

Isomerization of *n*-Butane over H-Mordenites under Nitrogen and Hydrogen: Influence of the Acid Site Density

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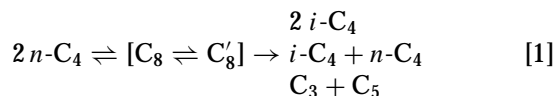
n-Butane transformation was investigated in a flow reactor at 523 K over a series of H-mordenite samples with Si/Al ratios of 6.6, 10, 20, 60, and 80. Under nitrogen, butane isomerization is accompanied by the formation in significant amounts of propane and pentanes. The reaction order with respect to *n*-butane is close to 2 for isobutane, for propane, and for pentane formation. These observations are in favor of a bimolecular mode of *n*-butane transformation involving successively formation of C₈ carbenium ions, isomerization, and cracking of these C₈ carbenium ions. A large positive effect of the density of acid sites is found, which can be related to the demanding character of this bimolecular process: two acid sites are required for the formation of the two *sec*-butyl carbenium ions involved as intermediates. Hydrogen strongly inhibits the transformation of *n*-butane, which can be explained by a decrease in the concentration of *sec*-butyl carbenium ions. An increase in the selectivity to isobutane and a decrease in the reaction order are observed, which seems to indicate participation of the very difficult monomolecular process (through the very unstable isobutyl carbenium ion) in butane isomerization. © 1998 Academic Press

INTRODUCTION

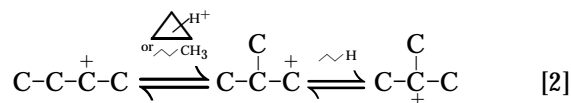
Isomerization of *n*-butane, a low value hydrocarbon, is an important commercial process. The isobutane produced can be used in alkylation processes or dehydrogenated into isobutene which can be transformed into methyl-*tert*-butylether (MTBE), *tert*-butylalcohol, polyisobutene, and other products (1, 2). Commercial processes of butane isomerization generally operate at relatively low temperatures (383–453 K) under high hydrogen pressure, with platinum chlorinated alumina being used as the catalyst (3).

The mechanism of *n*-butane isomerization has been thoroughly investigated in particular on mordenite (4–6), mazzite (7), and sulfated zirconia (8, 9) catalysts. It is generally admitted that this reaction occurs through a bimolec-

ular dimerization–cracking mechanism:



although the isomerization of C₅₊ alkanes occurs through a monomolecular mechanism. This difference in mechanism is related to the fact that monomolecular isomerization of *n*-butane would involve a primary (hence very unstable) carbenium ion as an intermediate (10, 11):



However, recent experiments with ¹³C-labeled butanes carried out with sulfated zirconia seems to indicate that, depending on the operating conditions, *n*-butane isomerization can occur either through a monomolecular mechanism (under hydrogen at 523 K) (8) or through a bimolecular one (in the absence of hydrogen at 453 K) (9). This change in mechanism would be due to the large inhibiting effect which hydrogen has on the bimolecular isomerization as well as to the higher value of the activation energy for the more difficult monomolecular isomerization (12). The relative significance of these isomerization modes could also depend on the density of the protonic sites. Indeed the rate of bimolecular isomerization which requires the formation of two carbenium ions would be extremely dependent on the acid site density (13), which would not be the case with monomolecular isomerization. In order to check the existence of different reaction mechanisms and to specify their dependence on the acid site density, butane isomerization was carried out at 523 K over a series of H-Mordenite samples with differing acid site densities. The acidity of all the samples has previously been determined (14). Two types of operating conditions favoring the bimolecular mode of isomerization (under nitrogen) or the monomolecular one (under hydrogen) were chosen.

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EXPERIMENTAL

Catalysts

All the mordenite samples were supplied by the "Institut Régional des Matériaux Avancés" (IRMA) in Ploemeur, France. The framework Si/Al ratio of the nondealuminated HMOR sample (HMOR6.6) was equal to 6.6 and those of the dealuminated samples was equal to approximately 10, 20, 60, and 80. The dealumination was carried out by steaming at 820–970 K (depending on the dealumination level required) and by subsequent acid leaching (HCl or HNO₃ 1.3–6 mol · dm⁻³). The physicochemical characteristics of the HMOR samples are given in Table 1. The pore volumes were determined by nitrogen adsorption at 77 K with a gas adsorption system ASAP2010 from Micromeritics. It can be noted that practically no Lewis acid sites are observed by pyridine adsorption (14). This indicates that only polymeric extraframework aluminium species remain in the samples after the acid treatment, these species having a very small surface area compared to that of zeolite pores.

