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Catalytic combustion of solvent containing air on base metal catalysts

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Abstract

Complete oxidation of solvents (e.g., acetone, butyl acetate and isopropanol) over base metal oxides was investigated using a fixed bed reactor. Mixed oxides with perovskite (e.g. $LaMnO_3$) or spinel structure (e.g. $CuMn_2O_4$) have been prepared and characterized by BET surface area measurements and X-ray diffraction. The influence of catalyst type and composition, reaction temperature and feed composition on the formation of CO_2 and partially oxidized intermediates has been examined.

Keywords: Organic oxidation; Base metal oxides

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1. Introduction

In air pollution control, catalytic combustion is used to oxidize volatile organic compounds (VOC) to CO_2 and H_2O. As the catalytic combustion is mainly applied at low VOC concentration [1], heat recovery by downstream heat exchangers or by catalyst-coated heat exchangers [2] is indicated. Typical catalysts are supported noble metals (e.g. platinum or palladium) or single/mixed metal oxides. As in many cases the formation of toxic intermediates (e.g. acetaldehyde) [3,4] has been observed, one focus of the present study is the investigation of the influence of catalyst type and composition on activity and selectivity. In the following, the study of acetone oxidation on different catalysts will be presented as an example, because the results obtained with different solvent species have proved to be quite similar. The acetone oxidation can be described by a simplified reaction network of parallel and consecutive reactions [3,4]:

$$CH_3COCH_3 \rightarrow 3CO_2 \qquad (1)$$

and

$$CH_3COCH_3 \rightarrow \text{intermediates} \rightarrow CO_2 \qquad (2)$$

Full attention was given to the development of catalysts showing an increase in selectivity for direct oxidation. The present study represents an attempt to prepare catalysts with both greater activity and selectivity for solvent combustion.

2. Experimental

The experimental details of catalyst characterization and activity testing are summarized

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below, catalyst preparation and results of activity testing are given in the next sections.

The BET surface areas of the catalysts were measured using either nitrogen or krypton adsorption at 77 K in a volumetric gas adsorption apparatus. The powder XRD patterns of all catalysts were recorded with a seifert diffractometer using Cu Kα radiation ($\lambda = 1.5405$ Å) and compared with ASTM reference data for phase identification.

The activity tests were carried out using a simple flow reactor. It was made of a 2.5 cm diameter quartz tube and located in a tubular furnace with a single heating zone. Temperatures were measured with a Ni–CrNi thermocouple positioned in the middle of the catalyst bed, containing 0.4 g of catalyst in each case. All data were taken under steady-state conditions using a standard reaction gas mixture (0.20 vol.-% solvent in air, 1000 ml/min, 1 atm). Solvent loading was made by passing nitrogen through a bubbler containing liquid solvent at 0°C and the successive addition of adequate quantities of oxygen and nitrogen (N_2:O_2 = 79:21). The solvent content was checked through a carbon balance using a second reactor in which all carbon containing compounds were oxidized to CO_2. Concentrations of CO and CO_2 were measured with nondispersive IR-analyzers (BINOS), organic species were analyzed by gas chromatography (Varian 3700, FID, HP-FFAP column). For each catalyst sample, a plot of the conversion of the solvent versus temperature (S-shaped curve) and a plot of the yield of intermediates versus temperature were constructed. The yield of intermediates was defined as the amount of carbon in the form of intermediates divided by the whole amount of carbon at reactor inlet. In the following, $T_{95\%}$ designates the temperature at which 95% conversion is achieved under the conditions stated above.

3. Copper manganate catalysts

Copper manganate ($CuMn_2O_4$), a well-known oxidation catalyst for VOC removal at low temperatures [5], was either commercially available (catalyst K1 and K2) or prepared by ourselves (K3). The preparation technique used was the coevaporation of aqueous solutions of copper and manganese nitrate (mole ratio Cu:Mn = 1:2) followed by calcination in air (900°C, 20 h). All catalysts were again calcined (550°C, 4 h) before using in the reactor. Table 1 gives a description of $CuMn_2O_4$-catalysts used in the study.

