Catalysis Letters Vol. 89, Nos. 3–4, September 2003 (© 2003)

A study of the oxidative dehydrogenation of cyclohexane over oxide catalysts

Marta Panizza[a], Carlo Resini[a], Guido Busca[a,*], Enrique Fernández López[b], and Vicente Sánchez Escribano[b]

[a]*Laboratorio di Chimica delle Superfici e Catalisi Industriale, Dipartimento di Ingegneria Chimica e di Processo, Università di Genova, P.le Kennedy, 16129 Genova (Italy)*

[b]*Departamento de Química Inorgánica, Facultad de Ciencias Químicas, P. de la Merced s/n, 37008-Salamanca (Spain)*

Recieved 1 April 2003; accpted 6 June 2003

The vapor-phase cyclohexane oxidative dehydrogenation has been investigated over several catalysts. A typical catalyst for total oxidation, as Mn_2O_3, materials applied in the field of oxide hydrogenation reactions, as silica-supported vanadia- and niobia-based catalysts, V-, Fe-, and Ce-phosphates used for partial oxidation reactions and ZSM5 zeolite, protonic and Co exchanged, have been tested. Over almost all the catalysts, benzene is the main product obtained, although cyclohexene is obtained with high selectivity at low conversion on phosphate catalysts.

KEY WORDS: cyclohexane; oxidative dehydrogenation; vapor phase; benzene.

1. Introduction

The oxidation of cyclohexane is performed industrially in liquid phase to produce cyclohexanone and cyclohexanol [1], which are intermediates in the synthesis of adipic acid and hexamethylenediamine, the monomers for Nylon 6,6, and of cyclohexanone oxime, the monomer for Nylon 6. The conversion per pass of cyclohexane is very low but attempts to develop more performant and environmentally benign heterogeneously catalyzed processes were not successful [2].

The oxidative dehydrogenation (ODH) of cyclohexane can produce cyclohexene and cyclohexadiene, potential useful intermediates and monomers for polyadditions, and benzene. Benzene cannot be considered to be a useful product because cyclohexane is mostly produced by hydrogenation of benzene itself [3]. However, cyclohexane is also available in large amounts in naphthas, so it can be recovered from them although with quite demanding procedures. In particular, a significant concentration of cyclohexane occurs in the side fraction of the so-called benzene heartcut tower, a refinery distillation tower, where a benzene-rich fraction (50% of benzene) is separated from a heavy gasoline bottom and a light gasoline head fraction, both fulfilling the 1% maximum limit for benzene in commercial gasoline [4]. This side fraction can be considered a relatively low-value by-product of the refinery and is used to provide benzene for petrochemical processes.

Due to the important role of benzene as an intermediate in petrochemistry, processes for conversion of low-value hydrocarbons into benzene, such as aromatization of light alkanes [5], are under development. In this context, the conversion of cyclohexane, either recovered from the benzene heartcut tower side fraction, or still in mixture with benzene, can be a way to enhance the production of benzene and to fulfil the need for benzene in some cases.

Actually, the conversion of cyclohexane into benzene, when useful, can be obtained either by pure catalytic dehydrogenation or by oxidative dehydrogenation. Pure dehydrogenation processes allow the coproduction of hydrogen, a very valuable coproduct, but are endothermic, thermodynamically limited and hindered by easy catalyst deactivation by coking [6]. In contrast, oxidative dehydrogenations are exothermic and thermodynamically definitely favored processes in which catalyst coking usually does not occur [7].

This paper reports the investigation of the feasibility of the cyclohexane ODH in vapor phase over different kinds of catalysts, some of which have already been tested for converting cyclohexane in liquid phase: transition metal oxides [8], transition metal phosphates [9,10], protonic and transition metal exchanged zeolites [11]. The aim is to obtain indication of possible catalytic systems allowing the production of benzene or cyclohexene in vapor phase.

2. Experimental

Catalytic activity tests have been realized over different oxides.

α-Mn_2O_3 bixbyte has been prepared starting from a solution of $Mn(CH_3COO)_2 \cdot 4H_2O$ (Aldrich) and calcination at 773 K for 4 h in air.

---

[*] To whom correspondence should be addressed.

