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ISOBUTANOL FROM SYNTHESIS GAS

Wilhelm KEIM and Wolfang FALTER

Institute of Technical Chemistry and Petrochemistry, Rheinisch-Westfälische Technische Hochschule Aachen, Worringer Weg 1, D-5100 Aachen, F.R.G.

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A highly active and selective Zr-Zn-Mn-Li-Pd catalyst for the one-step synthesis of 2-methyl-1-propanol (isobutanol) from synthesis gas is described. This catalyst produces 60 wt% isobutanol at a rate of 740 g isobutanol per liter catalyst and hour. The catalyst was optimized by a statistical method indicating that during catalyst preparation pH and temperature control are essential.

1. Introduction

Recent years have seen an impressive growth of MTBE production especially in Western Europe and USA. Also in the future great amounts of the available isobutene (by-product of processes as steam cracking, catalytic cracking and dehydration) will be allocated as raw material for the synthesis of MTBE and a shortage is foreseen. Therefore many attempts are undertaken to develop alternative routes such as butane isomerisation. An other approach is the direct hydrogenation of carbon monoxide which was commerically practized by BASF [1,2] or still is done in the German Democratic Republic (Isobutyloil-Synthesis). In this old process a mixture of alcohols is obtained with methanol dominating and 2-methyl-1-propanol (isobutanol) amounting up to 15 wt%.

2. Results and discussion

Some years ago [3] we became interested in resuming this CO hydrogenation route emphasizing the synthesis of isobutanol or isobutene (for chemical use) and the direct conversion to MTBE according to fig. 1. As others [4–8] we learned that alkali addition is essential for C_1^+ alcohol formation and that combinations of various metals change the activity and selectivity to alcohols drastically. Table 1 summarizes our results using various metal combinations.

The use of the hydrogenation metal palladium increased the selectivity to isobutanol significantly. It is assumed that palladium favours the methanol

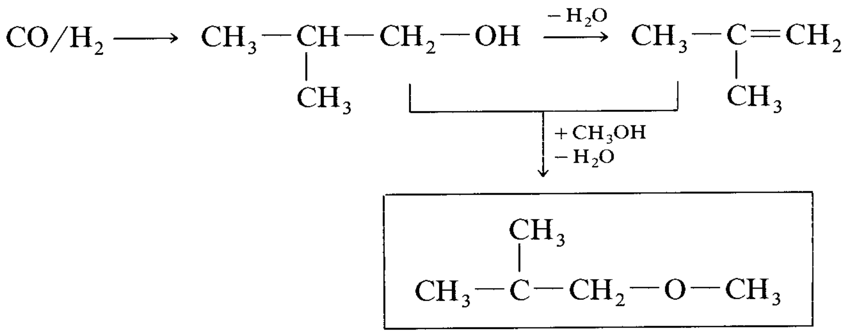

Fig. 1. Routes to MTBE.

synthesis and suppresses methane formation [9]. Variation of the reaction conditions changes selectivities to isobutanol. This is exemplified using catalyst 3, which allows the following conclusions:

INFLUENCE OF PRESSURE

With increasing reaction pressure the selectivity changes. The isobutanol fraction in the total liquid product reached with close to 60 wt% its maximum at 10 MPa and drops at 35 MPa to less than 20% in favour of methanol production. At pressures < 10 MPa the isobutanol selectivity also decreases favouring methane formation.

Table 1
Alcohol production with various catalysts

catalyst	1 [3] %	2 [9] %	3 [10] %
methanol	27	45	12
isobutanol	22	25	59
other alcohols	16	12	7
water	11	6	7
rest	24	12	15
yield isobutanol/g l^{-1} h^{-1}	176	200	740
GHSV/h^{-1}	12000	12000	20000

1: Zr (60.3 wt%); In (3.7 wt%); Cu (2.9 wt%); Zn (6.8 wt%); K (1.7 wt%)
2: Zr (58.5 wt%); Mn (14.7 wt%); Pd (1 wt%); K (0.8 wt%)
3: Zr (30.5 wt%); Mn (15.4 wt%); Zn (8.6 wt%); Pd (0.2 wt%); Li (1.5 wt%)
calculated as oxides from AAS measurements.
reaction conditions: temp. K 693, pressure MPa 25, CO/H_2 (vol.-% 1)

INFLUENCE OF REACTION TEMPERATURE

The reaction temperature was varied between 600 and 750 K showing minor effects on the activity. However the selectivity was altered drastically as is evident from fig. 2.

Whereas at low reaction temperature (625 K) about 72% methanol can be detected in the liquid product, this portion decreases to 6% at 725 K. Parallel the isobutanol portion in the liquid product increases from 4% at 625 K to 45% at 715 K. At even higher temperatures the isobutanol share decreases and higher alcohols are predominantly formed.

Water formation is independent of reaction temperature and remains at 10% in the liquid product. The formation of carbohydrates increases with increasing reaction temperature, especially the selectivity to methane.

