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The effect of loading, with chromium and manganese, on the activity of yttria-supported catalysts in the three-way neutralisation of gas emissions

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Maximum catalytic activity in NO + CO neutralisation and CH_4 combustion was observed for M/Y_2O_3 (M = Cr and Mn) at a M loading of 3–5%; this is understood to result from the stabilisation of active isolated M ions in yttria due to oxide-oxide interactions between the active transition metal oxide and the support.

In the development of three-way catalysts, increasing attention is being paid to heterogeneous systems based on oxides of rare earth elements and yttrium and containing oxides of manganese,[1,2] chromium,[3,4] and some other transition metals.[5,6] These multicomponent systems of perovskite-like structure possess a peculiar ability to stabilise transition metal ions in various oxidation states and provide high thermostability.[4]

This study was undertaken in order to scrutinise the compositional aspects with respect to the development of yttria-supported chromium and manganese oxide environmental catalysts. Here we report the results of separate studies on the catalytic reduction of NO by carbon monoxide and on complete methane oxidation by oxygen over M/Y_2O_3 (M = Cr and Mn) oxide systems, as a step towards overall comprehension of the operation of $Cr\text{-}Mn/Y_2O_3$ three-way catalysts in the simultaneous neutralization of CO, NO, C_xH_y.

Oxide catalysts, M/Y_2O_3 (1–20 at.% M, M: Cr, Mn), were prepared by hydroxide coprecipitation[7] (M = Cr) and by incipient wetness impregnation[8] (M = Mn), followed by calcination in a stream of air at 700–1300 K.

As Cr-containing catalysts are among the most active in NO reduction by CO,[4,9–11] the catalytic activity of M/Y_2O_3 was studied for Cr/Y_2O_3 samples. The experiments on conversion of a reaction mixture of NO + CO were carried out at 470–720 K and GHSV = 29000 h^{-1}, applying a pulse technique with GC analysis of reaction products; a gas mixture (pulse of 1 cm^3) with stoichiometric reagent ratio (NO:CO = 1:1) was used. Prior to the reaction run, the samples were pretreated in a stream of oxygen for 15 min at 870 K (gas flow rate 30 $cm^3\ min^{-1}$) followed by purging with helium for 1 h.

In turn, since Mn-containing oxide systems have proved to be highly effective in hydrocarbon oxidation,[1,2,12–14] Mn/Y_2O_3 catalysts in CH_4 combustion were studied. The flow reaction was examined in a quartz fixed-bed reactor at 970 K and 101.3 kPa, using the following reaction mixture: 25.3 kPa CH_4:5.1 kPa O_2 (GHSV ≈ 12000 h^{-1}), balanced with helium carrier gas. Under these conditions, complete oxidation of methane occurred. The reaction was carried out so that CH_4 conversion did not exceed 15%, so the activity of the catalysts was estimated from the initial reaction rates. The activity of Mn/Y_2O_3 samples was compared at the steady state reached after ≈ 1 h reaction time.

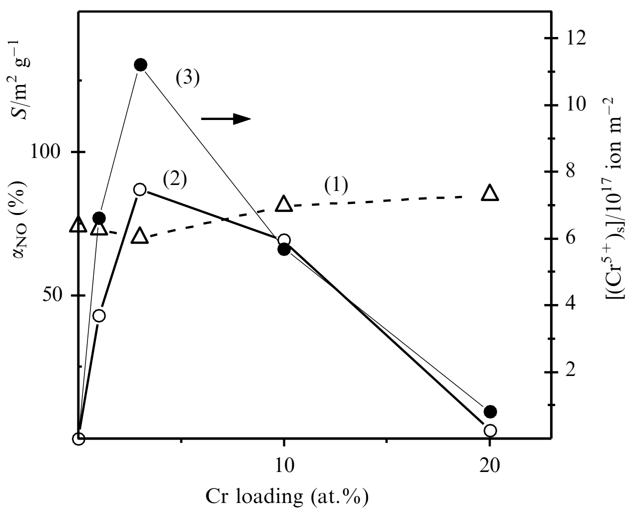

Figure 1 Variation of specific area S (1), NO conversion α_{NO} in reaction NO + CO at 620 K (2); and concentration $[(Cr^{5+})_s]$ of surface isolated Cr^{5+} ions (3) with total Cr loading in Cr/Y_2O_3 catalyst.

