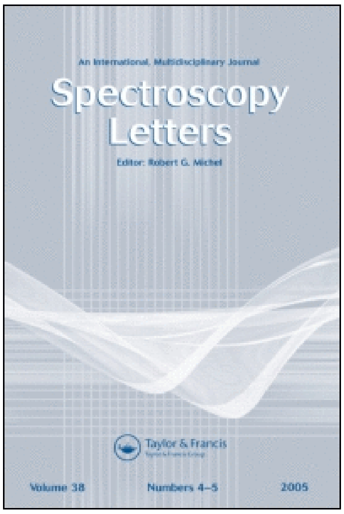

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FTIR STUDY OF THE ADSORPTION OF AMMONIA AND PYRIDINE ON V_2O_5/MgO CATALYSTS

Key words: V_2O_5/MgO Catalysts, Pyridine and Ammonia Adsorption, Brønsted and Lewis acid sites, FT-IR

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ABSTRACT

The adsorption of ammonia and pyridine on the surface of the V_2O_5/MgO catalysts has been studied for the determination of the Brønsted and Lewis acid sites. The data showed that the catalysts have medium Lewis acidity, but are also weak Brønsted acids, having active hydroxy groups able to interact with pyridine by H-bonding and by protonation. Pyridine is a suitable basic probe for the quantification of the catalysts. 32% V_2O_5/MgO catalyst is the most acidic catalyst.

INTRODUCTION

The surface acidity may have a relevant role on the oxidation activity and selectivity of the catalyst.

Vanadia supported on magnesia is of importance as a catalyst for the oxidative dehydrogenation of alkanes(1-5).

It has been well known that adsorption of bases such as ammonia and pyridine is widely used for the determination of the acidity of solid surfaces. The criterion for determination of the acid sites on the catalyst surfaces is the formation of ammonium and pyridinium ions for Brønsted centres and coordination of ammonia and pyridine on Lewis centres.

Infrared spectra of ammonia(6-8) and pyridine(9) adsorbed on magnesia which is a typical solid base catalyst, have been studied previously in detail. It was found that hydrogen-bonding is the only type of interaction and basic properties of the MgO surface generally predominate in the adsorption processes.

The interaction of ammonia with the surface of vanadia has also been investigated and stated that adsorption can take place on Brønsted acid sites(10,11), via hydrogen-bonding on V=O(12) or by coordinative bonding(13). The spectrum of pyridine adsorbed on vanadia was reported and found that vanadia showed the presence of both Lewis and Brønsted sites.

In this study, the types of acid sites present on V_2O_5/MgO catalysts were examined by taking FT-IR spectra from the surface during the adsorption of ammonia and pyridine.

EXPERIMENTAL

The preparation and characterization of the V_2O_5/MgO catalysts has been reported previously (5,14) and their main characteristics are summarized in Table 1.

IR measurements were performed using self-supporting pressed discs(0.1-0.2g) contained in a cell with NaCl windows, which allowed discs to be heated *in vacuo* or in the presence of gases. IR spectra have been recorded *in situ* at room or elevated temperatures by a Mattson 1000 FTIR instrument, equipped with a conventional evacuation-gas manipulation

TABLE 1.

Survey of the samples

Catalyst	Vanadium content, %	Surface area, m^2g^{-1}	Preparation methode
$15V_2O_5/MgO$	15	204	Impregnation
$33V_2O_5/MgO$	33	154	Impregnation
$32V_2O_5/MgO$	32	72	Grafting

BET surface area of support MgO was 72 m^2g^{-1}

ramp (10^{-3} Pa). The FTIR instrument was typically operated at a scan speed of 0.1 $cm^{-1}s^{-1}$ and a resolution of $2cm^{-1}$, collecting 50 scans per spectrum. All the catalyst samples were subjected to a standart pretreatment involving heat treatment at 673 K *in vacuo* for 8h. All the adsorption studies were carried out at 298 K and with the ammonia pressure of 0.4 kPa. Pyridine was adsorbed at the partial pressure of pyridine at 298 K *in vacuo*. After adsorption studies, desorption experiments were also done at elevated temperatures(373-673K) for 10 min. for the comparison of the strength of Brønsted and Lewis acid sites.

