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RESEARCH NOTE

Isomerization of 3-Phenyl-1-Propene (Allylbenzene) over Base Catalysts

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Several magnesium containing catalysts were tested for the 2-methyl-3-butyn-2-ol (MBOH) test reaction in a microcatalytic pulse reactor. All solids showed a selectivity close to 100% toward products formed on basic sites (mainly acetone and acetylene) in the 433–623 K range. However, no correlation was found between molar conversion per gram of catalyst and basic site density, determined by temperature-programmed desorption–mass spectrometry of CO_2 as the probe molecule. In the search for a process that fulfilled such a correlation, a new model reaction for base catalysts was found: isomerization of 3-phenyl-1-propene (allylbenzene) to 1-phenyl-1-propene (*cis* + *trans*). Therefore, a good correlation ($r = 0.986$) between molar conversion (per gram of catalyst) and basic site density was obtained at 523 K for all catalysts tested. © 2002 Elsevier Science (USA)

Key Words: **test reaction; 1-phenyl-1-propene; allylbenzene; MBOH; 2-methyl-3-butyn-2-ol; acid–base characterization; double-bond isomerization.**

INTRODUCTION

Despite the widely documented literature on the use of test reactions to characterize acidity in solids (mainly heterogeneous catalysts), there is still very little devoted to base characterization. Within this reduced group, aldol condensation (1, 2) or retrocondensation (3) together with Knoevenagel (4, 5) or Michael (6) reactions can be mentioned. However, it is important to point out that aldol condensation can also occur over acid catalysts, through a carbocationic process.

Some test reactions, such as alcohol transformation (7–12) or alkylation of toluene with methanol or formaldehyde (13), can be used to determine both the acidity and the basicity of catalysts. Moreover, there are some other processes, such as the transformation of 2-methyl-3-butyn-2-ol (14, 15), that allow us to carry out an acid, base and amphoteric characterization of heterogeneous catalysts.

Finally, double-bond isomerization processes have also been used for acid–base characterization. Thus, 1-butene (16–18), 2-methyl-2-pentene (19), and 2,3-dimethylbut-2-ene (20, 21) are some examples of the probe molecules. The present piece of research deals with the use of the transformation of 3-phenyl-1-propene (allylbenzene) as a test reaction in order to characterize the basicity of various solids consisting of one magnesium oxide. several mixed magnesium–titanium oxides, and a magnesium–zirconium oxide. Such a process is known to occur in the homogeneous phase through a carbanionic process (22).

Moreover, Tsuji *et al.* (23) studied the process at room temperature, in the liquid phase, for one magnesium oxide and different zeolitic materials modified with several metal oxides. Nevertheless they only found isomerization in the case of pure magnesia, probably due to diffusion problems inside the zeolitic micropores.

METHODS

Synthesis of the Solids

Catalysts were synthesized using the sol–gel technique, starting from $Mg(NO_3)_2 \cdot 6H_2O$, $ZrOCl_2 \cdot 6H_2O$ (Merck), and TiO_2 (Fluka). Different amounts of such chemicals were dissolved in distilled water (in the case of TiO_2, a suspension was formed). Then NaOH was added until pH 10 was reached. The gel was aged for 72 h and then filtered and air dried for 24 h and placed in an oven at 383 K. Calcination of gels in a furnace at 873 K for 3 h, either in the air (AIR) or in oxygen flow (OX), led to the solids in Table 1. Nomenclature is as follows: oxides present are represented by the symbol of the metal followed, in the case of mixed oxides, by the atomic Mg/Zr or Mg/Ti ratio, as determined by ICP (Perkin–Elmer Optima 3000 SC). Finally "AIR" or "OX" indicate that calcinations were performed either in the air or in the oxygen flow.