A 720 hours test ($T = 715$ K, $p = 25$ MPa, GHSV $= 20000$ h^{-1}) revealed that no decline in either activity or selectivity could be observed. Characterization of the catalyst before and after the 720 hours test showed no decline in BET surface area supporting high mechanic and thermal stability.

In comparison with data published in the literature our catalyst 3 is quite superior regarding activity and selectivity for isobutanol synthesis.

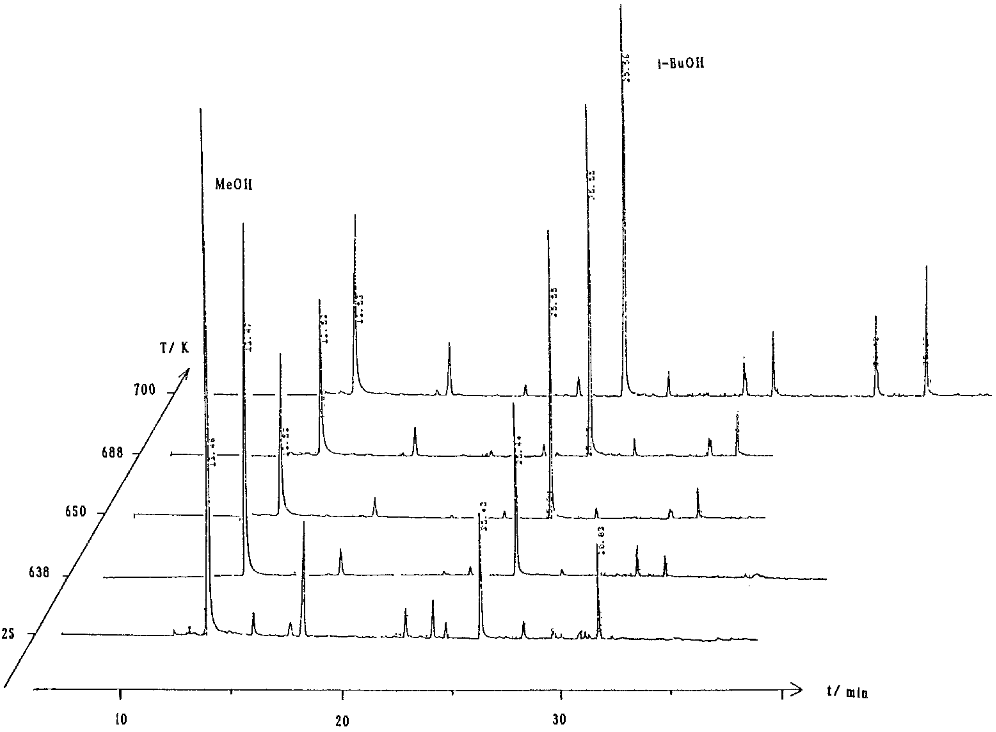

Fig. 2. Temperature dependence i-BuOH selectivity (Zr-Zn-Mn-Li-Pd catalyst, 10 MPa, GHSV 10000 h^{-1}).

3. Experimental [10,11]

The catalyst testing was carried out in a continuous flow system containing a 50 ml integral tubular reactor. Product analysis was carried out by capillary on-line gas chromatography, which is conducted by making use of a live switching system between a semipolar (CW 1500) and an apolar (OV 101) chromatography column. This multidimensional chromatography is necessary to separate isomeric hydrocarbons, starting from C_1 = methane, and alcohols, ending with C_8 = octanols.

A statistical Plackett-Burman plan [10] was carried out to check the individual influence of 18 variables on activity and selectivity. Only pH and temperature during catalyst preparation have been found to significantly influence the performance data. The preparation procedure is as follows: The catalysts are prepared by co-precipitation from the corresponding metal nitrates.

Temperature	350 K
concentration $M_x(OH)_y$	2-molar
$M_x(NO_3)_y$	0.5-molar
time of precipitation	1 hour
pH	11 (+/− 0.1)
ageing	5 hours
washing	twice with 1 l water/1 hour
drying	15 hours at 400 K
calcination	3 hours at 600 K/air
reduction	2 hours at 500 K and H_2 or N_2/H_2 (5 MPa)

The precipitation was carried out in a stirred batch reactor. The precipitates were filtered, washed twice with cold demineralized water, dried overnight and calcined in air. The composition of dried samples was determined by atomic absorption spectroscopy. Structural data were obtained by SIMS, electron diffraction, BET surface measurements and textural analysis by REM. The X-ray diffraction analysis shows the presence of Zr(IV), Zn(II), Alkali(I) and Mn(II). They are present before and after calcination as well as after reaction with CO/H_2. The thermal decomposition of catalysts before and after reaction was studied by TGA. All these data will be published in the near future. The palladium was added after calcination via impregnation technique.

Abbreviations

GHSV gas hourly space velocity defined as volume incoming syngas/volume catalyst and hour at standard conditions, MTBE methyl tert. butyl ether.

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