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ScienceDirect

Catalysis Today 133–135 (2008) 560–564

CATALYSIS TODAY

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Decomposition of nitric oxide on Pd-mordenite

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Abstract

The present work aims to evaluate mordenite as a support in Pd catalysts for the decomposition reaction of NO. In this way, two synthetic methods were used for mordenite preparation and compared with commercial mordenite (CBV10A). The mordenites were synthesized by two procedures: (1) employing sodium aluminate and Aerosil siliceous (Degussa) and (2) employing natural clay as an alternative source of Al and Si. The prepared materials showed specific superficial areas in the range of 300–360 $m^2\,g^{-1}$ and high crystallinity. The materials presented similar conversions for NO decomposition, suggesting that the different methods of preparing mordenite did not interfere in the catalytic activities of the palladium catalysts. Furthermore, the results of N_2O formation gave the following selectivity order: MOR-CBV10A > MOR-ARG > MOR-IZA.

Keywords: MOR; Pd catalyst; NO decomposition

1. Introduction

Over the last 40 years, the synthesis of zeolites has demanded a great deal of effort in several research groups around the world, which has resulted in a broad number of zeolites produced and about 100 different types of topologies determined [1].

Microporous zeolites are widely used as acid catalysts in the petrochemical industry, due to several desirable catalytic properties, such as: high superficial area, adjustable pore size, acidity and high thermal and chemical stabilities. Their exceptional catalytic properties are due to limitations imposed by their pore size, which may bring a shape selectivity regarding the products. The interest for zeolites as supports for transition metals is motivated by the possibility of creating unique catalytic sites, with a defined and ordered structure [2]. Zeolites can impart new catalytic properties to metals, attributed to the support–metal interaction. In the last two decades, the use of zeolites, such as mordenite, has aroused researchers' interest as a support to metals (Cu, Co, Ga, In and Fe among others) in reactions pertaining to the selective catalytic reduction of nitrogen oxide with hydrocarbons and in the direct decomposition of NO [3].

The economical importance of mordenite is extraordinary, because it has been used as a catalyst in reactions including hydrocracking, hydroisomerization, alkylation and dimethylamine production. Its crystalline structure is pyramidal orthorhombic (*mm*2), with the spatial group $Cmc2_1$ and a density of 2.12 $g\,L^{-1}$. The parameters of the unit cell are

$$A = 18.13\,\text{Å}\,, \qquad b = 29.49\,\text{Å} \qquad c = 7.52\,\text{Å}$$

It has unidirectional channels composed of rings of 12MR (6.5 × 7.0 Å). These channels are parallel in the z direction and interconnected through small channels of 8MR (4.8 Å) [2–5].

In recent studies using the reaction of selective reduction of NO with methane with Pd supported in zeolite, Loughram and Resasco [6,7] observed that the metallic sites and the acidic sites of zeolites MFI and MOR are preferably related to each other, and that acidity is necessary to disperse Pd in the form of

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doi:10.1016/j.cattod.2007.12.100

isolated Pd^{2+} ions, while the palladium in a non-acidic support tends to form palladium oxide aggregates. Carvil et al. [8] investigated the effect in the structure and in the performance of Pd–Mordenite catalysts related to the formation of Pd^{2+} complexes on the support. Satsuma et al. [9] studied crystallographic factors, such as the length of the channel and the distribution of Al atoms in the zeolitic framework, in order to evaluate their effects on the stability of Pd ions incorporated to the support. These researchers concluded that such ions were placed in side pocket channels (8MR) and would be more stable under hydrothermal conditions than those ions placed in the main channels (12MR).

The direct decomposition reactions of NO have been considered the best option for its removal since these offer the advantages of not using reducing agents. Over the last few years, several catalytic systems have been studied for this reaction, based on metals supported in zeolitic materials; the pioneer study using zeolite Y, in 1981, was attributed to Iwamoto's research group [10]. In previous work we have demonstrated that mordenite was an interesting support for Pd and Cu catalysts in the NO decomposition reaction leading to lower N_2O production than palladium based on alumina catalysts [11]. The aim of this work is to evaluate mordenite prepared by different methods and a commercial one as supports for Pd catalysts and test them in the NO decomposition reaction.

2. Experimental

2.1. Synthesis of supports

The commercial mordenite used was CBV10A supplied by ITQ, Valence, Spain.

The synthesized mordenite was obtained by a standard method of IZA [12] in two procedures: (1) using sodium aluminate as a source of aluminum, and silica Aerosil (Degussa) as a source of siliceous; and (2) using a natural clay (called MINA) as an alternative source of Al and Si [13].

