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Mixed 3*d*-metal oxides prepared using molten ammonium nitrate

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Highly dispersed spinel structure mixed 3*d*-metal oxides $M'_xM''_yO_4$ (M′, M″ = Cr, Mn, Co, Ni and Cu) with homogeneous distribution of components and high catalytic activity in CO and CH_4 oxidation were prepared using ammonium nitrate and characterised by thermal analysis, X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM).

The use of molten ammonium nitrate for obtaining oxide materials such as MnO_2, polycrystalline copper–ruthenium oxides, ceramic c-$YBa_2Cu_{3-x}Nb_xO_y$ and δ-$SrCoO_3$ was described.[1–4] A stage of washing out alkali metal salts is necessary if molten alkali metal nitrates are used for preparing oxide materials.[5] This stage can be avoided with the use of NH_4NO_3 because an excess of ammonium nitrate can be simply eliminated from the system by sublimation/decomposition at moderate temperatures.

We used NH_4NO_3 as a reaction medium to produce highly dispersed 3*d*-metal oxide catalysts. To optimise conditions for this reaction, we studied the interaction between ammonium nitrate and transition metal nitrates during thermal treatment. The catalytic activity of the oxide products was determined in the reactions of CO and CH_4 oxidation.[†]

Thermal behaviour of individual hydrated transition metal nitrates mixed with NH_4NO_3 was investigated at a low heating rate (< 1 K min^{-1}). At the first stage (100–140 °C), dehydratation resulted in nitrate complexes $(NH_4)_3M(NO_3)_5$ (M = Cu,[6] Co[7] and Mn[8]). At the second stage (160–220 °C), chemical reactions in molten ammonium nitrate resulted in the formation of the ammines $Cu(NH_3)_2(NO_3)_2$ and $Cu(NH_3)(NO_3)_2$ in the case of copper.[9] In the case of M = Cr, the oxidation of Cr^{III} to Cr^{VI} and the formation of ammonium chromate(VI) occurred at this stage. Next (T > 220 °C), the decomposition of the mixture resulted in the formation of oxides.

The mixtures of individual hydrated 3*d*-metal nitrates with a fivefold molar excess of NH_4NO_3 were investigated at a high heating rate (5 K min^{-1}) (Figure 1). Decomposition of individual NH_4NO_3 begins at 175 °C and finishes at T_{end} = 253 °C; an exo effect occurs at T_{max} = 234 °C. It was found that the addition of 3*d*-metal nitrates or ammonium dichromate decreases the decomposition temperature of NH_4NO_3 in the following sequence: $Cr_2O_7^{2-}$ (73) >> Mn^{2+} (41) > Co^{2+} (34) > Cu^{2+} (14). The difference between T_{end} for pure NH_4NO_3 and NH_4NO_3 + $M(NO_3)_n$ mixtures is presented in parentheses (ΔT_{end}/K).

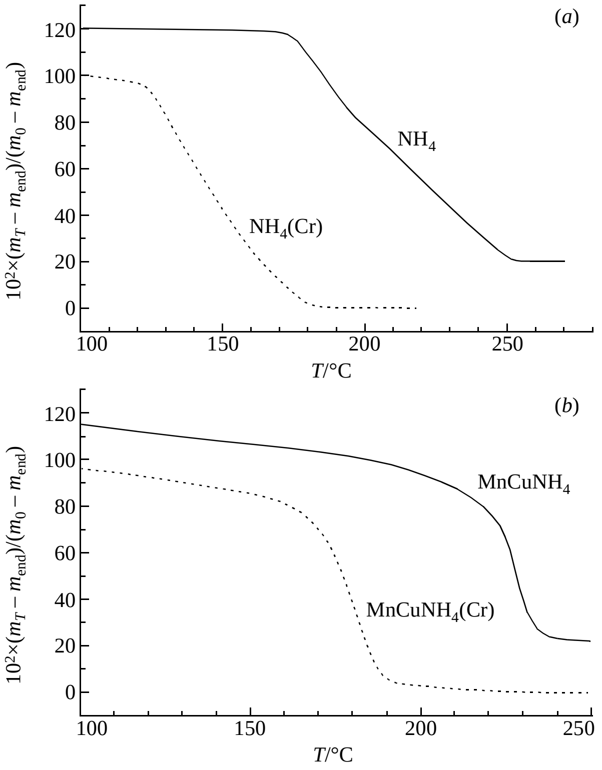

Figure 1 Thermal analysis of (*a*) NH_4NO_3 (NH_4) and NH_4NO_3 + 1 mol% $(NH_4)_2Cr_2O_7$ [NH_4(Cr)]; (*b*) $Mn(NO_3)_2\cdot 6H_2O$ + $Cu(NO_3)_2\cdot 3H_2O$ + NH_4NO_3 ($MnCuNH_4$) and $Mn(NO_3)_2\cdot 6H_2O$ + $Cu(NO_3)_2\cdot 3H_2O$ + NH_4NO_3 + 1 mol% $(NH_4)_2Cr_2O_7$ [$MnCuNH_4$(Cr)].

