

Hydrocarbons oxidation with hydrogen peroxide over germanic faujasites catalysts

V.I. Pârvulescu^{a,*}, D. Dumitriu^a, G. Poncelet^b

^a *University of Bucharest, Faculty of Chemistry, Department of Chemical Technology and Catalysis, B-dul Republicii 13, 70346, Bucharest, Romania*

^b *Université Catholique de Louvain, Unité de Catalyse et Chimie des Matériaux Divisés, Place Croix du Sud, 2 / 17, 1348 Louvain-la-Neuve, Belgium*

Received 15 December 1997; accepted 22 June 1998

Abstract

Highly crystalline near-faujasite Na–GeX, and its protonated and sulfated forms have been prepared and used as catalysts for the oxidation of several hydrocarbons with different structures (benzene, toluene, cyclohexane) in the presence of H₂O₂. The catalysts have been characterized using surface area measurements, X-ray diffraction (XRD) and infrared (IR) techniques. The catalytic experiments have been performed both at normal and autogenic pressure. Autogenic pressures highly improved the oxidation degree of the hydrocarbons. It was found that the oxidation of hydrocarbons in the presence of H₂O₂ depended not only on the formation of Ge–peroxo species but also on the acidic properties of the catalyst, and also involved the activation of O₂ formed in situ. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ge–faujasite; Sulfated Ge–faujasite; Oxidation with H₂O₂; Benzene; Toluene; Cyclohexane

1. Introduction

The use of molecular sieves in the liquid phase hydroxylation of hydrocarbons has been extensively studied in the last years due to their important advantages: shape selectivity and stability. The most investigated sieves are the titanosilicates (TS1 or TS2) obtained through the introduction of Ti(IV) species in the silicalite framework [1–14]. The catalytic performances of these zeolites have been accounted for by a concerted effect associating the presence of iso-

lated framework Ti(IV) species, high hydrophobicity of the surface, and shape selectivity conferred by the geometry of the channels [15–17]. Other authors have proved that the presence of cation exchange sites in the silicalite framework also induces a catalytic activity in the hydroxylation of hydrocarbons with H₂O₂. Studies over Y zeolites, mordenite and ZSM-5 with different Si/Al ratios have shown that the catalytic activity was depending on the number and strength of the Brönsted acid sites [18–22].

The aim of this study was to investigate the catalytic performances of a germanic near-faujasite molecular sieve in oxidation reactions using H₂O₂. Previous investigations of this sieve

* Corresponding author

were reported in the literature [23,24]. The amounts of adsorbed water and ammonia are lower for the germanic faujasite than for its silicic analogue, but the hydrophobic character of germanic faujasite is less pronounced than in titanosilicates. A greater instability of the Ge–O–Al linkages, due to the favoured sixfold coordination of germanium with respect to oxygen, was evidenced as a fundamental difference between germanic and silicic faujasites. Infrared (IR) study of the catalyst in the presence of water showed OH stretching bands originating from the decationation of the sieve.

Twenty years ago, Olah et al. [25] reported that a homogeneous superacid medium exhibits a high catalytic activity in the hydroxylation of hydrocarbons with H_2O_2 . On this basis, germanic faujasite has been sulfated using the procedure indicated for zirconia, characterized and tested [26].

2. Experimental

2.1. Catalysts preparation

A pure germanic near-faujasite (Na–GeX) synthesized at low temperature from Al–Ge gels according to the procedure described elsewhere has been used [27]. H–GeX was obtained by exchanging Na–GeX with a 0.2-M ammonium acetate solution. The NH_4 –GeX form was dried at room temperature and heated under a flow of helium at a rate of 1°C min^{-1} , using the following programme: from room temperature to 90°C and 2 h at 90°C ; from 90 to 250°C and 2 h at 250°C ; from 250 to 400°C and 4 h at 400°C . Cooling down was carried out under a helium flow.

Sulfated germanic near-faujasite was prepared by treating Na–GeX with a 0.1-M solution of ammonium sulfate for 7 h at 80°C . The mother liquors were filtered and the solid was washed with distilled water. After drying at room temperature the sample was heated using the programme described above.

2.2. X-ray diffraction (XRD)

The crystallinity of the different samples was controlled over the ‘as made’ samples by XRD analysis, using a DRON-2 equipment with iron-filtered Co $\text{K}\alpha$ radiation at a scanning speed of $2^\circ 2\theta \text{ min}^{-1}$.

2.3. IR spectroscopy

Self-supporting wafers (10 – 15 mg cm^{-2}) were prepared by compressing the zeolite in a stainless-steel die under a pressure of 0.5 ton cm^{-2} . The wafer was placed in the sample holder and introduced in an IR Pyrex cell fitted with NaCl windows. Before analysis, the samples were outgassed under a residual pressure of 10^{-6} Torr at a temperature of 300°C for 10 h. Temperature was increased at a rate of 1°C min^{-1} . The IR spectra were recorded with a Perkin-Elmer 180 spectrophotometer, after adsorption of pyridine and after outgassing.

2.4. Surface area measurements

Surface area measurements were performed using a Carlo-Erba equipment. Adsorption–desorption isotherms of N_2 at 77 K were obtained after outgassing the samples for 12 h at 200°C .

2.5. Catalytic tests

Catalytic tests were carried out under vigorous magnetic stirring at normal pressure in a glass reactor, and at autogenic pressure in a Teflon-lined stainless-steel autoclave. The reaction temperature was in the range 50 – 90°C . In order to eliminate O_2 eventually dissolved in the liquid phase, some experiments were performed by bubbling N_2 into the reactor through a gas disperser at a flow rate of 20 ml min^{-1} . For the experiments carried out in the autoclave, the vessel was firstly flushed with N_2 and this operation was repeated every 4 min. As aromatic hydrocarbons, benzene and toluene have been used, and cyclohexane as cycloalkane type

hydrocarbon. All the experiments were carried out with H_2O_2 (30 wt.% aqueous solution). The H_2O_2 /hydrocarbon molar ratio was 1:1 for the experiments conducted at normal pressure, and 2:1 for those at autogenic pressure. All the experiments were done over 0.1 g catalyst, using ca. 120 mmol of hydrocarbon. The catalyst activity was expressed in: mmol hydrocarbon transformed $\text{g}_{\text{cat}}^{-1} \text{h}^{-1}$. After reaction, the two phases were separated by filtration. The analyses were performed in a gas chromatograph (Hewlett Packard GC 5710A/30A) coupled to a ECD 18713A and equipped with a $4\text{-m} \times 1.8\text{-mm}$ packed column of Carbowax 20M on Chromosorb W-HP. The products were identified by GC-MS (Hewlett Packard MS-5988). The H_2O_2 transformation degree was established by iodometric titration. In order to put in evidence possible leaching of the catalyst during the reaction, the liquors resulting from the reaction were analyzed by atomic absorption spectroscopy.

