Tuning the Acid-Metal Balance in Pd/ and Pt/Zeolite Catalysts for the Hydroalkylation of m-Cresol

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Abstract

The liquid phase hydroalkylation of m-cresol catalyzed by zeolite catalysts doped with noble metals was investigated at 473K and 5200 kPa of H₂. Metals (Pt and Pd) were incorporated in HY (Si/Al=30) and H-Mor (Si/Al=10) zeolites by incipient wetness impregnation. The structural properties of the samples were characterized by NMR, XPS, and BET. Hydroalkylation of m-cresol involves a series of steps that start with the ring saturation to 3-methylcyclohexanone (MCONE), which is the primary product and is further hydrogenated to methylcyclohexanol (MCNOL) on the metal function. This, in turn, is dehydrated on the acid sites to 3-methyl-cyclohexene, which readily alkylates the unreacted m-cresol to form bicyclic compounds that fall in the desirable fuel range. In these bifunctional catalysts, differences in intrinsic hydrogenation activity of metals play an important role in determining the final selectivity to alkylated products. In fact, the ratio of number of acid sites (n_A) to exposed metal sites (n_M) can be tuned to maximize the selectivity towards bicyclic compounds because this selectivity is determined by the fate of the intermediate 3-methylcyclohexene (MCENE). That is, if the C=C hydrogenation on the metal is fast compared to alkylation on the acid site, the selectivity decreases. However, if the hydrogenation is too slow, the overall product yield decreases. Therefore, to optimize the hydroalkylation yield a delicate metal/acid balance is required. Moreover, in the absence of metal, the zeolite would deactivate very quickly. Therefore, having the metal and acid functions together is also important for extending the catalyst life. Finally, it has been observed that 3D-pore zeolites, like HY, are preferred over 1D-pore zeolites such as H-Mor, which sharply diminish the formation of alkylation compounds, despite being more acidic than HY.

Keywords: Hydrodeoxygenation, hydroalkylation, m-cresol, acid/metal balance, metal nature, hydrogenation activity, shape selectivity.

1. Introduction

Biomass-derived pyrolysis oil (bio-oil) is a promising alternative to fossil fuels [1,2]. However, upgrading is required before it can be used as a fuel, mainly due to the high oxygen content and low energy density [3]. Several strategies have been proposed to improve bio-oil properties. An extensive amount of work has focused primarily on hydrodeoxygenation of phenolic compounds [4-18] while some work has focused on improving carbon retention and enhancing molecular weight mainly by alkylation reactions [19 - 24]. Molecular weight enhancement of bio-oil molecules may become important for the production of molecules with the appropriate length to use them as components of the gasoline and, particularly, of the diesel pools.

Hydroalkylation of aromatics has been previously studied to improve molecular weight in the upgrading of conventional fossil fuels. As early as 1934, Truffault [25] reported the formation of cyclohexylbenzene during the hydrogenation of benzene in the presence of phosphoric anhydride and nickel-black catalysts. More recent studies [26-30] have reported results for this reaction over different supported transition metal catalysts. They all conclude that a combination of acidity and hydrogenation activity is necessary for the formation of cyclohexylbenzene. It is generally accepted that partially hydrogenated benzene intermediates alkylate unreacted benzene molecules to form cyclohexylbenzene. However, none of these intermediates have ever been observed. In fact, one would expect that at high H₂ pressures, full hydrogenation of the aromatic ring is kinetically favored upon adsorption of benzene on the surface. However, the presence of olefins seems to be necessary for the alkylation via a carbenium ion, which is much more difficult to form from paraffins than from olefins. Hydroalkylation of phenolics compounds, on the other hand, has a significant advantage over hydroalkylation of aromatics [31,32]. In the presence of bifunctional metal/acid catalysts phenolic molecules can undergo hydrogenation/dehydration reactions [10-14,16], which have among their intermediate products cyclohexanols and cyclohexenes, which are potential alkylation agents for phenolic rings via electrophilic aromatic substitution [31,32]. For example, Hong et al. [31] observed the hydroalkylation of phenol using Pt/HY, while Zhao et al. [32] used Pd/H β . Interestingly, while both groups operated at similar reaction temperature and H₂ pressure, the former reported selectivities to alkylation of only about 10% and the latter revealed alkylation selectivities as high as 56%.

This significant difference in selectivities can be related to differences in balance between hydrogenation and dehydration/alkylation activities of these two catalysts, which in turn depend on the nature and availability of the metal active sites, combined with the acid density of the support. These studies have emphasized the importance of the acid/metal balance for improving the selectivity to hydroalkylation of phenolics [31,32]. However, a fundamental understanding of the effects of varying the type of metal, the metal availability and location, as well as the acid density and zeolite topology on the hydrogenation/dehydration/alkylation balance is lacking. In the present contribution, we have investigated the effect of these parameters in the hydroalkylation selectivity of m-cresol over a series of bifunctional metal/acidic zeolite catalysts. Specifically, HY and H-mordenite acidic zeolites doped with varying amounts of Pd and Pt of different dispersion have been prepared, fully characterized, and tested in liquid-phase reactions. The observed trends are interpreted in terms of reaction pathways recently proposed in the literature and their relationship with specific catalyst properties.

2. Experimental

2.1. *Catalyst preparation and characterization*

The ammonia form of zeolite Mordenite (Alfa Aesar, Si/Al = 10, $S_{\text{BET}} = 500 \text{ m}^2/\text{g}$) was calcined in air at 400 °C for 8 hours to obtain the H form [33]. Zeolite HY (Zeolyst, CBV760, Si/Al=30 $S_{\text{BET}} = 734 \text{ m}^2/\text{g}$) and SiO_2 (HiSil 915, $S_{\text{BET}} = 167 \text{ m}^2/\text{g}$) were used as provided. All supported metal catalysts were prepared by incipient wetness impregnation (IWI). Chloroplatinic acid hexahydrate (H_2PtCl_6), palladium (II) nitrate hydrate ($\text{PdNO}_3\text{X}\cdot\text{H}_2\text{O}$), and palladium chloride (PdCl_2) were purchased from Sigma-Aldrich and used as precursors for all Pt and Pd catalysts. In a typical catalyst preparation, 1-5g of support was dried overnight in the oven at 100 °C. Subsequently, a fresh aqueous solution of metal precursor was prepared and added to the support by IWI. For Pd catalysts, combinations of a metal precursor (PdNO_3 or PdCl_2) and a solvent (water, HCl 36%, or isopropanol) were used to prepare catalysts with varying metal dispersion. Silica supported catalysts were prepared following the same impregnation procedure. That is, PdCl_2 and H_2PtCl_6 were dissolved in an HCl 36% aqueous solution to prepare the 1%Pt/ SiO_2 and 1%Pd/ SiO_2 catalysts, respectively.