In all cases, the last mass loss corresponds to melt decomposition accompanied by an exo effect at T_{max} on DT curves. It is interesting that the temperatures of exo effects on DT curves were practically equal to the temperatures of the end of decomposition (T_{end} = 170–230 °C). After 250 °C the weight loss was only 1–2%. Thus, the formation of a solid phase from a liquid proceeds very quickly in a narrow temperature interval and, in most cases, as combustion. As a result, highly dispersed homogeneous oxide products are formed.

There is a peak broadening in XRD patterns of the mixed oxide samples calcined at 400 °C. Therefore, these samples consist of amorphous, poorly crystallised or highly dispersed phases. After annealing at 600 °C for 2 h, mixed spinel phases were found in all samples. According to the results of XRD, all samples were monophase except the samples I and II, in which two phases were identified ($CuCr_2O_4$ and Cr_2O_3). A crystalline phase of γ-Al_2O_3 exists in all supported samples (Table 1, samples II, V and VII). In the case of sample XI [F-centered cubic spinel, a = 8.252(4) Å], local X-ray spectral analysis was performed. It was found that this sample has a homogeneous distribution of the components with a molar ratio practically equal to its initial composition (Mn:Cu:Co = 3:2:2): 45.1% Mn, 27.0% Co and 27.9% Cu (theoretical values are 42.9, 28.6 and 28.6%, respec-

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[†] Ammonium nitrate; hydrated nitrates of Mn, Co and Cu; $(NH_4)_2Cr_2O_7$ and γ-Al_2O_3 (specific surface area of 185 $m^2\,g^{-1}$) of analytical grade were used as precursors. The $(NH_4)_2Cr_2O_7$ additive (1 mol%) was used in some cases to decrease the temperature of mixture decomposition. The hydrated nitrates were mixed with a 2.5–5 molar excess of NH_4NO_3 and decomposed and annealed in a furnace at 500 °C for 1 h.

The thermal decomposition of the mixtures was studied by heating in N_2 from room temperature to 500 °C at a rate of 5 K min^{-1} using a Q-1500D Derivatograph.

X-ray diffraction (XRD) analysis was performed using a STADI/P (STOE) diffractometer (2θ = 5–80°, $CuK_{\alpha 1}$ radiation, Ge monochromator). The phases were identified using the PCPDFWIN database (PCPDFWIN, Version 2.2, June 2001, JCPDS-ICDD).

Specific surface areas of the samples were measured using the BET method.

The microstructure of the samples was analysed using a JEM-2000FXII electron microscope (Jeol, Japan) in a scanning mode.

The catalytic oxidation of CO or CH_4 was performed in a flow fixed-bed quartz reactor (the composition of a gas mixture was 2.4 ml of CH_4 + + 9.6 ml of O_2 or 6 ml of CO + 6 ml of O_2; the gas flow rate was 12 ml min^{-1}; the contact time was 2 s). The gas composition was determined on a gas chromatograph (Shimadzu 17A) with a thermal-conductivity detector.

Table 1 Rates of methane oxidation (R_1 and R_2) over $M'_xM''_yO_4$ catalysts, specific surface areas (A) and temperatures of 50% ($T_{50\%}$) conversion of methane to carbon dioxide.