Catalytic Experiments

n-Butane transformation was carried out in a flow reactor under the following conditions: 523 K, partial pressures of *n*-butane and of the carrier gas (nitrogen or hydrogen) equal to 0.1 and 0.9 bar, respectively. The weight hourly space velocity (WHSV) was chosen between 0.6 and 10 h⁻¹ in order to always obtain an initial conversion lower than 10%. Prior to being used, the zeolite samples were calcined *in situ* at 773 K under dry air flow (60 ml · min⁻¹) for 10 h, the samples being kept under nitrogen during cooling to reaction temperature. In the experiments carried out under hydrogen, nitrogen is then substituted by hydrogen at reaction temperature, with the samples being kept for 1 h before reaction. In order to obtain an accurate value of the initial activity and to limit the zeolite deactivation, short

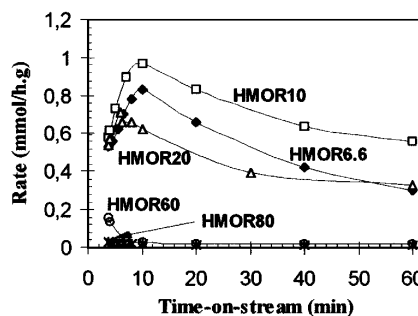


FIG. 1. Rate of *n*-butane transformation under nitrogen as a function of time-on-stream over mordenites.

values of time-on-stream were chosen (20 s to 5 min depending on WHSV). In every case, the minimum value of time-on-stream was chosen so as to have a constant value of the GC peak area, hence a constant value of the reactant pressure.

Analysis of reaction products was performed on line by gas chromatography with a 50-m fused-silica PLOT Al₂O₃/KCl capillary column with a flame ionization detector and a valco multiposition valve (10 positions).

RESULTS AND DISCUSSION

Transformation of *n*-Butane under Nitrogen

Figure 1 shows the change in the activity of mordenite samples as a function of time-on-stream. There is an initial increase in activity followed by a rapid decrease except with the more dealuminated samples (HMOR60 and 80). This increase in activity observed on H-mordenite (4, 15) and on the other catalysts (16, 17) can be attributed to the initiation step of a carbenium ion chain mechanism (16). The decrease in activity is most likely due to the formation of carbonaceous compounds (coke) inside the zeolite pores. Although the deactivation is rapid, the formation of coke is relatively slow: 0.1 to 0.3 wt% of coke after 1 h of reaction, which indicates a high deactivating effect of coke molecules. This high deactivating effect is related to the unidirectional pore system of mordenite: one coke molecule which deposits at the mouth of a large channel can block the access of the reactant to all the acid sites of the channel (18, 19).

The maximum activity is plotted in Fig. 2 as a function of *N*_{Al}, the number of framework aluminium atoms per unit cell. A maximum is found for a *N*_{Al} value between 3 and 4 (framework Si/Al value between 11 and 15). This *N*_{Al} value is practically the limiting value below which, according to the topological model (20, 21), all the protonic sites in mordenite are isolated and hence have a maximum acid strength and activity. Furthermore, for various reactions, *n*-pentane,

TABLE 1

Physicochemical Characteristics of HMOR Samples

Sample	(Si/Al) _{total}	(Si/Al) _{fr} ^a	Pore volume (cm ³ /g)		Protonic acidity ^b (μmol/g)	
			Micro-pores	Meso-pores	423 K	623 K
HMOR6.6	6.1	6.6	0.14	0.01	1017	632
HMOR10	7.5	10.5	0.186	0.070	545	316
HMOR20	16.7	19.9	0.203	0.058	350	190
HMOR60	35.5	59	0.178	0.086	256	151
HMOR80	65.3	79	0.18	0.1	121	59

^a Framework silicon to aluminium ratio.

^b Protonic acidity determined from the concentration of pyridinium ions measured after desorption at 423 and 623 K.

