

Gas-Phase Oxidative Dehydrogenation of Cyclohexanol over ETS-10 and Related Materials

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Received October 2, 2000; revised January 12, 2001; accepted January 12, 2001; published online April 11, 2001

The gas-phase oxidative dehydrogenation of cyclohexanol with air using ETS-10 and related materials is studied. At reaction temperatures below 200°C, ETS-10 was 100% selective to cyclohexanone and 75% cyclohexanol conversion was achieved. Catalyst deactivation was attributed to pore blockage. The catalyst is completely regenerated by calcination at 400°C. Cyclohexanol conversion increases with temperature and oxygen/cyclohexanol feed ratios. The introduction of Cr, Fe, K, or Cs in ETS-10 affects stability and decreases conversion and selectivity towards cyclohexanone. For comparison, some results on TS-1, zeolites NaX, and mordenite are also presented. © 2001 Academic Press

Key Words: gas-phase oxidative dehydrogenation; cyclohexanol; air; ETS-10; ETAS-10; transition metals; alkaline cations.

INTRODUCTION

The gas-phase dehydrogenation of cyclohexanol to cyclohexanone is a very important industrial process since the latter is an intermediate used in the production of nylon. Cyclohexanone is conventionally produced via the direct dehydrogenation of cyclohexanol over ZnO- or Cu-based catalysts (1–3). Oxidative dehydrogenation (OD) has great advantages when compared with conventional dehydrogenation processes. OD is a practically irreversible exothermic reaction while dehydrogenation is a reversible endothermic reaction (4). Therefore, dehydrogenation equilibrium conversions are thermodynamically limited and OD conversions are not thermodynamically limited.

Alkali-exchanged zeolites are known to promote base-catalysed dehydrogenation of alcohols (5, 6). Alkali doping poisons acidic centres and consequently suppresses dehydration activity and increases dehydrogenation selectivity. Cyclohexanol conversion is considered a test reaction for acid–base properties of solid catalysts (7, 8). The dehydration of cyclohexanol to cyclohexene takes

place on weak acid sites and the consecutive reactions (isomerization/disproportionation) take place on stronger acid sites (7). It is possible to expect that basic solids favour the dehydrogenation process over the dehydration one, producing mainly cyclohexanone (9).

ETS-10 is a tinosilicate molecular sieve with an open 12-membered-ring channel system (10). The structure consists of corner-sharing octahedral titanium(IV) and tetrahedral silicon. Each titanium ion in the framework has a 2– charge (balanced by Na and K cations: $(\text{NaK})_2\text{Si}_5\text{TiO}_{13}$) which furnishes ETS-10 with considerable basicity, as shown by its dehydrogenation activity for the “isopropanol to acetone” probe reaction (11). This material is a potential candidate as a catalyst for the conversion of cyclohexanol to cyclohexanone.

In this work we study the gas-phase oxydehydrogenation of cyclohexanol using air, at atmospheric pressure, in the presence of ETS-10 and related materials, prepared by the introduction of other elements in ETS-10 by ion-exchange (K, Cs, H, Cr, Fe) or during hydrothermal synthesis (Al, Cr, V, Fe). For comparison, some results on TS-1, zeolites NaX, and mordenite are also presented.

EXPERIMENTAL

Sample Preparation

ETS-10 and ETAS-10 (Al/Ti = 0.26) samples were prepared according to the methods described previously (12, 13). TS-1 was prepared according to a procedure described in (14).

Protonic ion-exchanged ETS-10 (H-ETS-10) was prepared by mixing 5.0 g of ETS-10 with 2.5 ml of acetic acid in 500 ml of H₂O, for 5 h, at room temperature. The K⁺ and Cs⁺ ion-exchanged ETS-10 samples (K-ETS-10 and Cs-ETS-10, respectively) were prepared as follows: 2.0 g of ETS-10 in 230 ml of H₂O was mixed with 2.33 g of KNO₃ or 3.88 g of CsCl, at 323 K and room temperature, respectively, for 12 h. ETS-10 was ion-exchanged with chromium

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and iron (Cr-ETS-10 and Fe-ETS-10, respectively) by mixing 2.0 g of ETS-10 with 0.59 g of $\text{Cr}_2(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ or 1.8 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 75 ml of H_2O (pH adjusted to ca. 7 by addition of NaOH solution), at 50°C , for 40 h. The ion-exchanged samples were filtered, thoroughly washed with distilled water, and dried at 393 K.

