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Synthesis of alcohols from carbon oxides and hydrogen on ZnCrTi oxides: preparation and catalytic activity

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Ternary systems of composition $(1-x)ZnCrO_{2.5}\cdot xZn_2TiO_4$ were tested in the synthesis of higher alcohols from syngas. The catalysts after calcination were found to be solid solutions of Zn, Cr and Ti oxides of spinel like structure, with only a small amount of crystalline ZnO phase segregated. After the catalytic test more important quantities of crystalline ZnO were formed in the catalysts revealing an intrinsic instability of the system. However, a significant maximum in selectivity to higher alcohols was found for $x = 0.1$ and is associated with an increased rate of isobutanol (2-methylpropanol) formation observed on this system.

Keywords: Higher alcohols synthesis; Zn–Cr–Ti oxides

1. Introduction

The direct synthesis of higher alcohols mixed with methanol from carbon oxide and hydrogen has recently been the object of considerable attention from both the fundamental and scientific points of view for the production of synthetic fuels to be mixed with gasoline. Among the systems proposed for the synthesis of alcohols from syngas are Zn–Cr oxides doped with an alkali and eventually other elements [1–3]. They were also developed and tested in a demonstration plant [4]. However, the binary Zn–Cr oxides show some decay with time on stream ascribable to a certain structural instability, due to the more severe conditions of synthesis which are necessary when higher alcohols are the major products desired. The decay seems to be related to a slow process of segregation of ZnO from the defective spinel phase structure of the Zn–Cr mixed oxide [2,3] and, therefore, to a decrease of the amount of zinc present in irregular non-stoichiometric octahedral positions.

In past work on the synthesis of higher alcohols on new catalytic systems [5], we showed that Zn–Ti oxides may crystallize in an inverse spinel phase of Zn_2TiO_4 stoichiometry, which was found to be thermally very stable in air during the calcination process. The intrinsic greater stability of the Zn_2TiO_4 system and the ability in the chain growth suggested an attempt to improve the performance of the Zn–Cr oxide system by forming a solid solution with Zn–Ti oxide, in the hope of keeping the methane formation low at the same time.

2. Experimental

Mixtures of Zn_2TiO_4 and $ZnCrO_{2.5}$, prepared by the method of complexation with citric acid [5–7] which normally favours the solid solution formation, here indicated with the formula $(1-x)ZnCrO_{2.5} \cdot xZn_2TiO_4$, were examined. The Zn/Cr ratio in the binary Zn–Cr oxide systems was chosen equal to 1, because for such a value the deactivation observed in reasonably slower [2,3].

Starting salts were Ti(IV) propoxide (tetraisopropyl orthotitanate), $Zn(NO_3)_2 \cdot 9H_2O$, $Cr(NO_3)_3 \cdot 6H_2O$ and citric acid. Preparations were such as to obtain 100 g of oxides after calcination; citric acid, in a ratio of 1/3 mol/equivalent of metal ions, was dissolved in 1 ℓ of water. Ti propoxide was dropped in the resulting solution; the product of hydrolysis was dissolved in about 1 h by heating at 363 K; as a result of the complexation, isopropyl alcohol was released.

The solution of zinc and chromium nitrates (dissolved in about 400 ml of water) was then added: the resulting solution was concentrated on a stirring heater until stirring was hindered by a strong increase of viscosity and foaminess; some NO_x were evolved during this time. The samples were then dried at 423 K by slowly heating in an air flow. A sudden elimination of the residual NO_x accompanied by swelling of the solid was observed.

The samples were then ground (< 48 mesh), calcined at 633 K with heating rate 1 K/min, kept in a thin layer at this temperature for 7 h with periodical stirring in order to completely eliminate the carbonaceous material and they were finally calcined at 743 K with a heating rate of 1 K/min and kept at this temperature for 3 h. The powder was then compressed at 3 tons cm^{-2} in order to obtain lamina which were broken into 14–20 mesh granules.

The surface area was measured using a Sorptomatic 1800 (Carlo Erba).

IR spectra were recorded with a Perkin Elmer 457 using KBr disks.

For the X-ray powder diffraction analysis a Philips diffractometer, fitted with a General Automation system 16/240 computer was used. Ni filtered Cu Kα radiation ($\lambda = 0.15418$ nm) was used with silicon or corundum as internal standards. Quantitative determination of ZnO crystalline phase was carried out when necessary by using the "matrix flushing method" described by Chung [8]. Approximate crystal sizes were evaluated by the Sherrer method; disorder effects were not taken into account. Before the catalytic tests the catalysts were prereduced in a N_2–H_2 atmosphere as already reported [5] and were dry impregnated with CH_3COOCs to obtain a 8.47 or 12.5% Cs_2O content (b.w. on an oxide base). The catalysts were finally reduced as before [5]. Cs doped catalysts were considered because it is known from the literature [1] that this alkali shows the greatest promoting effect for alcohol formation.