1011-372X/03/0900–0199/0 © 2003 Plenum Publishing Corporation

$V_2O_5/SiO_2 = 44.7:56.3$ w/w (denoted as VS) and V_2O_5–$Nb_2O_5/SiO_2 = 22.4:32.7:44.9$ w/w (denoted as VNS) have been prepared by sequential impregnations of a commercial amorphous silica (Carlo Erba, $296\,m^2/g$) with ammonium metavanadate and with niobium ethoxide, in oxalic acid and water solutions and calcined in air at 873 K for 4 h.

Ce-, V-, and Fe-phosphates: the Ce-phosphate precipitation was carried out with ammonium hydroxide from the metallic nitrate and phosphoric acid in order to have a ratio metal to phosphorous equal to 1 : 1. Then, the precipitate was aged for 24 h under continuous stirring and gentle heating, washed and dried overnight at 368 K. The sample was later milled and calcined at 773 K in a Nabertherm furnace for 4 h. The phase obtained is $CePO_4$ confirmed by X-ray diffraction (XRD) (ICDD file n° 75–1880).

V phosphate was synthesized according to a well-known method previously reported in literature [12]. Vanadium pentoxide (30 g) was stirred into 360 mL of a mixture (1 : 2) of benzyl and isobutyl alcohols. 19.2 mL of orthophosphoric acid (in order to keep a final atomic P : V ratio of 1 : 1) dissolved in 60 mL of isobutyl alcohol was denoted to form a slurry that gradually darkened upon heating to the reflux temperature (~378 K). After 12 h, the mixture was cooled with continuous stirring and the green product was isolated by filtration, washed with diethyl ether and milled and then dried overnight at 328 K. The final product was calcined at 773 K in the same conditions as above. The phase obtained is γ-$VOPO_4$ confirmed by XRD (ICDD file n° 47–0950).

Fe phosphate was prepared by the same method from Fe(II) oxalate and orthophosphoric acid. The amounts employed were 12 g of Fe(II) oxalate and 4 mL of H_3PO_4. The synthesis conditions were not changed. The phases obtained are $Fe_7(PO_4)_6$ and F_2O_3 confirmed by XRD (ICDD file n° 35–0282, ICDD file n° 73–0603, respectively).

H-ZSM5 and Co-ZSM5 have been obtained from the commercial NH_4-ZSM5 (Zeolyst, $SiO_2/Al_2O_3 = 50$). Co-ZSM5 has been prepared by cationic exchange: NH_4-ZSM5 in powder has been put in contact with a 0.02 M water solution of cobalt acetate $Co(CH_3COO)_2 \times 4H_2O$; the so-obtained solution has been kept in a continuous stirring at 80 °C for 24 h. At exchange completed, the solution has been filtered, the solid phase has been washed with deionized water and then separated by centrifugation and dried at 80 °C for 10 h. Afterwards, the material has been calcined in air at 550 °C for 4 h.

The operative conditions are summarized in table 1; in all the tests (but the empty reactor tests), the amount of catalyst is equal to 0.1 g gently mixed mechanically with 0.4 g of quartz. In the case of the tests over the metal phosphates, the operative conditions have been chosen according to the literature [13], so in the presence of water vapor; even over VS catalyst, a comparison in presence of water vapor has been investigated.

3. Results and discussion

Preliminary tests have been performed in the empty reactor with the aim to investigate the occurrence of gas-phase reactions in two different feeding conditions (figure 1(a) and (b)).

Table 1
Materials and operative conditions

Sample	Cyclohexane %	Oxygen %	H_2O %	Total flow (mL/min)	$C_6H_{12}:O_2$	App.$E_{act.}$ (kJ/mol)
Mn_2O_3	1	2		300	1 : 2	n.a.
VS	2	2		300	1 : 1	83
VS	1	2		300	1 : 2	88
VS	1	2	0.1	300	1 : 2	92
VNS	2	2		300	1 : 1	71
VNS	1	2		300	1 : 2	92
VNS	4	2		300	2 : 1	90
V-phosphate	1.7	1	2.4	270	1.7 : 1	50
Fe-phosphate	1.7	1	2.4	270	1.7 : 1	77
Ce-phosphate	1.7	1	2.4	270	1.7 : 1	88
H-ZSM5	0.2	2		300	0.2 : 2	63
H-ZSM5	2	2		300	1 : 1	71
H-ZSM5	4	2		300	2 : 1	59
Co-ZSM5	0.2	2		300	0.2 : 2	n.a.
	2	2		300	1 : 1	136
	4	2		300	2 : 1	90
Empty reactor	2	2		300	1 : 1	242
	4	2		300	2 : 1	328