The temperature dependency of acetone oxidation over $CuMn_2O_4$-catalysts is shown in Fig. 1 (left side). The catalytic activities of the three catalysts were very similar. In Fig. 1 (right side)

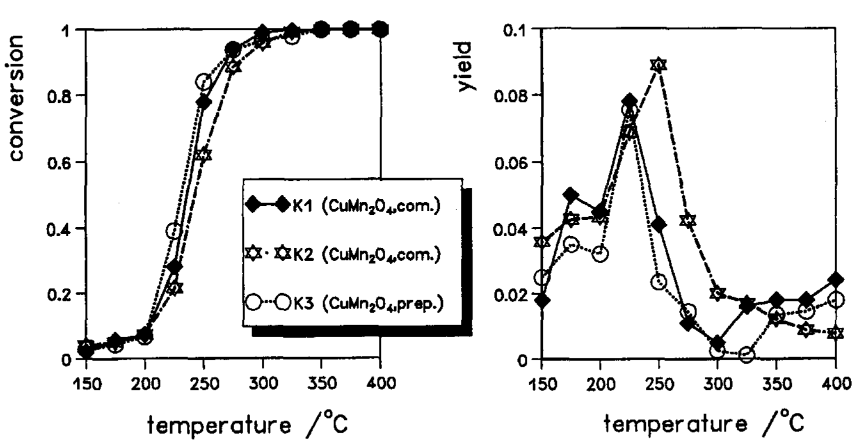

Fig. 1. Oxidation of acetone on three different copper manganate catalysts.

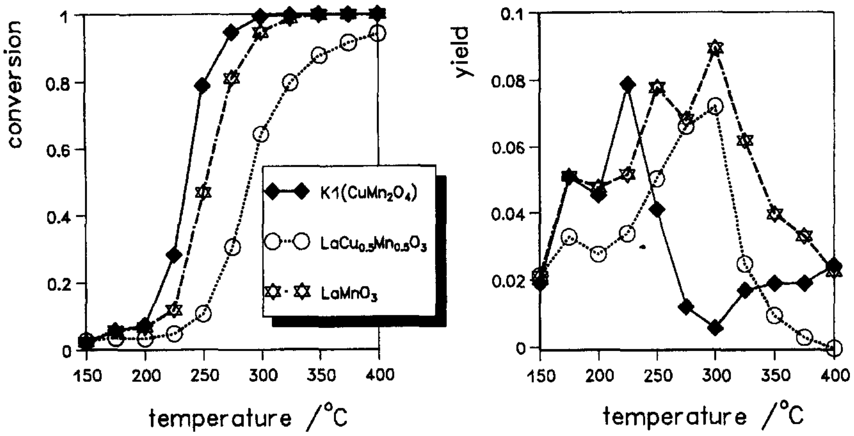

Fig. 2. Oxidation of acetone on copper manganate catalyst K1 and two perovskite type oxides.

the yield of intermediates is shown versus temperature. The commercial catalyst K1 and the self prepared catalyst K3 exhibited an almost similar level of intermediate-formation (maximum 8% at 225°C), while the commercial catalyst K2 showed both a higher yield of intermediates and a significant higher temperature for maximum yield. The main carbon containing intermediates for all three catalysts were acetaldehyde and carbon monoxide.

Table 1
Data of $CuMn_2O_4$-catalysts

	Calcination		Characterization	
	T / °C	Duration/h	BET-area / $m^2 g^{-1}$	$T_{95\%}$ / °C
K1 ($CuMn_2O_4$)	550	4	64	275
K2 ($CuMn_2O_4$)	550	4	99	300
K3 ($CuMn_2O_4$)	900	20	3.1	290

4. Perovskite-type catalysts

Since Voorhoeve et al. [6] reported the high catalytic activity of perovskite-type oxides for oxidation reactions, they were investigated in a multitude of studies. In the structure of perovskite ABO_3 the B site cation (transition metal) is surrounded octahedrally by oxygen and the A site cation (often La) is located in the cavity made by these octahedra. It is important that partial substitution of other cations for A and B cations is possible without affecting the fundamental crystal structure.