ETFes-10 was synthesised hydrothermally in a Teflon-lined autoclave, under autogeneous pressure, without agitation. An alkaline solution was prepared by mixing 11.3 g of H_2O , 2.57 g of NaOH, 1.39 g of KF, and 0.77 g of KCl. To this solution were added 1.07 g of FeCl_3 and 8.52 g of a TiCl_3 aqueous solution (1.9 M in 2.0 M HCl, Aldrich), followed by blending in of 17.43 g of sodium silicate solution (27 wt% SiO_2 , 8 wt% Na_2O , Merck). Fine seed crystals (0.20 g of ETS-10) were added to the final gel and carefully mixed. The autoclave was sealed and heated to 230°C . After 36 h the autoclaves were removed and quenched in cold water. The resulting crystals were filtered, washed at room temperature with distilled water, and dried at 90°C .

ETCrS-10 and ETVS-10 were prepared similarly. An alkaline aqueous solution was prepared by mixing a sodium silicate solution [(SiO_2 27 wt%, Na_2O 8 wt%, Merck), 9.50 g for Cr and 9.52 g for V] with H_2O (8.00 g for Cr and 7.61 g for V), NaOH (1.30 g for Cr and 1.1 g for V), KCl (0.99 g for Cr and 0.98 g for V), NaCl (1.43 g for Cr and 1.65 g for V) and TiCl_3 [TiCl_3 15 wt%, HCl 10 wt%, Merck), 4.12 g for Cr and V]. To this solution were added 1.16 g of $\text{Cr}_2(\text{SO}_4)_3 \cdot 15\text{H}_2\text{O}$ in H_2O (7.20 g) and 1.50 g of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ in H_2O (7.60 g) for ETCrS-10 and ETVS-10 synthesis, respectively. After seeding with 0.10 g of ETS-10 each sample mixture was stirred to give a gel that was heated at 230°C , under autogeneous pressure, for 40 h. The resulting crystalline product was filtered, washed with distilled water, and dried at 120°C .

Characterisation of Samples

Powder X-ray diffraction of the samples was carried out on a Philipps X'pert MPD diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Crystallinity was estimated by summing the areas of the peaks at 20.1 and $24.7^\circ 2\theta$ and normalizing them to the corresponding areas of the as-synthesised ETS-10 sample. Scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDS) were carried out on a Hitachi S-4100 microscope. Nitrogen adsorption data were recorded gravimetrically, at 77 K, using a CI electronic MK2-M5 microbalance. The equilibrium of each data point was monitored using CI Electronics Labweigh software and the pressure was monitored using an Edwards Barocel pressure sensor. The samples were outgassed at 573 K overnight (>14 h), to give a residual pressure of ca. 10^{-4} mbar, and then cooled to room temperature prior to adsorption measurements. The specific total pore vol-

umes (V_p) were estimated from the nitrogen uptake at $P/P_0 \sim 0.95$, using the density of N_2 in its normal liquid state ($\rho = 0.8081 \text{ g cm}^{-3}$).

Catalytic Reactions

The oxidative dehydrogenation of cyclohexanol was carried out in a continuous-flow fixed bed reactor (Pyrex glass, 7 mm i.d.) at atmospheric pressure. Prior to reaction the catalyst (ca. 100 mg) was heated *in situ* at 250°C , for 90 min, in a nitrogen stream ($20 \text{ cm}^3/\text{min}$) to remove moisture. At the reaction temperature N_2 was substituted by air ($15 \text{ cm}^3/\text{min}$) and cyclohexanol was introduced with a Cole-Parmer 74900 Series syringe pump. The oxygen/cyclohexanol molar ratio was varied between 9 and 89 and the reaction temperatures between 150°C and 300°C . Temperature was measured by a thermocouple inserted in the catalyst bed.

Effluent from the catalyst bed was periodically injected into a Varian 3800 gas chromatograph (with a FID detector) by a six-port VICI gas-sampling valve. A semicapillary CP-WAX 52 CB column ($30 \text{ m} \times 0.53 \text{ mm}$) was used to separate the products.