Catalytic activity runs were performed in a descending flow, copper lined, tubular reactor heated at 703 K by a fluidized sand bath. The reacting mixture ($H_2/CO = 1$) was supplied by cylinders and a compression loop (membrane compressor). The outlet gases from the reactor were cooled at 263 K to obtain condensation of most of the products and then expanded to atmospheric pressure. The expanded mixture of light boiling compounds (H_2, CO, CO_2, CH_4, C_2H_6) was periodically analysed during the run by an on-line Hewlett Packard gaschromatograph using H_2 as carrier gas, 3 m of Porapak QS packed column and both TCD and FID detectors. The condensed mixture was discharged (after outgassing) from the condenser at the end of each run and analyzed by a Varian 3400 series gas chromatograph equipped with a 3 m of Porapak QS packed column and TCD detector; He was employed as carrier gas.

The mean carbon numbers of C_{2+} hydrocarbons (nC_h) and of C_{2+} oxygenates (nC_{ox}) were determined by chromatographic analysis and identification of the peaks.

3. Results and discussion

Fig. 1 shows the percentages of crystalline ZnO in the catalysts calcined at 743 K, before impregnation with CH_3COOCs and after impregnation and use in

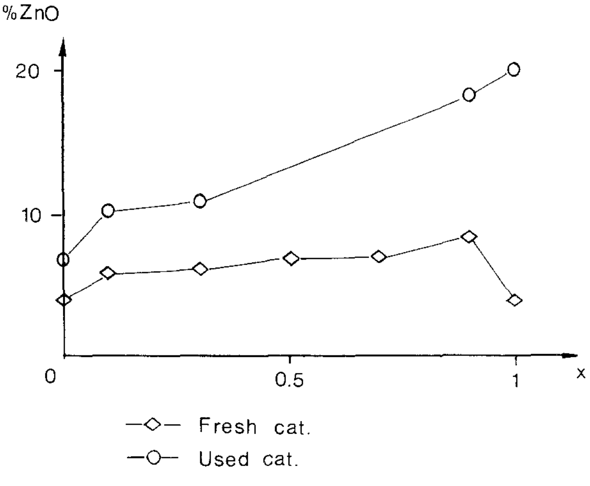

Fig. 1. Amount (% w/w) of crystalline ZnO formed in the calcined catalysts versus Ti/(Ti + Cr) molar fraction.

the reactor. The amount of crystalline ZnO is significant for all samples and ranges from 4 to 8 wt% for the fresh catalysts without showing any particular trend, whereas an increase with x is observable for discharged samples. Evidently the preparation of the catalysts suffers from some not completely controlled steps, most probably the calcination which is affected by sudden evolution of NO_x. The segregation of ZnO in the catalysts here considered is not surprising for non-stoichiometric Zn/Cr oxides ($x = 0$), in which it occurs simply as a thermal effect, the spinel $ZnCr_2O_4$ being the only stable compound at high temperature [2].

Zn–Ti oxides ($x = 1$), on the contrary, when calcined in air display octahedral zinc and are thermally very stable [5]. The fact that for $x = 1$ a relevant amount of segregated ZnO is found in the used catalysts shows that this system doped with alkali under reaction conditions is no longer stable.

The stabilisation effect of Ti on octahedral zinc is therefore lost for the ternary Zn–Cr–Ti oxides doped with alkali and under reducing conditions. Both fresh and discharged samples showed in addition to the segregated ZnO only another phase, a cubic spinel-type, the lattice parameter a of which varies almost regularly with x from the extreme values of $ZnCr_2O_4$ and $ZnTiO_4$, as shown in fig. 2, thus indicating the formation of a Zn/Ti/Cr/O solid solution in fresh catalysts, which persists in used catalysts without significant structural alterations in spite of the observed ZnO segregation. No significant sintering of spinel phases was detected, the mean crystal sizes (Sherrer method) being about 75 Å for fresh catalysts and about 80 Å for discharged ones.

