (885.9 μmol g⁻¹).

To elucidate the role of NO, the in situ FTIR technique was used to investigate soot oxidation with NO on K/MgAlO. The spectra evolutions of the reactions during the isothermal heating process at 500 °C and 400 °C are illustrated in Figs. 2 and 3, respectively. In Fig. 2, after heating at 500 °C for 20 min, a band at 2162 cm⁻¹ arises (see Fig. 2b), which can be attributed to the ketene group [25, 26]. This band reaches maximum after 100 min (see Fig. 2f) and progressively decreases as the reaction proceeds (see Figs. 2f–j). In Fig. 3, the presence of the band of the ketene group is also observed for soot oxidation with NO on K/MgAlO at 400 °C despite the extended time

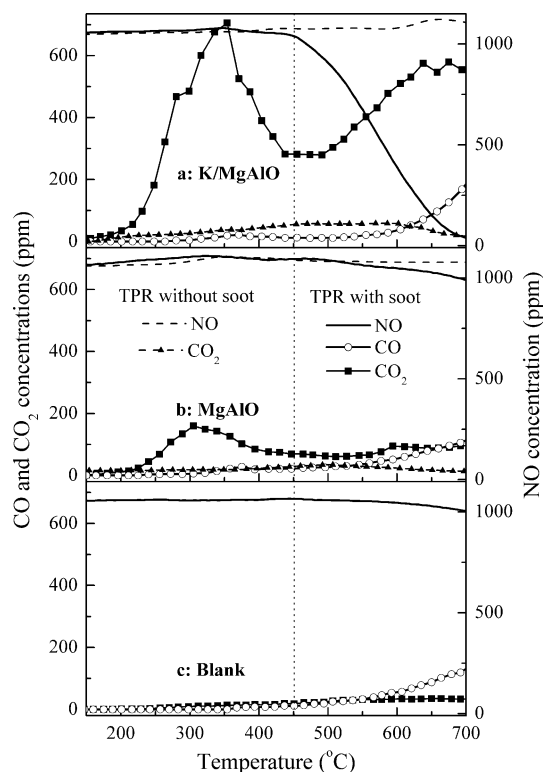


Figure 1. TPR patterns of CO₂, CO and NO for soot oxidation with NO on K/MgAlO (a), MgAlO (b) and the blank sample (c). The TPR patterns without soot are also given.

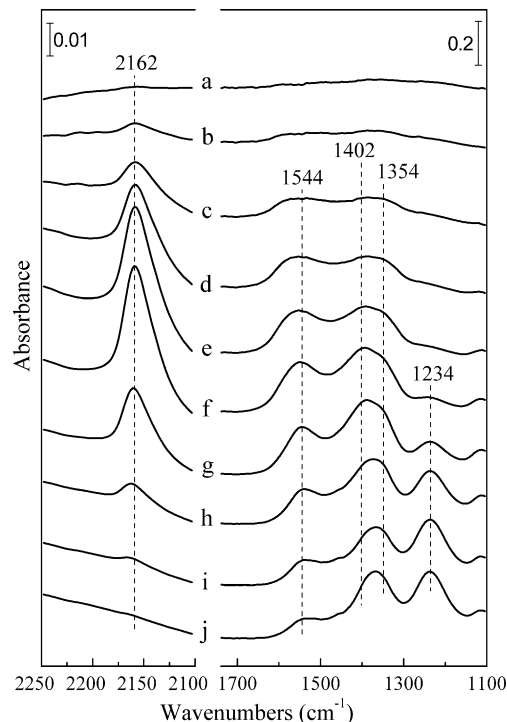


Figure 2. In situ FTIR spectra of the mixture of soot and K/MgAlO after heating at 500 °C for 0 min (a), 20 min (b), 40 min (c), 60 min (d), 80 min (e), 100 min (f), 120 min (g), 140 min (h), 160 min (i) and 180 min (j) in 1050 ppm NO + He.