Metal dispersions were estimated from dynamic pulse CO adsorption and reported as CO/M. Supported Pt samples were reduced under H_2 for 1 h at 300 °C, while Pd samples were reduced

at 200 °C. Subsequently, the samples were cooled down to room temperature, and flushed with He for 0.5 h to remove adsorbed H₂. Using a 100 µL sample loop, 5% CO/He gas mixture was pulsed onto the sample until saturation of the surface of the catalyst was reached. The CO consumption was monitored by a Cirrus mass spectrometer (MKS) connected to the outlet of the reactor.

The acid density of zeolites HY (Si/Al=30) and of H-Mor (Si/Al=10) as well as of metal-loaded zeolites was determined by temperature programmed desorption (TPD) of isopropylamine (IPA). In each case, 50 mg of catalyst sample was loaded into a 0.25 in o.d. quartz reactor. The catalyst was pretreated in He flow at 400 °C for 2 h to eliminate any adsorbed water, then the reactor was cooled down to 100 °C and held there for 20 min. While keeping the temperature at 100 °C, ten pulses of 2µL of isopropylamine (1 pulse/3 min) were sequentially sent over the sample using a manual syringe; then, the sample was flushed under He for 2 h to remove any weakly adsorbed IPA. A linear temperature ramp of 10 °C/min from 100 to 600 °C was used for the TPD. The evolution of desorbed species was continuously monitored by a Cirrus mass spectrometer (MKS) recording the following signals m/z = 18 (H₂O), 44 (IPA), and 41 (propylene). The density of acid sites was quantified by calibrating the MS signals using the average of 10 pulses of propylene gas standard.

For transmission electron microscopy (TEM), Pt catalysts were pre-reduced at 300°C for 1 h, while Pd catalysts were pre-reduced at 200°C. Then, the samples were dispersed in isopropanol and sonicated by a horn sonicator (Cole-Parmer), operating at an amplitude of 25% for 10 min before deposition onto holey carbon coated copper grids. The images were obtained on a JEOL 2000 field emission system operated at 200 kV. ²⁷Al NMR experiments were performed on a Bruker AVIII HD NMR spectrometer operating at a magnetic field strength of 11.74 T with a 4 mm Bruker MAS probe. For the MAS experiments of ²⁷Al (130.3754 MHz), a single pulse acquisition was applied with a spinning speed of 14 KHz and a short RF pulse (less than 15°) with a recycle delay of 0.5-1 s. Spectra were collected after 10240 scans and referenced to AlCl₃ (aq. 1 M) at 0 ppm. N₂ physisorption was performed on all samples by a Micromeritics ASAP 2010 unit. Prior to analysis, the zeolite samples were degassed in situ at 230°C for 24 h. Powder XRD (PXRD) patterns were recorded on a D8 Series II X-ray diffractometer (BRUKER AXS), in reflection geometry using Cu Kα radiation generated at 40 kV and 35 mA. Data were collected over 5-65° angle range with a step size of 0.05 and a count time of 1.0 s.

2.2. Catalytic activity measurements

Catalytic activity measurements for hydrodeoxygenation of m-cresol were carried out in a 300 mL Parr 4843 reactor, operating in batch mode. The temperature inside the reactor was controlled with a CAL 9500P controller (CAL Controls Ltd.). In a typical run, 0.030 g of catalyst sample and 60 mL of undecane were added to the stainless steel reaction vessel, then pressurized to 1050 kPa with N₂ and subsequently depressurized to purge the air from the system. In a similar way, the reactor was purged with 1050 kPa of H₂ to purge the N₂ out. The pressure was increased to 2100 kPa of H₂, while stirring at 400 rpm, and the reactor was heated up to the pre-reduction temperature (300 °C for platinum catalyst, 200 °C for Pd catalysts) and held at that temperature for 1h. Subsequently, the set-point was adjusted to the selected reaction temperature, usually 200 °C. After equilibration, 60 mL of a mixture of undecane containing the reactants was injected from a pressurized feeding cylinder. The pressure of the reactor was adjusted to 5200 kPa with additional H₂. The zero reaction time was taken as the moment when the specified reaction temperature and pressure was reached after injecting the feed. H₂ was constantly fed to the reactor to replace the gas consumed in the reaction and keep the pressure at 5200 kPa. At the end of the reaction period, the reactor was cooled to room temperature and depressurized, the products were filtered and analyzed by gas chromatography (GC-FID and GCMS). Typical GC chromatograms describing all the products observed are summarized in the supplementary information file (Figures S2 and S3). An Agilent GC-FID 7890B equipped with a capillary, low polarity column (Phenomenex ZB-5) of 60.0 m × 0.25 mm × 0.25 μm was used for quantitative analysis, while a Shimadzu QP2010 GC-MS equipped with a mid-polarity (Phenomenex ZB-1701) capillary column, 60.0 m × 0.25 μm × 0.25 μm nominal, was used for product identification. Commercially available standards were used when possible to confirm the identity of the products. In all the GC-FID analyses, isopropanol was used as internal standard to help close the mass balances. Carbon balance in all the runs was better than 92 %. Selectivity is defined in a carbon molar basis as.

$$\text{Selectivity \%} = \frac{\text{Carbon moles of product } i}{\text{Carbon moles of reactant converted}} \times 100$$

2.3. Computational methods

All of the calculations reported herein were carried out using periodic plane-wave gradient-corrected density functional theory methods as implemented in the Vienna ab initio Simulation Package (VASP). [34-37] The Perdew-Burke-Ernzerhof (PBE) [38,39] form of generalized gradient approximation (GGA) exchange correlation functional was used to provide the non-local gradient-corrections to exchange and correlation energies. Wave functions were constructed by using projector augmented wave potentials (PAW) [40] within a cutoff energy of 400 eV.

The close-packed 4x4 Pt (111) and Pd (111) surface with four metal layers and 15 Å of vacuum separating slabs in the z-direction was used for all of the calculations reported herein. The top two metal layers were allowed to relax in the calculations whereas the bottom two layers were held fixed to their bulk position. The electronic energies were converged to within 10^{-6} eV. The geometric structures for all of the calculations were optimized until the forces were converged to within 0.01 eV/Å using a $2 \times 2 \times 1$ Monkhorst-Pack k-point mesh to sample the first Brillouin zone. [41] The energies of the adsorbates in vacuum were calculated spin-polarized using an $18 \times 18 \times 18$ Å unit cell with the Γ only k-point mesh.