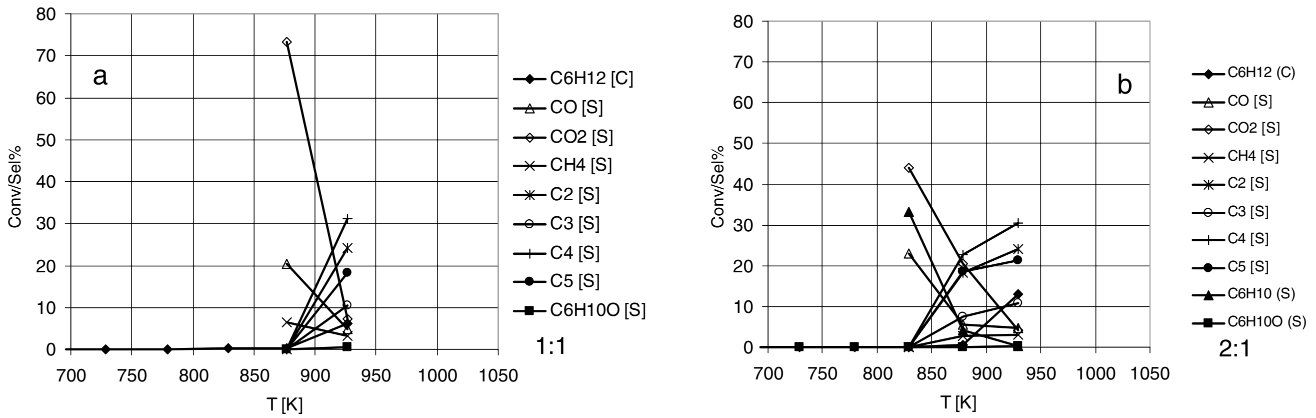

Figure 1. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products in the empty reactor. Feed: (a) 2 : 2 : 96 = C_6H_{12} : O_2: He (1 : 1) and (b) 4 : 2 : 94 = C_6H_{12} : O_2: He (2 : 1), total flow 300 mL/min.

In both tests, the conversion of cyclohexane starts above 850 K, and in any case does not exceed 15% at 930 K. The products obtained are typical of the cracking thermal reactions (i.e., C1–C5 hydrocarbons). Apparent activation energies (>240 kJ/mol, see table 1) are in both cases in the range typical of gas-phase reactions limited by chemical act [7].

Mn_2O_3 has been chosen in order to test the reactivity of the cyclohexane over a very active catalyst in total oxidation reactions [14]. The test has been realized with 1% of cyclohexane, 2% of oxygen in helium with a total flow equal to 300 mL/min. The activity of Mn-oxide catalyst is high also in the case of cyclohexane oxidation as expected. Conversion of C_6H_{12} starts to be significant above 573 K, it is higher than 20% at 623 K, and it is in constant increasing by increasing temperature reaching 44% at 759 K. Oxygen conversion becomes total in a range of 50 °, stressing the particular activity of the catalyst. The main product, according to the activity of the catalyst as a total oxidation catalyst, is in fact CO_2, which selectivity decreases after total oxygen consumption. Benzene is obtained in increasing amounts by increasing cyclohexane conversion reaching 50% of selectivity at 759 K.

Vanadia-based catalysts are well known as partial oxidation catalysts [15]. In a previous work [16], the activity of silica-supported niobium oxide and its role when it is associated to vanadia have been discussed. Tests have been conducted either with the cyclohexane : oxygen ratio equal to 1 : 2 or in the presence of water vapor (0.1%). The aim of this test is to check the effect of water vapor on the catalyst activity and on the distribution of the products. Figure 2 shows the distribution of reactants and products by increasing temperature of the reaction of oxidation of cyclohexane (see table 1) over VS and VNS. In these conditions, the VS catalyst seems to be more active than the VNS one; in fact, over VS cyclohexane conversion starts at a lower temperature and it reaches the highest conversion of 75% at 900 K, whereas over VNS the conversion does not exceed 20% at 880 K. Benzene is the main product in both cases even though its selectivity decreases by increasing temperature in favor of the increasing of CO_x selectivities. As for VS catalyst, traces of cyclohexene have been detected. Figure 2(c) shows the effect of water vapor on the trend of the conversion/selectivity curves. Comparing figure 2(c) to figure 2(a) it is evident that a decrease of cyclohexane conversion (reaching 62% at 620 K) corresponds to an increasing of selectivity to benzene (reaching a maximum of 75% at 400 K) and to a decrease of CO selectivity (lower than 10% in the whole temperature range considered).