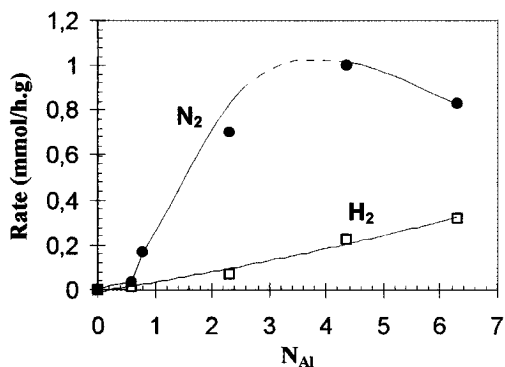


FIG. 2. Rate of *n*-butane transformation under nitrogen and hydrogen as a function of N_{Al} , the number of aluminium atoms per unit cell.

n-hexane isomerization (22–24), *n*- and isooctane cracking (22), ethylacetate hydrolysis (25), butene dehydration (26, 27), orthodichlorobenzene isomerization (27), etc., a maximum activity has been found at approximately this value. However the change in activity with N_{Al} , shown in Fig. 2, is not that as expected from the topological model: in particular at low N_{Al} values, there is no linear correlation between the activity and N_{Al} .

Average turnover frequency (TOF) values were estimated by dividing the activity by the total number of protonic acid sites retaining pyridine adsorbed at 423 K. Figure 3 shows that for the more dealuminated samples there is a large increase in TOF with the density of the acid sites. The same is observed if TOF is estimated by considering only the strong acid sites or the very strong acid sites (able to retain pyridine adsorbed above 623 and 723 K, respectively). This pronounced effect of the density of acid sites has been previously explained by the demanding character of butane transformation over H-mordenites (13). This transformation has previously been shown to occur through a dimerization-cracking mechanism in which

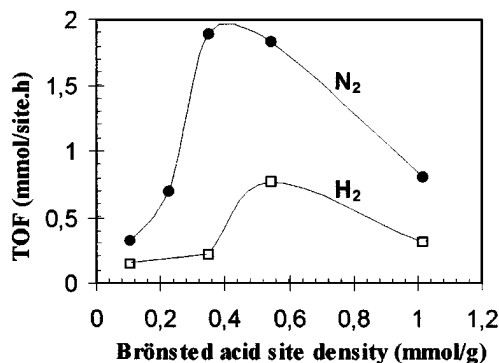


FIG. 3. *n*-Butane transformation under nitrogen and hydrogen. Turnover frequency (TOF) versus Brønsted acid site density (determined from the concentration of pyridinium ions measured after desorption at 423 K).

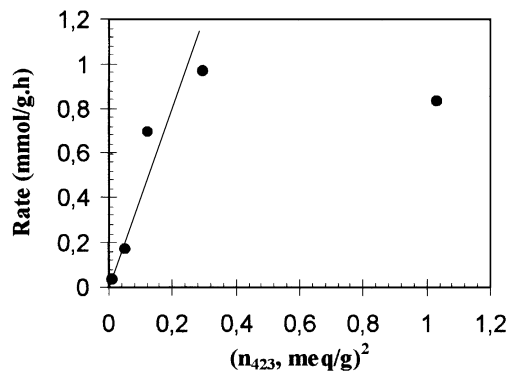


FIG. 4. *n*-Butane transformation under nitrogen. Change of the reaction rate of the mordenites vs square of the density of mordenite acid sites (n_{423} : determined from the concentration of pyridinium ions measured after desorption at 423 K).

at least two acid sites are required (15). In agreement with this proposal, the activity is practically proportional to the square of the acid site density provided that the value corresponding to HMOR6.6 is excluded (Fig. 4). The activity found for this latter zeolite is lower, which can be explained by its weaker acidity. This lower activity may also be due to a faster initial deactivation of this sample (before the activity measurement). Indeed this sample is the only one which does not present mesopores (Table 1) which are known to decrease greatly the toxicity of coke in unidirectional pore systems (28).

