EVIDENCE OF THE ROLE OF NON-STOICHIOMETRY IN Zn-Cr CATALYSTS BY THERMAL INVESTIGATIONS.

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ABSTRACT

The formation, stability and surface reactivity of monophasic non-stoichiometric spinel-type Zn/Cr catalysts (NSS) were investigated by different thermal techniques. It was found that they form prevalently via chromate intermediates and are non-equilibrium phases, which upon use as catalysts or when heated tend to form ZnO and $ZnCr_2O_4$. The non-stoichiometry increases the CO adsorption capacity considerably, with a large fraction of high energy sites identifiable as modified chromium atoms present at the NSS surface. Data from the TPD of methanol, show that the deviation from the stoichiometry decreases the oxidizing power of the surface and creates new stable active sites, which may be identified as surface zinc species.

INTRODUCTION

Renewed interest in Zn/Cr mixed oxides, widely employed in the past in the catalytic synthesis of methanol from syn-gas at high temperature and pressure, has resulted from the discovery that modifications in their composition allow higher alcohol mixtures to be obtained (1,2). A family of well defined Zn/Cr mixed oxides with different Zn/Cr ratio has been characterized (3,4). The members of this series of compounds are monophasic with Zn/Cr ratios which range from 33:67 to 50:50 and can be regarded as excess zinc non-stoichiometric spinels. The excess Zn^{2+} ions are located in B-type sites of the lattice i.e. in octahedral coordination typical of trivalent cations in normal AB_2O_4 spinel. The increased zinc content is accompanied by a parallel increase in the lattice parameter (4,5). Above the 50:50 ratio, the systems are biphasic with a separate ZnO phase in addition to non-stoichiometric spinel (NSS). Stoichiometric $ZnCr_2O_4$ (Zn/Cr= 33:67) is practically inactive, while NSS exhibits catalytic activity in

the synthesis of methanol (3,4).

In the present work various thermal techniques were employed in order to evidence i) the chemical processes leading to the formation of NSS and the range of stability of these phases, and ii) the correspondence between non-stoichiometry and the appearance of peculiar surface properties in CO adsorption and CH_3OH decomposition, which are not observed in the cases of $ZnCr_2O_4$, ZnO and Cr_2O_3.

EXPERIMENTAL

The samples were prepared by coprecipitation at 333K from a solution of the nitrates of the elements with a slight excess of $NaHCO_3$ (pH 8.0 ± 0.1) (5). The characteristics of the samples calcined at 653K for 24h are shown in Table I. Differential scanning calorimetry (DSC) and infrared (IR) analyses were obtained using a Perkin Elmer DSC-2C and a Jasco A-202 spectrophotometer, respectively. X-ray diffraction (XRD) powder patterns were obtained using nickel-filtered $CuK_{\bar{\alpha}}$ radiation (λ = 0.15418nm) and a Philips goniometer equipped with a stepping motor and automated with a General Automation 16/240 computer. The heats of CO adsorption were measured using a Tian-Calvet calorimeter connected to a volumetric apparatus, following a technique described previously, which allows the simultaneous determination of adsorbed amounts and related heats (6). Temperature programmed desorption (TPD) measurements of methanol were performed in the 430-770K range using a laboratory apparatus. After pretreatment for 24h in He or H_2 at 770K, the catalysts were saturated with pulses of CH_3OH (5:95 v/v) at 430K and kept for 1h under pure He flow; then, the temperature was increased at a rate of 25K min^{-1}. The desorbed species were analyzed by a hot-wire detector (HWD) and a quadrupole mass spectrometer (QMS) (7).

RESULTS AND DISCUSSION

Formation and stability of non-stoichiometric phases.

The DSC thermograms of the dried precipitates show the presence of five endothermic peaks (Fig. 1A): the first two at about 373 and 473K due to losses of water and the third at 523-543K to the decomposition of the hydroxycarbonates to amorphous oxides. The amorphous oxides react in two stages at about 740-790K and 880-920K to form NSS The intensities of these transitions increase with increasing chromium content. The samples calcined at 573K for 24h present broad XRD spectra (Fig. 1D) typical of quasi-amorphous compounds, and on the corresponding IR spectra (Fig. 1C) the presence of considerable amounts of amorphous chromate is observed (8). The main feature of the DSC thermograms of these samples, is the presence of a very large peak with the maximum at 630-

TABLE I - Compositions and physical-chemical characteristics of the catalysts calcined at 653K for 24h.