Cyclohexane conversion over transition metal phosphates has been tested. Catalytic activity has been evaluated feeding cyclohexane, oxygen and water with the following concentrations: 1.7% of cyclohexane, 1% oxygen in presence of 2.4% of water stream (see table 1). Figures 3, 4, and 5 report the trend of the conversion/selectivity versus temperature curves of the carbon-containing compounds. Cyclohexane conversion over vanadium phosphate (figure 3) becomes important at 620 K and reaches the maximum values of 60% at near 950 K. The main product is benzene with a selectivity higher than 75% in the range of temperature considered. At low conversions, traces of cyclohexene have been detected. In the presence of Fe-phosphates (figure 4), cyclohexane conversion starts at near 520 K, and it is still below 40% at 920 K. At very low conversion, the main product is cyclohexene and its selectivity decreases from 100 to 5% by increasing temperature. At the same time the selectivity to benzene increases and reaches 85% at 950 K. As similar behavior of Fe-phosphate is observed over Ce-phosphate (figure 5) in a range of temperature 570–750 K. In fact, cyclohexane conversion starts at 570 K and the main product at low conversion is cyclohexene with a selectivity of 55% at 570 K. Selectivity to benzene increases from 40% at 570 K and it stabilizes at 85% from 750 K becoming the main product at higher conversions. At temperatures above