RESULTS AND DISCUSSION

Characterisation

ETS-10 and ETMS-10 samples have similar crystalline structures, as revealed by their powder XRD patterns (Fig. 1), and similar morphology, as revealed by their SEM images (Fig. 2). M/Ti ratios of the ETMS-10 samples were estimated by EDS, which gave $\text{Fe/Ti} = 0.23$; $\text{Cr/Ti} = 0.32$; $\text{V/Ti} = 0.87$. For ETAS-10 $\text{Al/Ti} = 0.26$ (13). The MFI structure of synthesised TS-1 was confirmed by XRD. The Si/Ti ratio in TS-1 ($\text{Si/Ti} = 101$) was confirmed by EDS.

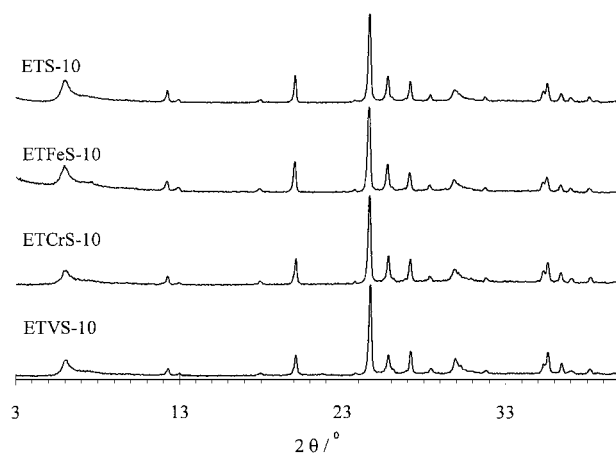


FIG. 1. X-ray diffraction patterns of ETS-10 and ETMS-10 samples.

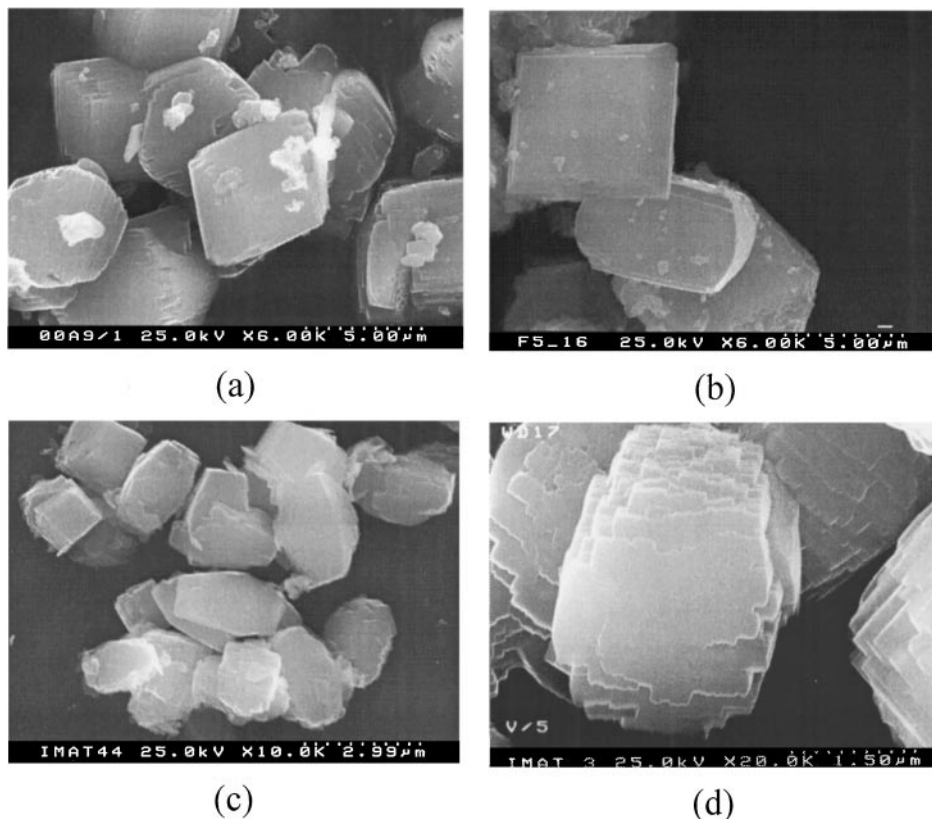


FIG. 2. SEM images of (a) ETS-10, (b) ETS-10, (c) ETS-10, and (d) ETS-10.

The N_2 adsorption isotherms of ETS-10, ETMS-10, and X-ETS-10 materials are of Type I (IUPAC), characteristic of microporous solids. Texture parameters, such as specific surface area (S_{BET}) and total pore volume (V_p), were determined from the adsorption isotherms. These values, given in Table 1, are roughly the same for all samples with the exception of Cs-ETS-10 for which S_{BET} and V_p values decreased ca. 28%.

