Pd Supported on Zn^{II}-Cr^{III} Mixed Oxide as Catalyst for One-Step Synthesis of Methyl Isobutyl Ketone

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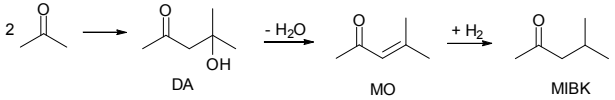
Introduction

Methyl isobutyl ketone (MIBK) is produced on industrial scale and widely used as a solvent for paint and protective coatings [1]. Traditionally, MIBK is manufactured via a three-step process involving base-catalysed aldol condensation of acetone to diacetone alcohol (DA), acid-catalysed dehydration of DA to mesityl oxide (MO) and metal-catalysed hydrogenation of MO to MIBK [2]. Heterogeneous multifunctional catalysts that contain acid-base and metal functionalities and are therefore capable of carrying out all three reactions in one step in the liquid or gas phase without separating the intermediate DA and MO have attracted considerable interest [2]. Because the one-step process is simpler and more economical, there is an incentive to find new, more efficient catalysts for this process.



Here we report the one-step synthesis of MIBK in the gas and liquid phase over a new catalyst: palladium supported on ZnO-Cr_2O_3 mixed oxide, Pd/Zn-Cr. Although Zn-Cr oxide has long been used as a catalyst for various reactions, neither Zn-Cr oxide nor Pd/Zn-Cr has been used for the synthesis of MIBK prior to our work.

Materials and Methods

A series of Zn-Cr oxides with a Zn/Cr atomic ratio of 1:30-20:1 were prepared by co-precipitation of Zn^{II} and Cr^{III} hydroxides and doped with Pd [3,4]. The catalysts were characterised using BET (surface and porosity), TGA (water content), XRD (crystallinity), NH_3 and pyridine adsorption (acidity - by DRIFT and calorimetry) and H_2 adsorption (Pd dispersion) (Table 1). The gas-phase synthesis of MIBK was performed under atmospheric pressure in a Pyrex glass fixed-bed microreactor. The liquid-phase reaction was carried out in a stainless steel autoclave. Product analysis was conducted by gas chromatography.

Results and Discussion

Pd metal supported on Zn^{II}-Cr^{III} mixed oxide was found to be an efficient bifunctional catalyst for one-step synthesis of methyl isobutyl ketone (MIBK) from acetone and H_2 in the gas and liquid phases. Diisobutyl ketone (DIBK) formed a useful by-product in this process. In the gas phase, the catalyst reached a steady state in ca. 1 h and showed constant activity and selectivity for at least 10 h on stream (Fig. 1). For both the continuous gas-phase process (300°C, ambient pressure) and the batch liquid-phase process (180°C, 7.5 bar H_2 pressure), the preferred catalyst formulation comprised 0.3 wt% Pd on the amorphous Zn-Cr (1:1) oxide (S_{BET} = 132 m^2/g) possessing Lewis acid sites (1.2 mmol/g density) with an enthalpy of NH_3 adsorption of -155 kJ/mol. Both processes produced MIBK with a selectivity of 70-78% and 90% MIBK + DIBK total selectivity at 38-40% acetone conversion, on a par with the best results reported to date. Evidence is provided that hydrogenation of mesityl oxide to MIBK is the rate-limiting step in the gas-phase process.

Table 1. Catalyst characterization.

Catalyst	S_{BET} (m^2/g)	Pore diameter [a] (Å)	Pore volume[b] (cm^3/g)	H_2O content (wt%)	D[c]	ΔH (NH_3)[d] (kJ/mol)
Zn-Cr (1:30)	223	29	0.16	8.95		-193
Zn-Cr (1:10)	193	31	0.15	9.19		-180
Zn-Cr (1:1)	132	33	0.11	8.97		-155
Zn-Cr (10:1)	33	112	0.09	2.83		-150
Zn-Cr (20:1)	36	91	0.08	2.02		-127
0.3%Pd/Zn-Cr (1:30)	189	36	0.16		0.83	
0.3%Pd/Zn-Cr (1:10)	180	31	0.14		0.79	
0.3%Pd/Zn-Cr (1:1)	112	35	0.09	9.32	0.37	
0.3%Pd/Zn-Cr (10:1)	32	103	0.09		0.58	
0.3%Pd/Zn-Cr (20:1)	19	87	0.04	1.73	0.58	

(a) Average pore diameter by BET method, (b) Single point total pore volume, (c) Pd dispersion, and (d) Initial enthalpy of NH_3 adsorption at zero adsorption coverage at 100°C.

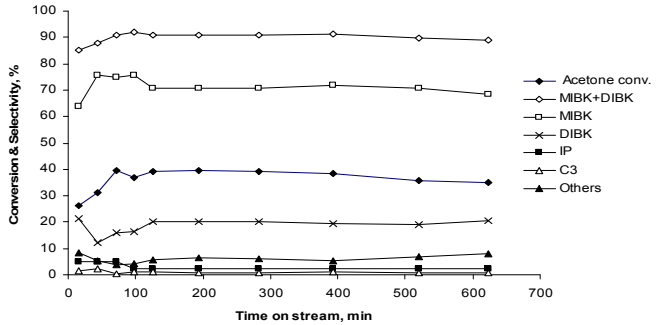


Figure 1. Acetone conversion and product selectivities vs. time on stream (0.2 g 0.3%Pd/Zn-Cr (1:1), 10 ml/min H_2 flow, acetone/H_2 = 37:63 mol/mol, 300°C).

Significance

New bifunctional catalyst Pd/Zn-Cr for the one-step MIBK synthesis has been developed and thoroughly characterised.

References

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