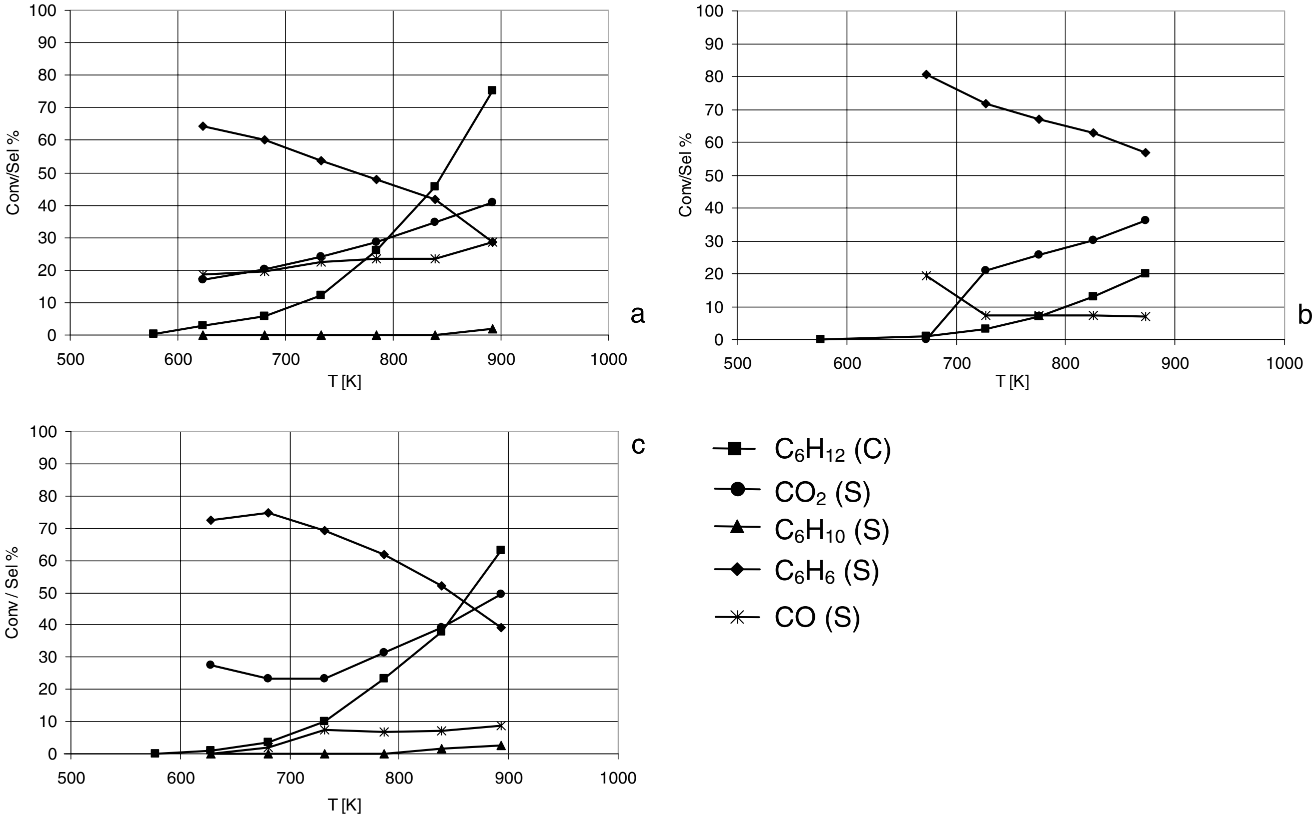

Figure 2. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over VS (a, c) and VNS (b) catalysts. Feed: total flow 300 mL/min, (a) and (b) 1 : 2 : 97 = C_6H_{12} : O_2:He; (c) 1 : 2 : 0.1 : 97 = C_6H_{12} : O_2 : H_2O : He.

750 K cyclohexane conversion is stable around 35%. In all cases, selectivity to CO_x does not exceed 20%. The apparent activation energy calculated for the reaction over transition metal phosphates (reported in table 1) are typical of reactions under kinetic control.

Tests over H- and Co-exchanged ZSM5 zeolite have been performed in order to investigate the role of Co and of Brønsted sites on the activity as well as on the selectivity towards partial oxidation products. Figures 6, 7, and 8 report the results of tests performed in different feeding conditions. Figure 6 shows the results of the tests performed with a cyclohexane/oxygen ratio of 1 : 10 over protonic and Co-exchanged zeolites. Cyclohexane conversion over H-ZSM5 starts at high temperature and remains always below 5%. The products detected are CO_x, benzene and traces of cracking products. In these conditions, the apparent activation energy of cyclohexane is 63 kJ/mol. When the zeolite is exchanged with cobalt (figure 6(b)), the catalyst activity increases. In fact, cyclohexane conversion starts at 720 K and

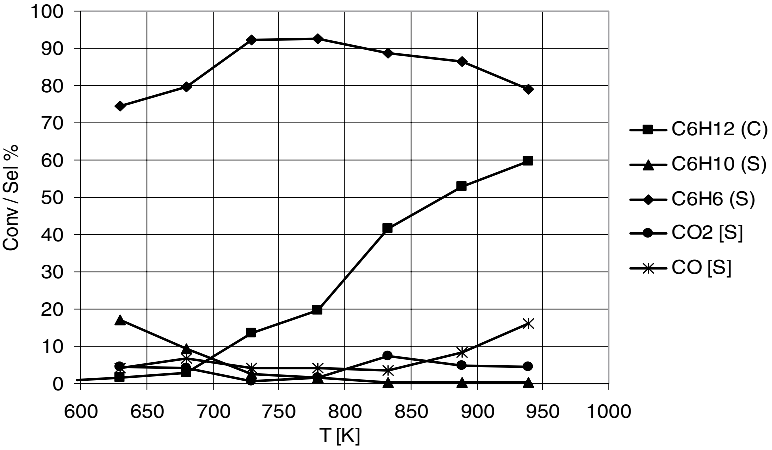

Figure 3. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over V-phosphate catalyst. Feed: 1.7 : 1 : 2.4 : 94.9 = C_6H_{12} : O_2 : H_2O : He, total flow 270 mL/min.