One object of the present study was to prepare (substituted) perovskites containing La and Sr as A cation and the same metals as in the $CuMn_2O_4$-spinel as B cation and to compare their catalytic behaviour with that of $CuMn_2O_4$.

The different perovskites were obtained by dissolving the adequate amounts of the nitrates

Table 2
Data of perovskites

	Preparation	Calcination		Characterization	
	Glucose	T /°C	Duration/h	BET-area /m^2g^{-1}	$T_{95\%}$ /°C
$LaMnO_3$	–	1050	6	1.4	300
$LaCu_{0.5}Mn_{0.5}O_3$	–	1050	6	0.3	400
$La_{0.8}Sr_{0.2}MnO_3$ (prep. 1)	–	1050	6	0.9	320
$La_{0.8}Sr_{0.2}MnO_3$ (prep. 2)	yes	750	6	19.4	250

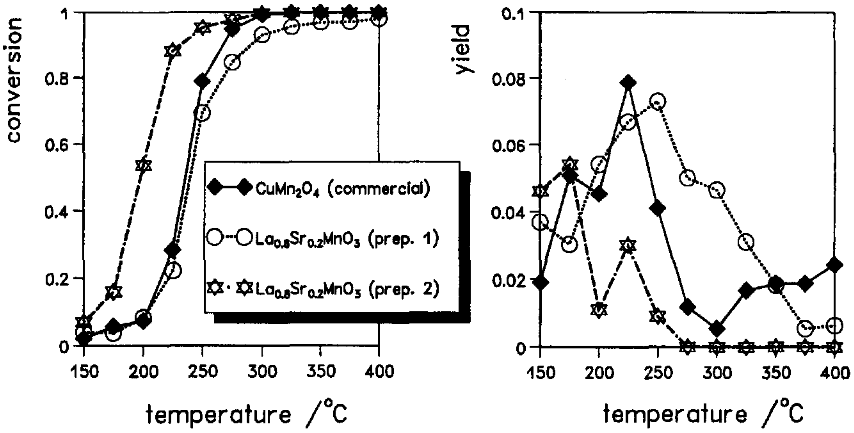

Fig. 3. Oxidation of acetone on copper manganate catalyst K1 and two different prepared $La_{0.8}Sr_{0.2}MnO_3$-perovskites.

of La, Sr, Cu and Mn in water followed by coevaporation and calcination at 750 or 1050°C for 6 h. Segregation of the nitrates during evaporation was avoided by rapid drying and addition of hydroxyethylcellulose (HEC) to the solution in order to increase the viscosity. Adding glucose to the solution in a molar ratio 1:1 and calcination at lower temperatures resulted in a dramatic increase of specific surface area [7]. Exemplarily some results of various prepared and tested perovskites will be discussed below. Data of these selected perovkites are shown in Table 2.

Fig. 2 shows the conversion of acetone and yield of carbon containing intermediates for the most active $CuMn_2O_4$-catalyst K1, $LaMnO_3$-perovskite and $LaCu_{0.5}Mn_{0.5}O_3$-perovskite. $CuMn_2O_4$ was more active than the perovskites. The $LaCu_{0.5}Mn_{0.5}O_3$-perovskite containing the same transition-metals as the $CuMn_2O_4$ -spinel was shown to be the most inactive catalyst ($T_{95\%} = 400$°C). Although all three catalysts showed qualitatively similar intermediate-formation, temperatures of maximum intermediate yield varied as shown in Fig. 2 (right side).