3. Results

3.1. Textural characterization

Changing from the Na to the H form did not modify the textural properties of germanic faujasite. Both sieves exhibited a specific surface area of about $208 \text{ m}^2 \text{ g}^{-1}$. Sulfatation of germanic near-faujasite caused an increase of the surface area ($248 \text{ m}^2 \text{ g}^{-1}$) which may be related to the advanced destruction of the sieve framework.

3.2. XRD

The X-ray diffractograms of germanic faujasites showed (Fig. 1A) a crystalline structure, the parameters of which have been previously reported [27]. After sulfatation, the germanic faujasite was severely damaged and no diffraction line could be observed (Fig. 1B). These results show that after heating the sulfated sieve, only an amorphous structure was obtained. The

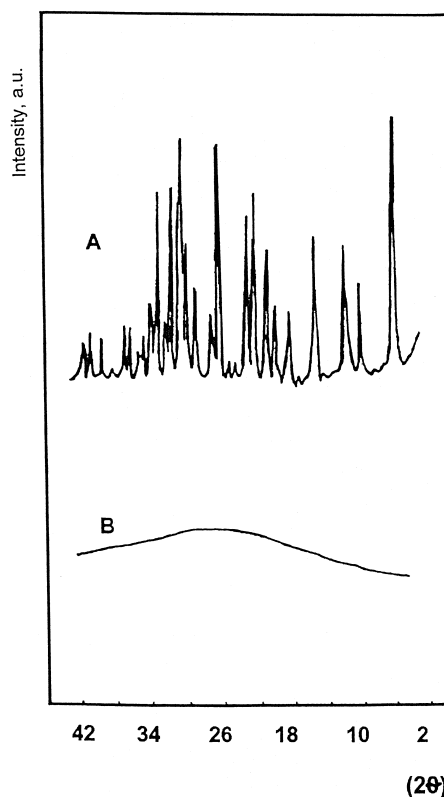


Fig. 1. XRD patterns of the germanic faujasite (A) and of sulfated germanic faujasite (B).

effect of the sulfatation is evident: heating under similar conditions pure germanic faujasite resulted in only a small loss of crystallinity.

3.3. IR spectroscopy

Pyridine may be adsorbed on solid surfaces in different ways: physisorbed by weak van der Waals interaction (IR absorption band near 1450 cm^{-1}), hydrogen bonded pyridine (absorption band at the same position), pyridine in interaction with Lewis acid sites (band at about 1457 cm^{-1}), and pyridine in interaction with Brönsted acid sites (band at about 1540 cm^{-1}).

In the case of the starting Na-GeX, merely physisorbed pyridine was put in evidence (Fig. 2A and B). The band located at wave numbers higher than 1576 cm^{-1} as well as those at 1150 and 1220 cm^{-1} are assigned to pyridine coordi-

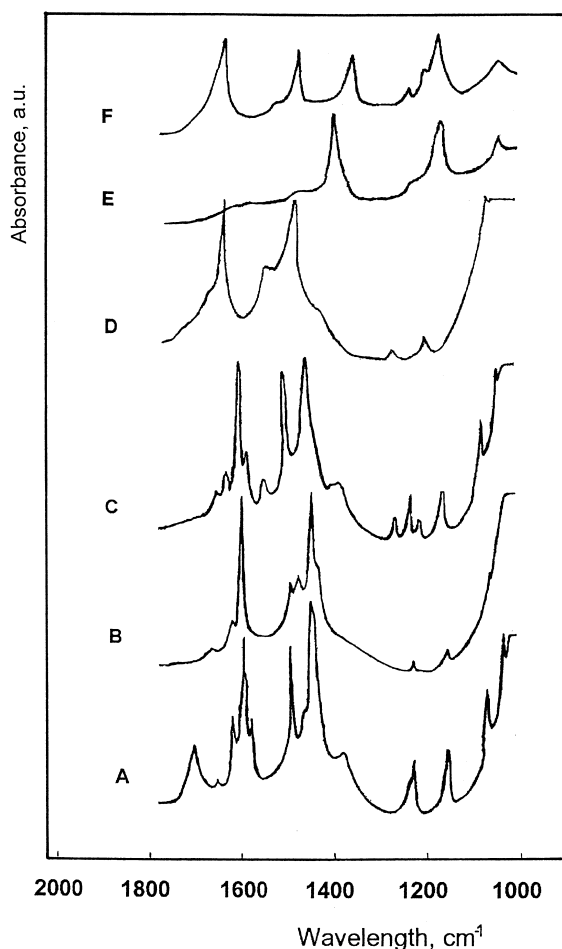


Fig. 2. IR spectra of pyridine adsorbed on Na-GeX near-faujasite after adsorption (A) and outgassing at 250°C (B), on H-GeX near-faujasite after adsorption (C) and outgassing at 250°C (D) and on sulfated germanic faujasite (F). Spectrum (E) shows the IR-spectrum of sulfated germanic faujasite.

nately bound to Na⁺ ions. The band at 1475 cm⁻¹ could be due both to an interaction of pyridine with the Na⁺ ions and to the presence of Lewis sites. It could also be due to a chemisorbed carbonate species [28]. Furthermore, the removal of pyridine during outgassing at 250°C resulted in a diminution of all the bands.