With all the samples, *n*-butane is mainly transformed into isobutane and propane + pentanes (approximately 65% iso, 35% *n*). Traces of C_2 and C_6 are also observed. Deactivation does not affect the selectivity as shown by comparing the yields in isobutane, propane, and pentanes over HMOR10 (Fig. 5). Apparently the products are directly formed from *n*-butane transformation (Fig. 5). This suggests that all these products result from a bimolecular transformation of *n*-butane (pathway 1). In agreement with

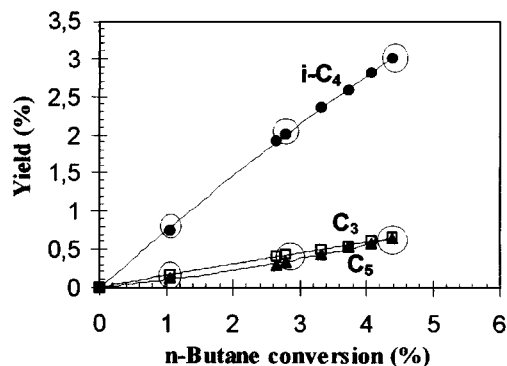


FIG. 5. Yields of propane, pentanes, and isobutane as a function of *n*-butane conversion under nitrogen over HMOR10 at 523 K (○, fresh catalyst; ●, points taken during the deactivation).

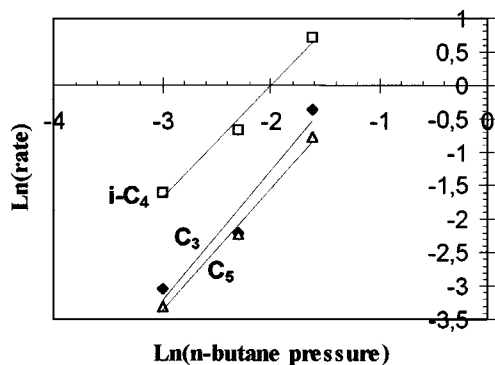


FIG. 6. *n*-Butane transformation under nitrogen over HMOR10. Estimation of the reaction orders.

this proposal the reaction orders with respect to *n*-butane were found to be between 1.7 and 1.9 for the formation of C_3 , *i*- C_4 , and C_5 over HMOR10 (Fig. 6). With all the samples (except HMOR6.6) the product distribution is practically independent on N_{Al} : approximately 70% (mol) of *i*- C_4 (80% with HMOR80), 18% of C_3 , and 12% of C_5 (Fig. 7). With HMOR6.6, propane is extremely favored: 65% (mol) C_3 , 25% *i*- C_4 , 10% C_5 . The same abrupt change in selectivity with the zeolite composition has been found by Asuquo *et al.* (6). These authors related the particular selectivity of the nondealuminated sample to its high concentration of protonic sites. This explanation seems unlikely for such an abrupt change, with the theoretical density of protonic sites of HMOR6.6 being only 1.45 times greater than that of HMOR10. This particular selectivity of HMOR6.6 may be due to the absence of mesopores in this zeolite and, therefore, to the much longer diffusion pathway for organic molecules. Therefore, while the reactant molecules diffuse through the channels, they can undergo many successive intermolecular reactions with consequently a preferential formation of propane. Indeed butanes and pentanes are very reactive compared to propane and can be transformed

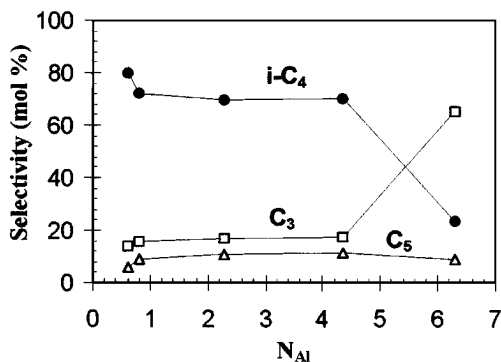
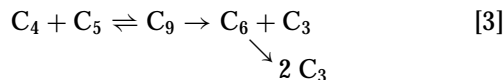


FIG. 7. Product selectivity for *n*-butane transformation under nitrogen vs N_{Al} , the number of aluminium atoms per unit cell after 1 h on stream. Conversion values between 1 and 3%.

into this product, e.g.,



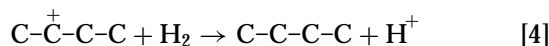
This type of shape selectivity related to the unidirectional pore system of mordenite has recently been observed in xylene isomerization over unidirectional mesoporous MCM-41 aluminosilicates and is called tunnel shape selectivity (29). It can be noted that for all the samples, the C_3/C_5 molar ratio is greater than 1, which indicates that the successive Scheme [3] occurs over all the mordenites even in the presence of mesopores.