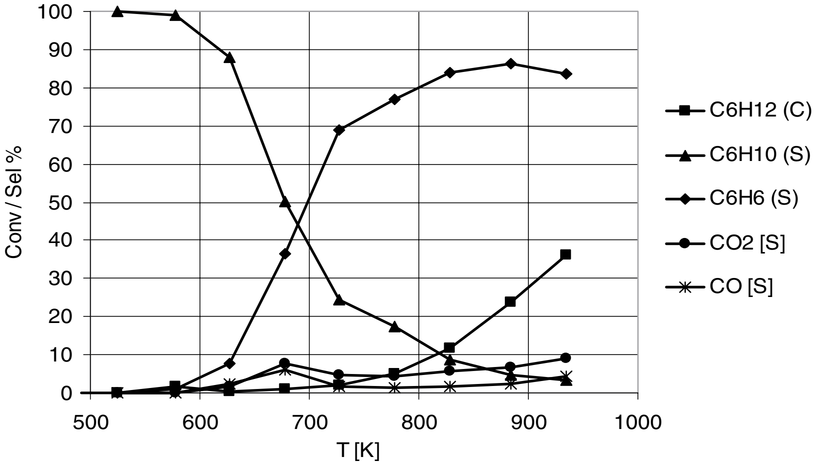

Figure 4. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over Fe-phosphate catalyst. Feed: 1.7 : 1 : 2.4 : 94.9 = C_6H_{12} : O_2 : H_2O : He, total flow 270 mL/min.

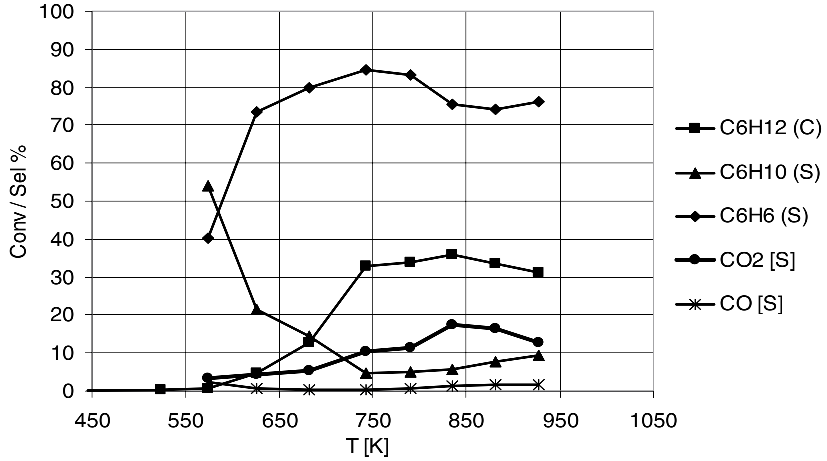

Figure 5. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over Ce-phosphate catalyst. Feed: 1.7 : 1 : 2.4 : 94.9 = C_6H_{12} : O_2 : H_2O : He, total flow 270 mL/min.

becomes nearly complete at 940 K. The main product is CO_2 and its selectivity reaches 100% at the highest temperature investigated here. The results of the test with a 1 : 1 feed are reported in figure 7. In the presence of H-ZSM5 (figure 7(a)), the conversion of the reactant is very low (it does not exceed 8%) and the main products, in these conditions, are CO and CO_2. On the contrary, cyclohexane conversion over Co-ZSM5 (figure 7(b)) starts at 580 K and reaches the values of 90% at 900 K. The main product becomes benzene whereas the