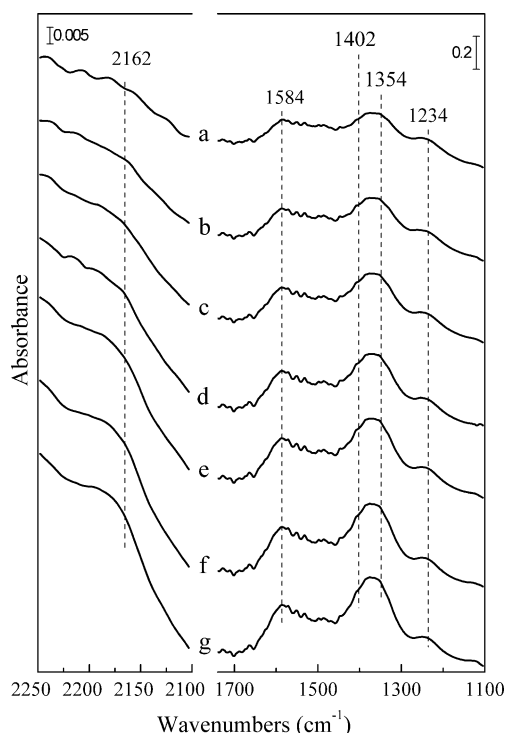


Figure 3. In situ FTIR spectra of the mixture of soot and K/MgAlO after heating at 400 °C for 100 min (a), 150 min (b), 200 min (c), 250 min (d), 300 min (e), 350 min (f), and 400 min (g) in 1050 ppm NO + He.

(≥ 150 min) due to the slow reaction rate at this temperature. The ketene group has been identified as the intermediate of soot oxidation with O_2 or NO_2 [18, 22], which is a surface-oxygen complex formed on the surface of soot with graphite structures [2, 6]. Likewise, the ketene group can serve as the intermediate of soot oxidation with NO. In Fig. 2, with the progress of the ketene group from the presence and reaching maximum to the final disappearance, soot oxidation is complete. During this process, chelating bidentate carbonate (1544 and 1354 cm^{-1}) and ionic carbonate (1402 cm^{-1}) are formed, which have been observed in soot oxidation with O_2 [22]. These carbonates originate from the adsorption of the produced CO_2 on potassium sites.

The adsorption of NO on potassium sites will result in the formation of ionic nitrites (nitrates are negligible) [22], as shown below:



K^+-O^* indicates the surface oxygen on potassium sites. However, as shown in Fig. 2f, only after the oxidation reaction has proceeded 100 min at 500 °C is the ionic nitrite (1234 cm^{-1}) present. Thereafter, the ionic nitrite increases. Simultaneously, the ketene group gradually decreases and finally disappears. As indicated above, this is a signal that soot oxidation is complete, implying that a relationship might exist between the ketene group (on the surface of the soot) and the ionic nitrite (on the surface of K/MgAlO). To make it clear, the

following in situ FTIR experiments of the surface reaction of free (active) carbon sites with the nitrite were designed, as shown in Fig. 4. At first, the mixture of soot and K/MgAlO was heated to 430 °C in O_2 + He followed by cooling down to 200 °C with purging with He. In this step, some soot was depleted and thus a clear FTIR signal and lots of free carbon sites were obtained. The corresponding spectra are shown in Fig. 4a, illustrating the presence of chelating bidentate carbonate and ionic carbonate on K/MgAlO. NO was introduced and switched off when the spectrum did not change significantly. As expected, the band of the ionic nitrite was observed (see Fig. 4b). At this time, free carbon sites and ionic nitrite were abundant on the surfaces of soot and K/MgAlO, respectively. The mixture was progressively heated up to higher temperatures in He (see Figs. 4c–g). During this period, the band of the ionic nitrite gradually decreases in intensity, simultaneously with the formation of the ketene group. When the band of the ketene group reaches maximum at 500 °C for 5 min (see Fig. 4h), the ionic nitrite is completely absent. These facts suggest that the ionic nitrite may be consumed with the production of the ketene group. In other words, the ionic nitrite on K/MgAlO interacts with the free carbon sites on the soot to form the ketene group, which can be described as:

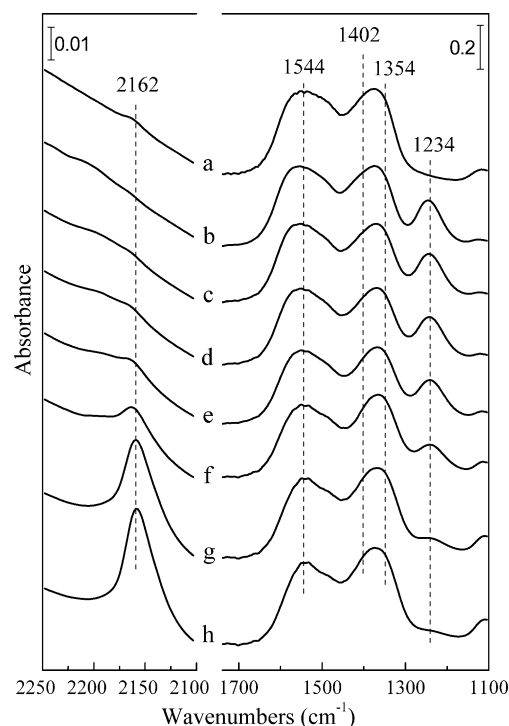
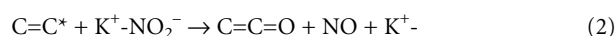


Figure 4. In situ FTIR spectra of the mixture of soot and K/MgAlO after the following consecutive treatments: heating up to 430 °C in 5 vol.-% O_2 + He and cooling down to 200 °C with purging of He (a), introduction of 1050 ppm NO + He at 200 °C for 80 min followed by purging of He (b), and heating up to 300 °C (c), 350 °C (d), 400 °C (e), 450 °C (f), 500 °C (g) and maintaining at 500 °C for 5 min (h).

$C=C^*$ represents the free carbon sites on soot, while $C=C=O$ indicates the ketene group. The free carbon sites are the unsaturated carbon atoms on the defects in the graphitic structure of soot and thus possess high reactivity [27].

The as-formed ketene group can be further oxidized into CO_x by adjacent ionic nitrites via reaction (3) or (4):



Reaction (3) stands for soot oxidation without NO consumption below 450 °C (see Fig. 1), which is supported by the results shown in Figs. 3 and 4. Reaction (4) is predominant at higher temperatures, responsible for the reduction of NO (above 450 °C). This conclusion is reasonable concerning the fact that the reaction barrier needed for reaction (4) is higher than that for reaction (3). In reaction (4), five electrons are transferred for the reduction of NO_2^- to N_2 , whereas only three electrons are transferred for the reduction of NO_2^- to NO in Reaction (3).

Reactions (1) to (4) constitute the mechanism of soot oxidation with NO on potassium sites as depicted in Fig. 5, which may be called the nitrite-ketene mechanism. In this mechanism, NO first combines with the active oxygen on surface K sites of K/MgAlO forming nitrites. Then, the nitrites interact with the free carbon sites on soot to produce the ketene group. Finally, the ketene group is further oxidized to CO_x by adjacent nitrites, regenerating NO at lower temperatures and/or producing N_2 at higher temperatures. In the mechanism, surface oxygen on potassium sites is involved in the reaction via the nitrites. The nitrite was reported to be mobile, and its formation leads to a more flexible surface than the clean surface [28]. Therefore, the nitrite can reach the free carbon sites more easily than the surface active oxygen. This can explain why the activity observed in NO atmosphere is higher than that in inert atmosphere at lower temperatures.

In fact, the nitrite-ketene mechanism is analogous to the mechanism of soot oxidation with $NO + O_2$ [22]. For both mechanisms, NO plays the same role of the oxygen carrier that transfers the active oxygen to the surface of soot in the form of nitrites (in NO) or NO_2 (in $NO + O_2$). The active oxygen is derived from K/MgAlO in NO below 450 °C, whereas it is from gas phase O_2 in $NO + O_2$. This kind of active oxygen is not reusable but can be replenished in the presence of gas phase O_2 . It is reported that the reaction order of O_2 is between 0.5 and 1 [19, 29]. Therefore, soot oxidation with NO is slow in the absence of gas phase O_2 at lower temperatures (see Fig. 3).