Fig. 3 shows the IR spectra of the calcined samples for $x = 0$, 0.5, 1 and of ZnO as a reference. The spectrum for $x = 0$ is characterized by bands about 1600 cm^{-1} indicating the presence of some hydroxycarbonates (SADTLER ST. SP. 1743 of $Zn_5(OH)_6(CO_3)_2$), bands at 480–620 cm^{-1} which are typical of the

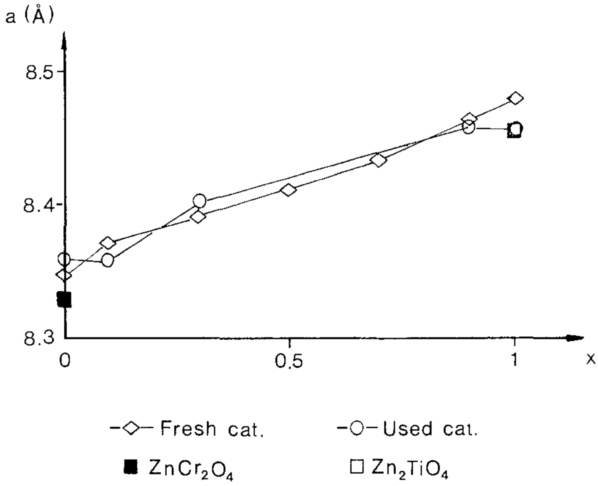

Fig. 2. Cubic spinel type parameter a versus x.

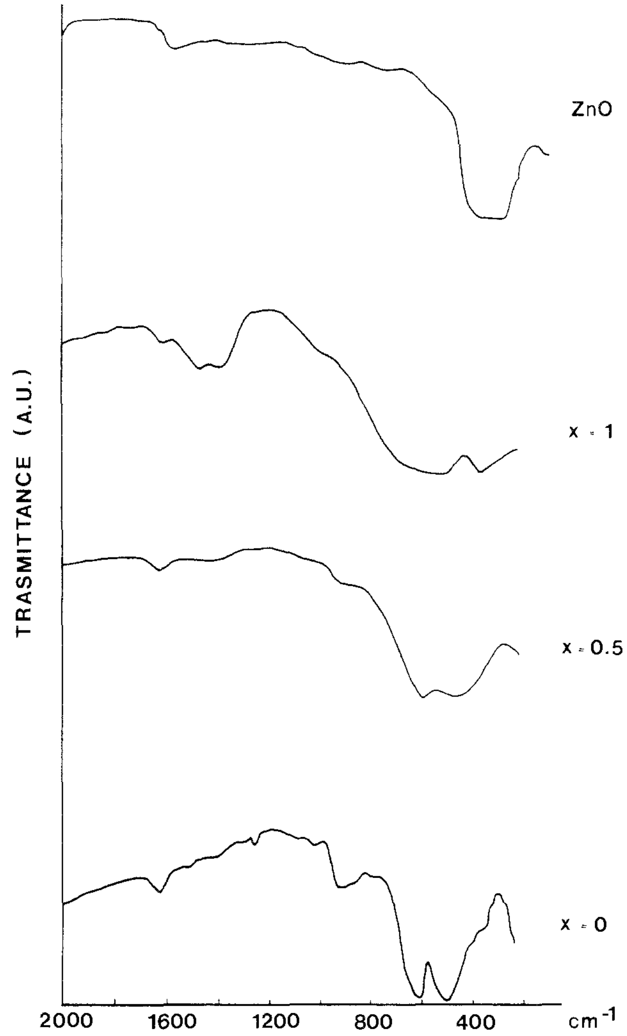

Fig. 3. IR spectra of ZnO and samples with $x = 0, 0.5, 1$.

spinel phase and bands at 910 cm^{-1} which may be ascribed to Cr^{VI} present in the structure [3]. By increasing x the bands at 480 and 620 cm^{-1} gradually broaden to give a single band in the 400–600 cm^{-1} region, which is also typical of ZnO, while the band at 910 cm^{-1} ascribed to Cr^{VI} gradually disappears.

Catalysts discharged from the reactor did not display the band at 910 cm^{-1} characteristic of Cr^{VI}, the other main features of the spectra remaining the same. Surface area of the calcined samples were in the 45–65 m^2 g^{-1} range and were some 10–15% less in the discharged samples.