The IR spectra of pyridine adsorbed on H-GeX near-faujasite clearly indicate the presence of both Lewis (1440 cm⁻¹) and Brønsted (1540 cm⁻¹) sites (Fig. 2C and D). It is seen that the band at 1473 cm⁻¹ has disappeared, which

makes more probable the assignment of this band to a chemisorbed carbonate species. The bands at 1205, 1219 and 1244 cm⁻¹ are probably due to pyridine-Brønsted sites interactions. Outgassing these samples also resulted in a diminution of all the bands.

The spectra shown in Fig. 2E and F were recorded on sulfated germanic faujasites. The shape of the spectra evidently differed from those of the former germanic faujasites, evidencing the well known shifted asymmetrical stretching frequency of S=O (1350 cm⁻¹) [26,29]. Sulfated GeX (spectrum E) showed bands at 1032, 1160 and 1380 cm⁻¹, and a shoulder at 1210 cm⁻¹ which are typically assigned to bidentate sulfate coordinated to metal clusters [26,29]. The IR spectrum of pyridine adsorbed on SO₄/GeX (spectrum F) only exhibited the presence of coordinately bonded pyridine (1440 and 1612 cm⁻¹). No band was observed near 1540 cm⁻¹, indicating the absence of pyridinium ion. This means that the new structure only contained Lewis acidity. In such a way, a structure similar to the one found after sulfatation of Zr, Ti, Sn, or Fe oxides—as named ‘superacid structure’ [30]—is formed.

IR spectra as well as XRD patterns of the tested catalysts did not indicate structural degradation during the reaction.

3.4. Catalytic tests

The reagents conversion, the H₂O₂ selectivity (calculated as: [mol H₂O₂ utilized in the formation of the oxidation products/mol H₂O₂ consumed] × 100), the H₂O₂ conversion calculated as: [mol H₂O₂ decomposed/mol H₂O₂ introduced at the beginning of reaction] × 100, the product distribution and the number of millimoles of hydrocarbon transformed per gram of catalyst and per hour for the oxidation reaction of benzene, toluene, and cyclohexane are presented in Tables 1–3, respectively. The number of millimoles of hydrocarbon transformed was very different according to the nature of the

Table 1
Reaction of benzene over investigated catalysts

Catalyst	Temperature (°C)	Reaction time (h)	Benzene conversion (mol%)	H ₂ O ₂ selectivity (mol%)	H ₂ O ₂ conversion (mol%)	Product distribution (mol%)			Reaction rate (mmol C ₆ H ₆ g _{cat} ⁻¹ h ⁻¹)
						Phenol	1,2-Dihydroxybenzene	1,4-Dihydroxybenzene	
Na–GeX, under autogenic pressure	50	3	0	0	20	0	0	0	0
	60	3	0.5	1.5	33.3	100	0	0	2
	70	3	1.99	6.25	31.84	100	0	0	7.99
H–GeX, under normal pressure	50	3	0	0	18.6	0	0	0	0
	60	3	25.65	13.66	94.16	99.7	0.15	0.15	102.6
	70	3	65.7	33.47	98.68	99.45	0.18	0.37	262.81
Sulfated GeX, under autogenic pressure	50	6	0	0	24.5	0	0	0	0
	60	6	0.045	0.074	60.81	100	0	0	0.09
	70	6	0.075	0.113	66.36	100	0	0	0.15
	50	2	13.33	8.28	80.49	100	0	0	80
	60	2	29.16	16.39	91.4	97.2	2.8	0	175
	70	2	92.33	53.97	90.21	94.53	5.47	0	554

Table 2
Reaction of toluene over investigated catalysts

Catalyst	Temperature (°C)	Reaction time (h)	Toluene conversion (mol%)	H ₂ O ₂ conversion (mol%)	H ₂ O ₂ selectivity (mol%)	Product distribution (mol%)					Aromatic ring/methyl oxidation ratio ^a (mol.mol ⁻¹)	Reaction rate (mmol C ₇ H ₈ g _{cat} ⁻¹ h ⁻¹)
						<i>o</i> -Cresol	<i>p</i> -Cresol	Benzylic alcohol	Benzylic aldehyde	Benzoic acid		
Na–GeX, under normal pressure	50	3	0.725	43.15	1.68	71.3	0	28.7	0	0	2.48	2.9
	60	3	0.8	48.84	2.35	50.4	0	25.4	4.2	20	1.01	3.2
	70	3	0.85	54.25	2.78	48.2	0	10.4	5.6	36	0.93	3.4
	80	3	0.4	48.6	1.56	40	0	11	8.4	40.6	0.66	1.6
	90	3	0.23	54.22	0.8	38.2	0	12.2	10.6	39	0.61	0.92
Na–GeX, under autogenic pressure	50	3	13.55	88.21	7.68	0	100	0	0	0	–	54.2
	60	3	17.7	90.21	10.82	20.9	50.6	18.2	10.3	0	2.5	70.8
	70	3	40.17	89.4	25.97	43.4	27.8	13.2	15.6	0	2.47	160.7
	80	3	56.35	96.7	38.42	50.59	10.38	7.12	31.89	0	1.56	225.4
	90	3	57.125	94.59	42.68	46.02	11.5	3.45	36.59	2.4	1.35	228.5
H–GeX, under normal pressure	50	6	0.195	62.29	0.37	15.15	0	75.76	0	9.1	0.17	0.39
	60	6	0.375	59.85	0.76	15.3	3.4	70	1.3	10	0.23	0.75
	70	6	0.6	70.92	1.06	16.4	5.2	64.1	3.3	11	0.27	1.2
	80	6	1.15	68.05	2.19	17	10.8	54.6	5.6	12	0.38	2.3
	90	6	1.49	50.16	.05	18.56	12.42	46.52	9.93	13	0.44	2.98
Sulfated GeX, under autogenic pressure	50	1.5	22.5	44.16	40.76	0	0	40	60	0	0	180
	60	1.5	31.25	62.5	62.5	0	0	25	75	0	0	250
	70	1.5	51.21	91.8	55.78	0	0	0	100	0	0	409.75
	80	1.5	56.35	93.41	63.34	0	0	0	90	10	0	450.8
	90	1.5	59.41	96.81	66.89	0	0	0	82	18	0	475.3

^aCresols isomers/methyl oxidation products.