The nudged elastic band (NEB) method [42] was used to find reaction coordinates by linearly interpolating 8 images between the initial and final states and then minimizing the energy of the string of images until the forces perpendicular to the reaction path converged within 0.25 eV/Å. Reliable estimations of the transition state and reaction mode were obtained from the NEB results and used in the dimer method [43] to isolate the transition states and establish the lowest energy path. The dimer methods use two images that close to the transition state to form a ‘dimer’ structure. The transition state was located by moving the ‘dimer’ uphill along the potential energy surface. The ‘dimer’ is also rotated along this path in order to follow the lowest curvature mode of the potential energy. The dimer calculations were carried out until the forces perpendicular to the reaction mode were converged to within 0.01 eV/Å at a $2 \times 2 \times 1$ k-point mesh to sample the first Brillouin zone.

The binding energies of the surface species were calculated as:

$$E_{ads,i} = E_{surf+i} - E_{surf} - E_i$$

where E_{surf+i} is the total energy of the metal surface with the adsorbate i bound to the metal surface, E_{surf} is the total energy of the bare metal surface and E_i is the total energy of the adsorbate in gas phase. The activation barriers and reaction energies were calculated as:

$$\Delta E_{ACT} = E_{TS} - E_R$$

$$\Delta E_{RXN} = E_P - E_R$$

respectively; where E_{TS} is the total energy of the transition state, E_R is the total energy of the reactant state and E_P is the total energy of the product state.

3. Results and discussion

3.1. Catalyst Characterization

To quantify the effects of acid density and metal sites in the catalytic HDO/HDAlk of m-cresol, a full characterization of the composition and structure was performed on the Pt/ and Pd/zeolite catalysts. The analytical techniques selected for this study provide detailed information of the zeolite topology and distribution of metal clusters. Table 1 summarizes the list of all metal-doped zeolites used in this study. Non-zeolitic samples, Pd/SiO₂ and Pt/SiO₂, were also investigated for comparison. The metal dispersion was estimated from CO chemisorption analysis. To attain varying levels of metal dispersion a combination of catalyst precursors and impregnation methods were selected. The dispersion of Pt catalysts obtained by impregnation of an aqueous solution of H₂PtCl₆ precursor resulted in moderately high metal dispersion on HY zeolite (~55-65%) and lower on silica. To achieve a wider range of metal dispersions, the synthesis of Pd/HY catalysts was carried out combining different metal precursors and solvents (Table 1). As a result, three levels of dispersion were attained on the zeolite. The highest Pd dispersion on HY (43%) was obtained by using PdCl₂ in water/HCl as the impregnating solution. By contrast, when the solution was PdNO₃ dissolved in water, the resulting metal dispersion was much lower (24%); and when it was PdNO₃ dissolved in isopropanol, the dispersion was even lower (5%). Figure 1 illustrates TEM images of the three Pd/HY catalysts with different levels of dispersion, the difference in particle size associated with different dispersion values is evident. Very fine particles are observed for the high dispersion catalyst and much bigger particles for the lower dispersion catalysts. While the metal dispersion for Pd/SiO₂ and Pt/SiO₂ was about the same on the two samples, due to the difference in atomic weight, the Pd catalyst contained approximately twice as much surface atoms as the Pt sample.

The results of acid density as quantified by TPD of adsorbed IPA are also included in Table 1. As expected, zeolite H-Mor (Si/Al=10) is more acidic than zeolite HY (Si/Al=30) since it has a higher content of Al atoms associated with Brønsted acid sites. Deposition of metals on the surface of the zeolites did not greatly affect the acidity of the zeolite. Only a minor reduction in acid density was observed on the metal-containing catalysts. From the information of Table 1, the ratio of mmol of Brønsted sites per gram (n_A) to mmol of exposed metal atoms per gram (n_M) is calculated for each catalyst. These n_A/n_M values will be important in discussing the effect of the acid/metal balance on the hydroalkylation selectivity.

In Figure 2, the XRD patterns of the metal-doped catalysts are compared to those of the bare zeolite samples. Clearly, no significant differences in relative intensity or position of the peaks were observed upon metal addition, which indicates that the deposition of Pd has minimal effects on the zeolite crystallinity. Overall, the structures of H-Mor and HY 30 zeolite after the metal loading remained intact.

However, as shown in Figure 3, the ^{27}Al NMR spectra of the Pd/H-Mor and Pd/HY 30 catalysts are somewhat different from those of the H-Mor and HY 30 parent zeolites, respectively. The peaks at 55 and 61 ppm are assigned to tetrahedrally coordinated Al in the framework, while the one at 0 ppm peak is due to extraframework octahedral Al species [44]. In general, the metal-doped zeolites show a slightly higher and broader peak for the octahedral species, indicating a small degree of framework attack during the metal loading treatment.

Also, it is clear that the HY catalysts show a relatively higher content of extraframework Al than the H-Mor catalysts. This is due to the method employed to reach the high Si/Al ratio (30) of the HY material used in this study. While the exact technique is not reported by the supplier, it is expected that the high Si/Al ratio is obtained by dealumination of the parent HY zeolite with lower Si/Al ratio (e.g. 2.3), upon which, the fraction of extraframework Al atoms greatly increases [45].

3.2. *Hydroalkylation of m-cresol over Pt- and Pd- loaded zeolite HY*

The conversion of m-cresol over different noble metal-doped zeolite catalysts was investigated in the batch reactor. As shown in Table 2, the main products were 3-methylcyclohexanone (MCONE), 3-methylcyclohexanol (MCNOL), 3-methylcyclohexene (MCENE), toluene, and methylcyclohexane (MCANE). In addition, alkylated products

containing two or more six-carbon rings were formed in significant amounts. The distribution of alkylated products was estimated from combined analysis of GC-MS and GC-FID. A typical distribution at an intermediate conversion level (~45%) is illustrated in Figure S1 of the supplementary information file.

At higher conversions, the selectivity toward alkylated deoxygenated compounds such as 3-methylcyclohexyl-1-methylcyclohexane is increased. That is, increasing the residence time after alkylation results in higher yields of deoxygenated compounds in the desired range of molecular weights. Therefore, for the analysis of product distribution, oxygenated and deoxygenated alkylation products are considered together. Additional detailed information about the determination of the alkylation product distribution is included in the supplementary information file.

Table 2 summarizes the catalytic activity data of the different catalysts with varying noble metal loadings, dispersions, and zeolite type. Catalysts identified as 1%Pd/HY A, B, and C have high (0.43), medium (0.24), and low (0.05) metal dispersions, respectively. With all catalysts, except the monometallic 1%Pt/SiO₂, 3-methylcyclohexanone (MCONE), 3-methylcyclohexane (MCANE), and alkylated products were the dominant products.

