Gas-phase pinacol conversion on $AlPO_4$, γ-Al_2O_3 and SiO_2 catalysts

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Pinacol (2,3-dimethyl-2,3-butanediol) conversion over $AlPO_4$ ($Al/P = 1$) and γ-Al_2O_3 catalysts proceeded in two parallel reaction pathways with formation of 2,3-dimethyl-1,3-butadiene (by 1,2-elimination) and 3,3-dimethyl-2-butanone (by rearrangement), the latter being the main reaction product. The activity was in accordance with the surface acidity data as measured versus cyclohexene skeletal isomerization reaction. Thus, $AlPO_4$ showed the highest activity (almost total conversion at 523 K). The 1,2-elimination/rearrangement ratio depended on the type of catalyst used and diene formation increased with reaction temperature. Moreover, pinacolone was a reaction intermediate for diene production.

Keywords: $AlPO_4$, Al_2O_3, SiO_2, 2,3-dimethyl-2,3-butanediol conversion, activity, selectivity, poisoning by bases, pyridine, 2,6-dimethylpyridine, hexamethyldisilazane

1. Introduction

It has been well established [1] that the conversion of pinacol (2,3-dimethyl-2,3-butanediol) proceeded in the presence of strong acids via a carbenium ion and with migration of the substituent to a neighboring carbon atom. The formation of a carbonyl compound (3,3-dimethyl-2-butanone) by rearrangement was accompanied by the formation of an alkene (2,3-dimethyl-1,3-butadiene) by 1,2-elimination. Concentrated sulfuric acid was the usual catalyst although the process can also be carried out using different acid catalysts, such as silica–alumina [2], zeolites [3–5], silicoaluminophosphates [6], heteropoly acids [7] and perfluorinated (Nafion-H) resinsulfonic acids [5]. Faujasite zeolites such as LaHY and CaHY exhibited higher activities than H-ZSM-5. However, an advantage of ZSM-5 was the high resistance to coke formation. Within the faujasite group it was found [3] that differences in Brønsted acidity resulted in differences in selectivity for ketone and diene formation. Moreover, when the reaction temperature was raised above 673 K, diene was mainly formed. So, lower reaction temperatures strongly favoured the pinacol rearrangement vs. 1,2-elimination. As for other acid catalysts, the conversion of pinacol over silicoaluminophosphate (SAPO) molecular sieves proceeded in two parallel ways [6]. The pore dimensions of the SAPO molecular sieve were important for catalytic activity while the ratio between the two reaction products did not considerably depend on the type of molecular sieve used. The results observed were in accordance with the data on catalytic activity of SAPO towards hydrocarbons [8].

The aim of the present work was to study 2,3-dimethyl-2,3-butanediol (pinacol) conversion over commercial silica and γ-alumina and amorphous $AlPO_4$ catalysts.

2. Experimental

2.1. Catalysts

Three catalysts were used: an $AlPO_4$ ($Al/P = 1$) obtained by precipitation from aluminum chloride and H_3PO_4 (85 wt%), using aqueous ammonia [9], dried at 393 K (24 h) and calcined at 773 K ($AlPO_4$-773) or 1073 K ($AlPO_4$-1073) for 3 h; a commercial γ-Al_2O_3 from Merck calcined at 773 K (Al_2O_3-773) or 1073 K (Al_2O_3-1073); and a commercial SiO_2 from Merck calcined at 773 K (SiO_2-773) or 1073 K (SiO_2-1073). The textural properties, surface area (S_{BET}), pore volume (V_P) and main pore radius (r_P), as well as the pore volume distributions are shown in table 1.

2.2. Surface acidity

The surface acidity was measured in a dynamic mode by means of the rate constants of the gas-phase cyclohexene skeletal isomerization (reaction that is catalyzed by strong acid sites) according to a method described elsewhere [10]. The reaction rates of cyclohexene isomerization (k_a) were also shown in table 1.