Influence of Hydrogen on *n*-Butane Transformation

As has previously been reported (12), hydrogen has an inhibiting effect on *n*-butane transformation over H-mordenite. Furthermore, under hydrogen, the initiation period found with the mildly dealuminated samples (Fig. 8) is suppressed and the deactivation is faster than under nitrogen. The inhibiting effect is much more pronounced with the mildly dealuminated samples than with the very dealuminated samples. Thus with HMOR10, substitution of hydrogen for nitrogen divides the maximum activity by 3.5 and the activity after 1-h reaction by 15 against 1.7 and 4, respectively, with HMOR80 (Fig. 8).

The initial activity is plotted in Fig. 2 as a function of N_{Al} the number of framework aluminium atoms. The greater the N_{Al} the higher the activity, quasi-identical values of the activity however being observed for HMOR10 ($N_{Al} = 4.3$) and HMOR6.6 ($N_{Al} = 6.3$). This curve is completely different from that expected from the topological model (no maximum, no proportionality of the activity with N_{Al} for the most dealuminated samples) and from that found under nitrogen. The TOF values were calculated and plotted in Fig. 3 as a function of the density of the protonic acid sites. As under nitrogen, a maximum in TOF is obtained but for a greater value of the acid site density.

The inhibiting effect of hydrogen has been explained by a large decrease in the concentration of the *sec*-butyl carbenium ions caused by the reaction



(i.e., by the reverse reaction of the protolytic dehydrogenation of *n*-butane). This type of reaction has already been proposed in order to explain the decrease in the rate of toluene disproportionation caused by hydrogen (30, 31). The large decrease in the concentration of *sec*-butyl carbenium ions would render practically impossible the encounter between these ions and butene molecules resulting from their desorption, hence the bimolecular isomerization.

The product distribution is also modified by hydrogen, the proportion of isobutane increasing at the expense of

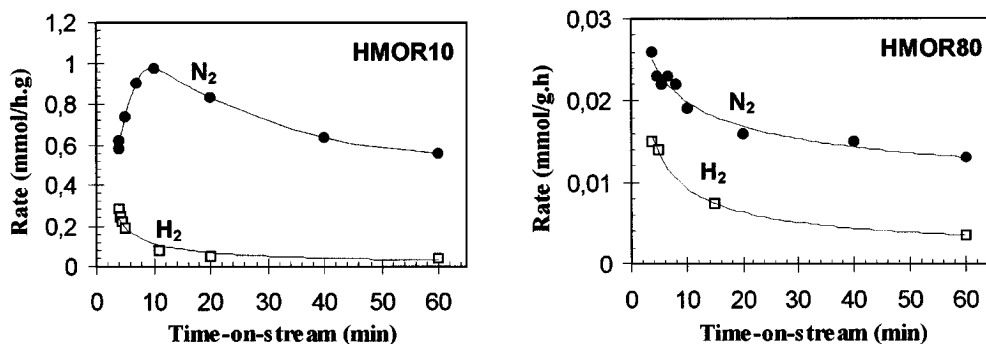


FIG. 8. Rates of *n*-butane transformation under nitrogen and hydrogen over HMOR10 and HMOR80 as a function of time-on-stream.

propane + pentanes. Thus, for approximately the same conversion (1–2%) the molar percentage of isobutane in the product mixture is generally greater than 80 (except with HMOR6.6: 75%) whereas it was close to 70% under nitrogen for all the samples except for HMOR6.6 (25%). The large change in selectivity found with this latter zeolite is probably due to the large decrease in the reaction rate. Therefore, the number of successive reactions undergone by *n*-butane molecules during their passage through the channel would be much lower under hydrogen than under nitrogen.