Table 3
Reaction of cyclohexane over investigated catalysts

Catalyst	Temperature (°C)	Reaction time (h)	Cyclohexane conversion (mol%)	H ₂ O ₂ selectivity (mol%)	H ₂ O ₂ selectivity (mol%)	Product distribution (mol%)				Reaction rate (mmol C ₆ H ₁₂ g _{cat} ⁻¹ h ⁻¹)
						Cyclohexanol	Cyclohexanone	Hydroxycyclohexanone	Adipic acid	
Na–GeX, under normal pressure	50	6	0.805	86.00	1.83	4.28	95.72	0	0	1.61
	60	6	0.99	80.51	2.54	3.8	85.8	10.4	0	1.98
	70	6	1.26	97.96	2.9	0	74.49	25.5	0	2.52
Na–GeX, under autogenic pressure	50	3	15.12	59.95	20.31	44.22	52.21	1.84	1.73	60.5
	60	3	32.6	82.52	30.24	50.1	48.2	1.2	0.5	130.4
	70	3	66.45	79.07	58.65	60.4	39.6	0	0	265.8
Sulfated GeX, under autogenic pressure	50	1.5	16.75	91.25	14.5	42	58	0	0	134
	60	1.5	24	88.61	23.02	30	70	0	0	192
	70	1.5	42.01	88.21	88.22	25	75	0	0	336.08
H–GeX, under normal pressure	50	6	0.075	81.14	1.75	58	42	0	0	0.15
	60	6	0.16	59.04	0.42	45	55	0	0	0.32
	70	6	0.375	60.13	1.06	30	70	0	0	0.75

hydrocarbon. Generally, in the experimental conditions employed, the number of millimoles of hydrocarbon transformed increased with increasing temperature and it was much higher under autogenic pressure; for toluene, a small decrease of the number of millimoles transformed on Na–GeX could be observed at temperatures higher than 70°C and at normal pressure.

3.4.1. Benzene oxidation

For benzene, no transformation was observed at 50°C over Na–GeX catalyst, both under normal and autogenic pressure. The increase of temperature improved the conversion. On H–GeX and Na–GeX catalysts, the selectivity to phenol was 100% at normal pressure (Table 1). Under autogenic pressure, low selectivities to dihydroxybenzenes were observed and no *p*-benzoquinone was detected.

3.4.2. Toluene oxidation

Table 2 shows the selectivities of toluene transformation on Na–GeX and H–GeX, at normal and autogenic pressures. A higher selectivity to cresol isomers was obtained on the Na-form of the catalyst, while on the H-form, the methyl group oxidation was the main reaction. These results suggest that the sodium form and the acid form are promoting two different reaction pathways. Generally, an electrophilic mechanism is proposed for the hydroxylation of the aromatic ring, whereas the oxidation of the methyl group would occur via a radical pathway [15,31].

The selectivities to benzoic acid, benzylic aldehyde, and benzylic alcohol in the reaction of toluene over H–GeX at normal pressure suggest that the transformation of benzylic aldehyde into benzoic acid proceeds rapidly on the catalytic sites, even at 50°C, while the increase of temperature facilitates the desorption of aldehyde from the catalyst surface.

3.4.3. Cyclohexane oxidation

The results of the transformation of cyclohexane on H–GeX and Na–GeX catalyst, at

normal and autogenic pressures, are presented in Table 3. At normal pressure, high selectivities to cyclohexanone were obtained. Adipic acid was not formed. The high selectivities to cyclohexanol, the low selectivities to cyclohexanone and hydroxycyclohexanone, and the formation of adipic acid under autogenic pressure indicate that the transformation of hydroxycyclohexanone to adipic acid is favoured, while under similar experimental conditions, the transformation of cyclohexanol to cyclohexanone and the transformation of cyclohexanone to hydroxycyclohexanone are diminished.

It should be mentioned that in the absence of catalyst, the reaction of cyclohexane with H₂O₂ at normal pressure occurred with a low conversion (0.09 mmol cyclohexane transformed h⁻¹ at 70°C) and total selectivity to cyclohexanone. Without catalyst but at autogenic pressure, the cyclohexane oxidation exhibited a much lower conversion (1.13 mmol cyclohexane transformed h⁻¹ at 70°C) than in the presence of catalyst, but with higher selectivities to cyclohexanone (56%) and lower selectivities to cyclohexanol (24.3%) and adipic acid (19.6%). Cyclohexane is very difficult to be activated. We suppose that cyclohexane and its oxidation products are able to react with H₂O₂, both in the chemisorbed phase and in the liquid phase. However, the possibility for cyclohexanol to be oxidized non-catalytically by H₂O₂ was already reported [32].

Table 4 shows the evolution of the conversion of cyclohexane vs. time on Na–GeX catalyst at 70°C and at normal pressure. The transformation of cyclohexane started after an induction period of 1.5 h, which suggests that the reaction process was possibly occurring through an autocatalytic process involving the participation of cyclohexanol or cyclohexanone in the catalytic act. When catalytic amounts of cyclohexanol were introduced at the beginning of the reaction, the conversion of cyclohexane was immediately put in evidence. The same behaviour was previously reported by Allian et al. [21] who also observed an induction period

Table 4

Selectivities for cyclohexane transformation over Na–GeX catalyst, at 70°C under normal pressure

Reaction time (min)	Product distribution (mol%)				Reaction rate (mmol C ₆ H ₁₂ g _{cat} ⁻¹ h ⁻¹)
	Cyclohexanol	Cyclohexanone	Hydroxycyclohexanone	Adipic acid	
60	100	0	0	0	0.01
75	94.8	5.2	0	0	0.12
90	72.4	27.6	0	0	0.73
105	69.9	30.1	0	0	1.15
120	35.0	57.3	7.7	0	1.68
135	15.0	66.6	18.4	0	2.24
150	0	74.5	25.5	0	2.52

during the hydroxylation of phenol over acidic solids. The induction time was considerably reduced by the addition of one of the components of the quinonic redox couple. On the other hand, cyclohexane oxidation over TS1 with H₂O₂ was not influenced upon addition of cyclohexanol to the reaction mixture [32]. The fundamental differences between the reaction pathways promoted by GeX and TS1 seem to be the consequence of the differences of the hydrophilic/hydrophobic surface character of these solids.