RESULTS AND DISCUSSION

Figure 1, 2 and 3 shows the infrared spectra of ammonia adsorbed on 15, 33 and 32 % V_2O_5/MgO catalysts, respectively. In the region of 2000-1000 cm^{-1}, an absorption band assignable to the bending vibration of NH_4^+ ion was not observed at 1410-1420 cm^{-1}, which generally indicates the presence of the Brønsted acid sites on the catalyst surfaces. Since the i.r. bands of ammonia in the gas phase are at 1628, 3336 and 3414 cm^{-1}, characteristics of the $\delta_{asym.}$, $\nu_{sym.}$ and $\nu_{asym.}$ of ammonia. Whereas the bands at 1460 and 3280 cm-1 are the $\delta_{asym.}$ and $\nu_{asym.}$ of NH_4^+.

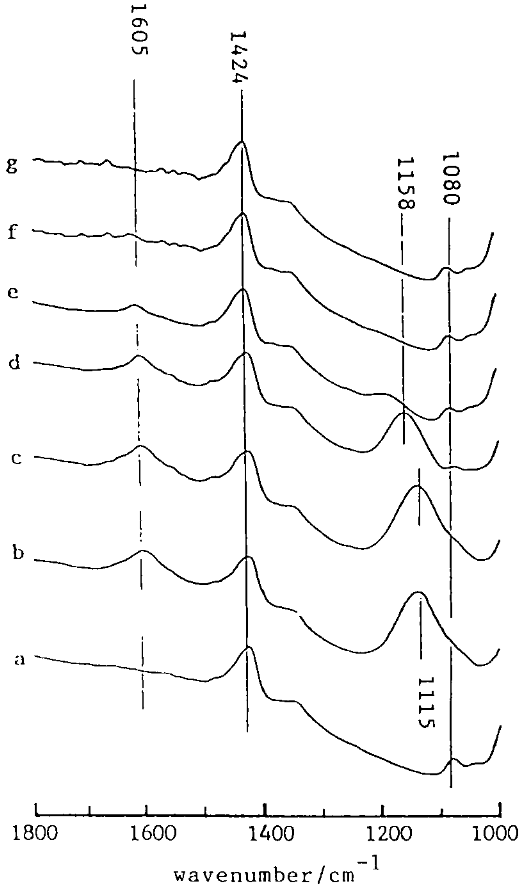


Fig. 1. FTIR spectra of ammonia adsorbed on 15% V_2O_5/MgO catalyst
a) reference b) 5h ads. c) 298K, des. d) 373K, des.
e) 473K, des. f) 573K, des. g) 673K, des.

On the other hand, the reaction of ammonia with Lewis acid sites resulted in the presence of i.r. bands at 1605 cm^{-1}, characteristic of the ammonia bonded to Lewis acid sites, while the band at 1424 cm^{-1} resulted the sorption of ammonia on Brønsted acid sites as NH_4^+. The extinction coefficient of the band at 1460 cm^{-1} was given as 0.147cm^{2}μmol^{-1}(23).

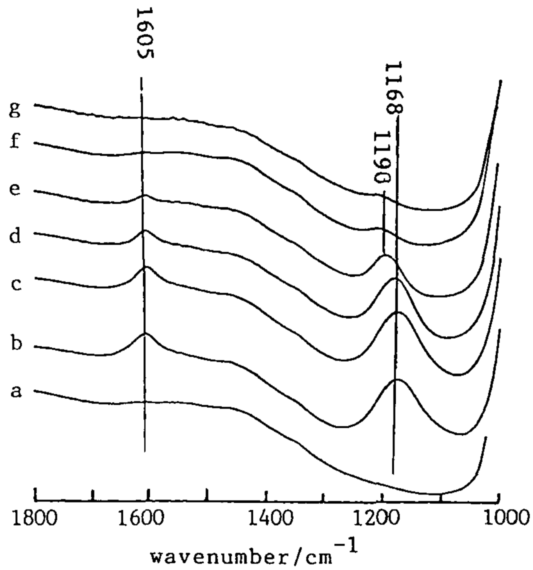


Fig. 2. FTIR spectra of ammonia adsorbed on 33% V_2O_5/MgO catalyst
a) reference b) 5h ads. c) 298K, des. d) 373K, des.
e) 473K, des. f) 573K, des. g) 673K, des.

This band was not observed in the sorption spectra of ammonia on 33 and 32% V_2O_5/MgO catalysts. In the case of 15% V_2O_5/MgO catalyst, a band at 1424 cm^{-1} was observed only the difference spectra which overlaped the reference spectra of the sample. Moreover, this absorption band in the case of the other catalysts presented a very irregular shape, very weak and unclear.