2.3. Catalytic measurements

The catalytic properties of $AlPO_4$, γ-Al_2O_3 and SiO_2 catalysts in 2,3-dimethyl-2,3-butanediol (pinacol) conversion were studied by using a pulsed fixed bed reactor inserted between the sample inlet and the analytical column of a HP-5890 II GC with FID. Catalytic measurements were

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Table 1
Surface area (S_{BET}), pore volume (V_{P}), pore radius (r_{P}), pore volume distribution and acid properties, as apparent rate constants (k_a, at 673 K) for cyclohexene skeletal isomerization, of $AlPO_4$, γ-Al_2O_3 and SiO_2 catalysts.

Catalyst	S_{BET}	V_{P}	r_{P}	Pore volume distribution (vol%)					$k_a \times 10^6$
	(m^2/g)	(ml/g)	(nm)	>20 nm	10–20	5–10	2–5	<2	(mol/atm g s)
$AlPO_4$-773	235	1.08	18.4	29.7	61.5	8.8	–	–	15.3
$AlPO_4$-1073	220	1.02	18.5	53.2	39.1	6.1	1.6	–	11.3
Al_2O_3-773	100	0.22	8.5	26.0	9.0	39.9	25.1	–	1.6
Al_2O_3-1073	82	0.22	10.3	28.0	14.5	42.1	15.4	–	0.1
SiO_2-773	392	0.74	7.6	0.9	17.9	58.5	22.7	–	–[a]
SiO_2-1073	289	0.55	7.4	0.7	20.0	56.2	21.8	1.3	–[a]

[a] There is no reaction.

Table 2
2,3-dimethyl-2,3-butanediol and 3,3-dimethyl-2-butanone conversions over $AlPO_4$, γ-Al_2O_3 and SiO_2 catalysts.

Catalyst	2,3-dimethyl-2,3-butanediol				3,3-dimethyl-2-butanone		
	T (K)	X (mol%)	S_{DIENE} (mol%)	S_{ONE} (mol%)	T (K)	X (mol%)	S_{DIENE} (mol%)
$AlPO_4$-773	523	99.9	33.5	66.5	673	31.3	100.0
$AlPO_4$-1073	523	99.5	32.8	67.2	673	24.9	100.0
Al_2O_3-773	523	60.6	15.2	84.8	673	13.5	100.0
Al_2O_3-1073	523	55.0	10.2	89.8	673	10.3	100.0
SiO_2-773	523	1.0	–	100.0	673	–[a]	–
SiO_2-1073	523	–[a]	–	–	673	–[a]	–

[a] There is no reaction.

performed under the following conditions: pulse size 1 μl 10 M pinacol in acetonitrile; reaction temperature, 523–673 K (at 50 K intervals); catalyst weight, 5–30 mg in powder form; flow rate of nitrogen carrier gas, 30 ml min^{-1}. A fresh catalyst was used in each run, and before use, the catalyst was pretreated by *in situ* heating under nitrogen (30 ml min^{-1}) for 1 h at 573 K. The reaction products, 2,3-dimethyl-1,3-butadiene and 3,3-dimethyl-2-butanone (pinacolone) were analyzed by using a cross-linked methyl silicone gum (12 m, 0.2 mm × 0.32 μm film thickness) capillary column. Product characterization was performed by GC-MS (HP-5890 GC coupled with a HP-5970 MS detector) using products condensed in a cold trap and comparing their retention times with those of commercially available reagents.

In order to understand the pinacol reaction path, the 3,3-dimethyl-2-butanone and 2,3-dimethyl-1,3-butadiene conversions were also studied under the same experimental conditions.

Blank runs at 523–673 K showed that under the experimental conditions used in this work, thermal effects could be neglected.

3. Results and discussion

As for other solid acid catalysts, the conversion of pinacol (2,3-dimethyl-2,3-butanediol) on $AlPO_4$, γ-Al_2O_3 and SiO_2 proceeded in two parallel pathways, giving either 3,3-dimethyl-2-butanone (by rearrangement) or 2,3-dimethyl-1,3-butadiene (by 1,2-elimination). Besides, pinacol conversion mainly proceeded via rearrangement (table 2).