3.4.4. Oxidation of benzene, toluene and cyclohexane over sulfated GeX

Much higher transformation degrees were achieved on sulfated GeX compared with Na–GeX, which was a better catalyst than H–GeX. These results could be related with the amorphous structure of sulfated GeX calcined at 400°C. Not only a higher strength of the active sites but also the absence of structural constraints could be possible reasons for the increase of activity. Also, sulfated GeX is a more selective catalyst. Toluene transformation on sulfated GeX occurred only on the methyl group and merely to benzylic aldehyde (see Table 2). The remarkable transformation of toluene to benzylic aldehyde occurs with relatively high conversions. Hydroxycyclohexanone and adipic acid were not produced in the transformation of cyclohexane (see Table 3). In order to identify eventual reaction products strongly adsorbed on

the catalyst surface, the used catalyst was stirred for 6 h in methanol at 50°C under reflux. Only trace amounts of benzoic acid were detected in these solutions when the reactions were performed between 50–70°C. Increasing the reaction temperature (80–90°C) resulted in the formation of large amounts of benzoic acid. One of the reasons for this behaviour could be the modification of the solubility of the components in the reaction mixture with increase of temperature. No other compounds were identified.

3.4.5. Catalysts leaching

Several experiments in which the catalyst was filtered and the mother liquor was allowed to react further were also made. After removal of the catalyst, no further reaction was evidenced, irrespective of the molecule subjected to the reaction and of the reaction conditions.

3.4.6. Experiments performed under N₂ atmosphere

In order to elucidate some aspects concerning the reaction pathways promoted by germanic faujasites, few experiments were performed in bubbling N₂ in the reaction mixture. A fast removal of O₂ formed in situ by H₂O₂ decomposition or even dissolved from the air was expected.

Over Na–GeX and at normal pressure, oxidation of toluene occurred with a slow decrease of the conversion, and also with a slow decrease in the amount of benzylic oxidation products

Table 5
Reaction of toluene over investigated catalysts under N₂ atmosphere

Catalyst	Temperature (°C)	Reaction time (h)	Toluene conversion (mol%)	H ₂ O ₂ conversion (mol%)	H ₂ O ₂ selectivity (mol%)	Product distribution (mol%)					Aromatic ring/methyl oxidation ratio ^a (mol mol ⁻¹)	Reaction rate (mmol C ₇ H ₈ g _{cat} ⁻¹ h ⁻¹)
						<i>o</i> -Cresol	<i>p</i> -Cresol	Benzylic alcohol	Benzylic aldehyde	Benzoic acid		
Na-GeX, under normal pressure	50	3	0.70	43.20	1.60	72.00	0	28.00	0	0	2.57	2.8
	60	3	0.80	49.00	2.30	50.50	0	25.40	4.20	19.90	1.02	3.2
	70	3	0.84	53.80	2.75	48.72	0	10.40	5.10	35.78	0.95	3.4
	80	3	0.32	48.50	1.17	47.37	0	10.00	6.70	35.90	0.90	1.3
	90	3	0.18	54.00	0.59	47.30	0	9.80	7.90	35.00	0.89	0.7
Na-GeX, autogenic pressure	50	3	12.40	88.20	7.02	0	100	0	0	0	0	49.6
	60	3	14.50	90.00	8.40	25.33	61.33	8.20	5.13	0	6.5	58.0
	70	3	12.80	90.30	7.44	55.40	35.51	4.09	5.00	0	10.0	51.2
	80	3	36.30	97.00	19.56	78.35	16.10	1.00	4.55	0	17.0	145.2
	90	3	34.64	95.00	19.10	75.74	19.00	0.44	4.82	0	18.8	138.6
H-GeX, under normal pressure	50	6	traces	63.1	0	traces	traces	0	0	0	–	0
	60	6	traces	60.2	0	traces	traces	0	0	0	–	0
	70	6	traces	70.5	0	traces	traces	0	0	0	–	0
	80	6	traces	69.4	0	traces	traces	0	0	0	–	0
	90	6	traces	50.0	0	traces	traces	0	0	0	–	0
Sulfated GeX, under autogenic pressure	50	1.5	4.5	45.0	7.73	6.1	3.0	36.1	54.8	0	0.1	36.0
	60	1.5	6.9	62.0	8.80	10.5	6.2	25.0	58.3	0	0.2	55.2
	70	1.5	9.6	92.0	8.89	8.4	8.3	12.8	70.5	0	0.2	76.8
	80	1.5	8.9	93.9	8.64	5.4	3.7	9.3	80.7	0.9	0.1	71.2
	90	1.5	4.2	96.5	4.45	0	0	0	95.1	4.9	0	33.9

^aCresols isomers/methyl oxidation products.

Table 6
Reaction of cyclohexane over investigated catalysts under N₂ atmosphere

Catalyst	Temperature (°C)	Reaction time (h)	Cyclohexane conversion (mol%)	H ₂ O ₂ selectivity (mol%)	H ₂ O ₂ selectivity (mol%)	Product distribution (mol%)				Reaction rate (mmol C ₆ H ₁₂ g _{cat} ⁻¹ h ⁻¹)
						Cyclohexanol	Cyclohexanone	Hydroxycyclohexanone	Adipic acid	
Na-GeX, under normal pressure	50	6	0.75	85.00	1.71	4.5	95.5	0	0	1.5
	60	6	0.85	80.50	2.16	3.9	86.8	9.3	0	1.7
	70	6	0.90	96.90	2.07	1.3	74.2	24.5	0	2.0
Na-GeX, under autogenic pressure	50	3	10.5	60.50	9.97	85.00	15.00	0	0	43.5
	60	3	20.4	81.50	14.05	86.67	13.33	0	0	81.6
	70	3	26.5	80.00	19.41	82.76	17.24	0	0	106.0
Sulfated GeX, under autogenic pressure	50	1.5	8.4	91.20	5.69	76.20	23.80	0	0	67.2
	60	1.5	15.7	89.10	10.2	84.13	15.87	0	0	125.6
	70	1.5	18.9	87.80	12.25	86.12	13.88	0	0	151.2
H-GeX, under normal pressure	50	6	traces	82.00	0	0	traces	0	0	0
	60	6	traces	60.0	0	0	traces	0	0	0
	70	6	traces	59.4	0	0	traces	0	0	0