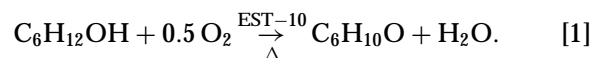
TABLE 1

Texture Parameters of the Catalyst Samples Derived from N_2 Isotherms (77 K)

Sample	S_{BET} ($m^2 g^{-1}$)	V_p ($cm^3 g^{-1}$)
ETS-10	275.7	0.145
ETFeS-10	297.7	0.142
ETCrS-10	240.9	0.116
ETVS-10	318.2	0.153
Fe-ETS-10	327.7	0.161
Cr-ETS-10	248.0	0.137
K-ETS-10	244.9	0.135
Cs-ETS-10	196.2	0.108
H-ETS-10	257.8	0.143
ETAS-10	268.3	0.128

Catalytic Reactions

ETS-10 was the most active catalyst among the studied materials for the oxidative dehydrogenation (OD) of cyclohexanol using air as oxygen source, at $150^\circ C$ and atmospheric pressure (37% conversion after 120 min on stream, Fig. 3). Cyclohexanone was the only product observed and is formed according to the stoichiometric reaction [1].



The OD of cyclohexanol over ETS-10 was demonstrated by using nitrogen instead of air, under identical experimental conditions, which gave 1.5% conversion. The thermal reaction of cyclohexanol (shown in a blank experiment without catalyst) gave ca. 3% conversion at $150^\circ C$ (Fig. 3) and ca. 5% conversion at $250^\circ C$.

The introduction of acidity in ETS-10 by ion-exchange with acetic acid (H-ETS-10) or by isomorphous substitution with aluminium (ETAS-10) reduces both activity and selectivity towards cyclohexanone (Fig. 3). It has been claimed that dehydration activity is related to the catalysts' surface acidity and that selectivity to cyclohexanone decreases with increasing acidity (7, 8, 15–19). The presence of weak acid sites is sufficient for the dehydration of cyclohexanol to

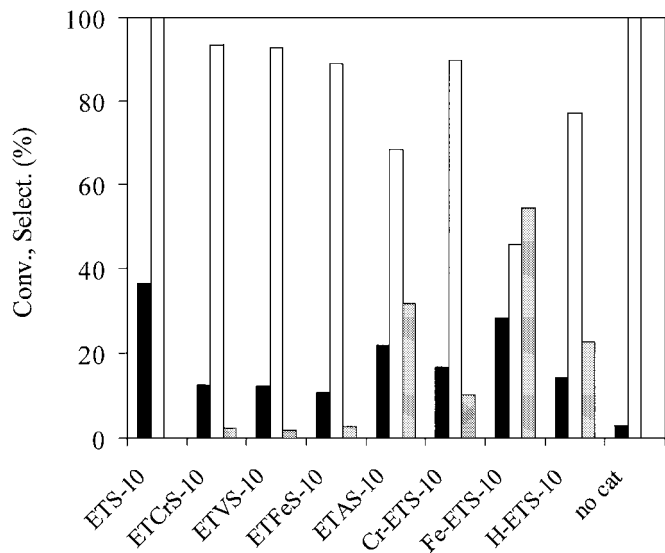


FIG. 3. Oxidative dehydrogenation of cyclohexanol by air at 150°C over different metallosilicate materials and without catalyst: (■) conversion, (□) selectivity to cyclohexanone, (▨) selectivity to cyclohexene. Reaction conditions: 150°C; 100 mg catalyst; 15 cm³/min air; oxygen/cyclohexanol molar ratio = 89; TOS = 120 min.

cyclohexene, which is a by-product. Since parent ETS-10 shows no dehydration activity, under the same reaction conditions, it is thought that the OD process involves mainly basic sites.