A solution containing 10 g of H_2O and 2.064 g of NaOH was prepared. Then, a solution of 3.575 g of sodium aluminate was added. Next, 161.25 g of H_2O was added followed by 24.80 g of SiO_2. The gel was kept shaking for 30 min. The prepared gel, with the following composition [14]: $6Na_2O:A1_2O_3:30SiO_2:780H_2O$, was placed in three stainless steel autoclaves internally coated with Teflon (60 mL capacity). The temperature of crystallization used was 448 K under shaking. The prepared mordenite was called MOR-IZA. The other synthetic method uses as a source of aluminum 5.826 g of natural clay (instead of sodium aluminate), and 21.46 g of SiO_2 was added to reach the same gel composition as in the MOR-IZA. The same procedure of synthesis as described above was carried out to prepare the mordenite called MOR-ARG. The zeolites used as supports were called MOR-CBV10A (commercial), MOR-IZA (standard synthesis) and MOR-ARG (synthesis using clay).

2.2. Catalysts preparation

The supports were treated at 673 K for 3 h (5 K min^{-1}). Before reaching the desired temperature, they undergo two constant temperature steps (1 h each) at 423 K and 573 K. Palladium was incorporated into the supports (3 g) by an ionic exchange with a solution of $Pd(NO_3)_2$ 0.8 mmol L^{-1} at 323 K during 36 h. The material was filtered, washed with deionized water, dried at 373 K for 24 h and calcinated at 673 K under synthetic airflow for 5 h. This method was adapted from Aylor et al. [15]. The catalysts were called PdMOR-CBV10A (commercial), PdMOR-IZA (standard synthesis) and PdMOR-ARG (synthesis using clay).

2.3. Characterization of materials

The materials prepared were characterized by several complementary techniques: X-ray diffraction (XRD), chemical analysis, textural analysis by isotherm adsorption of nitrogen and temperature programmed reduction (TPR).

The X-ray diffraction patterns were obtained on a Siemens D 5000 instrument operated at 40 kV and 25 mA with Ni filter and Cu Kα (λ = 1.54 Å) radiation.

Chemical analyses were performed using induced coupled plasma technique (ICP-OES) in a PerkinElmer Optima 2000DV instrument.

Textural analysis (specific surface area, BET method) were determined from nitrogen isotherms of adsorption at 77 K using Micromeritics Gemini adsorciometer. Prior to analysis, the catalysts were degassed at 673 K during 12 h.

Temperature programmed reduction profiles were taken in a multi-purpose unit coupled to a thermal conductivity detector. The catalysts went through a prior treatment at 673 K with a heating rate of 5 K min^{-1} under a flow of argon (30 mL min^{-1}) during 1 h. After cooling at 253 K, catalyst reduction was performed by flowing a mixture of 1.5% of H_2 in argon up to 773 K.

2.4. Catalytic activity

Catalytic experiments with NO were carried out in a fixed-bed reactor. Prior to reaction, the catalysts were reduced *in situ* at 573 K for 2 h. The NO decomposition reaction was studied as a function of time using a feed mixture containing 500 ppm of NO in an argon background. The temperature of 673 K was chosen based on previous studies conducted by our research group [16]. The flow rate was adjusted to maintain the space velocity at 15,000 h^{-1}. The effluent gases were analysed by a FTIR MB100-BOMEM spectrometer equipped with a multiple reflection gas cell (7.0 m path length and 2.1 L volume). The NO, NO_2 and N_2O stretching bands at 1955–1790 cm^{-1}, 1658–1565 cm^{-1} and 2266–2159 cm^{-1}, respectively, were monitored. In order to calculate the NO conversions from the IR data, a method of treating the measured absorbance values was used to determine the NO concentration at the entrance of the gas IR cell (reactor exit) [17].

Table 1
Characterization of Mina clay

Chemical analysis[a]	%	Mineralogical analysis	%
SiO_2	54.45	Kaolinite	79
Al_2O_3	34.33		
Fe_2O_3	1.43	Mica	4
MgO	0.09		
MnO	0.01	Quartz	12
CaO	0.09		
K_2O	0.21	Gibbsite	5
Na_2O	0.05		
P_2O_5	0.04		
Zr	0.08		

[a] Hydrated form (9.22% corresponds to water lost).

3. Results and discussion

3.1. Synthesis of support

Table 1 shows the characterization data of the clay used to prepare the mordenite MOR-ARG. We observed that the clay is essentially a kaolinite and it has a high content of Si and Al, being indicated as a source of these elements for the zeolite synthesis. It was also observed that it has small quantities of several charge compensating metals that might bear an influence in the synthetic process.