Moreover, the activity data were in accordance with the data on surface acidity, measured versus the cyclohexene skeletal isomerization reaction, and thus, amorphous $AlPO_4$ exhibited the highest activity (almost total conversion at 523 K) while commercial silica was practically inactive. Furthermore, the ratio between the two products also depended on the type of catalyst used and, besides, diene formation increased as the reaction temperature increased while less pinacolone was produced.

With respect to pinacolone (3,3-dimethyl-2-butanone) conversion, the results obtained also appear in table 2. As can be seen from table 2, pinacolone conversion yielded only 2,3-dimethyl-1,3-butadiene and the activity results correlated with surface acidity data, amorphous $AlPO_4$ being the most active catalyst. Moreover, commercial silica does not exhibit catalytic activity. On the other hand, 2,3-dimethyl-1,3-butadiene remained unaltered on all catalysts, even at a reaction temperature of 673 K.

In order to better understand the reaction pathway in pinacol conversion, several *in situ* poisoning experiments were carried out at 573 K using different probe base molecules: pyridine (PY), 2,6-dimethylpyridine (DMPY) and hexamethyldisilazane (HMDS). The poisoning of the active acid sites on $AlPO_4$-773 and γ-Al_2O_3-773 catalysts with probe base molecules was performed according to the following procedure. After measuring the activity of the fresh catalyst at 573 K (in triplicate: ∼8% error), the catalyst was saturated with pulses of pure base. After satura-

Table 3
Poisoning experiments in 2,3-dimethyl-2,3-butanediol conversion over $AlPO_4$-773 and Al_2O_3-773 catalysts.

Catalyst	Poison	T (K)	X (mol%)	S_{DIENE} (mol%)	S_{ONE} (mol%)
$AlPO_4$-773	–	573	99.8	35.9	64.1
	PY	573	99.8	35.9	64.1
	DMPY	573	99.8	36.0	64.0
	HMDS	573	97.6	33.8	66.2
Al_2O_3-773	–	573	90.2	20.9	79.1
	PY	573	89.7	20.1	79.9
	DMPY	573	89.3	19.2	80.8
	HMDS	573	79.3	17.4	82.6

tion, the catalyst was maintained in nitrogen at 573 K for 30 min (in order to remove traces of unreacted base) and then, the activity of the catalyst was again measured at the same temperature. The results obtained with respect to the influence of probe base reagents in catalytic activities and product selectivities, at a reaction temperature of 573 K, are shown in table 3.

As can be seen from table 3, the activities and product selectivities remained almost unchanged by PY and DMPY poisoning. In contrast, HMDS treatment lowered the activity, thus poisoning some of the acid sites. In this way, the method using HMDS was different from the method using PY and DMPY. The HMDS silylating agent reacts easily with Brønsted acidic hydroxyl groups, with the formation of stable trimethylsilyl (TMS) ethers [11,12], i.e., a covalent bond rather than the acid–base reaction characteristic of PY or DMPY probes. The poisoning of acid sites with HMDS was accompanied by an increase in pinacolone selectivity (S_{ONE}) showing that diene formation needed higher surface acidity. Furthermore, HMDS treatment suppressed the activity of $AlPO_4$ and γ-Al_2O_3 catalysts for pinacolone conversion into 2,3-dimethyl-1,3-butadiene.

4. Conclusions

Pinacol (2,3-dimethyl-2,3-butanediol) conversion over $AlPO_4$ ($Al/P = 1$) and γ-Al_2O_3 catalysts proceeded in two parallel reaction pathways with formation of 2,3-dimethyl-1,3-butadiene (by 1,2-elimination) and 3,3-dimethyl-2-butanone (by rearrangement), the latter being the main reaction product. The activity was in accordance with the surface acidity data measured versus cyclohexene skeletal isomerization reaction. Thus, $AlPO_4$ showed the highest activity (almost total conversion at 523 K). The 1,2-elimination/rearrangement ratio depended on the type of catalyst used and diene formation increased with reaction temperature. Moreover, pinacolone was a reaction intermediate for diene production.

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