The mechanism proposed above might be extended to other K-supported metal oxides. Fig. 6 shows the activity of K/ZrO₂ for soot oxidation with NO by TPR (a) and the corresponding in situ FTIR spectra (b). Comparison of Fig. 6a with Fig. 1a shows that the activity of K/ZrO₂ is

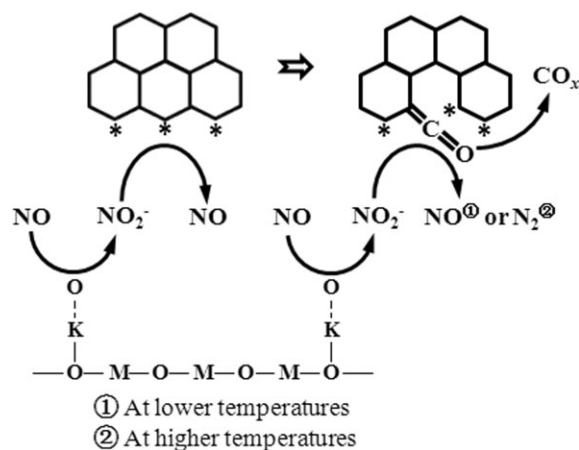


Figure 5. Nitrite-ketene mechanism for soot oxidation with NO on K/MgAlO in the absence of O_2 . M stands for metal Mg or Al; the carbon body is polyaromatic.

much lower than that of K/MgAlO at lower temperature. However, the ketene group (2162 cm^{-1}) is also observed on K/ZrO₂ (see Fig. 6b), indicating that the nitrite-ketene mechanism is suitable to K/ZrO₂. The higher activity of K/MgAlO compared to that of K/ZrO₂ might be attributed to the higher potassium dispersion on MgAlO due to the strong interaction between potassium and MgAlO [18].

4 Conclusions

Soot oxidation with NO is much more active on K-supported Mg-Al hydrotalcite mixed oxides (K/MgAlO) than on MgAlO oxides. The nitrites and the ketene group were identified as reaction intermediates. A nitrite-ketene mechanism was proposed in which NO first combines with surface oxygen on

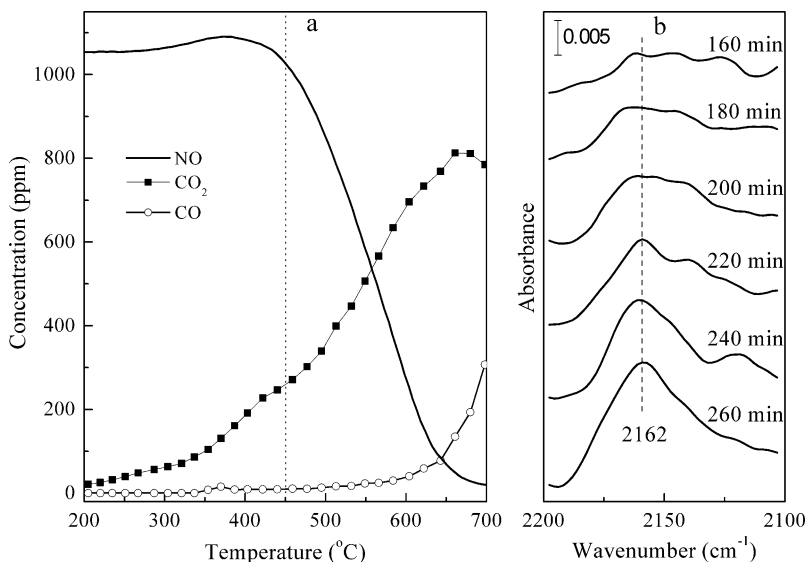


Figure 6. TPR patterns of CO_2 , CO and NO for soot oxidation with NO on K/ZrO₂ (a) and the corresponding in situ FTIR spectra at 500 °C (b).

potassium sites of K/MgAlO forming nitrites. Then, the nitrites interact with the free carbon sites on soot to produce the ketene group. Finally, the ketene group is further oxidized to CO₂ by adjacent nitrites, regenerating NO at lower temperatures and/or producing N₂ at higher temperatures.

In the absence of gas phase O₂, soot oxidation with NO at lower temperatures (below 450 °C) is limited by the amount of active oxygen from the potassium sites. This kind of active oxygen is not reusable but can be replenished in the presence of gas phase O₂. The presented mechanism is an effective complement to soot oxidation in NO + O₂.

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The authors have declared no conflict of interest.

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