Minachev *et al.* (20 and references therein) reported the strong effect of the alkaline cations compensating the net negative charge of several zeolite structures, on the catalyst activity for oxidative dehydrogenation of several organic compounds. The base strength depends on the exchangeable cations and increases in the following order: Na < K < Cs (21). Other authors have developed alkali-treated catalysts for cyclohexanol dehydrogenation to promote the formation of cyclohexanone (3, 22). To study the influence of the alkaline cation on the catalytic performance of ETS-10, two experiments were carried out using K-ETS-10 and Cs-ETS-10 catalysts, at 200°C. No changes in selectivity were observed (selectivity to cyclohexanone remained 100%), suggesting that alkali doping did not cause significant changes in the surface properties of ETS-10. Furthermore, no promotional effect in terms of activity of ETS-10 was observed: cyclohexanol conversions decrease upon ion-exchange with bulkier K⁺ or Cs⁺ cations, and catalyst deactivation is significantly accelerated (Fig. 4). A possible explanation for these results is severe pore blockage of the microporous structure caused by the bulkier exchanged cations, accounting for rapid deactivation.

Metallosilicates containing different transition metals have been used in the dehydrogenation of alcohols to carbonyl compounds (23 and references therein). It is possible to expect that ETS-10 with different types of transition metal dopant give different catalytic activities in the OD of

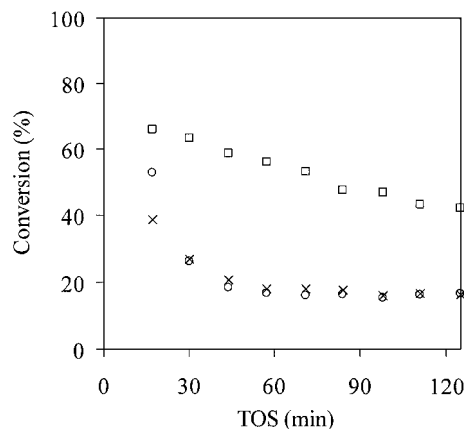


FIG. 4. Conversion profiles for the oxidative dehydrogenation of cyclohexanol, over ETS-10 (□), K-ETS-10 (×), and Cs-ETS-10 (○). Reaction conditions: 200°C; 100 mg of catalyst; 15 cm³/min air; oxygen/cyclohexanol molar ratio = 89.

cyclohexanol due to the nature of these various cations. Transition metals were introduced in ETS-10 by ion-exchange (X-ETS-10, X = Cr, Fe) or during hydrothermal synthesis (ETMS-10, M = Cr, V, Fe). No promotional effect in terms of overall activity and selectivity was observed. For all these materials cyclohexanol conversion and selectivity towards cyclohexanone were lower than those of the undoped ETS-10 material (Figs. 3 and 5). The catalysts exhibited dehydration activity, yielding cyclohexene as a by-product. A comparison of ETMS-10 with X-ETS-10 materials shows that the latter have greater dehydration activity than the former: Fe-ETS-10 gave the highest selectivity to cyclohexene (54.2%, at 38.5% conversion) and the lowest selectivity to cyclohexanone (45.8%). It has been reported

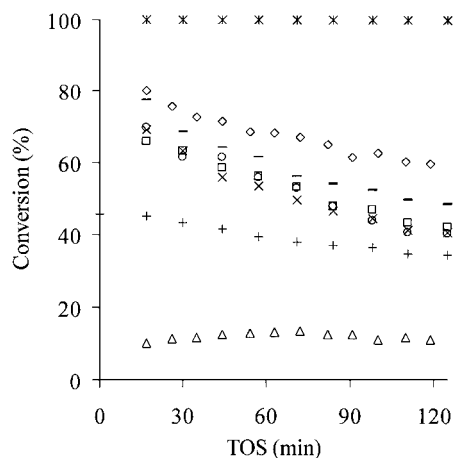


FIG. 5. Conversion profiles for the oxidative dehydrogenation of cyclohexanol, with air at 150°C over ETS-10 (+) and ETFeS-10 (Δ); 200°C over fresh ETS-10 (□), reactivated (ETS-10 reactivated by calcination with air, at 400°C) once (○), and reactivated twice (×); 250°C (—); 275°C (◇); 300°C (*). Reaction conditions: 100 mg of catalyst; 15 cm³/min air; oxygen/cyclohexanol molar ratio = 89.

TABLE 2

Influence of Reaction Temperature on Cyclohexanol Conversion and Selectivity, over ETS-10^a

Temperature (°C)	Conversion (%)	TON ^b (mmol/g _{cat})	Selectivity (%)	
			Cyclohexene	Cyclohexanone
150	36.6	0.7	0	100
200	42.2	0.8	0	100
250	49.7	0.9	20.3	67.7
275	59.8	1.1	68.4	34.8
300	100	1.9	79.3 ^c	0

^a Reaction conditions: 100 mg of catalyst, 15 cm³/min air; oxygen/cyclohexanol molar ratio = 89; TOS = 120 min.