It can be seen that, in general, at similar conversions and conditions, higher selectivity to MCONE was observed for catalysts containing Pd in comparison to those containing Pt. This difference can be ascribed to the high activity of Pt for hydrogenating the carbonyl in MCONE. However, the selectivity to MCNOL is low in all cases in which the acidic zeolite is present. Clearly, the dehydration to MCENE is fast under the reaction conditions and the subsequent reaction is crucial for the hydroalkylation selectivity, since this olefin can further react either as an alkylating agent of the aromatic ring or getting hydrogenated to MCANE, which is the undesirable side product.

On the monometallic 1%Pt/SiO₂ catalyst the situation is different since the lack of acidity precludes the dehydration of MCNOL, which accounts for the high selectivity to MCNOL and the absence of alkylated products. The low selectivity to toluene in all cases is due to the high H₂ pressure and relatively low temperatures used in this case, compared to previous studies conducted in the vapor phase at lower pressures and higher temperatures, in which toluene was a dominant product over bifunctional catalysts [7-,8,9,16]. A run was conducted at a lower hydrogen pressure (2100 instead of 5200 kPa). The product distribution is summarized in Figure

S4 of the supplementary information file. It was observed that the overall conversion greatly decreased, probably because the initial hydrogenation of the m-cresol aromatic ring is decreased. An increased selectivity towards alkylation was observed at short reaction times and low conversions. However, the rate of deactivation increased and, since the reaction was so much slower it needed to react for much longer time or required an increased amount of catalyst to achieve a significant conversion. Therefore, we kept the pressure at 5200 kPa for the rest of the runs.

To evaluate the role of varying the n_A/n_M ratio in the bifunctional catalysts, the product selectivities of two Pt/HY catalysts with varying metal loading were evaluated at similar conversions. Figure 4 compares the product distribution at the same conversion of about 62 % over two Pt/HY catalysts with 1 and 0.2 wt % Pt. It is observed that as the n_A/n_M ratio increases the alkylation selectivity goes up moderately while the selectivity to MCANE goes down. This trend shows that by controlling the number of acid sites that catalyze dehydration and alkylation, compared to the metal sites that catalyze hydrogenation one could optimize the production of alkylated compounds. However, it seems that Pt is too active for hydrogenation and, even at low metal/acid ratios, it is not an effective metal for hydroalkylation.

A better performance is observed using Pd. When comparing the results at similar conversion levels over three Pd/HY catalysts of the same metal loading but varying dispersion (Figure 5), we observe that, as the metal dispersion decreases and the n_A/n_M ratio increases, the selectivity towards alkylation is greatly enhanced. As the number of exposed metal atoms decreases the overall reaction rate also decreases since the initial step in the reaction scheme requires hydrogenation. In fact, to reach the same conversion level, different amounts of catalyst were used for each sample. The one with the lowest metal dispersion required 9 times more catalyst than the one with the highest dispersion. Therefore, the amount of exposed Pd cannot become too small since, eventually, the alkylation yield would go to zero as depicted in Figure 5. Hydroalkylation is a sequential reaction and obviously selectivity should vary with the level of conversion. Therefore, we take precautions to make the comparisons at the same conversion.

While it is clear in Figures 4 and 5 that Pd/HY is more effective than Pt/HY, the difference is even more convincing when we compare in Figure 6 the alkylation/MCANE ratio over the two series of catalysts at varying acid/metal ratios at the same conversion of 61 %. It is clear that the alkylation/MCANE ratio is much higher on Pd/HY than on Pt/HY. This is important because

these are the two final products. Over Pd, the concentration of MCONE is kept higher than on Pt for a very broad range of m-cresol conversion, and as shown below this has a strong positive effect on alkylation selectivity.

As illustrated in Figure 7, the variation of selectivity with conversion is much smaller than the variation from one catalyst to another. For instance, it can be seen that high selectivities to alkylated products can be kept on catalysts with appropriate acid/metal site ratios up to very high conversions (Figure 7 and Table 2).

Figure 8 shows the proposed reaction pathway for the hydrodeoxygenation and hydroalkylation of m-cresol. As recently proposed in a detailed kinetic study of our group [9], it is reasonable to suggest that m-cresol can undergo tautomerization before ring hydrogenation. Subsequent hydrogenation of the keto-tautomer ring produces MCONE as the dominant primary product (step 1). Further hydrogenation of the carbonyl in MCONE produces MCNOL (step 2), which in turn can undergo a rapid dehydration to MCENE (step 3). This is the important intermediate, which depending on the acid/metal balance can either undergo hydrogenation to MCANE (undesirable step 4) or alkylation of an unreacted m-cresol molecule via electrophilic aromatic substitution (desirable step 5) [32]. While MCNOL could also act as an alkylating agent via an oxonium intermediate, we have observed that, in the present conditions, the dehydration rate is much higher than the alkylation rate, which indicates that the alkylating agent is the olefin, MCENE.

In line with the reaction pathway shown in Figure 8, the n_A/n_M ratio directly affects the selectivity towards alkylation, as mentioned above. However, it is important to analyze the relative rates of hydrogenation of the carbonyl in MCONE and of hydrogenation of the double bond in MCENE compared to the rates of acid catalyzed dehydration and alkylation. A simple analysis of the reaction pathway would suggest that, to enhance alkylated products, one would want to maximize the conversion of MCONE to MCNOL on the metal catalyst (step 1). However, we will see below that this is not necessarily the case.

After MCNOL is dehydrated on the acid site, a fast C=C hydrogenation of the MCENE to MCANE (step 4) would be undesirable. In fact, from a process point of view, one might consider separate reactors, one undergoing full hydrogenation of cresol to MCNOL on a metal catalyst and a second one in which MCNOL will be co-fed with fresh cresol on an acidic material that would catalyze dehydration and alkylation. However, it is well-known that without a metal and

H₂ present, an acid catalyst rapidly deactivates under conditions favorable for dehydration and alkylation. Numerous examples in the literature [46-48] demonstrate that a close proximity of metal and acid sites in the zeolite can greatly improve catalyst stability as well as selectivity for reactions that require bifunctionality. Therefore, it is desirable to find a catalyst with the right metal/acid balance that can undergo the hydrogenation/dehydration/alkylation in one pot.

It seems that Pt is a more active hydrogenation catalyst than Pd and, as a result, the rates for both hydrogenation of the carbonyl (C=O) bond in MCONE and the double bond (C=C) in MCENE are high compared to the tandem dehydration/alkylation rates. Thus, high yields of MCANE are obtained with Pt/HY. In contrast, C=O double bond hydrogenation rates on Pd catalysts are low compared to dehydration/alkylation. Therefore, the MCONE yields are high. Therefore, it is important to evaluate experimentally and theoretically the relative rates and energy barriers over the two metals in the absence of the acid to compare their intrinsic activities.

