

Reaction of cyclohexene over crystalline and amorphous modified silicoaluminophosphate catalysts[†]

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The reaction of cyclohexene with H₂O₂ has been carried out over silicoaluminophosphate-37 (SAPO-37) molecular sieve, and crystalline and amorphous vanadium-silicoaluminophosphate catalysts, synthesized by hydrothermal method. The products formed in the reaction are cyclohexenone, cyclohexanol, cyclohexanone, cyclohexaneoxide and 1,2 cyclohexanediol. The selectivity among the products depends on the nature of the catalyst, oxidant and solvent.

Titanium and vanadium substituted silicalites (TS-1, VS-1, etc.) are reported in the literature as active catalysts in the hydroxylation and oxidation reactions¹⁻³. The selectivity is predominantly affected by the nature of the catalyst, solvent and oxidant. The reaction of cyclohexene has been reported by Tuel and Ben Taarit⁴ over TS-1 and TiSAPO-5 molecular sieves. In this note, we report the activity and selectivity of silicoaluminophosphate-37 (SAPO-37) molecular sieve and crystalline and amorphous vanadium substituted SAPO and TiSAPO-37 catalysts, synthesized by hydrothermal method, in the reaction of cyclohexene.

Experimental

Vanadium-silicoaluminophosphate VSAPO (DiPA), VSAPO (TPA), VSAPO-37, VSAPO (TBA), VSAPO (TriPA) and TiSAPO-37 catalysts were synthesized using aluminium sulphate, sodium silicate, vanadium oxide and an organic template by hydrothermal method as reported in the literature^{5,6}. The synthesis and physicochemical characterization is given elsewhere⁷. The following templates were used as given in the literature^{5,6}, dipropylamine (DiPA), tetrapropylammonium bromide (TPA), tetrabutylammonium bromide (TBA)

and tripropylamine (TriPA).

The reaction of cyclohexene was carried out taking 20 ml of acetone, 1 g of the powdered catalyst and about 1 g of cyclohexene in a round bottom flask. The reaction was carried out under refluxing conditions for about 20 h, with cyclohexene to H₂O₂ ratio, 1:2 molar. The products were analysed by gas chromatography using SE-30 (30%) and OV-17 columns. The analysis was confirmed by GC-Mass.

Results and discussion

All the "as-synthesized" catalysts reported here are crystalline⁷. Except SAPO-37, VSAPO-37 and TiSAPO-37, all the catalysts in Table 1 lost > 90% of their crystallinity during the removal of template. SAPO-37 molecular sieve is thermally stable (400°C) and > 80% crystalline.

The results of the reaction of cyclohexene over various vanadium-silicoaluminophosphate catalysts (VSAPO) and SAPO-37 molecular sieve are given in Table 1. In the reaction of cyclohexene over VSAPO (DiPA), the yields of cyclohexanol, cyclohexanone and cyclohexenone were 14.4, 7.6 and 65.3 wt% based on cyclohexene respectively. The higher yields of cyclohexenone were 65.3 and 61.7% obtained over VSAPO (DiPA) and VSAPO (TPA). Titanium substituted SAPO showed higher activity in the formation of cyclohexeneoxide and dihydroxylated product as given in Table 1. This indicated different reaction mechanisms due to the cation effect in the presence of H₂O₂.

The effect of solvent, mixed solvent system and *t*-BuOOH is depicted in Table 2. The selectivity of cyclohexenone was 63.0, 42.8 and 80.6% for acetone, methanol and acetonitrile as solvents, respectively. Probably with the increase in polarity of the solvent, the selectivity for cyclohexenone increases. In the case of benzene and water the yield of total products and cyclohexenone was negligibly small (< 5%) compared to organic polar solvents, under our experimental conditions. In the case of mixed solvent systems, like (acetone + water) and (methanol + water) the selectivity of cyclohexenone was 21.0 and 46.6 respectively i.e. intermediate compared to that in pure solvent systems. The cyclohexeneoxide and diol formation is more in the case of tertiary-butyl hydroper-