(see Table 5). This behaviour was more evident at temperatures over 70°C. A different situation was found for H–GeX, where N₂ bubbling resulted in a drastic decrease of the conversion. Only traces of cresols were found in the reaction mixture after 6 h. Such results agree with other literature studies, which reported radical acid-catalyzed reactions using O₂ as oxidizing agent and hydroperoxides as initiators [33]. The presence of Brønsted acid sites was found to decrease the induction period which obviously characterizes such oxidation processes. The behaviour of Na–GeX in the oxidation of cyclohexane at normal pressure and N₂ bubbling is also in concord with such observations (see Table 6). Only a slow decrease of cyclohexane conversion and almost no modification in the product distribution were observed. On the contrary, on H–GeX, bubbling of N₂ resulted in an almost total suppression of cyclohexane transformation. Only traces of cyclohexanone were detected in the reaction products. In all the cases, H₂O₂ conversion was not affected by N₂ bubbling, but H₂O₂ efficiency was drastically diminished.

For all the experiments carried out in the autoclave with continuous renewal of the gaseous atmosphere by pure N₂, a decrease of the conversion was observed. This decrease was more evident for sulfated GeX (Table 5). But even in such conditions, the conversions of the hydrocarbons (toluene or cyclohexane) still remained higher than at normal pressure. These experiments came to prove that oxidation occurs not only with H₂O₂ as oxidizing agent, but also O₂ formed in situ strongly contributes to these reaction.

The modification of the conversion brought about a modification of the selectivity. In the oxidation of toluene on Na–GeX, an increase of the aromatic ring/methyl oxidation products molar ratio was observed, and in the reaction of cyclohexane, an increase of cyclohexanol/cyclohexanone molar ratio occurred (Table 6). On sulfated GeX, the formation of cresols has also been detected.

4. Discussion

Na–GeX and H–GeX near-faujasites have similar textural characteristics but different acidic–basic properties. The H–GeX sieve exhibits weaker acid properties than H–SiX faujasite [24]. At the same time, the surface of the germanic sieves is hydrophilic, even though this characteristics is less marked compared with the silicic faujasite [23].

Sulfatation of GeX faujasite determines, after calcination, the formation of a solid with properties remembering those of sulfated zirconium and titanium oxides but more particularly of tin or iron [34]. GeX loses its structural characteristics, the X-ray analysis evidencing an amorphous solid even at a very low heating rate in helium atmosphere. At the same time, the acidic properties of the sieve are totally changed, the IR spectra of adsorbed pyridine showing a band structure typical of ‘superacid’ solids.

The exchange of Na⁺ with NH⁴⁺, followed by calcination, resulted in highly H⁺ exchanged form which was labile enough as to be destroyed during the thermal treatment by the adsorbed sulfate species. Decationation of the sieve in the presence of water has been already proved [24] and this behaviour, together with the six-fold coordination tendency of germanium, could be the reasons for the interaction with sulfate adsorbed species.

The numbers of millimoles of hydrocarbon transformed per gram of catalyst and per hour on Na–GeX near-faujasites under autogenic pressure are comparable or higher than those reported in the literature for titanosilicates [6,14], but the H₂O₂ selectivities are less pronounced.

Also, Na–GeX near-faujasite has proved to be a more efficient catalyst than Na–ZSM-5 [18]. The differences of the transformation degree of the hydrocarbons at normal pressure cannot be interpreted as an effect of diffusion phenomena, because faujasite is characterized by relatively larger pores and, therefore, should not give rise to such restrictions. The different transformation degrees for the hydrocarbons in-

vestigated should be assigned to the different thermodynamic stabilities and reactivities of the substrates, and to some selective adsorption processes of the reaction products, which are functions of their polarity and of the hydrophilicity of the surface of faujasite [35] leading to the blockage of the active sites.

The variation of the number of molecules of hydrocarbon transformed vs. temperature should be assigned to some concurrent effects: one of them is that higher temperatures facilitate the desorption of the polar products from the catalyst surface, unblocking the active sites; the other effect is that the increase of temperature involves a decrease of the stability of H_2O_2 in aqueous solution, and its non-selective decomposition to water and dioxygen. A decrease of the solubility of oxygen molecules at higher reaction temperatures occurs concomitantly.

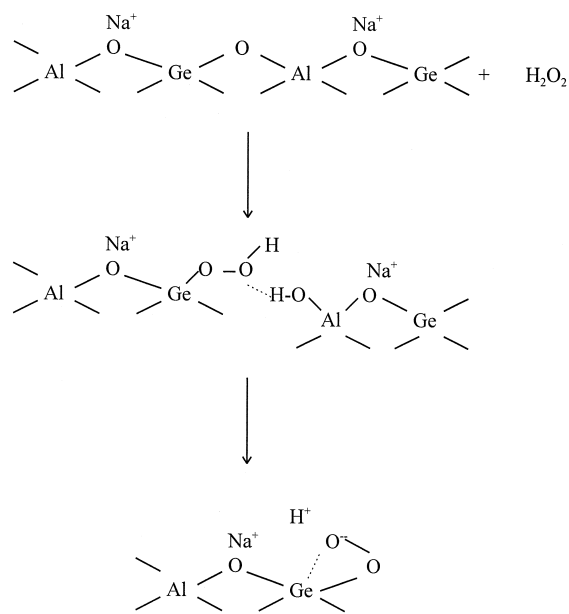
For the oxidation of cyclohexane, it is possible that cyclohexanol acts as a solvent for cyclohexane, but the induction period (1.5 h) could be explained mainly by the cyclohexyl hydroperoxide formation from cyclohexanol through an acid-catalyzed reaction with H_2O_2 . Thermal decomposition of the cyclohexylhydroperoxide could lead to alkoxy radicals which initiate an auto-oxidation process.