3.3. Hydrogenation of 3-methylcyclohexanone and 3-methylcyclohexene over Pt and Pd. DFT calculations on Pt (111) and Pd (111).

Our DFT calculations show that 3-MCONE adsorbs on both Pd (111) and Pt(111) surfaces through the carbonyl oxygen. Without van der Waals interactions, the binding energy of 3-MCONE to Pd (111) surface is calculated to be -35 kJ/mol, which is stronger than on the Pt (111) surface (-25 kJ/mol). This is consistent with the relative oxophilicity of these two metals and the resulting shorter metal-oxygen (M-O) bond determined for Pd (0.282 nm) than for Pt (111). When van der Waals interactions are considered, the adsorption energy increases for both metals (-91 kJ/mol for Pd and -85 kJ/mol for Pt), which makes the relative difference smaller, but still shows that the M-O bond is stronger on Pd. The adsorption energy of hydrogen was also calculated for the two metals and also found to be stronger for Pd (-56 kJ/mol) than for Pt (-44 kJ/mol).

After calculating the adsorption energies, we calculated the energy barriers for the hydrogenation reaction. It is generally accepted that hydrogenation proceeds through two sequential steps [49]. In the case of hydrogenation of the -C=O bond of MCONE to form MCNOL the sequential H incorporation could occur by two different paths depending on whether the first H is added to the oxygen or the carbon of the carbonyl group, involving respectively a hydroxyalkyl or an alkoxide intermediate. We examined both paths and found that

the one involving the hydroxyalkyl intermediate was more favorable, which is in agreement with the previously reported hydrogenation of other ketones and aldehydes. [49] As illustrated in Figure 9 (a) for the case of Pd (111), the first H atom adsorbed on the metal surface can be added to the oxygen of the carbonyl group of MCONE to form a hydroxyalkyl intermediate via the metal-insertion mechanism. That is, in the transition state, the H atom inserts into the adsorbed carbonyl O and M atom. The energy barrier for this path was calculated to be 68 kJ/mol on Pd(111) but only 15 kJ/mol on Pt(111). The reaction energy was calculated to be 31 kJ/mol on Pd(111), which is also more endothermic than on the Pt(111) surface (-2 kJ/mol). This higher energy barrier and the more endothermic reaction energy on the Pd(111) surface than on the Pt(111) surface is in consistent with the stronger binding energy of MCONE as well as hydrogen on these two metal surfaces. In the second step, the formed hydroxyalkyl intermediate undergoes the second hydrogen incorporation to form MCNOL with an energy barrier of 88 kJ/mol on Pd(111) and 59 kJ/mol on Pt(111). Thus, the overall energy barrier for the hydrogenation of MCONE to form MCNOL is calculated to be 120 kJ/mol on Pd(111) surface, while 57 kJ/mol on the Pt(111) surface as summarized in the energy diagrams in Figure 9 (b). The calculated much lower energy barrier on the Pt(111) surface for the hydrogenation of MCONE than on the Pd(111) surface is in agreement with the experimental observation herein that on the Pt/HY catalyst, the majority of MCONE is hydrogenated to the alcohol MCNOL which then goes through the further dehydration and alkylation reactions, while on Pd/HY catalyst, we still see significant amounts of MCONE, as it is more difficult to hydrogenate on this metal.

In agreement with our results, previous DFT calculations [50-52] indicate that the free energy barrier for hydrogenation of C=O bonds is higher (i.e. lower rates) on Pd than on Pt surfaces. The lower activity of Pd has been usually linked to the stronger interactions of O with Pd than with Pt [53-55]. The stronger interaction of the reactant with the catalyst surface leading to lower rates indicates that Pt, on the activity volcano plot, is closer than Pd to the optimum M-O strength that maximizes hydrogenation. The latter, located to the right of the maximum in the volcano plot, would interact too strongly and would result in lower rate.

One could search for a metal that optimizes the binding with C and O atoms to reach the appropriate level of hydrogenation activity. However, by inspecting the reaction scheme in Figure 8, one can see that an ideal hydrogenation metal catalyst for maximizing alkylation selectivity would be one that maximizes the hydrogenation of the carbonyl double bond (C=O),

but not the C=C double bond in MCENE. That is, we would need to maximize the concentration of the alkylating agent (3-methylcyclohexene) by enhancing the rate of step (1) and reducing step (4). As mentioned above, under our reaction conditions, the dehydration reaction is fast enough to consider MCENE as the only alkylating agent.

Therefore, it is important to compare the energy barriers for the hydrogenation of MCENE, which will compete with the desirable alkylation reaction on Pd/HY and Pt/HY catalysts. Our DFT calculations indicate that MCENE adsorbs on both Pd(111) surface and Pt(111) surface through the 'di- σ ' modes with the binding energy of -50 kJ/mol on the Pd(111) surface and -71 kJ/mol on the Pt(111) surface. The weaker binding energy of the MCENE through the C=C double bond on the Pd(111) surface is in agreement with ethylene which also binds on the metal surfaces through the C=C double bond as the experiments showed that ethylene adsorbs more weakly on Pd(111) than on Pt(111) [56].

Similar to the hydrogenation of MCONE, the hydrogenation of MCENE also proceeds through two sequential elementary steps, as illustrated in Figure 10 (a) for Pd(111). The first H addition to one of the carbons of the C=C double bond in MCENE forms an alkyl intermediate, via a typical C-H-metal triangle transition state. In contrary to the case of MCONE, the energy barrier for this step is significantly lower on the Pd(111) surface (72 kJ/mol) than on the Pt(111) surface (82 kJ/mol). As shown in Figure 10 (a), the second step in the sequence also proceeds via the metal insertion mechanism. Again, the energy barrier for this step is also lower for Pd(111) than for Pt(111).

Therefore, according to the DFT calculations, Pd should not be as effective as Pt for hydroalkylation since Pd seems to have a lower activity than Pt for C=O hydrogenation and a higher activity for C=C hydrogenation. However, contrary to the predictions for the most effective metal drawn from the sequence in Scheme 1, Pd is much more effective than Pt at all metal/acid molar ratios (see Figure 6). As it will be shown in the experiments described below, the reason for this discrepancy might be that in the calculations we have not considered the role of competitive adsorption of MCONE, which forms stronger M-O bonds with Pd than with Pt. In addition, due to higher hydrogenation rate of Pt, neither MCONE nor MCNOL accumulates in the gas phase working with Pt catalysts as much as when working with Pd catalysts. Therefore, the rate of C=C bond hydrogenation may be much more significantly reduced in the presence of ketones on Pd than on Pt.