Fig. 3 (left side) illustrates the high catalytic

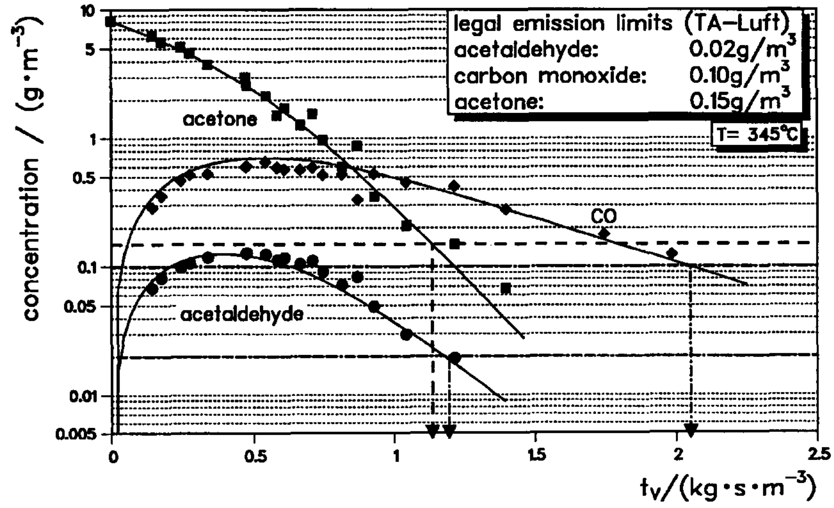

Fig. 4. Mass concentration of acetone, CO and acetaldehyde plottet against the modified residence time for the case of acetone oxidation on copper manganate catalyst K1.

activity that can be achieved with perovskites prepared with glucose (prep. 2). The $T_{95\%}$ value was decreased from 320 to 250°C, the $La_{0.8}Sr_{0.2}MnO_3$ (prep. 2) was even more active than the commercial $CuMn_2O_4$-catalyst K1. The temperatures of intermediate-maximum increased with increasing $T_{95\%}$.

5. Discussion

One has to consider both the S-shaped activity curves and the formation of partially oxidized intermediates to determine the minimum temperature T_{min} required for complete oxidation (achieving the legal emission limit). Such measurements lead to a first estimation of the reactor dimensions and its operation. However, it necessitates the sufficiently precise knowledge of the reaction kinetics to dimension a technical reactor safely. We therefore investigate the complete oxidation kinetics of different solvents on various mixed oxides [3,4], if ever the screening experiments led to interesting results. Fig. 4 illustrates typical results of the kinetic study in the case of acetone oxidation on $CuMn_2O_4$-catalyst K1 using a catalyst bed of 1.75 m length. The mass concentrations of acetone, carbon monoxide and acetaldehyde are plotted against the modified residence time. The legal emission limits (TA-Luft) in the Federal Republic of Germany are much lower for the intermediates (carbon monoxide: 0.10 g m^{-3}, acetaldehyde: 0.02 g m^{-3}) then for the solvent (acetone: 0.15 g m^{-3}) itself. This leads to the somewhat surprising result that the emission limit of the primary solvent is already attained (here 1.1 kg s m^{-3}) when the concentrations of the secondary intermediates are still too high. Sometimes residence times have to be doubled (in this case from 1.1 to 2.1 kg s m^{-3}) to eliminate all compounds. The combustion of the investigated solvents can always be described by simplified parallel-consecutive reaction networks, including the intermediates, and rate expressions for each reaction. The curves shown in Fig. 4 have been calculated in this way. Using the kinetic data the reactor can now be designed and operated in a way that the outlet concentrations of both solvent and intermediates are below the legal limits.

6. Conclusions

The following conclusions can be drawn from this study.

- In all cases formation of partially oxidized intermediates was observed.
- The presence of glucose in the nitrate solution of metal precursor led to a dramatic increase of BET surface area and catalytic activity of perovskite-type oxides.
- The most active catalyst in this study (equal mass basis) was a $La_{0.8}Sr_{0.2}MnO_3$-perovskite prepared in the presence of glucose.
- Measurement of activity and selectivity as a function of temperature can help to estimate the optimal reactor temperature for a technical reactor, the final decision is facilitated by the knowledge of the complete reaction network [3].

Acknowledgements

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