Sample	Composition		A/m^2 g^{-1}	m_{cat}/mg	R_1/10^{-5} mmol m^{-2} min^{-1}	R_2/10^{-4} mmol g^{-1} min^{-1}	$T_{50\%}$/°C
	3*d*-metal ratio (at%)	Al_2O_3 (wt.%)					
I	Cu:Cr = 1:4		35	384	35	124	362
II	Cu:Cr = 1:4	50	97	321	9	89	395
III	Cu:Mn = 1:1[a]		34	436	26	88	380
IV	Cu:Mn = 1:1		28	400	26	73	380
V	Cu:Mn = 2:3	60	125	277	7	91	386
VI	Cu:Co = 1:1[a]		8	776	95	76	375
VII	Co:Cr = 3:2	50	105	339	25	261	370
VIII	Co:Mn = 2:1[a]		48	362	44	213	350
IX	Mn:Ni:Co = 3:2:2[a]		80	244	81	648	310
X	Mn:Cu:Co = 3:2:2[a]		60	304	56	335	335
XI	Mn:Cu:Co = 3:2:2		53	363	36	193	335

[a] Samples synthesised without $(NH_4)_2Cr_2O_7$.

tively). The formation of spinels at relatively low temperatures proceeds due to the high homogeneity of the samples.

All the individual oxides synthesised (CuO, MnO_2, Co_3O_4 and Cr_2O_3) have similar morphologies, as can be seen in the images obtained by SEM. They consist of nanoparticles with a size of about 10–50 nm, which agglomerate (2–10 μm) as a result of partial sintering. Note that oxides prepared in molten NH_4NO_3 have smaller particles than oxides obtained by individual nitrate decomposition or synthesised in molten KNO_3. For instance, the average sizes of CuO particles obtained in molten NH_4NO_3, molten KNO_3 and by individual copper nitrate decomposition are 40, 2000 and 250 nm, respectively. According to SEM, mixed oxides have a morphology similar to that of the individual oxides.

The sintering degree of the oxide depends on its nature. Thus, a sample of manganese dioxide exhibited the largest specific surface area (SA) (94 m^2 g^{-1}); therefore, it has the lowest degree of sintering. The sintering degree of nanoparticles in CuO and Co_3O_4 samples is higher than that in MnO_2.

Decomposition of the initial nitrate melt in the presence of γ-Al_2O_3 powder leads to the formation of samples with a large SA and high catalytic activity (Table 1) because alumina absorbs the heat released during decomposition and hinders the sintering of oxide particles.

All the test samples are highly active in the conversion of CO. Thus, 95% conversion took place over samples I and V at room temperature.

All the oxide samples possessed a good catalytic activity in the reaction of complete CH_4 oxidation (Figure 2), comparable with published data.[10–13] Temperatures of 50% conversion and catalytic activity of the samples as relative rates refer to sample surface area (R_1) and weight (R_2) are presented in Table 1. These values were calculated from the following equations: $R_1 = \nu\eta/VmS$, $R_2 = \nu\eta/Vm$, where ν is methane flow rate (2.4 ml min^{-1}), η is conversion at 300 °C, V is methane molar volume (24.45 ml mmol^{-1}), m is the catalyst weight (g), S is the SA of the catalyst (m^2 g^{-1}). A temperature of 300 °C was chosen for calculations because η < 10% at this temperature (only in the case of sample IX, η = 16%).

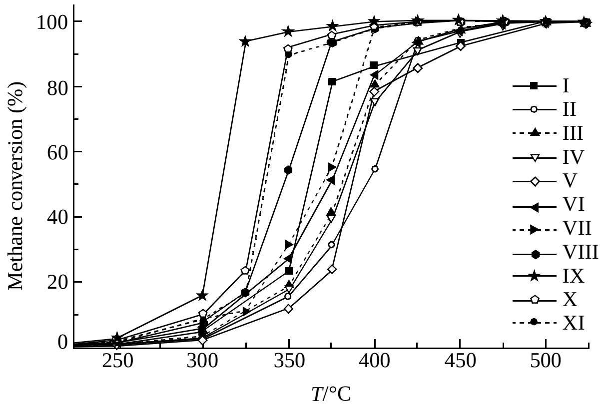

Figure 2 Catalytic activity of samples I–XI in methane oxidation.

Thus, samples I and VII are the most active samples among double samples. The catalytic activity R_1 of sample I (a mixture of $CuCr_2O_4$ and Cr_2O_3) was about 20 times higher than the activity[13] of a sample $CuCr_2O_4$. Ternary samples IX–XI are more active than binary samples I–VIII. In the reaction of methane oxidation the most active sample was IX, which gave 95% conversion of CH_4 at 335 °C. Its catalytic activity is about 60% of the activity of a $NiCo_2O_4$ sample, which was described previously.[13]

Therefore, all the samples demonstrated high activity in the total oxidation of CO and CH_4. These results are consistent with published data on the oxides of Cu, Co, Mn, and Cr as very active catalysts in oxidation reactions.[10–12]

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