A broad band assignable to coordinately held ammonia was observed at 1170-1185 cm^{-1} suggesting the presence of Lewis acid sites on the surface of all V_2O_5/MgO catalysts. Another band around 1605 cm^{-1} which is also assignable to the coordinately held ammonia, was observed. These two major bands can be attributed to the symmetric and antisymmetric deformation modes of coordinatively bonded ammonia.

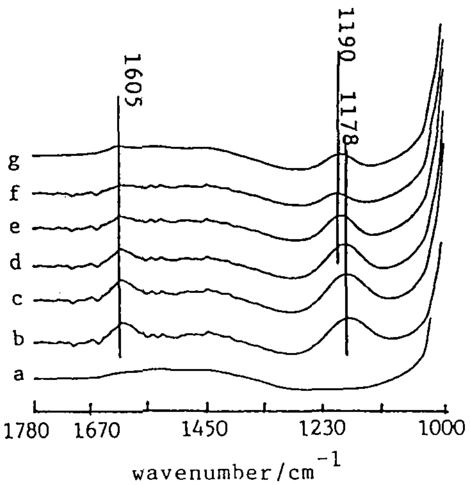


Fig. 3. FTIR spectra of ammonia adsorbed on 32% V_2O_5/MgO catalyst
a) reference b) 5h ads. c) 298K, des. d) 373K, des.
e) 473K, des. f) 573K, des. g) 673K, des.

For this reason, the quantitative evaluation of acidity was not made from the sorption data of ammonia.

Ammonia is a strong Lewis base and it is small in size. Furthermore, ammonia interacts even with weak sites with an appreciable heat evolution because of the lower basicity of pyridine than ammonia, and thus will not react with some of the weaker sites that would react with ammonia. The IR spectra of pyridine coordination compounds are clearly distinct from pyridinium ion and H-bonded pyridine can easily be distinguished. The ring vibration modes 19b and 8a are the most sensitive vibrations with regard to the nature of intermolecular interactions via nitrogen lone pair electrons(15). These two modes are observed at 1440 to 1447 and at 1580 to 1600 cm^{-1}, respectively, for H-bonded pyridine, at 1535 to 1550 and around 1640 $cm^{-1}$for pyridinium ion, and at 1447 to 1464 and 1600 to 1634 cm^{-1} for coordination compounds.

The spectrum of pyridine adsorbed on vanadia pretreated *in vacuo* at 573K was reported(16). It was observed that both chemisorbed pyridine (ν8a 1608 cm^{-1}, ν8b 1575cm^{-1}, ν19a 1487 cm^{-1} and ν19b 1446 cm^{-1}) and pyridinium cations (ν8a,8b 1640,1635 cm^{-1}, ν19b 1534 cm^{-1}) were formed, showing the presence of both Lewis and Brønsted sites.

In the view of the above statements, the presence of the acid sites was also confirmed by pyridine adsorption studies. Figure 4-6 show the IR spectra obtained from pyridine adsorbed on 15% V_2O_5/MgO, 33% V_2O_5/MgO and 32% V_2O_5/MgO catalyst. The spectra of pyridine on all of the catalysts in the region 1300-1000 cm^{-1} show the same pattern with the bands at nearly 1260, 1150, 1068, 1033 cm^{-1}. These bands persist after outgassing at room temperature (Fig. 4f, Fig. 5h, Fig. 6h,i), and their intensities decreased gradually by further evacuation at higher temperature above 373K. The spectra of pyridine adsorbed on 33% and 32% V_2O_5/MgO catalysts show the bands at 1600-1608, 1587-1581, 1490-1484, 1438-1446 cm^{-1}, associated with pyridine coordinated over Lewis acid sites.(Fig. 5 and Fig. 6). For the 32% V_2O_5/MgO which was prepared as a grafted catalyst, the intensities of the bands in the spectra(Fig. 6) are somewhat higher than that of spectra of 33% V_2O_5/MgO (Fig. 5).

The spectra of pyridine adsorbed on 15% V_2O_5/MgO in the region 1300-2000 cm^{-1}, show different pattern from the case of the other catalysts. Additionally, the weak bands in the region of 1600-1800cm^{-1}, namely, 1716,1683, 1652, 1646 cm^{-1} and the band at 1520 cm^{-1} are also evident, and persist after outgassing at 373K and 673K(Fig. 4g-j). These bands are associated typically with pyridinium ion adsorbed on Brønsted acid sites.