The X-ray diffractogram of the natural clay is presented in Fig. 1, where the presence of kaolinite, mica, gibbsite and quartz is seen. Kaolinite has a lamellar structure formed by regular pilling of layers 1:1 where each layer consists of a sheet of tetrahedral of Si and a sheet of octahedral of Al parallel to each other, with a basal space of approximately 7.0 Å [18].

The diffractogram of the prepared materials using the standard synthesis and the synthesis using clay are presented in Fig. 2. Comparing the peaks obtained in this figure with those of the literature [19], we can observe that the zeolitic phase present is the mordenite zeolite, proving that it is possible to use clays as an alternative source of aluminum and silicon.

Table 2 presents the values of BET superficial areas obtained by N_2 adsorption data and the values of crystallinity obtained by XRD. The areas of catalysts are in the range of 300–360 $m^2\ g^{-1}$ compatible with the values of mordenites. If compared to the commercial sample CBV10A, it can be seen that synthesized materials have high crystallinity reaching, in some cases, values higher than 100%, indicating that the samples prepared have a higher degree of crystallinity than the commercial mordenite.

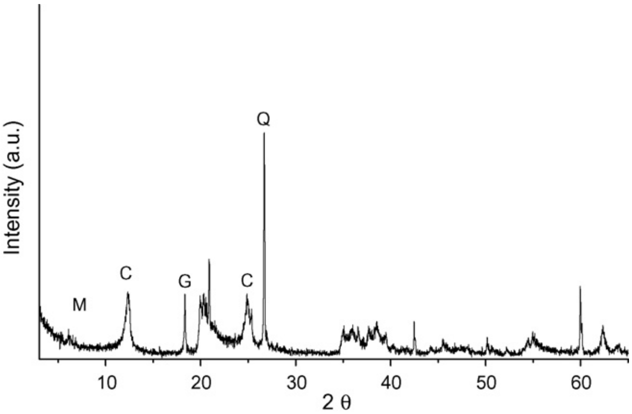

Fig. 1. Diffractogram of Mina natural clay. C: kaolinite; Q: quartz; M: mica; G: gibbsite.

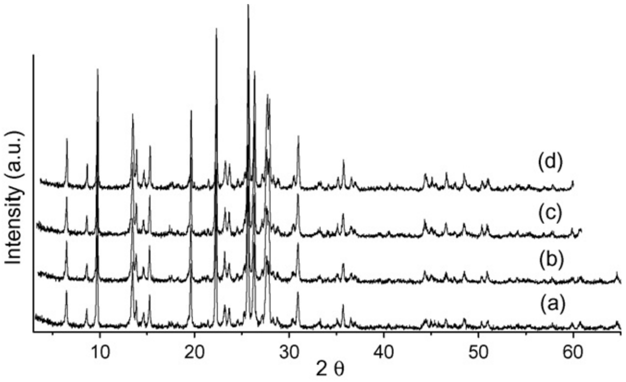

Fig. 2. Diffractograms of X-ray of the materials prepared: (a) standard synthesis 12 h; (b) standard synthesis 24 h; (c) synthesis using clays 12 h; (d) synthesis using clays 24 h.

Table 2
Specific surface areas and crystallinities of the materials

Support	Crystallization time (h)	Surface area BET ($m^2\ g^{-1}$)	Crystallinity (%)
Standard synthesis	12	361	112
MOR-IZA	24	334	115
Clay synthesis	12	315	80
MOR-ARG	24	331	72
Commercial MOR-CBV10A	–	358	100

Crystallinity was calculated using the ratio of the sum of the areas of the five most intense peaks of the samples prepared ($2\theta = 10.8°$; $20.6°$; $23.2°$; $26.6°$; $27.3°$) with the same peaks of the standard (CBV10A) and multiplied by 100.

3.2. Catalysts preparation

In Fig. 3, we can observe that every catalyst presents standard X-ray diffraction patterns in accord with the topology of zeolite mordenite and that the process of palladium impregnation did not affect the integrity of the zeolitic structure. The loss of crystallinity could be evidenced by the elevation on the baseline, in the region between $2\theta = 10–40°$, or by an increase in the noise. The diffractograms did not show peaks related to Pd and PdO (33.9° and 42.3°) aggregates [20–22]. That might be attributed to low Pd loadings and high dispersion.