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Table 1—Reaction of cyclohexene over VSAPO and SAPO-37 molecular sieves

Reaction temp.: 80°C; Catalyst wt.: 1 g; Duration: 20 h; Cyclohexene : H₂O₂ = 1 : 2 molar; Solvent : Acetone; DPA : Dipropylamine; TBA : Tetrabutylammonium bromide; TPA : Tetrapropylammonium bromide

Catalyst	Conversion of cyclohexene (%)	Product distribution (%)			Other products ^b
		Cyclohexenone	Cyclohexanol	Cyclohexanone	
VSAPO (DPA)	98.7	65.3	14.4	7.6	11.4
VSAPO (TBA)	88.2	56.2	4.7	9.3	18.0
VSAPO (TPA)	98.8	61.7	30.9	4.8	1.4
VSAPO ^a (DPA)	54.7	14.2	16.4	15.5	8.6
SAPO-37	83.3	33.3	25.0	14.2	8.4
TiSAPO-37	96.4	19.2	9.6	—	65.8

^aCyclohexene : H₂O₂ = 1 : 0.2 molar; ^b Cyclohexene-oxide & 1,2 Cyclohexanediol.

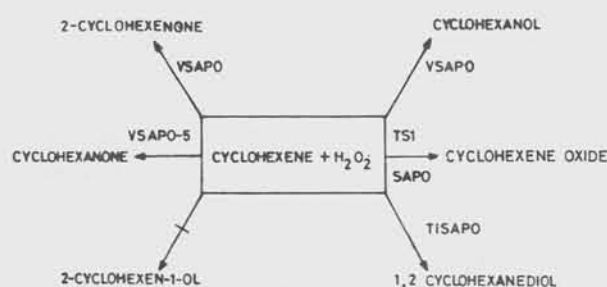
Table 2—Reaction of cyclohexene over VSAPO (TriPA) : Solvent effect

Catalyst	Solvent	Conversion of cyclohexene (%)	Product Distribution (%)			Other Products ^a
			Cyclohexanol	Cyclohexanone	Cyclohexenone	
VSAPO (TriPA)	Acetone	91.5	8.4	3.7	63.0	16.4
	Methanol	95.4	26.2	3.2	42.8	23.0
	Acetonitrile	96.5	12.9	—	80.6	3.0
	Benzene	—	—	—	—	—
	(Acetone + H ₂ O)	50.7	9.5	0.7	21.0	19.6
	(MeOH + H ₂ O)	75.0	16.6	—	46.6	11.8
	Acetone ^b	44.5	7.2	3.0	8.0	21.0 + 5.2 ^c

^aEpoxide + 1,2-cyclohexenediol; ^btert-butyl hydroperoxide (*t*-BuOOH); ^ccyclohexeneoxide
Experimental conditions given in Table 1.

eroxide (oxidant) (*t*-BuOOH) as given in Table 2. Probably due to the high polarity of the solvent, cyclohexene and oxygen are carried effectively to the active centres like vanadium and titanium present in the channels or cages of the molecular sieves or catalyst.

The reaction scheme for cyclohexene is depicted in Scheme 1. As far as the oxidizing strength of the catalyst is considered, titanium silicalite (TS-1) is having low strength leading to preferentially epoxide, followed by hydroxylation of epoxide depending on the solvent⁴. On the other hand, vanadium-SAPO catalysts are medium-strength oxidizing centres leading to the cyclic ketone formation. In the case of VSAPO catalyst, products with and without bond-breaking are obtained. Cyclohexenone is formed by homolytic allylic attack through preferential radical formation. Cyclohexeneoxide is formed by homolytic or heterolytic epoxidation; cyclohexanediol, cyclohexanol and cyclohexanone are formed via double bond addition or cyclohexanediol through hydrolysis⁸.