The quantitative analysis were carried out after 3h pyridine ammonia adsorption and followed by evacuation at 298 K for 10 min. At a pressure of 10^{-3} Pa. The bands at 1490 and 1450 cm^{-1} were employed for

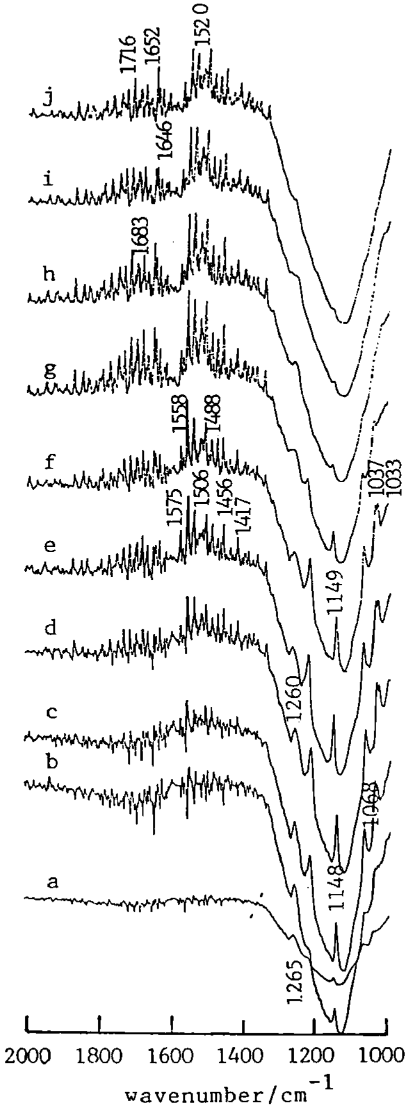


Fig. 4. FTIR spectra of pyridine adsorbed on 15% V_2O_5/MgO catalyst
a) reference b) initial ads. c) 1h ads. d) 2h ads. e) 3h ads.
f) 298K, des. g) 373K, des. h) 473K, des. i) 573K, des.
j) 673K, des.

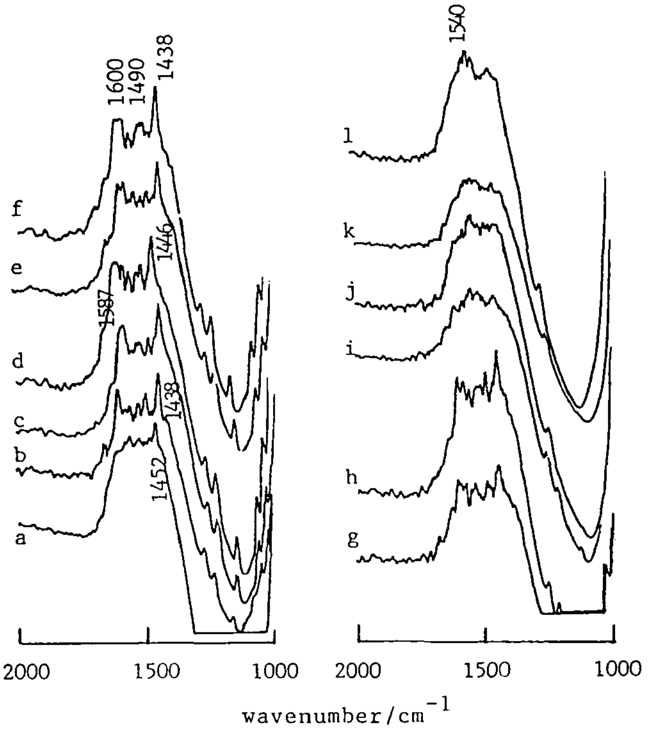


Fig. 5. FTIR spectra of pyridine adsorbed on 33% V_2O_5/MgO catalyst
a) reference b) initial ads. c) 15 min. ads. d) 30 min. ads.
e) 1h ads. f) 2h ads. g) 3h ads. h)298K, des. i) 373K, des.
j) 473K, des. k) 573K, des. l) 673K, des.