Zn/Cr (at. ratio %)	33:67	38:62	44:56	50:50
lattice parameter (nm)	0.8341	0.8334	0.8359	0.8360
crystal size (nm)	8.0	6.0	5.5	5.0
surface area (m^2g^{-1})	80	115	106	119
x^a	0.250	0.290	0.344	0.400
excess ZnO^b	0.000	0.060	0.135	0.213

a On the basis of a general formula $Zn_xCr_{2/3}$ $_{(1-x)}O$.
b Excess ZnO inside the spinel-type structure (g of ZnO per g of catalyst)

680K attributable to the decomposition of the chromate to chromite (Fig. 1B). In fact, after the precursors have been calcined at 653K for 24h, the formation of NSS is observed (Fig. 1D), with a corresponding decrease in the IR band of chromate (Fig. 1C). The broadness of the DSC peaks indicate that the decomposition of the chromate probably takes place in two stages as previously reported (9). Furthermore, the redox reaction via chromate may also favour the direct formation of spinel, in a way similar to that reported in the literature (10).

NSS, however, is unstable and evolves towards stoichiometric $ZnCr_2O_4$ with increasing temperature and parallel segregation of ZnO (Fig. 1C and 1D). As previously reported (3), this phenomenon is responsible for the loss of catalytic activity in NSS.

Active sites for CO adsorption.

The CO molecule is directly involved in syngas catalytic reactions and is usually activated by adsorption in "carbon down" form onto the catalysts. The evaluation of the number of sites for CO coordination present on the active solids is therefore of interest. Reported in Figures 2A and 2B the calorimetric and volumetric CO adsorption isotherms for monophasic samples having Zn/Cr ratios from 33:67 to 50:50. The samples were previously subjected to a mild reduction treatment in order to eliminate the surface chromates. In this way all the CO is adsorbed in the coordinative, reversible form. The adsorptive capacity of $ZnCr_2O_4$ is quite poor, but increases considerably for NSS. In particular the amount of adsorbed CO and the corresponding heat evolved show a maximum value corresponding to the deviation from stoichiometry, and then slowly decrease with increasing zinc content. The differential heat plots for CO adsorption are reported in Figure 3, which has been obtained by interpolation of the experimental points by means of a best-fitting computer program. Figure 3 indicates that, despite the marked differences in adsorptive capacity, the
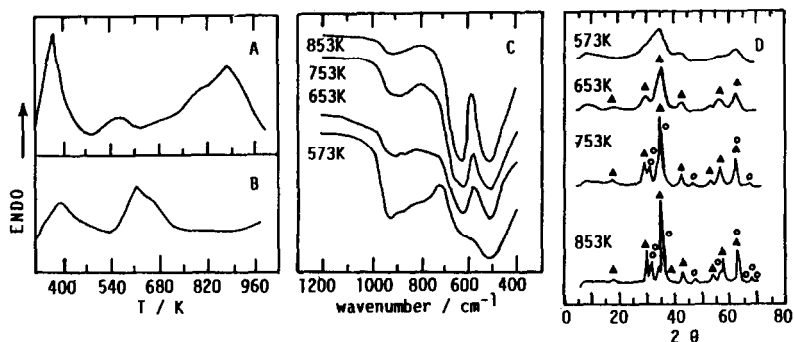
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Fig. 1. DSC thermograms of the Zn/Cr= 50:50 sample dried at 363K (A) and
calcined at 573K for 24h (B). IR spectra (C) and XRD powder patterns
(D) of the same sample calcined for 24h at different temperatures: (▲)
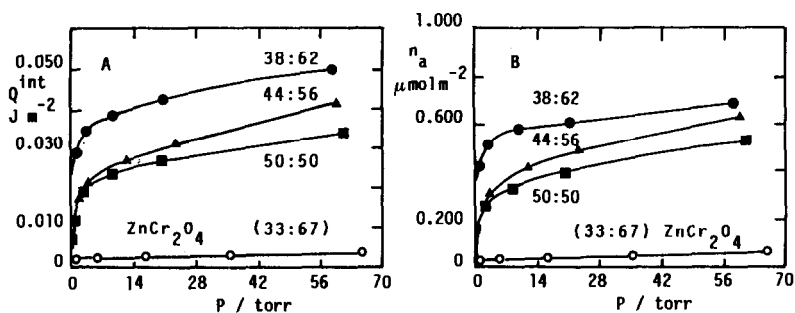spinel-type phase, (o) ZnO.