Table 3 presents the chemical analysis of the catalysts. The $Pd(NO_3)_2$ solution was used to lead the Pd concentration to a level of ~0.8% on the support. The ion-exchange level is estimated by assuming that two Na^+ ions are exchanged by one Pd^{2+} ion compensating the anions AlO_2^- present in the structure. A metallic cation/AlO_2^- ratio equal to 0.5 gives an

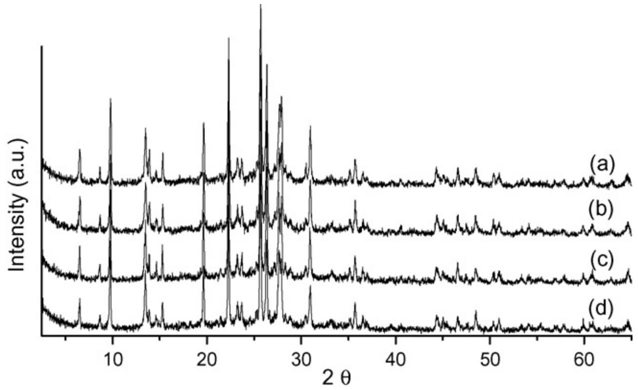

Fig. 3. Diffractogram of X-rays of material before and after the impregnation of palladium: (a) Mordenite; (b) PdMOR-CBV10A; (c) PdMOR-IZA; (d) PdMOR-ARG.

Table 3
Chemical analysis of the catalysts

Catalyst	Pd (wt.%)	Na (wt.%)	Al (wt.%)
PdMOR-IZA	0.72	3.31	2.74
PdMOR-ARG	0.76	3.29	2.44
PdMOR-CBV10A	0.77	2.85	4.14

ion-exchanged level of 100%. In all samples this level was chosen to be less than 100%.

Fig. 4 presents the TPR profiles obtained for the samples. Similar profiles for PdMOR-IZA and PdMOR-ARG are observed, however a well-differentiated profile is obtained in the sample PdMOR-CBV10A. The profiles obtained with the samples PdMOR-IZA and PdMOR-ARG are common profiles of zeolites containing Pd when the catalyst precursor is $Pd(NO_3)_2$ [15]. The catalyst PdMOR-IZA presents a peak at 723 K attributed to Pd^{1+} [23] not seen in the other catalysts. A peak due to a hydride is observed at 338 K. In sample PdMOR-CBV10A, two peaks at 298 K and 358 K, which are not present in the profiles obtained for PdMOR-IZA and PdMOR-ARG, are due to crystalline PdO and to PdO that interacts strongly with the support. The appearance of these peaks might be related to a higher dispersion of the palladium in this catalyst when compared to the others. Additionally, these peaks appear in the same region as the peak referent to the β-hydride phase that appears as an inverted shoulder. The intensity of the β-hydride phase peak is related to the particle size, suggesting that in the commercial mordenite sample the particles are smaller leading to higher metallic dispersion.

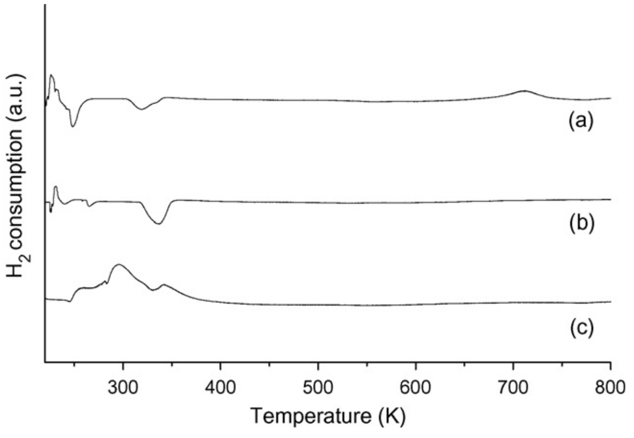

Fig. 4. TPR profiles of the catalysts: (a) PdMOR-IZA; (b) PdMOR-ARG; (c) PdMOR-CBV10A.

Table 4
Quantities of hydrogen consumed in the TPR analysis

Catalyst	H_2 consume 253 K (μmol g^{-1} cat)	H_2 consume 253 K to 443 K (μmol g^{-1} cat)	H_2 consume from β-hydride (μmol g^{-1} cat)
PdMOR-CBV10A	16.74	44.94	–
PdMOR-ARG	29.64	–	8.87
PdMOR-IZA	7.86	–	3.75

Table 4 presents the consumed quantities of H_2 obtained from the TPR analysis. It was observed that MOR-CBV10A consumes more hydrogen, followed by the catalyst PdMOR-ARG.

3.3. Catalytic activity

Fig. 5 presents the results of the catalytic activity for the three catalysts at a temperature of 723 K. The catalytic activities of the catalysts in the direct decomposition reaction of NO were studied for PdMOR-CBV10A in the temperature range of 623–773 K. The best temperature for comparing was selected as 723 K.