the determination of Brønsted and Lewis acid sites in the case of pyridine adsorption, respectively. The extinction coefficients (ε) of these bands are available from the literature(17-22). The concentration of Brønsted and Lewis acid sites referenced to unit weight of dry sample [q_H(μequiv.g^{-1})] has been obtained according to (22):

$$q_H=(A\ \pi\ R^2)/w\ \varepsilon \qquad (1)$$

where R(cm) is the radius of the catalyst wafer and w(g) is the weight of the dry sample. A values were evaluated from the difference

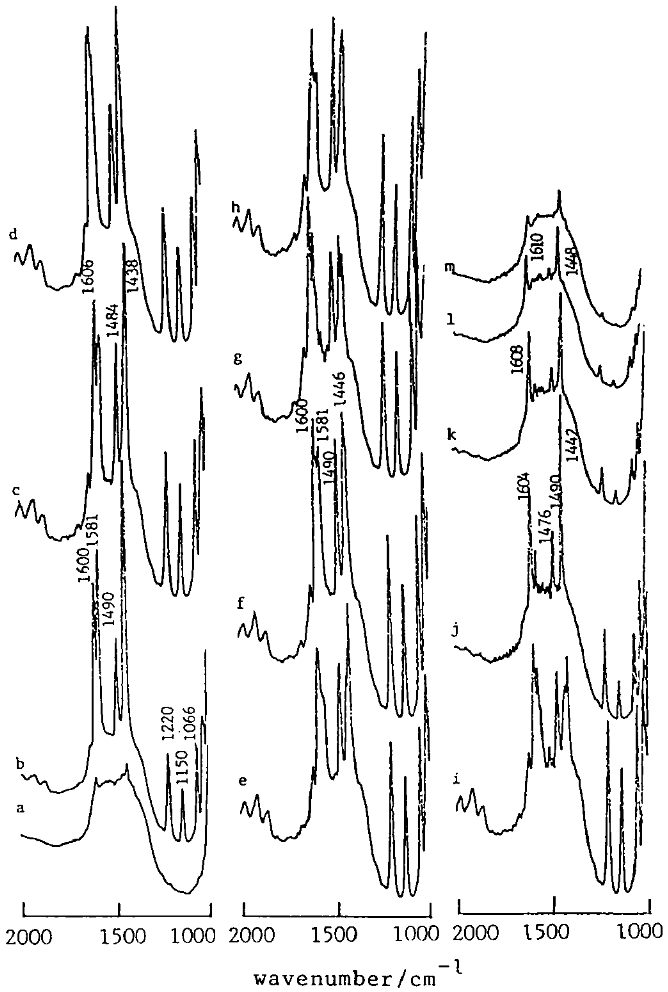
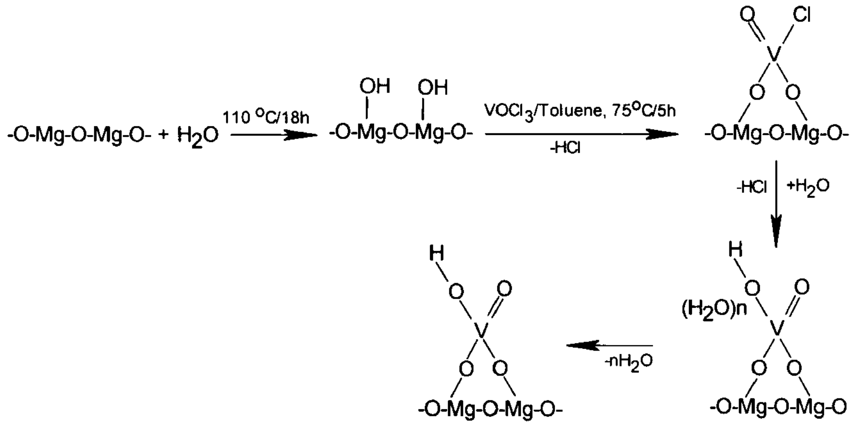


Fig. 6. FTIR spectra of pyridine adsorbed on 32% V_2O_5/MgO catalyst
a) reference b) initial ads. c) 15 min. ads. d) 30 min. ads. e) 1h ads. f) 2h ads. g) 3h ads. h) 298K, 10 min. des. i) 298K, 30 min. des. j) 373K, des. k) 473K, des. l) 573K, des. m) 673K, des.

spectra relative to all samples after baseline correction. ε values relative to the absorption bands at 1490 cm^{-1} (Brønsted sites, ε_B) and at 1450 cm^{-1} (Lewis sites, ε_L) were used as 1.67 and 2.22 $cm^2\mu mol^{-1}$ which were reported in the literature 18. The calculated values according to the above equation are given in Table 2.