Fig. 2.   Calorimetric (A) and volumetric (B) isotherms for CO adsorption on
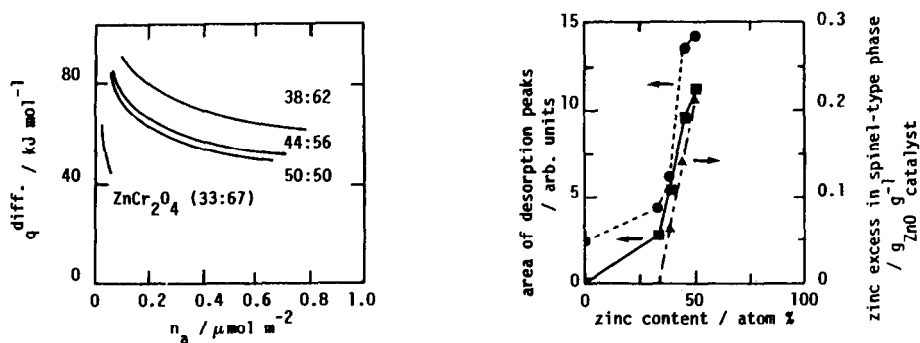$ZnCr_2O_4$ and three non-stoichiometric monophasic spinels.

Fig. 3. Differential heats of CO adsorption ($q^{diff}= dQ^{int}/dn_a$) on $ZnCr_2O_4$ and
three non-stoichiometric monophasic spinels.

Fig. 4. Amount of excess ZnO inside the NSS phases (▲) and TPD peak area for
catalysts pretreated in helium (●) and in hydrogen (■).

TABLE II - Methanol adsorption during the saturation experiments and $H_2/(CO+CO_2)$ and CO/CO_2 ratios in the TPD peaks.

Zn/Cr at. ratio %	Pretreatment T(K)	Flow	Pulses for saturation	First pulse with CH_3OH	$H_2/(CO+CO_2)$ ratio	CO/CO_2 ratio
33:67	770	He	10	5	only H_2O and CO_2	
	770	H_2	9	3	only H_2, H_2O and CO_2	
38:62	770	He	15	7	1.2	0.6
	770	H_2	12	5	1.5	0.7
44:56	770	He	20	10	1.2	0.4
	770	H_2	15	6	1.8	0.6
50:50	770	He	21	11	1.3	0.3
	670	He	16	10	1.2	0.3
	770	H_2	20	10	1.9	0.8
	670	H_2	15	8	2.0	0.5
ZnO	770	He	5	3	2.0	1.1
	770	H_2	2	1	not detectable	
Cr_2O_3	770	He	2	1	not detectable	
	670	He	3	1	only CO and CO_2	
	770	H_2	no adsorption		no desorption	

nature of the adsorption sites is basically the same in all the samples since their energy ranges between 80 and 40 kJ mol^{-1}. In particular the main differences among the various samples are determined by the different contents of sites with heats of adsorption higher than 60kJ mol^{-1}.

On the basis of the heats of interaction and the IR frequencies of adsorbed CO, the adsorption sites have been identified as surface Cr^{3+} ions (11), whose adsorptive capacity is related to the presence of excess Zn^{2+} ions in the octahedral positions of the spinel structure, which modifies, in comparison with the stoichiometric $ZnCr_2O_4$, both the environment of each Cr^{3+} ion and the collective properties of the whole solid (3-5). This interpretation agrees with the order followed by the various NSS phases in CO adsorptive capacity, which is proportional to the chromium content. However, a minor role of the surface Zn^{2+} ions located at the B sites in the adsorption of CO cannot be excluded (11).