^b Based on conversion at 120 min.

^c Remaining products are cyclohexane, benzene, and unidentified products with retention times very close to that of cyclohexene.

that the interaction of water with divalent cations in zeolites can form Brønsted acid sites, responsible for dehydration activity (5).

The best performance of ETS-10 in the OD of cyclohexanol stimulated us to further explore its catalytic behaviour.

The dependence of the conversion on time-on-stream (TOS) at different temperatures is shown in Fig. 5. ETS-10 shows high initial overall activity, which rapidly decreases with time-on-stream, in the temperature range 200–275°C. Turnover numbers (TON) increase from 0.7 mmol/g_{cat} at 150°C to 1.9 mmol/g_{cat} at 300°C (Table 2). At 300°C complete conversion of cyclohexanol was observed for 120 min on-stream. No loss of crystallinity (as ascertained by XRD) of the catalyst used at the different reaction temperatures was observed.

The product distribution, presented in Table 2 for ETS-10 at different reaction temperatures, remains almost unchanged for 120 min on-stream. Up to 200°C cyclohexanone is the only observed product. At 250°C cyclohexene (formed via dehydration) is a side product (20% selectivity) and becomes the main reaction product at 300°C (79% selectivity). Other products formed at 300°C are hydrocarbons such as benzene, resulting from aromatization activity, and cyclohexane, probably formed via hydrogenolytic splitting of the alcoholic OH group (24). Thus, cyclohexanol dehydration is favoured at high reaction temperatures causing a large drop in selectivity to cyclohexanone.

The influence of the oxygen to cyclohexanol feed ratio on conversion was studied at 200°C, by changing the feed rate of cyclohexanol. A 10-fold decrease of the oxygen/cyclohexanol molar ratio decreases conversion substantially (Fig. 6). Selectivity to cyclohexanone remained unchanged, i.e., 100%. The catalyst deactivation rate increases with decreasing oxygen/cyclohexanol molar ratio. This might be a result of partial pore blockage of the microporous structure since it was observed that the origi-

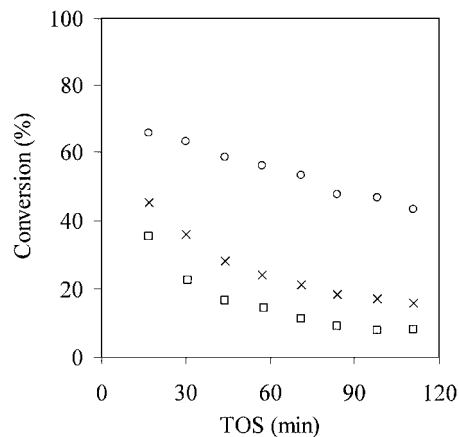


FIG. 6. Influence of oxygen concentration on OD of cyclohexanol, over ETS-10 at 200°C. Oxygen/cyclohexanol molar ratio: (O) 89, (X) 18, (□) 9.

nally white catalyst powder (ETS-10) turned a yellow to light brown colour after reaction. Lin *et al.* (4) reported the formation of oligomers of cyclohexanone in the OD of cyclohexanol over CuO–ZnO, at 240°C. Extraction of the used ETS-10 catalysts (200 and 250°C) with different solvents (acetonitrile, acetone, dichloromethane) revealed the presence of cyclohexanone in the resulting solutions (as determined by GC analysis). It is noteworthy that after extraction with different solvents the colour of the catalyst remained practically unchanged, suggesting that the extraction of organic matter was not complete and that products are partially retained in the porous system (probably subject to sterical constraints inside the pores).

The specific total pore volumes of fresh and used ETS-10 samples were evaluated from the nitrogen uptake at $P/P_0 \sim 0.95$ and 77 K. Both samples were outgassed at room temperature for 24 h. After the OD of cyclohexanol at 250°C, the values of specific surface area and total pore volume of ETS-10 decreased ca. 60%. On the other hand, no loss of crystallinity of the used sample was observed. These results suggest the presence of organic matter inside the ETS-10 structure.

