CHEMPHYSCHEM

Supporting Information

Clean diesel power via microwave susceptible oxidation catalysts

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Influence of catalyst preparation on crystal structure, surface area and activity. Three preparation methods were employed, of which low thermal decomposition of nitrates is the simplest. The nitrates are heated together with glycerol as reducing agent, the liquid is evaporated and the sample is calcined at 600–800 °C.[1] The resulting perovskites have surface areas of around 10 m^2g^{-1}. Both $LaMnO_3$ catalysts **16** and **17**, prepared by co-precipitation and thermal decomposition, perform equally well in CO and propane oxidation (Table 1), and have similarly high mw susceptibilities. On the other hand, from the six unsubstituted perovskites we prepared via this method, three did not form a single perovskite phase, as determined by XRD, and one of them, a $LaCrO_3$ perovskite, was not mw susceptible. The calcination step was equal to that of the samples prepared by co-precipitation.

Co-precipitation enables a more controlled formation of the catalyst precursor. The metal nitrates are dissolved in water and a specific pH is set by adding NaOH.[2] The metals precipitate as hydroxides, and the precipitate is washed, filtered and dried before calcination. This method can give perovskites with surface areas as high as 30 m^2g^{-1}. The disadvantage is that every metal has a distinct pH where the optimum hydroxide precipitation will occur, making the synthesis of multimetallic combinations difficult. ICP analysis of our $La_{0.8}A_{0.2}MnO_3$ catalysts (A = Ba, Ca, Mg), showed that little of the substituent was incorporated into the perovskite lattice. Indeed, the hydroxides of these elements are more soluble than Ce under our preparation conditions. Furthermore, a $La_{0.8}Ce_{0.2}FeO_3$ catalyst prepared via co-precipitation was not mw susceptible.

[1] A. Delmastro, D. Mazza, S. Ronchetti, M. Vallino, R. Spinicci, P. Brovetto, M. Salis, *Mater. Sci. Eng. B* **2001**, *79*, 140.
[2] Y. Zhang-Steenwinkel, J. Beckers, A. Bliek, *Appl. Catal. A: Gen.* **2002**, *235*, 79.

Since spray pyrolysis starts from metal nitrate solutions it avoids these solubility problems. The solutions are sprayed into the top part of an oven, and the powder sinks to the bottom. There are degrees of freedom in concentration, oven temperature, feed rate, and residence time. The latter is altered by adjusting the angle of the rotating oven. The production of large batches is possible, with surface areas from 3 to 10 m^2g^{-1}. All of the spray pyrolysis samples gave high purity, mw susceptible perovskites.

Selectivity towards ethene and propene in the presence of SO$_2$. Besides ethene and propene, an increase in the trace amounts of unidentified components is observed for most catalysts in the presence of SO$_2$. This decrease in selectivity can be explained either by an actual increase in the formation of side products or the weakening of their bond with the surface. Note that under these conditions a heterogeneous surface is present, with adsorbed SO$_2$, unaffected perovskite surface and sulphates, sulphites and oxides of the constituting atoms all possibly present and influencing the oxidation reaction. Furthermore, as oxidation of propane yields water, sulphurous acid may be formed at the catalysts surface together with SO$_2$. All of these species may affect the surface reactions.

The different phases formed after the SO$_2$ treatment. As the irreversible poisoning is caused by the destruction of the perovskite due to the formation of sulphites, sulphates and oxides of the constituting elements, and because the LaCrO$_3$ type catalysts show superior SO$_2$ tolerance, the amount of La$_2$(SO$_4$)$_3$ formed is likely to be lower in the presence of chromium. If lanthanum had the same susceptibility of forming sulphates in the presence of SO$_2$ regardless of the *B*-type atom, we would not expect the large difference in SO$_2$ tolerance between the Cr-containing perovskites and the ones with Mn, Fe, Co, Ni and Cu. The SO$_2$ tolerance for Cr type perovskites may reflect the lower affinity of chromium to adsorb SO$_2$, compared to the other *B*-atoms.[3] The high SO$_2$ tolerance and low activity of the Cr containing catalysts may be explained by the low adsorption of both poison and substrate.