The experiments performed at autogenic pressure led to much higher conversions than those carried out at normal pressure (Tables 1–3). These results should be assigned to a higher concentration of O_2 dissolved in the liquid phase and also to a decrease of the non-selective decomposition of H_2O_2 to O_2 and H_2O under autogenic pressure, occurring for thermodynamic reasons. A contribution of molecular dioxygen in a similar manner as that proposed by Howard and Ingold [36] and Walling and Johnson [37] for Fenton O_2 -saturated systems is difficult to conceive because in our case, metallic species known to be active in such reactions were inexistent, and no leaching of the zeolite was noticed. Moreover, recycling of used Na–GeX and H–GeX catalysts in successive experiments gave repro-

ducible catalytic properties. However, the O_2 dissolved in the aqueous phase is playing a role in the oxidation process, which occurs as a radicalic chain reaction process as previously reported by Sheldon [38]. The H_2O_2 efficiencies are still lower than 100%, even for reactions at autogenic pressure.

Moreover, the aromatic ring/methyl oxidation products ratio (Table 2) for toluene oxidation suggests that for Na–GeX, oxidation occurs predominantly through an electrophilic mechanism, while the H form seems to favour a radical mechanism.

The main difference between silicic faujasite and Ge–faujasite is that the latter one exhibits a low stability of Ge in tetracoordinated state. As in the case of titanosilicalites, where isolated framework Ti(IV) species are able to interact with H_2O_2 to form Ti–OOH species which act as oxidants for organic substrates, the interaction of framework Ge(IV) with H_2O_2 to produce Ge–OOH oxidant species could be reasonably supposed. The formation of a neighbouring hydroxylic aluminium bonded group (Scheme 1), which can interact with peroxidic oxygen via



Scheme 1.

a hydrogen bond, could be assumed. In these conditions, the oxidation involves the participation of an electrophilic oxygen (similarly as in the mechanism proposed for the olefins oxidation [3,12].

The auto-oxidation process involving O_2 seems to be the principal pathway in oxidation on H–GeX. It is initiated by acid-catalyzed or even thermal decomposition of hydroperoxides formed in a primary stage of oxidation with H_2O_2 . Additionally, Brönsted acid sites could decompose H_2O_2 in H_2O and O_2 , as it was proposed by other authors [22]. On Na–GeX, such a reaction pathway is not excluded, but its contribution is less pronounced. Some acidic properties could be gained by Na–GeX even after interaction with H_2O_2 (Scheme 1). The formation of Ge–peroxo species could liberate protons, this behaviour being favoured by the tendency of germanium to increase its coordination number.

Sulfatation of the GeX sieves strongly enhanced the catalytic activity. This enhancement is not due to an improvement of the properties of the sieve, but to the modification of its structural and textural characteristics. Batamack et al. [39] described this ‘superacid’ as chemisorbed H_2SO_4 , in fact SO_4^{2-} and H_3O^+ adsorbed species in the presence of a large excess of water. Probably the interaction of water with Lewis acid sites of sulfated GeX results in the formation of Brönsted acid sites, which are responsible for a radical-type oxidation pathway involving O_2 . But an electrophilic oxidation pathway is not excluded, mainly in the absence of O_2 .

5. Conclusions

Na–GeX, H–GeX and sulfated GeX are active catalysts in the hydroxylation of benzene, toluene, and cyclohexane. Under autogenic pressure, the reaction rate is improved. O_2 dissolved in the aqueous phase has an important contribution. An electrophilic oxidation mecha-

nism occurring over Na–GeX form is suggested by the selectivities to the cresol isomers obtained in the oxidation of toluene, while the H–GeX form seems to favour a radical-type mechanism. Sulfatation of the GeX sieves enhanced the catalytic activity. Modifications of the structural and textural characteristics seem to be the principal reason for this enhancement. A strong acidic character and a loss of crystallinity have been detected for the sulfated form.

References

- [1] J.S. Reddy, R. Kumar, *J. Catal.* 130 (1991) 440.
- [2] G. Deo, A.M. Turek, I.E. Wachs, D.R.C. Huybrechts, P.A. Jacobs, *Zeolites* 13 (1993) 365.
- [3] B. Notari, Symposium on New Catalyst Chemistry Utilizing Molecular Sieves, Division of Petroleum Chem., 206th National Meeting, American Chem. Soc., Chicago, IL, August 22–29, 1993, p. 761.
- [4] B. Notari, in: P.J. Grobet, W.J. Mortier, E.F. Vansant, G. Schulz-Ekloff (Eds.), *Innovation in Zeolite Materials Science*, Stud. Surf. Sci. Catal., Vol. 37, Elsevier, Amsterdam, 1987, p. 413.
- [5] C.B. Khow, C.B. Dartt, H.X. Li, M.E. Davis, Symposium on New Catalyst Chemistry Utilizing Molecular Sieves, Division of Petroleum Chem., 206th National Meeting, American Chem. Soc., Chicago, IL, August 22–29, 1993, p. 769.
- [6] A.V. Ramaswamy, S. Sivasanker, P. Ratnasamy, Symposium on New Catalyst Chemistry Utilizing Molecular Sieves, Division of Petroleum Chem., 206th National Meeting, American Chem. Soc., Chicago, IL, August 22–29, 1993, p. 765.
- [7] G. Perego, G. Bellussi, C. Corno, M. Taramasso, F. Buonomo, A. Esposito, in: Y. Murakami, A. Iijima, J.W. Ward (Eds.), *Proceeding 7th Int. Conf. on Zeolites*, Stud. Surf. Sci. Catal., Vol. 28, Elsevier, Amsterdam, 1987, p. 129.
- [8] R. Millini, E.P. Massara, G. Perego, G. Bellussi, *J. Catal.* 137 (1992) 497.
- [9] R. Millini, G. Perego, K. Seiti, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Holderich (Eds.), *Zeolites and Related Microporous Materials, State of the Art 1994*, Stud. Surf. Sci. Catal., Vol. 84, Elsevier, Amsterdam, 1994, p. 2261.
- [10] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti, in: C. Martena, A. Zecchina, G. Costa (Eds.), *Structure and Reactivity of Surfaces*, Stud. Surf. Sci. Catal., Vol. 48, Elsevier, Amsterdam, 1988, p. 133.
- [11] A. Tuel, Y. Ben Taarit, *Appl. Catal. A: General* 102 (1993) 69.
- [12] R.A. Sheldon, J. Dakka, *Catal. Today* 19 (1994) 215.
- [13] E. Astorino, J.B. Peri, R.J. Willey, G. Busca, *J. Catal.* 157 (1995) 482.
- [14] U. Schuchardt, H.O. Pastore, E.V. Spinace, in: J. Weitkamp,