These data show that there is an increase both the Brønsted and Lewis acid sites with the increase in V_2O_5 content. In the case of 33 and 32% V_2O_5/MgO catalysts, the later is more acidic than the former as far as the concentration of the acid sites concerned. This may be due to the preparation methods in which 32% V_2O_5/MgO catalyst was prepared according to the grafting procedure. This is grafting of V_2O_5 to MgO; for this purpose MgO and $VOCl_3$/toluene solution was used. The mechanism of the preparation reaction is as in the following:



The other catalysts were obtained by VMgO precursors generated by adding an appropriate amount of $Mg(OH)_2$ to a basic solution containing NH_4VO_3 .

As a result, FTIR spectroscopy has been used successfully with pyridine as a basic probe, to determine the Brønsted and Lewis acid sites

TABLE 2.
The concentration of Brønsted and Lewis acid sites calculated from the pyridine adsorption data

Catalyst	q_H^B/ μequiv.g^{-1}	q_H^L/ μequiv.g^{-1}
$15V_2O_5/MgO$	0.07	0.13
$33V_2O_5/MgO$	3.06	1.35
$32V_2O_5/MgO$	9.27	13.90

on the surface of the catalysts. The catalysts have medium Lewis acidity, but are also a weak Brønsted acids, having active active hydroxy groups able to interact with pyridine by H-bonding and by protonation. The V_2O_5 content and preparation methods are naturally important on the acidity of the samples. Ammonia seems to be not a suitable basic probe for quantitative acid site analysis in this case.

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REFERENCES

1. Chaar M. A., Patel D., Kung M. C. and Kung H. H., J. Catal.,1987; 105: 483.
2. Chaar M. A., Patel D. and Kung H. H., J. Catal.,1988; 109: 463.
3. Siew Hew Sam D., Coennen V. and Volta J. C., J. Catal., 1990; 123: 417.
4. Patel D., Andersen P. J. and Kung H. H., J. Catal., 1990; 125: 132.

5. Yurdakoc K. and Hönicke D., *Infrarotspektroskopische Untersuchung der Adsorptionsstructuren von Propan und Propen an V_2O_5/MgO Katalysatoren,* in Wissenschaftliche Abschlußberihte, 25. Internationales Seminar, Universität Karlsruhe(TH), W. Germany, Juli 1990, p.104-114.

6. Knözinger H., Adv. Catal., 1976; 25: 184.

7. Tench A. J. and Giles D., J. Chem. Soc., Faraday Trans. I, 1972; 68: 193.

8. Tench A. J., J. Chem. Soc., Faraday Trans. I, 1972; 68: 197.

9. Tretyakov N. E. and Filimonov V. N., Kinet. Catal. (USSR), 1970; 11: 815.

10. Inomata M., Miyamoto A., Murakami Y., J. Catal., 1980; 62:140.

11. Belokopytov Yu. V., Kholyavenko K. M. and Gerei S. V., J. Catal., 1979; 60: 1.

12. Janssen F. J. J. G., F. Van der Kerkhof M. G., Bosch H. and Ross J. R. H., J. Phys. Chem., 1987; 91: 5921.

13. Bosch H., Bongers A., Enoch G., Snel R., Ross J. R. H., Catal Today, 1989; 4: 139.

14. Yurdakoc M. K., Häffner R. and Hönicke D., Materials Chemistry and Physics , 1996; 44: 273.

15. Kline C. H. and Turkevich J., J. Chem. Phys., 1944; 12: 300.

16. Busca G., Ramis G. and Lorenzelli V., J. Mol. Catal., 1989; 50: 231.

17. Hughes T. R. and White H. M., J. Phys. Chem., 1967; 71: 2192.

18. Emeis C. A., J. Catal., 1993; 141: 347.

19. Makarova M. A., Karim K. and Dwyer J., Microporous Mater., 1995; 4: 243.

20. Khabtou S., Chevreau T. and Lavalley J. C., Microporous Mater., 1994; 3: 133.

21. Datka J., Turek A. M., Jehng J. H. and Wachs I. E., J. Catal., 1992; 135: 186.

22. T Barzetti., Selli E., Moscotti D. and Forni L., J. Chem. Soc. Faraday Trans.,1996; 92(8): 1401.

23. Datka J., Gil B. and Kubacka A., Zeolites, 1995; 15: 501.

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