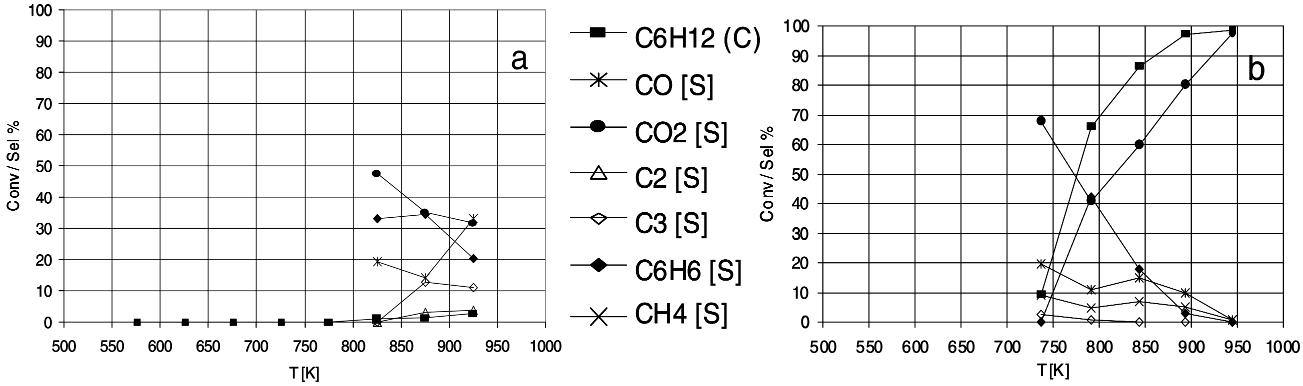

Figure 6. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over H-ZSM5 (a) and Co-ZSM5 (b) catalysts. Feed: 0.2 : 2 : 97.8 = C_6H_{12} : O_2 : He, total flow 300 mL/min.

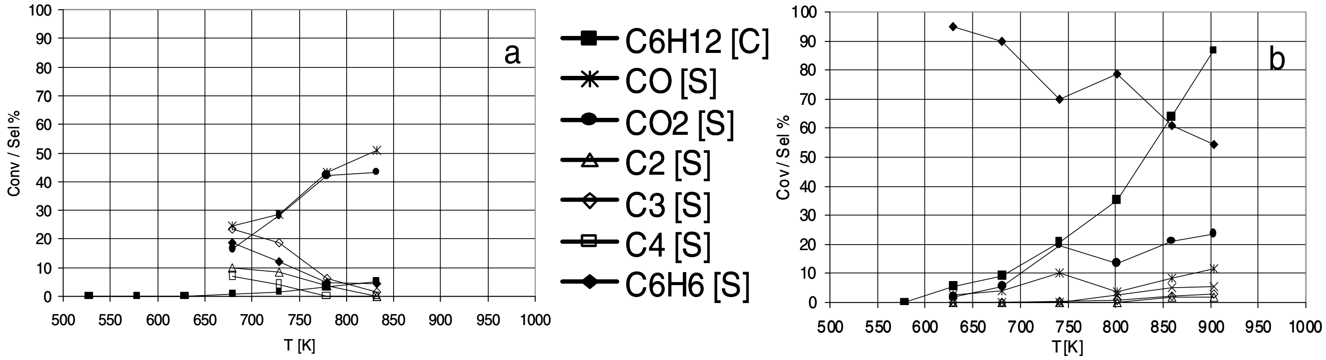

Figure 7. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over H-ZSM5 (a) and Co-ZSM5 (b) catalysts. Feed: $2:2:96 = C_6H_{12}:O_2:He$, total flow 300 mL/min.

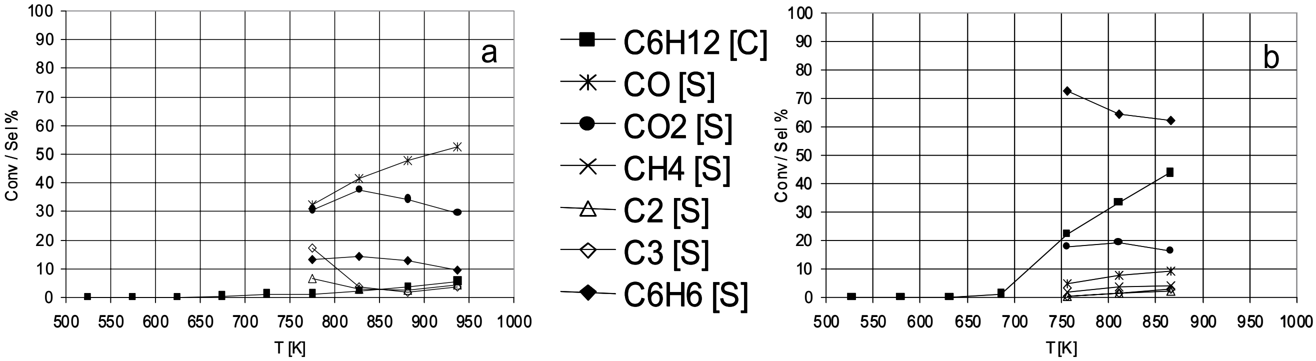

Figure 8. Variation of the conversion (C) of cyclohexane and the selectivities (S) to the main reaction products over H-ZSM5 (a) and Co-ZSM5 (b) catalysts. Feed: $4:2:94 = C_6H_{12}:O_2:He$, total flow 300 mL/min.