Differential scanning calorimetry (DSC) analysis, under air atmosphere, also supports the assumption that the primary cause of ETS-10 deactivation is pore blockage. The results (Fig. 7) show a broad exothermic band between 280°C and 390°C for the used catalysts that does not appear for the fresh ETS-10 sample, suggesting that it is due to organic matter present in the solid. A similar exothermic band is also present in the DSC analysis data of a fresh ETS-10 sample doped with a small quantity of cyclohexanone. The removal of organic matter from ETS-10, which has an onset at 280°C, may account for the facile diffusion of the reaction products out of the pores, thus avoiding deactivation at 300°C (Fig. 5).

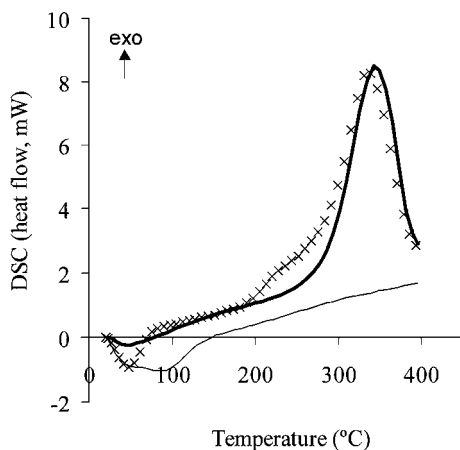


FIG. 7. DSC analysis of fresh ETS-10 (thin line), ETS-10 after reaction at 250°C (bold line), and sample mixture of ETS-10 plus cyclohexanone (×).

After the reaction at 200°C the catalyst was regenerated *in situ* by calcination at 400°C and recycled twice. The conversion profiles are shown in Fig. 5. The catalyst activity is completely regenerated with no loss of crystallinity and selectivity to cyclohexanone remained 100% throughout each cycle.

The activity of ETS-10 at 150°C was compared with that of known microporous siliceous materials such as TS-1 and zeolites NaX (25) and mordenite (25). Table 3 shows the overall activity, the conversion at 120 min on-stream, and the product distribution obtained for each individual catalyst, under the same experimental conditions described in Fig. 2. The activity of ETS-10 is higher than that of TS-1 and similar to that observed for mordenite and faujasite NaX (Table 3). Both microporous titanosilicates (ETS-10 and TS-1) and NaX were 100% selective to cyclohexanone. Mordenite was less selective towards cyclohexanone: it exhibits some dehydration activity, which accounts for the formation of cyclohexene. The dehydrogenation can be catalysed by acidic or basic sites present in these materials (8 and references therein). Presently, work is being carried out to

TABLE 3

OD of Cyclohexanol over Various Metallosilicates at 150°C^a

Catalyst	Conversion (%)	Activity ^b ($\mu\text{mol g}_{\text{cat}}^{-1} \text{min}^{-1}$)	Selectivity (%)	
			Cyclohexene	Cyclohexanone
ETS-10	36.6	5.8	0	100
TS-1	7.6	1.2	0	100
Mordenite	30.9	4.9	6.7	93.3
NaX	31.3	4.9	0	100

^aReaction conditions: same as in Fig. 2.

^bActivity = (degree of conversion in percent/100) × (molar flow rate/mass of catalyst).

understand the type of active sites of ETS-10 involved in the oxydehydrogenation of cyclohexanol and gain a better mechanistic insight.

CONCLUSION

ETS-10 is an active catalyst for the oxidative dehydrogenation of cyclohexanol with air and cyclohexanone is the only reaction product formed at reaction temperatures up to 200°C. Its catalytic performance was superior to that observed for other related materials, prepared by ion-exchange or hydrothermal synthesis. The introduction of other transition metals, aluminium, or protons in ETS-10 decreases selectivity to cyclohexanone, yielding cyclohexene which is a dehydration product. Alkali doping has no promotional effect on activity and causes rapid deactivation of the catalyst.

High reaction temperatures (>200°C) increase the dehydration activity of ETS-10, yielding mainly cyclohexene at 300°C. Increasing oxygen/cyclohexanol feed ratios increases the conversion of cyclohexanol in the presence of ETS-10. The catalyst deactivation observed up to 250°C is thought to be caused by partial blockage of the porous structure of ETS-10 which is overcome at higher reaction temperatures. The catalytic activity of ETS-10 is completely regenerated by calcination at 400°C. The overall activity of ETS-10 is higher than that of TS-1 and comparable to those of mordenite and faujasite NaX. ETS-10 shows higher oxydehydrogenation activity than zeolites NaX and mordenite.

ACKNOWLEDGMENTS

We thank PRAXIS XXI and FEDER for financial support.

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