All the tests were performed three times and catalytic activity was regenerated after an activation reduction process.

We observed that the catalysts present similar conversions, which remained at 100% conversion for about 100 min, signifying that no ν(NO) band was detected in the infrared spectrometer. This result indicates that the synthesis methods do not influence the catalytic activity, even if the PdMOR-CBV10A presented different TPR profiles. It is generally accepted that the catalytic decomposition of NO occurs on

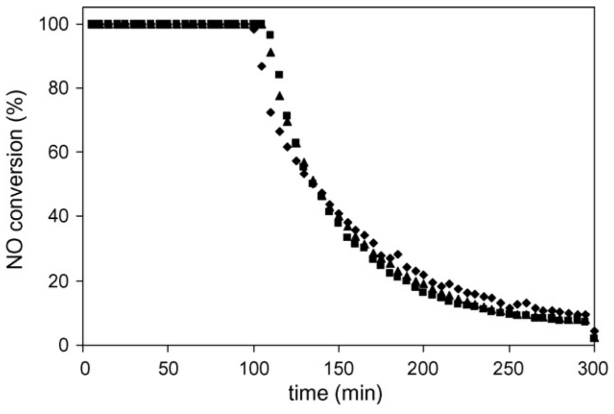

Fig. 5. NO decomposition as a function of reaction time at 673 K: (◆) PdMOR-CBV10A; (■) PdMOR-ARG; (▲) PdMOR-IZA.

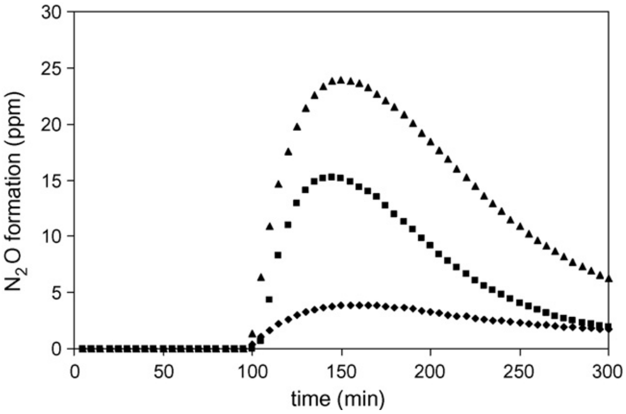

Fig. 6. N_2O formation as a function of reaction time at 673 K: (◆) PdMOR-CBV10A; (■) PdMOR-ARG; (▲) PdMOR-IZA.

reduced metals [24]. The reaction mechanism involves the adsorption of NO on the metal surface followed by dissociation into nitrogen and oxygen, and the recombination of adsorbed nitrogen to form N_2. However, the oxygen produced remains strongly adsorbed, inhibiting further adsorption of NO and consequently the catalyst deactivates. Depending on the reaction conditions the tightly bound oxygen may even lead to oxidation of the metal. Another reaction that takes place is the adsorbed species NO and N reacting together and giving N_2O.

As far as the results for the formation of N_2O are concerned (Fig. 6), the catalyst PdMOR-CBV10A is the most selective, followed by PdMOR-ARG and then by PdMOR-IZA. The quantity of N_2O formed measures indirectly the selectivity of the reaction, that is, the higher the proportion of this oxide, the lower the selectivity to N_2 and O_2 of the reaction. These results are interesting since the catalysts studied have similar areas, crystallinity and quantities of Pd. The most selective sample, PdMOR-CBV10A is the sample that presented a higher consumption of hydrogen in the TPR analysis. Another interesting result is that zeolitic materials synthesized with raw materials, such as clay, can be used as catalysts. In this case the catalyst obtained from MOR-ARG was more selective and also had a higher H_2 consumption than the one obtained from MOR-IZA. However, N_2O production using these catalysts is lower than with palladium catalysts supported on alumina (100 ppm) [25]. This might be related to the acidic properties of mordenite. Therefore, the selectivity in this case is directly related to the palladium-exposed atoms on the support. Furthermore, only traces of NO_2 were detected for the three catalysts.

4. Conclusions

The use of clay as a source of Al and Si led to the production of zeolite mordenite. The two methods of synthesis led to materials that were used as a support for palladium and were shown to be active in the decomposition of NO. The commercial sample was more selective followed by the Pd MOR-ARG and PdMOR-IZA. The catalyst obtained from the zeolite MOR-ARG is more selective than PdMOR-IZA. This indicates that the initial impurities of the clay, present in the zeolitic structure, do not interfere with the reaction.

Acknowledgements

The authors acknowledge the financial support provided by URI-Campus Erechim, CNPq, FAPERGS and COPESUL.

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