The increase in isobutane selectivity with the substitution of hydrogen for nitrogen has been previously explained by the coexistence of bimolecular and monomolecular modes of butane isomerization with very different sensitivities to hydrogen (12). The bimolecular mode which requires two *sec*-butyl carbenium ions as intermediates would be much more inhibited by hydrogen than the monomolecular mode which requires only one. Furthermore, hydrogen was found to have little effect on *n*-hexane isomerization which occurs through a monomolecular mechanism (12). Through the bimolecular mode, *n*-butane leads to a mixture of isobutane and of propane + pentanes while the monomolecular mode is very selective to isobutane. By admitting that the selectivity of *n*-butane transformation through the bimolecular mechanism is roughly the same as that found under nitrogen with the mildly dealuminated samples (i.e., 70% *i*-C₄), it can be estimated from the selectivity that, under hydrogen, 30 to 50% of isomerization occurs through the monomolecular mechanism. It can be also suggested that even under nitrogen the monomolecular mechanism plays a nonnegligible role in *n*-butane isomerization over the very dealuminated samples HMOR60 and HMOR80. In agreement with this proposal, the reaction order with respect to *n*-butane over HMOR80 and under nitrogen is close to 1 for butane isomerization whereas it was close to 2 over HMOR10. This greater significance of the monomolecular mechanism found with the more dealuminated samples can be related to their low acid site density. Indeed the TOF of bimolecular *n*-butane transformation which most likely requires

two acid sites is very dependent on the acid site density while that of monomolecular transformation should not be dependent.

The effect of hydrogen pressure over the reaction rates was determined by carrying out *n*-butane transformation over fresh samples of HMOR10 under various hydrogen pressures from 0 to 0.9 bar, with the pressure of *n*-butane being kept at 0.1 bar. Figure 9 shows the lower the hydrogen pressure the greater the reaction rate. A reaction order of -1.2 was found by considering the maximum activity for all the experiments carried out in the presence of hydrogen. The effect of *n*-butane pressure on the reaction rates was also determined under hydrogen by using fresh samples of HMOR10. In these experiments, the hydrogen pressure was kept as 0.8 bar and the *n*-butane pressure was varied from 0.05 to 0.2 bar. A reaction order close to 1 was found for the production of *n*-butane, i.e., a value lower than that found under nitrogen. This suggests a change in the reaction mechanism from a bimolecular mode to a monomolecular one. It can also be emphasized that with the lower *n*-butane pressure (0.05 bar) a relatively large amount of methane, ethane, and ethylene is observed, 20% (mol), which was not the case with the higher pressure (0.2 bar).

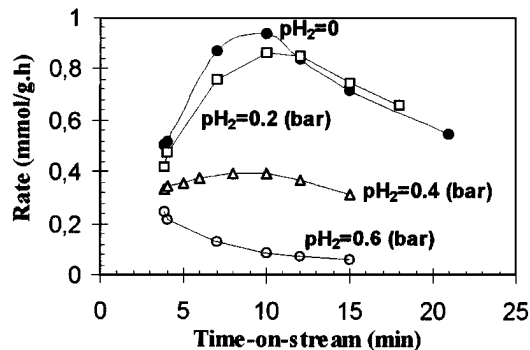


FIG. 9. Effect of hydrogen partial pressure on the rate of *n*-butane transformation.

CONCLUSION

From the effect of the acid site density of HMOR samples on their activity and selectivity in *n*-butane transformation under nitrogen and under hydrogen, the following main conclusions can be drawn:

(i) Under nitrogen, *n*-butane isomerization mainly occurs through a bimolecular process involving C₈ carbenium ions as intermediates. This is shown in particular by the relatively low selectivity to isobutane (a relatively large amount of propane and pentanes is simultaneously formed) and by the reaction order of 2 with respect to *n*-butane. This bimolecular process which requires two acid sites for its catalysis is extremely favored by the acid site density.

(ii) Hydrogen has a very large inhibiting effect on butane transformation, most likely due to the decrease in the concentration of *sec*-butyl carbenium ions. The bimolecular process which requires two *sec*-butyl carbenium ions as intermediates is very inhibited, much more so than the monomolecular isomerization which requires only one *sec*-butyl carbenium ion intermediate. Therefore, under hydrogen, the monomolecular mechanism could play an important role in butane isomerization indicating that mordenites have very strong acid sites capable of catalyzing this very difficult reaction.

(iii) Mesopores created by dealumination play a significant role in *n*-butane isomerization particularly under nitrogen. They limit the deactivating effect of coke and especially the number of secondary transformations undergone by the reaction products during their diffusion through the unidirectional channels of the mordenite samples. These secondary transformations explain the very high selectivity to propane of the non dealuminated sample which does not present mesopores.

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