- H.G. Karge, H. Pfeifer, W. Holderich (Eds.), Zeolites and Related Microporous Materials, State of the Art 1994, Stud. Surf. Sci. Catal., Vol. 84, Elsevier, Amsterdam, 1994, p. 1877.
- [15] A. Bhaumik, R. Kumar, P. Ratnasamy, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Holderich (Eds.), Zeolites and Related Microporous Materials, State of the Art 1994, Stud. Surf. Sci. Catal., Vol. 84, Elsevier, Amsterdam, 1994, p. 1883.
- [16] F. Maspero, U. Romano, J. Catal. 146 (1994) 215.
- [17] T. Tatsumi, K. Asano, K. Yanagi-Sawa, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Holderich (Eds.), Zeolites and Related Microporous Materials, State of the Art 1994, Stud. Surf. Sci. Catal., Vol. 84, Elsevier, Amsterdam, 1994, p. 1861.
- [18] T. Yashima, Y. Kobayashi, T. Komatsu, S. Namba, New frontiers, in: L. Guzzi, P. Tetenyi, F. Solymosi (Eds.), Catalysis, Proceedings of 10th International Congress on Catalysis, Budapest, Kyado Academy, 1992, p. 1689.
- [19] T. Yashima, T. Nagase, T. Komatsu, S. Namba, in: T. Inui, K. Fujimoto, T. Uchijima, M. Masai (Eds.), New Aspects of Spillover Effect in Catalysis, Stud. Surf. Sci. Catal., Vol. 77, Elsevier, Amsterdam, 1993, p. 417.
- [20] M. Allian, A. Germain, F. Figueras, Abstracts of TOCAT-2 Conference, Tokyo, Japan, 1994.
- [21] M. Allian, A. Germain, F. Figueras, Catal. Lett. 28 (1994) 409.
- [22] J.S. Reddy, R. Kumar, S.M. Csicsery, J. Catal. 145 (1994) 73.
- [23] L. Lerot, G. Poncelet, M.L. Dubru, J.J. Fripiat, J. Catal. 37 (1975) 396.
- [24] G. Poncelet, M.L. Dubru, J. Catal. 52 (1978) 321.
- [25] G.A. Olah, N. Yoneda, D.G. Parker, J. Am. Chem. Soc. 99 (2) (1977) 483.
- [26] T. Jin, T. Yamaguchi, K. Tanabe, J. Phys. Chem. 90 (1986) 4794.
- [27] L. Lerot, G. Poncelet, J.J. Fripiat, Mater. Res. Bull. 9 (1974) 979.
- [28] P.A. Jacobs, F.H. van Cauwelaert, E.F. Vansant, J.B. Uytterhoeven, J. Chem. Soc., Faraday Trans. 1 69 (1973) 1056.
- [29] K. Arata, Adv. Catal. 37 (1992) 165.
- [30] K. Tanabe, H. Hattori, in: G. Ertl, H. Knozinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis: A. General Principles, Methods and Reaction Engineering, Vol. 1, VCH Verlagsgesellschaft, 1997, p. 404.
- [31] P. Ratnasamy, R. Kumar, in: L. Bonnevot, S. Kaliaguine (Eds.), Zeolites: A Refined Tool For Designing Catalytic Sites, Proceedings of the International Zeolite Symposium, Vol. 97, Elsevier, Quebec, 1995, p. 367.
- [32] E.V. Spinace, H.O. Pastore, U. Schuchardt, J. Catal. 157 (1995) 631.
- [33] P.S.E. Dai, J.H. Lunsford, J. Catal. 64 (1980) 184.
- [34] K. Tanabe, M. Misono, Y. Ono, H. Hattori, New Solid Acids and Bases, Stud. Surf. Sci. Catal., Vol. 51, Elsevier, Amsterdam, 1989, p. 54.
- [35] F. Thibault-Starzyk, R.F. Parton, P.A. Jacobs, in: J. Weitkamp, H.G. Karge, H. Pfeifer, W. Holderich (Eds.), Zeolites and Related Microporous Materials, State of the Art 1994, Stud. Surf. Sci. Catal., Vol. 84, Elsevier, Amsterdam, 1994, p. 1419.
- [36] J.A. Howard, K.U. Ingold, Can. J. Chem. 45 (1967) 785.
- [37] C. Walling, R.A. Johnson, J. Am. Chem. Soc. 97 (2) (1975) 363.
- [38] R.A. Sheldon, in: E.G. Derouane, J. Haber, M. Guisnet, F. Lemos, F.R. Ribeiro, M. Guisnet (Eds.), Catalytic Activation and Functionalization of Light Alkanes: Advances and Challenges, 3. High Technology, Vol. 44, Kluwer Academic Publishers, 1997, p. 73.
- [39] P. Batamack, G. Coudurier, C. Doremieux-Morin, F. Garin, M. Hachoumi, V. Semmer, J. Sommer, J.C. Vedrine, Book of Abstracts EUROPACAT II Congress, September 3–8, Maastricht 1995, 351.