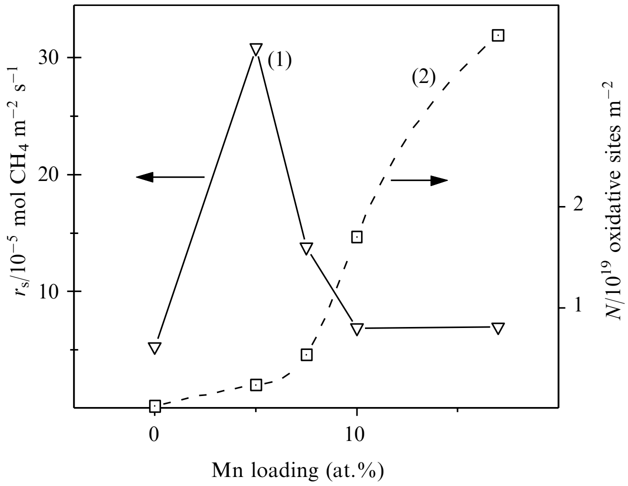

Figure 2 Activity in CH_4 combustion, r_s, at 970 K (1) and the number of oxidative sites N reactive towards H_2 (970 K) (2) for Mn/Y_2O_3 catalysts with different Mn loading.

Comparison of EPR data for Cr- and Mn-containing yttria† revealed a resemblance in the formation of mixed oxide microstructures. Calcined at 570–970 K, where the hydroxides decompose,[7,16] the samples with low (1–20 at.%) Cr content reveal an EPR signal from isolated or weakly interacting Cr^{5+} ions. Magnetic resonance data,[7,15] together with cubic Y_2O_3 lattice evaluation, enable us to conclude that the symmetry of the Cr^{5+} ion localisation site is close to that of chromium in the stoichiometric double oxide $YCrO_4$ with a structure of the zircon type. The catalytic behaviour of Cr/Y_2O_3 (T_{cal} = 870 K) in the reaction of NO + CO is governed by dispersed Cr^{5+} ions, available on the sample surface. For the Cr-containing catalysts, with nearly the same specific areas (*cf.* Figure 1, curve 1), the variation of catalytic activity in the reaction of NO + CO (Figure 1, curve 2) followed the surface concentration of isolated chromium ions[7] (Figure 1, curve 3) and activity was found to be highest at a Cr loading of 3 at.%. Thus, for Cr/Y_2O_3 (T_{cal} = 870 K), isolated Cr^{5+} ions appear to be the catalytic sites in the reduction of NO by carbon monoxide.

For high-temperature CH_4 combustion on Mn/Y_2O_3 samples, maximum activity was also seen on catalysts with low transition metal loading (5% Mn/Y_2O_3) (Figure 2, curve 1). This was the case (Figure 2, curve 2) even though the total concentration of reactive oxidative sites in Mn/Y_2O_3 catalysts, *i.e.* content of labile oxygen, steadily increases with Mn loading as measured at 970 K by hydrogen uptake. This result shows that the capacity of labile oxygen is not a universal criterion of activity of manganese catalysts in hydrocarbon oxidation, as was supposed earlier.[17,18]

For Mn/Y_2O_3 catalysts the reduced state is important and we have shown that isolated ions Mn^{2+} are stabilised by the Y_2O_3 matrix. Since the reagent ratio ($5CH_4$:$1O_2$) provided a reducing medium during the experiment, the Mn/Y_2O_3 samples were found to be reduced after catalysed combustion of CH_4. In the course of the reaction manganese entered some stable microstructures of mixed Mn-Y oxides. These paramagnetic species were found[15] in all reduced Mn/Y_2O_3 samples in nearly the same concentration (3–4×10^{18} spin g^{-1}). EPR signals of these isolated Mn^{2+} ions had approximately the same linewidth (15–18 G), showing that the arrangement of weakly interacting manganese ions in yttria was virtually independent of Mn loading. Therefore, for Mn/Y_2O_3 catalysts, isolated Mn^{2+} ions became stabilised by yttria under the reaction conditions employed, even though simultaneous aggregation of manganese oxide definitely occurred, being evidenced by the rising of a wide ($H \approx 500$ G) signal from superparamagnetic aggregates of MnO.

† Results of an EPR study of M/Y_2O_3 (M = Cr, Mn) are discussed in detail elsewhere.[7,15]

Thus, comparison of spectral and catalytic data reveals that isolated Cr^{5+} and Mn^{2+} ions stabilised in interstices of the Y_2O_3 structure, as mixed oxide fragments or defects, seem to operate as active sites in the studied reactions, which are related to three-way catalysis. Conversely, the development of some microstructures, in which isolated M^{n+} ions are stable, seems to be indicative of a strong oxide–oxide interaction (SOOI) in M/Y_2O_3 systems.

After having been discovered by Lund and Dumesic,[19,20] the effects of a SOOI were observed for various mixed oxides.[15,19–26] SOOI usually results in the stabilisation of an ionic form of a transition metal ion (iron,[19–24] cobalt,[24] nickel[24] or manganese[15,25,26]) in mixed oxide microstructures with an oxide support. Generally, these stable microstructures evolve in the catalysts as a result of multiple redox treatments. This is also the case with redox reactions, wherein the SOOI effect for Cr/Y_2O_3 and Mn/Y_2O_3 has been revealed in this paper. Of special interest is the fact that SOOI-domains with isolated ions of transition metals appear to be the very active species in M/Y_2O_3 (M = Cr, Mn) catalysts of reactions of relevance to three-way exhaust neutralisation.

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