Scheme 1:—VARIOUS REACTION PRODUCTS IN THE REACTION OF CYCLOHEXENE OVER MSAPOs

The reaction of cyclohexene over SAPO-37 was carried out by varying solvents and the results are given in Table 3. The yields of cyclohexanone were 33.8 and 22.1% in the presence of acetone and methanol as solvents respectively. In the presence of water as a solvent and H₂O₂ as an oxidant, the yield of cyclohexene-epoxide was 57.2%. The results in Table 3 indicate the dominating effect of solvent over the product distribution. The effect of solvent is due to the solubility of reactants and products, its polarity, solvent's

Table 3—Reaction of cyclohexene over SAPO-37: Effect of solvent
Reaction temp.: 80°C; Duration = 20 h; Solvent used = 20 ml; Catalyst = SAPO-37; wt = 1 g

Solvent	Conversion of cyclohexene (%)	Product distribution (%)				Other Products ^a
		Cyclohexenone	Cyclohexanol	Cyclohexanone	Cyclohexene-oxide	
Acetone	83.9	33.3	25.0	14.2	—	8.4
Methanol	32.4	22.1	—	10.3	—	—
(Methanol + H ₂ O)	98.8	—	—	—	37.0	61.7
H ₂ O	57.2	—	—	—	57.2	—

^amajor product is 1,2 cyclohexanediol

Table 4—Reaction of cyclohexene over MSAPO-5 molecular sieves

Catalyst	Conversion of cyclohexene, %	Solvent	Product distribution (wt%)			Others products
			Cyclohexenone	Cyclohexanol	Cyclohexanone	
TiSAPO-5 (0.7 wt% Ti ²⁺)	100	Methanol	36.1	30.1	—	33.8
VSAPO-5 (0.8 wt% V ⁴⁺)	100	Methanol	24.5	42.8	—	3.0 + 29.7 epoxide diol
CrSAPO-5 (0.9 wt% Cr ³⁺)	97	CH ₃ CN	50.4	30.1	—	16.5
MnSAPO-5 (0.9 wt% Mn ⁴⁺)	69.8	CH ₃ CN	38.1	31.7	—	30.2
CoSAPO-5 (0.7 wt% Co ²⁺)	71.9	CH ₃ CN	47.6	21.4	—	1.5 + 7.4 epoxide diol
NiSAPO-5 (0.9 wt% Ni ²⁺)	50	CH ₃ CN	31.9	14.6	—	4.2
CuSAPO-5 (1.1 wt% Cu ²⁺)	25.3	CH ₃ CN	13.6	11.7	—	—
ZnSAPO-5 (1.1 wt% Zn ²⁺)	63.4	CH ₃ CN	25.6	36.0	—	1.8 (epoxide)

Conditions are given in Table 1

acidity-basicity and competitive chemisorption⁸, as discussed by Gilbert and Mercier. The detailed work is in progress.

The reaction of cyclohexene was carried out over transition metal (M) silicoaluminophosphate-5 molecular sieves and the results are given in Table 4. The trend in the formation of cyclohexenone was CrSAPO-5 > CoSAPO-5 > MnSAPO-5 > TiSAPO-5 > NiSAPO-5 > VSAPO-5. Apparently this trend in the activity in the formation of cyclohexenone cannot be correlated with the aqueous redox potentials. The trend in the total conversion of cyclohexene with respect to cation (M) was V(100) ≈ Ti(100) > Cr(97) > Co(71.9) > Mn(69.8) > Cu(25.3%) which may be approximately correlated with the redox potential with the exception of Cu. The number in bracket indicates the per cent conversion, as given in Table 4. The formation of epoxide was lower. Thus by the variation of catalyst, solvent, oxidant and time on stream (duration), the selectivity in the liquid phase oxidation reaction of cyclohexene

(olefin) in the presence of H₂O₂/TBHP can be changed.

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