3.4. *Hydrogenation of 3-methylcyclohexanone and 3-methylcyclohexene over Pt and Pd. Experimental measurements over Pt/SiO₂ and Pd/SiO₂.*

As shown in Table 3, in agreement with the DFT predictions, it is experimentally verified that the rate of C=O hydrogenation is much higher on Pt than on Pd, which also agrees with the higher selectivity to MCONE obtained over Pd/HY catalyst compared to Pt/HY catalysts in the reaction of m-cresol. Also, in agreement with the trend in energy barriers calculated by DFT, Pd is much faster than Pt to hydrogenate the C=C bond. However, as mentioned above, the higher selectivity to alkylation on Pd/HY compared to Pt/HY (Table 1) would indicate that Pd should be less active than Pt for C=C hydrogenation (step 4 in Figure 8), which is the opposite trend to that observed in the direct comparison of the two rates (Table 3).

The most plausible explanation for this difference is that the high concentration of MCONE remaining in the gas phase when Pd is used as a catalyst may result in a strong competitive adsorption that inhibits the rate of MCENE hydrogenation. In fact, our DFT calculations indicate that the adsorption energy of MCONE on Pd (111) (-91 kJ/mol) is much higher than that of MCENE (-50 kJ/mol). Furthermore, the experimental evidence clearly shows that this is the case. As summarized in Table 3, co-feeding MCONE and MCENE (1:1 molar) results in a dramatic decrease in the rate of C=C hydrogenation. Moreover, this effect may be further enhanced during the reaction of m-cresol on Pd/HY, since under those conditions, the MCONE to MCENE ratio can be as high as 60:1 (Table 1). By contrast, the effect should be much lower over Pt catalysts. First, the adsorption energy is somewhat lower; second, and more important, during the m-cresol reaction over Pt/HY the MCONE to MCENE ratio is always low, thus reducing the effect of adsorption competition. As mentioned before, Pt is very active for hydrogenation of MCONE, and the zeolite is very active for the dehydration of MCNOL. Therefore, the self-inhibiting effect of Pd/HY catalysts that favors the selectivity to hydroalkylation is not present on Pt catalysts. That is, the low C=O hydrogenation rate on Pd/HY (step 1), which in principle is not desirable, causes the enhanced concentration of MCONE that in turn competes for active sites with MCENE, thus diminishing the C=C hydrogenation and consequently improving the alkylation selectivity (step 4 relative to 5 in Figure 8).

3.5. *Comparison of Hydroalkylation activity of Pd/HY and Pd/H-Mor zeolites*

Figure 11 illustrates the influence of the zeolite structure on the alkylation selectivity. When zeolite H-Mor was used as a support instead of HY the selectivity towards alkylated products severely decreased. Interestingly, in the two catalysts, the loading and dispersion of Pd were very similar and the overall conversion level was about the same. However, the Pd/H-Mor resulted in much lower yield of alkylated products. The main differences between these two zeolite supports are their density of acid sites and their structure. The lower Si/Al ratio of H-Mor makes it more acidic than HY. In fact, the IPA-TPD results confirm that the acid density in H-Mor is almost 4 times higher than HY (Table 1). Therefore, based on this characteristic alone, one would expect a higher alkylation activity since, as shown in Figure 5, the alkylation/MCANE ratio increases with the n_A/n_M ratio. That is, the large differences in hydroalkylation yields must be linked to the difference in structure of the two zeolites. In fact, this effect seems to be a clear example of shape selectivity, in which the three dimensional arrangement of zeolite HY supercages allows for the larger-sized alkylated molecules to form and leave the zeolite resulting in higher selectivity towards these products (Table 2). By contrast, the one-dimensional structure of zeolite H-Mor limits the formation of alkylation molecules leading to a dramatically lower selectivity. It can be observed that MCNOL and MCENE are readily formed but, without a favorable environment for alkylation (step 5), they undergo the unselective route (step 4) to MCANE. These results are in agreement with previous results reported by Zhao et al. [32], who compared the phenol hydroalkylation activity over H β and HZSM-5 zeolites and showed that the smaller pores in the latter limited the formation of alkylation products, which were more abundant in the former.

To further confirm the shape limiting effect of zeolite HMor for the formation of alkylation products we have co-fed m-Cresol and MCNOL over the bare HMor and HY zeolites. That is, by cofeeding the phenolic and the hydrogenated intermediate in the absence of metal, we could directly compare the role of the zeolites. In agreement with the results over the Pd containing zeolites, it was found that although HMor has a much higher acid density than HY, the yields of alkylation products were much lower over HMor than over HY (Figure 12), even when using a much longer reaction period for the former than for the latter. This result seems to confirm that the one-dimensional structure of zeolite H-Mor limits the formation of alkylation compounds compared to a zeolite (HY) with a more open three-dimensional pore structure.

3.6. *Changes in product distribution with catalyst deactivation and role of the metal*

Under conditions favorable for alkylation and dehydration over zeolites catalyst, deactivation by coke formation could potentially be a major drawback. It is thus important to investigate the extent of deactivation and its effects on product distribution since, as mentioned above, product selectivity is a function of a delicate acid/metal balance. A non-uniform deactivation of the acid and metal functions might disrupt the balance and, consequently, alter the product selectivity. Product selectivity is compared on Figure 13 as a function of conversion over two different series. In one of them, the conversion was varied by changing the catalyst mass, while keeping the reaction time constant and short. In the other series, the catalyst mass was kept constant, while the reaction time increased. In a batch reactor without deactivation, increasing the catalyst mass is equivalent to increasing the reaction time. However, when a significant deactivation is present, by running in the two different modes, we can uncouple the effects of conversion Vs. deactivation on product selectivity. The runs at short times minimize deactivation and show the variation of selectivity with conversion. The runs at longer times exhibit the different deactivation behavior of the two functions. Figure 13 shows that, in the case of the runs with minimum deactivation (conversion as a function of catalyst mass), the selectivity towards alkylation products (step 5) remains high over a broad range of conversion. In contrast, when deactivation is significant, the selectivity towards alkylation compounds drops considerably whereas selectivity towards MCANE (step 4) increases. Therefore, although the catalyst is not completely deactivated, partial deactivation causes a significant shift in product selectivity. Moreover, the preferential decrease in selectivity towards alkylation compounds suggests that the acid function in the Pd/HY catalyst is being deactivated more than the metal function. In fact, the selectivity towards MCONE (steps 1 and 2) does not change significantly with or without deactivation, suggesting that the metal function of the catalyst is not considerably deactivated. In essence, the effective acid/metal ratio in the catalyst decreases with catalyst deactivation and, consequently, the selectivity to alkylation products also decreases.