Catalysts that are affected by SO$_2$ show a typical distribution of the newly formed phases (see Figure S1). Figure S1a shows a top view of the reactor bed of catalyst **3**. A brown, ring shaped phase is formed. Two phases are seen for catalyst **10** (Figure S1b). Analysis of this sample showed that both the brown and grey phase contain lanthanum,

[3] I. Rosso, G. Saracco, V. Specchia, E. Garrone, *Appl. Catal. B: Environ.* **2003**, *40*, 195.

manganese and cerium. The lanthanum is present as $La_2(SO_4)_3$ and the manganese as MnO. XPS showed that the brown phase contains slightly more Mn and Ce^{4+} as compared to the grey phase.[4] The ring shapes are not caused by flow differences in the bed, as the samples consist of uniformly sized particles. Temperature differences due to non-uniform mw heating are also excluded as the mw energy is directed towards the sample from one side, so this cannot account for the circular shapes observed. However, as in mw heating energy is applied to the mw susceptible catalyst bed itself, the inner part of the bed will be hotter than the outer part, that is in contact with the relatively cool reactor wall. The ring may be the area of the bed where the temperature is ideal for the formation of sulphates or oxides of the elements present in the perovskite.
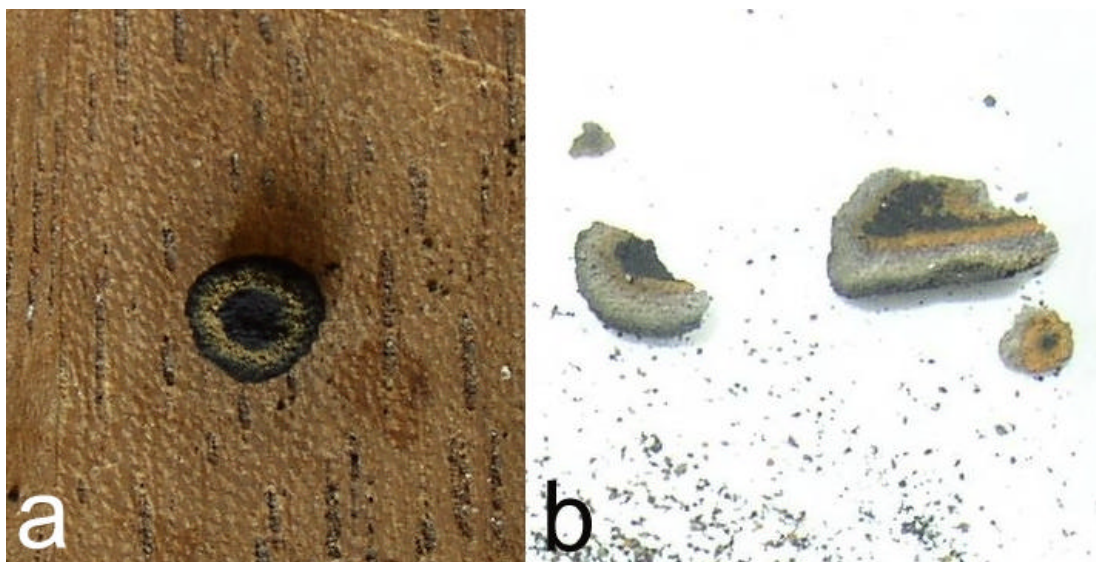
Figure S1. The typical phase distribution of SO_2 poisoned $La_{0.8}Sr_{0.2}MnO_3$, **3** (photo a, top view) and $La_{0.8}Ce_{0.2}MnO_3$, **10** (photo b), taken after long term exposure to SO_2 at elevated temperature.

Deposits at the reactor exit after SO$_2$ treatment. At the reactor exit, a brownish-black deposit was observed for most catalysts after the SO_2 experiments. This deposit was present at the inner wall of the reactor, at the point of exit from the mw cavity. It ranged from wet to tarry, with a pH <1. This deposit was observed only at the point of exit, regardless of the reactor positioning in the cavity, and was also present when

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[4] Y. Zhang-Steenwinkel, H. L. Castricum, J. Beckers, E. Eiser, A. Bliek, *J. Catal.* **2004**, *221*, 523.

conventional heating was employed. ICP analysis showed that the deposit contained mainly sulphur, and traces of elements used in the perovskite library, but with no direct correlation to the perovskite loaded during the specific run. We think that water formed during the oxidation condenses on the cold part of the reactor, in which SO_2, CO, CO_2 and unreacted hydrocarbons dissolve to form this dark deposit.