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TABLE 1

Specific Surface Area (S_{BET}) and Basic Site Density, as Determined by TPD of CO_2, for the Different Catalysts

		Basic site density (a.u./m^2)			
Catalyst	S_{BET} (m$^2 \cdot$ g^{-1})	Low strength (<673 K)	Medium strength (673–873 K)	High strength (>873 K)	Total
Mg–AIR	53	5.3	0.9	1.4	7.6
Mg–OX	47	6.7	0.3	2.4	9.4
MgTi5–OX	52	7.2	2.4	2.1	11.7
MgTi19–OX	67	8.8	1.1	4.0	13.9
MgTi31–OX	78	8.3	2.2	2.1	12.6
MgZr27–OX	74	6.4	3.0	6.2	15.6

Physical Characterization

The textural properties of solids were determined from nitrogen adsorption–desorption isotherms at liquid nitrogen temperature by using a Micromeritics ASAP-2000 instrument. Surface areas were calculated by the BET method.

X-ray investigation of the solids was carried out using a Siemens D-500 diffractometer provided with an automatic control and data acquisition system (DACO-MP). The patterns were run with nickel-filtered copper radiation ($\lambda = 1.5405$ A) at 35 kV and 20 mA; the diffraction angle 2θ was scanned at a rate of 2° min^{-1}.

FT-Raman spectra were obtained on a Perkin–Elmer 2000 NIR FT-Raman system with a diode-pumped NdYAG laser (9394.69 cm^{-1}). It was operated at a resolution of 4 cm^{-1} throughout the 3600- to 200-cm^{-1} range to gather 64 scans.

Base Characterization of the Solids

Base characterization of the solids was carried out by temperature-programmed desorption–mass spectrometry (TPD–MS), using carbon dioxide as the probe molecule, as described elsewhere (15).

Reactivity Tests

Experiments were conducted in a microcatalytic pulse reactor described in a previous paper (15). Experimental conditions are as follows:

- MBOH pulses, 0.5 μL; temperature, 433–623 K; N_2 flow, 75 mL min^{-1}; FID detector (523 K); Supelcowax capillary column (30-m length and 0.20-mm i.d.); oven temperature, 333 K (3 min); increase in temperature up to 473 K (at 8°C min^{-1}), final temperature kept for 5 min.
- Allylbenzene pulses, 0.1 μL; temperature, 433–623 K; N_2 flow, 75 mL min^{-1}; FID detector (523 K); Supelcowax capillary column (30-m length and 0.20-mm i.d.) and SPB-50 (60-m length and 0.25-mm i.d.); oven temperature, 393 K.

RESULTS AND DISCUSSION

Physical and Base Characterization of the Solids

BET surface areas of all the solids are shown in Table 1. Pure magnesia catalysts (Mg-AIR and Mg-OX) consist of periclase (bands at $2\theta = 37.2$, 43.1, and 62.5 in the X-ray spectra). As far as magnesium–titanium oxides are concerned, no mixed phases are detected except for MgO (periclase) and TiO_2 (mainly anatase), individually. The presence of TiO_2 as anatase is confirmed by Raman spectra (bands at 199, 398, 516, and 640 cm^{-1}). Finally, MgZr27-OX consists of MgO (periclase) and tetragonal ZrO_2 (bands in the X-ray spectrum at $2\theta = 60.2, 50.6, 35.3$, and 30.4). Mixed oxides are not detected.

Results regarding base characterization are also included in Table 1. An example of the TPD profiles is depicted in Fig. 1. As can be seen, basic sites can be classified according to their different strengths (different carbon dioxide desorption temperature). Therefore, there are low-strength (desorption temperature below 673 K), medium-strength (desorption between 673 and 873 K), and high-strength basic sites (desorption over 873 K).

Reactivity Tests

Due to their base character all solids are carbonated as confirmed by XPS and DRIFT. Therefore, prior to catalytic tests the solids were heated at 823 K (50 K below their calcination temperatures) for 30 min. Moreover, such a process was monitored by mass spectrometry observing the loss of water and carbon dioxide.