Figure 14 compares the evolution of activity of catalyst Pd/HY-A (high metal dispersion) and Pd/HY-C (low metal dispersion), with catalyst amounts adjusted to obtain the same initial conversion. While Pd/HY-A had a lower selectivity to alkylation and a lower overall activity, its rate of deactivation is slower than that of Pd/HY-C. It is clear that, with a higher metal dispersion, Pd/HY-A is more efficient in keeping the surface clean. The higher dispersion on

this catalyst not only provides a larger amount of surface metal available, but also maximizes the proximity of the particles to the acid sites. At the same time, the enhanced hydrogenation activity degrades the selectivity towards alkylation, as shown in Figure 5.

This result is a clear demonstration that it is important to use a bifunctional system to conduct simultaneously hydrogenation and alkylation. In principle, one could have proposed a two-reactor process, separately conducting hydrogenation of m-cresol to MCNOL first and then co-feed MCNOL and m-cresol over an acidic catalyst. A process like this would eliminate the problem of competing steps 4 and 5 (Figure 8). However, as shown here, the rate of deactivation of an acidic catalyst in the presence of an olefin (MCENE) and a phenolic compound, without metal and hydrogen present, is very fast. In fact, this problem is illustrated in Figure 15, which shows the evolution of conversion and selectivity when co-feeding m-cresol and MCNOL over bare HY zeolite in the batch reactor. It is clear that the alkylation reaction completely stops after the first hour even when there is enough m-cresol and MCENE to continue reacting.

We have also made a direct comparison of the deactivation behavior of HY and Pd/HY catalysts by comparing their activities as a function of time. Table 4 shows the conversion and alkylation selectivity for Pd/HY-C and bare HY at 1h and 7h. In the case of HY, the reaction stops after the first hour and there is no significant change in conversion or selectivity. On the other hand, over Pd/HY-C the conversion doubles from 1 to 7 hours, and even though the selectivity to alkylation is decreasing, the alkylation yield is still increasing. Demonstrating that even though the metal function seems to keep itself cleaner and hydrogenation is less affected than alkylation, the acid function is much better preserved in the presence of a metal than when it is by itself.

Conclusions

The selectivity of hydroalkylation of m-cresol catalyzed by bifunctional metal-doped zeolites depends on a delicate balance between the metal and acid activities. The former catalyzes hydrogenation of the aromatic ring that yields an intermediate ketone, which also needs to be hydrogenated to a saturated ring alcohol (methylcyclohexanol). The latter catalyzes the dehydration of this alcohol to an olefin that acts as the alkylating agent. At the same time, the metal can also catalyze hydrogenation of the olefin before it can alkylate an aromatic ring. Likewise, excessive hydrogenation activity may deplete the amount of unreacted aromatic rings,

thus reducing the alkylation rate. Therefore, to maximize hydroalkylation yield and selectivity a controlled hydrogenation activity is necessary. Moreover, a good metal/acid balance is also important to improve the catalyst life. Without a metal, the acid sites deactivate very quickly in the presence of MCENE and m-cresol. The metal helps keeping the acid sites active.

Since dehydration of MCNOL is much faster than alkylation, MCENE is more likely to be the main alkylating agent of the unreacted m-cresol to form bicyclic products. Therefore, by tuning the hydrogenating/alkylating activity of the catalyst, one could favor the hydrogenation of the double bond to form MCANE or else, favor the acid catalyzed alkylation of the aromatic ring of m-cresol. The ratio of acid sites to exposed metal sites in the catalyst (n_A/n_M) can be tuned to control the alkylation/hydrogenation activity ratio. Similarly, changing the nature of the metal catalyst results in improved selectivity towards alkylated products since it changes the hydrogenation activity.

Finally, it has been shown that the hydroalkylation of m-cresol requires a 3-dimensional pore structure like that of HY zeolite due to shape effects that dominate in this reaction. It is observed that despite having a higher acid density than the HY zeolite, a one-dimensional pore structure like that of H-Mor results in a much lower activity towards alkylation, both with and without the hydrogenation function.

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Figure 1. Transmission Electron Microscopy (TEM) images of Pd/HY catalyst (1%Pd, Zeolite Si/Al=30) of different dispersion levels. (A) High dispersion (CO/Pd = 0.43); (B) Medium dispersion (CO/Pd = 0.24; and (C) Lowest dispersion (CO/Pd = 0.05).

Figure 2. X-ray diffraction (XRD) of zeolites HY (Si/Al=30) and H-Mor (Si/Al=10) before and after depositing Pd metal, (a) HY; (b) Pd/HY-A; (c) H-Mor; (d) Pd/H-Mor

Figure 3. ^{27}Al MAS NMR of zeolites HY (Si/Al=30) and H-Mor (Si/Al=10) before and after depositing Pd metal, (a) HY; (b) Pd/HY-A; (c) Pd/HY-B; (d) Pd/HY-C; (e) H-Mor; (f) Pd/H-Mor

Figure 4. Effect of molar acid/metal ratio on alkylated products selectivity for Pt catalysts. Conversion: 62%. Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst reduction: 300 °C, 2100 kPa H₂, 1 hour. Catalyst amount: 1%Pt/HY30 (0.030g), 0.2%Pt/HY30 (0.150g).

Figure 5 . Effect of molar acid/metal ratio on alkylated products selectivity for Pd catalysts. Conversion: $\sim 62 \pm 3\%$. Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H_2 , stirring speed 400 rpm. Catalyst reduction: 200 $^{\circ}C$, 2100 kPa H_2 , 1 hour. Catalyst amount: Pd/HY-A (0.010g), Pd/HY-B (0.060g), Pd/HY-C (0.090g), Pd/HY-D (0.120g)

Figure 6. Comparison of ratio of yields of alkylation/MCANE for Pd and Pt catalysts as a function of acid/metal ratio. Conversion $\sim 62 \pm 3\%$. Reaction conditions: *m*-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H_2 , stirring speed 400 rpm, 1h. Catalyst reduction: 200 °C (Pd), 300 °C (Pt) 2100 kPa H_2 , 1 hour.

Figure 7. Effect of conversion on product selectivity for Pt (left) and Pd (right) catalysts. Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst reduction: 200 °C , 2100 kPa H₂, 1 h. Catalyst amount: Pd/HY-A (0.005g, 0.010g, 0.030g); Pd/HY-C (0.030g, 0.060g, 0.090g, 0.0120g)

Figure 8. Proposed pathway of m-Cresol hydrodeoxygenation and hydroalkylation

Figure 9 (a). Reactant, transition state and product structures for the two sequential steps hydrogenation of 3-methylcyclohexanone on Pd (111) surface.

Figure 9 (b). Energy diagrams for the two-step sequential hydrogenation of 3-methylcyclohexanone on Pd (111) and Pt(111) surfaces.