selectivity to CO_x is less than 30% in the whole range of temperature. Doubling again the volume of the hydrocarbon in the feed, in the presence of acidic zeolite (figure 8(a)), the cyclohexane conversion starts at 720 K and it is still below 8% at 940 K. At very low conversions, the main products are benzene and hydrocarbons with three carbon atoms, whereas, above 780 K, CO_x become the largest products. On the contrary, in the same conditions over Co-ZSM5 (figure 8(b)), the cyclohexane conversion becomes significant above 700 K and increases by increasing of temperature to 45% at 880 K. The main products at low conversion are CO_x whereas at higher temperature benzene becomes the most important product.

4. Conclusions

The catalytic tests have pointed out gas-phase reactions occur above 850 K. Easy reducible Mn oxide as expected works as a total oxidation catalyst (giving rise to CO_x as main product); this confirms that it could be used as combustion catalyst at low temperature (below 600 K).

A higher selectivity to benzene has been obtained using a partial oxidation catalyst (VS). Tests conducted in the presence of water vapor (even though in small concentration) show an increasing of the benzene selectivity. The role of Nb oxide results in an increasing of benzene selectivity and a corresponding decreasing of cyclohexane conversion.

In the case of transition metal phosphates, cyclohexane conversion is significant in spite of the high water vapor concentration. High selectivity to benzene is obtained whereas at very low conversion high selectivity to cyclohexene is found as well.

Protonic zeolite shows a low activity with CO_x as main products, whereas the same zeolites exchanged with cobalt shows a much higher activity with benzene as main product. The comparison between the two tests points out the role of Co as active site for cyclohexane dehydrogenation.

Further studies will be done on metal phosphates, which can be considered the most interesting catalytic materials for benzene and cyclohexene production.

References

[1] K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry*, 3rd ed. p. 240.

[2] U. Schuchardt, D. Cardoso, R. Sercheli, R. Pereira, R.S. da Cruz, M.C. Guerreiro, D. Mandelli, E.V. Spinaci and E.L. Pires, Appl. Catal. A: Gen. 211 (2001) 1.

[3] K. Weissermel and H.-J. Arpe, *Industrial Organic Chemistry*, 3rd ed. p. 345.

[4] J. Blomberg, P.J. Schoenmakers and U.A. Th. Brinkman, J. Chromatogr. A, 972 (2002) 137–173.

[5] K. Nishi, S. Komai, K. Inagaki, A. Satsuma and T. Hattori, Appl. Catal. A: Gen. 223 (2002) 187–193.

[6] D. Sanfilippo, F. Buonomo, G. Fusco and I. Miracca, in *Natural Gas Conversion V*, P.A. Parmaliana, D. Sanfilippo, F. Frusteri, A. Vaccari and F. Arena (eds) (Elsevier, Amsterdam, 1998) pp. 919–924.

[7] H.H. Kung, Advan. Catal. 40 (1994) 1.

[8] C. Hettige, K.R.R. Mahanama and D.P. Dissanayake, Chemosphere 43 (2001) 1079.

[9] M. Ai, Catal. Today 52 (1999) 65–69.

[10] R.A.W. Johnstone, J. Liu and D. Whittaker, J. Mol. Catal. A: Chem. 174 (2001) 159–168.

[11] E.L. Pires, M.Wallau and U. Schuchardt, J. Mol. Catal. A: Chem. 136 (1998) 69–74.

[12] G. Busca and G. Centi, J. Am. Chem. Soc. 111(1) (1989).

[13] J.M. Millet, D. Rouzies and J.C. Vedrine, Appl. Catal. A: Gen. 124 (1995) 205–219.

[14] M. Baldi, V. Sanchez Escribano, J.M. Gallardo Amores, F. Milella and G. Busca, Appl. Catal. B: Environ. 17 (1998) L175–182.

[15] J.G. Eon, R. Olie and J.C. Volta, J. Catal. 145 (1994) 318–326.

[16] C. Resini, M. Panizza, F. Raccoli, M. Fadda, G. Busca, E. Fernandez Lopez and V. Sanchez Escribano, Submitted paper.