2-Methyl-3-butyn-2-ol (MBOH) test reaction. All solids tested showed a selectivity close to 100% to the main

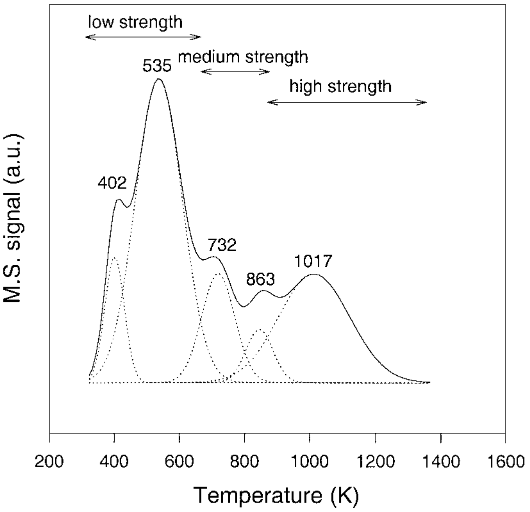


FIG. 1. Temperature-programmed desorption–mass spectrometry (TPD–MS) profile of catalyst Mg–OX deconvoluted into peaks corresponding to low-, medium-, and high-strength basic sites.

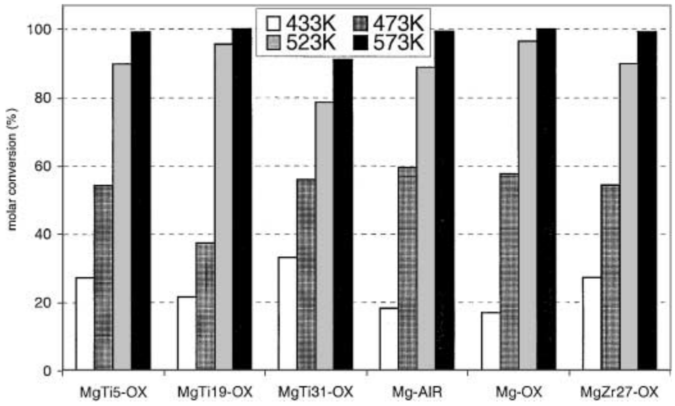
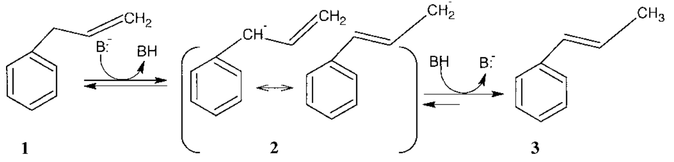


FIG. 2. 2-Methyl-3-butyn-2-ol (MBOH) test reaction. Results found for different catalysts expressed in terms of variation of molar conversion with temperature. Catalyst weight was 20 mg in all cases.

products formed on basic sites (acetone and acetylene) within the 433- to 623-K range, which allows us to classify them with base catalysts. Figure 2 shows the conversions found for all the catalysts at four different temperatures. Catalyst weight remained constant (20 mg). Any attempt to correlate either molar conversion at low temperatures with high-strength basic site density or molar conversion at high temperatures with total basic site density did not lead to good results. This is consistent with results reported by Handa *et al.*, who found that MBOH decomposition is not a sensitive test reaction for estimating the nature of very strong basic catalysts (20). According to Handa *et al.*, these results could be explained in terms of the strong adsorption of acetylene and acetone on the catalyst. Moreover, as temperature increases, some secondary products coming from aldol condensation of acetone are formed, which contribute to carbon deposition (11, 24).

3-Phenyl-1-propene (allylbenzene) test reaction. In the search for a test reaction which allowed us to correlate basic site densities with molar conversion, we considered alkene isomerizations. These reactions seem to be a more effective means to estimate the nature of strong basic sites than the MBOH one (20). In this sense, isomerization of 3-phenyl-1-propene (allylbenzene) to 1-phenyl-1-propene (β-methylstyrene), *cis* + *trans* (Scheme 1), could yield some interesting results. According to Scheme 1, **3** (*cis* + *trans* stereoisomers) is more stable than **1**, due to the conjugation of the olefin bond with the aromatic ring. Moreover, the *trans* form is the main product, since it is more stable than the *cis* one.