Figure 10 (a). Reactant, transition state and product structures for the hydrogenation of 3-methylcyclohexene on Pd (111) surface.

Figure 10 (b). Energy diagrams for the two-step sequential hydrogenation of 3-methylcyclohexanone on Pd (111) and Pt(111) surfaces.

Figure 11. Effect of zeolite support on alkylated products selectivity for Pd catalysts. Conversion 60%. Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst reduction: 200 °C, 2100 kPa psi H₂, 1 h. Catalyst amount: Pd/H-Mor (0.090g), Pd/HY (0.060g)

Figure 12. Alkylation activity of bare zeolite HY and H-Mor presented as yield from 3-methylcyclohexanol. Reaction conditions: m-Cresol (0.036 mol), methylcyclohexanol (0.036mol), Undecane (111.6 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst amount 0.030g. Reaction time: HY (1h), H-Mor (16 h). The initial moles of m-Cresol and MCNOL equal. Therefore the yield to alkylation from m-Cresol is the same as the yield to alkylation from MCNOL

Figure 13. Comparison of deactivation of Pd/HY-C for m-Cresol runs as a function of time and as a function of catalyst amount. FULL SYMBOL: Varying catalyst mass. OPEN SYMBOL: Varying time. Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst reduction: 200 °C , 2100 kPa psi H₂, 1 h.. VARYING TIME: Pd/HY-C (0.030g), time (1,3,5,7h). VARYING CATALYST MAS: Pd/HY-C (0.030g, 0.060g, 0.090g, 0.0120g), time (1h).

Figure 14. m-Cresol conversion Pd/HY-A (high metal dispersion) and Pd/HY-C (low metal dispersion) catalysts as a function of time. Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst reduction: 200 °C , 2100 kPa H₂, 1 h. Catalyst mas: 1%Pd/HY-A (5mg), 1%Pd/HY-C (30mg)

Figure 15. (a) Yield of products for m-Cresol + 3-methylcyclohexanol over bare HY. (b) Rate of alkylation as a function of time over bare HY. Reaction conditions: m-Cresol (0.036 mol), methylcyclohexanol (0.036mol), Undecane (111.6 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst amount 0.030g. Reaction time 1, 3, 5 and 16h.

Table 1. Ratio of acid sites to exposed metal sites in mmol H⁺/mmol metal exposed. Dispersion estimated from CO chemisorption; Acid density estimated from IPA-TPD

Catalyst	ICP Metal content	Dispersion	IPA TPD Acidity	BET surface area	Acid/metal molar ratio
	Weight %	CO/M	mmol H ⁺ /g	m ² /g	mmol H ⁺ /mmol M exposed
HY	0	-	0.35	734	-
HY (theoretical)	0	-	0.54	-	-
1%Pt/HY	0.9	0.56	0.26	678	10
0.2%Pt/HY	0.2	0.64	0.30	685	72
Pd/HY-A	1.0	0.43	0.33	697	8
Pd/HY-B	0.4	0.24	0.36	671	42
Pd/HY-C	0.8	0.05	0.35	708	77
Pd/HY-D	0.2	0.23	0.35		98
H-Mor	0	-	1.3	500	-
H-Mor (theoretical)	0	-	1.5	-	-
1%Pd/H-Mor	0.8	0.38	0.93	517	26
1%Pt/SiO ₂	0.8	0.23	-	167	0
1%Pd/SiO ₂	0.8	0.23	-	167	0

Table 2. Hydrodeoxygenation and hydroalkylation of m-cresol over different catalysts.· Reaction conditions: m-Cresol (0.036 mol), undecane (116.8 mL), stirring speed 400 rpm. Catalyst reduction: 300 °C (Pt) or 200 °C (Pd), 2100 kPa H₂, 1 hour

Entry	Catalyst	Catalyst Mass	Reaction Time	Pressure H ₂	m-Cresol Conversion	MCNONE	MCNOL	MCENE	Toluene	MCANE	Alkylated
		mg	h	kPa	%	Selectivity (%)					
1	1%Pt/HY30	30	1	5200	62	1.8	2.5	0.3	1.0	80	14
2	0.2%Pt/HY30	150	1	5200	62	1.3	Traces	0.3	1.3	76	20
3	0.2%Pt/HY30	150	8	2100	76	Traces	Traces	0.5	2.4	74	21
4	1%Pt/SiO ₂	30	1	5200	21	22	72	Traces	Traces	4.8	0.8
5	1%Pd/H-Mor	90	1	5200	61	74	1.4	0.2	0.6	19	4.7
6	1%Pd/HY30-A	10	1	5200	59	68	4.4	0.1	0.2	14	11
7	1%Pd/HY30-B	60	1	5200	66	35	0.2	0.4	0.6	21	40
8	1%Pd/HY30-C	90	1	5200	61	33	Traces	0.7	0.7	21	45

Table 3. Hydrogenation rates of methylcyclohexene and methylcyclohexanone over Pt and Pd supported on silica. .
 Reaction conditions: reactant (0.036 mol), undecane (116.8 mL), stirring speed 400 rpm, 5200 kPa H₂. Catalyst reduction: 300 °C (Pt) or 200 °C (Pd), 2100 kPa H₂, 1 hour

Catalyst	Reactant	Catalyst mass (mg)	T (°C)	time (h)	x (%)	Hydrogenation Rate mol / (mole-M s) ^a
1%Pt/SiO ₂	MCONE	90	200	13	57	0.09
1%Pd/SiO ₂	MCONE	90	200	12	41	0.04
1%Pt/SiO ₂	MCENE	60	50	1	4	0.13
1%Pd/SiO ₂	MCENE	30	50	1	48	1.7
1%Pd/SiO ₂	MCENE + MCONE (1:1)	30	50	1	17	0.3 ^b

^a Moles of reactant converted per mol of metal per second

^b Reflects the hydrogenation rate of methylcyclohexene. The hydrogenation rate of methylcyclohexanone is negligible at this temperature

Table 4. Comparison of conversion of m-Cresol and selectivity to alkylation of Pd/HY30-C and bare HY30.

Catalyst	Cresol Conversion 1 h	Cresol Conversion 7 h	Alkylation Selectivity 1 h	Alkylation Selectivity 7 h
HY ^(a)	25	27	30	32
Pd/HY-C ^(b)	21	42	48	30

^(a) Feed: m-Cresol (0.036 mol), methylcyclohexanol (0.036mol), Undecane (111.6 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst amount 0.030g.

^(b) Feed: m-Cresol (0.036 mol), undecane (116.8 mL), 5200 kPa H₂, stirring speed 400 rpm. Catalyst amount 0.030g. Catalyst reduction: 200 °C 2100 kPa H₂, 1 hour