Temperature programmed desorption of methanol.

Methanol decomposition tests were carried out in order to examine the surface reactivity more completely.The data reported in Table II and Figure 4, show the relationship between excess zinc inside the NSS structure and the amount of methanol adsorbed during the saturation experiments as well as the amount of

desorbed species in the TPD experiments. These two amounts can be taken as an indication of the number of active sites. The observed correlation is present for both the pretreatments, in He or H_2, however, the reducing pretreatment decreases the adsorption capacity of NSS phases, and completly destroys that of pure ZnO and Cr_2O_3 (Table II). On the other hand, the two treatments slightly modify the TPD peak profiles for the NSS phases (Fig. 5). In all cases a maximum at 590K and a shoulder at a higher temperature were observed. The first peak is formed by H_2, CO and CO_2 (as found in the case of ZnO), while the shoulder at ca. 770K is due to successive desorption of CO_2 (as found in the case of $ZnCr_2O_4$). The two CO_2 desorption maxima at different temperatures may be attributed to the presence of two centers having different basicities.

According to the pretreatment adopted, the behaviour of NSS is similar either to that of ZnO or to that of $ZnCr_2O_4$. The reducing treatment of NSS results in $H_2/(CO+CO_2)$ ratios near 2.0 and CO/CO_2 ratios near 1.0, typical of ZnO (7, 12) (Table II). However, unlike ZnO, NSS has a higher number of adsorption centers, that are not destroyed by H_2. After pretreatment in He, NSS phases show $H_2/(CO+CO_2)$ ratios lower than 2.0 and CO/CO_2 ratios near to 0.5, indicating the presence of oxidizing centers on the surface, in agreement with the IR data (Fig. 1C). This behaviour is similar to that of $ZnCr_2O_4$, which has a higher oxidizing power, and also is stable in a reducing atmosphere.

Therefore the deviation from stoichiometry decreases the oxidizing power and creates new sites for methanol adsorption, which also are stable in a hydrogen atmosphere. On the basis of the desorption temperatures, these sites may be identified as zinc surface species, which adsorb methanol and stabilize it as methoxy and formate species (7).

CONCLUSIONS

The investigations of excess zinc Zn/Cr spinels active in the synthesis of methanol from CO and H_2, have shown that they are metastable phases whose formation depends on the preparation route adopted. Thermal treatment at temperatures higher than 753K destroys the NSS and a biphasic solid composed of ZnO and $ZnCr_2O_4$ is obtained. This process also occurs during catalytic tests and leads to deactivation of the catalysts.

When compared with stoichiometric $ZnCr_2O_4$ (catalytically inactive) NSS shows a marked enhancement of the chemisorptive capacity towards CO (proportional to chromium content) as well as an increse in the CH_3OH decomposition capacity proportional to the zinc content. Both Cr^{3+} and Zn^{2+} sites play a role in the catalytic activity of NSS, which probably depends on the delicate balance between CO activation (occurring on Cr^{3+}) and H_2 activation occurring on Zn^{2+} sites (13).

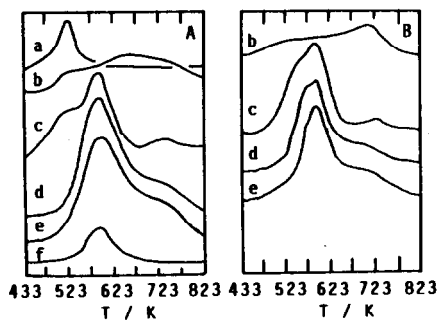Fig. 5. TPD peaks for Cr_2O_3 (a), ZnO (f) and catalysts with Zn/Cr= 33:67 (b), 38:62 (c), 44:56 (d) and 50:50 (e) pretreated at 770K in helium (A) and hydrogen (B).

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