SCHEME 1. Mechanism for isomerization of allylbenzene in a basic medium.

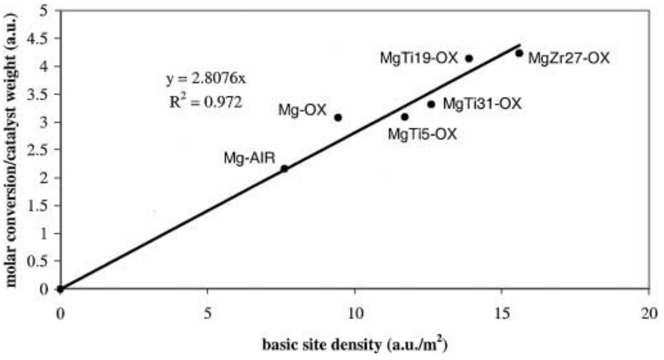


FIG. 3. Allylbenzene test reaction. Correlation between molar conversion/gram of catalyst and basic site density (a.u./m^2), at 523 K, for different catalysts.

Blank reactions (in the absence of the catalyst) did not lead to isomerization of allylbenzene in the 443- to 623-K range. Unlike blank reactions, allylbenzene underwent isomerization in the presence of any of the basic solids, yielding β-methylstyrene (*cis* + *trans*). Chain isomerization, which would have yielded α-methylstyrene, did not occur. Finally, three new experiments were carried out in order to cast further light on the nature of the process. (i) The injection of pure *trans*-β-methylstyrene (without catalyst) only yielded 1% of the other isomer (*cis*-β-methylstyrene). Therefore, the distribution of products is not purely determined by thermodynamic equilibrium. (ii) The injection of pure *trans*-β-methylstyrene, in the presence of catalyst, yielded small quantities of both allylbenzene and *cis*-β-methylstyrene. This is evidence of the existence of an equilibrium among the three species, as expressed in Scheme 1. (iii) Poisoning of the catalyst with carbon dioxide led to a sharp decrease in activity. Thus, the process is catalysed by bases.

Figure 3 depicts the favorable correlation ($r = 0.986$) between molar conversion (per gram of catalyst) and total basic site density for all catalysts, at 523 K. The inclusion of either only low- and medium-strength basic sites ($r = 0.935$) or medium- and high-strength basic sites ($r = 0.716$) worsened the results. This is hardly surprising since double-bond isomerization is quite an easy process, not requiring a high basic strength. At temperatures below 523 K, the different products are greatly retained, which results in the tailing of the peaks. On the other hand, at high temperatures (over 523 K) coke formation, and therefore catalyst deactivation, is very important. The *trans*/*cis* ratio was about 6 for all the catalysts.

CONCLUSIONS

The 2-methyl-3-butyn-2-ol test reaction allowed us to classify a series of catalysts as basic solids but no correlation between molar conversion and basic site density could be drawn. In the search for such a correlation, isomerization of 3-phenyl-1-propene (allylbenzene) to β-methylstyrene ($cis + trans$) was proposed as a new test reaction for base catalysts. A good correlation ($r = 0.986$) between molar conversion (per gram of catalyst) and total basic site density for all catalysts was obtained at 523 K. However, it must be taken into account that β-methylstyrene ($cis + trans$) could also be obtained over acid sites through a carbocationic process. Therefore, allylbenzene isomerization might be used as a test reaction for either base or acid catalysts but not amphoteric ones since, in this case, two different mechanisms (carbocationic + carbanionic) would be involved. Nevertheless, this is hardly surprising since the same can be said of all alkene isomerizations. Even some other test reactions undeniably useful and extensively used for basic characterization of solids (such as aldol condensations) can also occur on acid materials.

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