Fig. 4 gives the results of the catalytic tests for 8.47% Cs_2O samples. For $x > 0.3$ the yields to higher alcohols and to C_{2+} hydrocarbons decreases, while CH_4 increases substantially. For $x = 0.1$ a minimum in methanol formation and

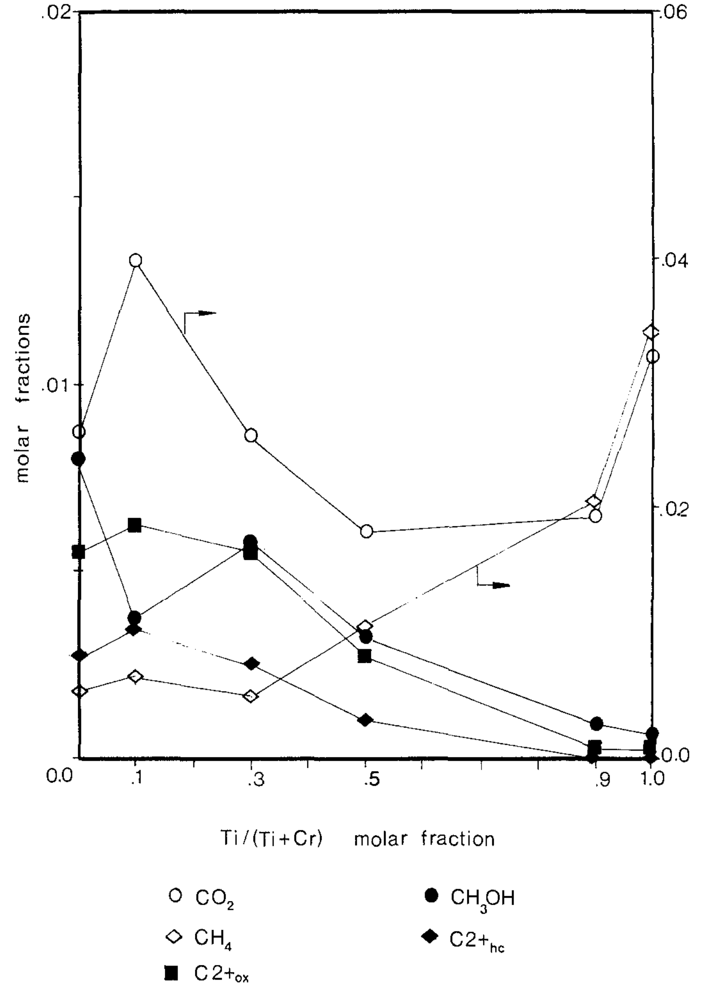

Fig. 4. Product distribution (as molar fractions in reactor's outlet gases) versus x measured at 703 K, $H_2/CO = 1$ and 8.47% Cs_2O.

a corresponding pronounced maximum in CO_2 and a less significant maximum in the oxygenates and hydrocarbons formation is observed.

This datum may be interpreted as an increased ability in chain growth caused by this system, and it is even more pronounced for the 12.5% Cs_2O samples. Indeed, it was found that for $x = 0.1$ the molar yield to 2-methylpropanol was 39% greater than for $x = 0$; while, on the contrary, for $x = 0.2$ was 31% lower than for $x = 0$.

The increased amount of C_{2+} oxygenates observed for $x = 0.1$ must be ascribed to a greater amount of isobutanol production (table 1) and to a greater ability in chain growth both for the C_{2+} alcohols and C_{2+} hydrocarbons as shown by their mean carbon number (table 2).

Table 1
Molar fraction of alcohols in the reaction outlet (mol%) for 12.5% Cs_2O, $T = 703$ K

Cat	CH_3OH	C_2H_5OH	n-C_3H_7OH	i-C_4H_9OH
$x = 0$	0.6690	0.0230	0.0624	0.2627
$x = 0.1$	0.6395	0.0160	0.0543	0.3647

Table 2
Mean carbon number of C_{2+} alcohols (nC_{ox}) and of C_{2+} hydrocarbons (nC_h) for 8.74% Cs_2O, $T = 703$ K

	$x = 0$	$x = 0.1$	$x = 0.3$	$x = 0.5$	$x = 0.9$	$x = 1.0$
nC_{ox}	4.04	4.39	4.18	4.00	3	2.75
nC_h	3.36	4.28	3.69	4.80	5	5.05

The primary assumption which leads us to perform this work, i.e. the stabilisation of the catalyst by admixing Zn–Cr oxides with Ti oxides, was therefore not verified; however, an interesting maximum of isobutanol production, which is more evident by adding larger amounts of cesium, is observed. The increased production of isobutanol may be ascribed to a greater chain growth ability of the catalytic system for $x = 0.1$ as shown by the higher mean carbon number of both $C_{2+,ox}$ and $C_{2+,hc}$ and also the lower molar fraction of methanol itself as well as ethanol and propanol.

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