Adsorbed species in transition metal catalyzed transformations studied by IR spectroscopy

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Abstract

Results of IR investigations are reported on several surface reactions over Pd and Ni catalysts supported on fumed silica (Cab-O-Sil). The catalysts were of low dispersion and were studied in: (a) double-bond isomerization of methylenecyclohexane (MCH), (b) ring opening of 1,1-dimethylcyclopropane (DMCP), and (c) ring opening of DMCP in the presence of D_2. It was found that during double-bond isomerization of MCH, H–D exchange (and OH–OD exchange on the support) also took place and an appreciable amount of hydrocarbon-like species remained attached to the surface of the catalysts. When DMCP 'alone' was introduced into the system, dissociative adsorption occurred (scission of one or more C–H bonds preceded C–C bond rupture). Strongly adsorbed hydrocarbon-like residues were also formed. When a DMCP + D_2 mixture was allowed to react on the catalysts, measurements indicated adsorption of a dissociative type over Pd/CS and Ni/CS. In the presence of D_2 coking was slow, there was no sign of hydrocarbon-like residues in the IR spectra of Pd/CS, i.e., product precursors could be desorbed with the help and participation of D_2. At 473 K Ni/CS probably underwent coking, however, these hydrogen-poor carbonaceous species were not detectable by IR spectroscopy.

Keywords: H–D exchange; Methylenecyclohexane; 1,1-Dimethylcyclopropane; 1,1-Dimethylcyclopropane and D_2 mixture; Silica-supported Pd and Ni catalysts; Surface IR spectroscopy

1. Introduction

In understanding the behavior of heterogeneous catalysts, information concerning surface chemistry of various transformations is crucial. Since a catalytic reaction involves several, often not very easily resolvable steps, obtaining reliable knowledge requires many, usually complementary methods. Kinetic investigations give rate and selectivity data and frequently serve with indirect indications about the adsorbed species as well. Acquiring direct information about the mode of adsorption is indispensable, though it is not easy by far. Surface sensitive instrumental methods, which see adsorbed species, have very poor time resolution at least in the timescale of surface chemical reactions, and even poorer resolution in that of the elementary steps. In spite of this drawback, instrumental methods are able to give valuable information about surface chemistry [1]. The reliability of the observations is enhanced if knowledge obtained from instrumental methods is complemented with kinetic measurements, i.e., the cat-

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alysts *and* the probe molecule(s) are studied together [2,3].

In this contribution we report on possible adsorption modes of various probe molecules over silica-supported Pd and Ni catalysts. The molecular probes were methylenecyclohexane, 1,1-dimethylcyclopropane, and 1,1-dimethyl-cyclopropane in the presence of D_2.

The double-bond isomerization reactivity of methylenecyclohexane was observed before [4,5].

Kinetically speaking, 1,1-dimethylcyclopropane did not react over these metals since they did not give a desorbed product. Neither was D-exchanged cyclopropane formed [6].

We have published a series of papers on the ring opening and occasionally isomerization activities of, among other substituted derivatives, 1,1-dimethylcyclopropane in the presence of hydrogen over silica-supported Pd [7] and Ni [8] catalysts. As part of the discussion, the main conclusions of these kinetic studies will also be summarized.

2. Experimental

2.1. Materials

2.1.1. Support and catalysts

Cab-O-Sil M5 (CS) is a non-acidic fumed silica of BDH, which is widely used as a catalyst support when inertness is a requirement (BET surface area: 241.6 m^2 g^{-1}, the number of surface OH groups after 1-hour flow under dry N_2 at 673 K is 1.9×10^{18} m^{-2}, determined with dimethylzinc tetrahydrofuranate following the method described in Ref. [9]). It was used in the preparation of the catalysts in this study.

The 3.0% Pd/Cab-O-Sil (Pd/CS) and the 3.0% Ni/Cab-O-Sil (Ni/CS) catalysts were prepared by impregnating the support with the aqueous solution of the appropriate metal salts ($PdCl_2$ and $Ni(NO_3)_2$, respectively), followed by reduction in flowing hydrogen at 773 K for 16 hours. The high-temperature hydrogen treat-

ment diminished the chlorine content of the Pd/CS catalyst, as revealed by X-ray fluorescence spectroscopy: for details, see Ref. [7]. The dispersion values (number of exposed metal atoms/number of total metal atoms) of the catalysts were 15.4% for Pd/CS and 6.8% for Ni/CS. The latter value was determined by H_2 chemisorption. Dispersion value of the Pd/CS catalyst was measured by CO chemisorption in a pulse system at room temperature. In all the calculations 1:1 adsorption stoichiometry was assumed and applied.

2.1.2. Compounds

1,1-Dimethylcyclopropane (DMCP) was prepared and purified via published methods [10]. The compounds were gas chromatographically pure and were used after several freeze–thaw–evacuate cycles (2.66 kPa for a run).

Methylenecyclohexane (MCH) was a Fluka product with purity higher than 98%. It was used without further purification (1.33 kPa for a run).

Oxygen-free D_2 was obtained from a Matheson 8326 generator, operating with a palladium membrane. 13.3 kPa of D_2 was used for a run and 79.8 kPa for pretreatment.

2.2. Instrumentation and procedure

2.2.1. Kinetic measurements

Kinetic investigation was carried out in a conventional closed circulation apparatus. The volume of the reactor was 54 cm^3, and the total volume of the system was 175 cm^3. The reactor was heated with an air thermostat. The volume of the sampling capillary was 0.05 cm^3, and the total sampling volume was 0.3 cm^3. A Carlo Erba Fractovap 2150 gas chromatograph with a flame ionization detector was attached to the system. A 4-m-long all-glass column filled with 5% bis(2-methoxyethyl)adipate on Chromosorb PAW 80/100 mesh was used for analysis.

Before the reaction the catalyst was activated for an hour under flowing hydrogen at the reaction temperature and the reactants (1.33 kPa of

DMCP and various amounts of hydrogen) were premixed in the circulation part of the system.

At a certain hydrogen pressure, initial rates were determined always over a fresh sample of catalysts (10 mg). These rates were converted to turnover frequency (TOF: molecule exp. atom^{-1} s^{-1}) data on the basis of exposed metal atoms, calculated from dispersion values.

2.2.2. Infrared measurements

Infrared (IR) spectroscopic studies were performed in a Specord 71 IR apparatus (Carl Zeiss, Jena) equipped with a static cell. Self-supporting wafers made from 24.0 ± 0.5 mg of catalyst were used in the measurements. Evacuation after pretreatment was carried out to a residual pressure of 10^{-2} Pa before the spectra were registered. Spectra were taken in transmittance mode in the 4000–2000 cm^{-1} (though no bands were found between 2400 and 2000 cm^{-1}). Under 2000 cm^{-1} the strong bands of silica largely covered the weak CH vibrations.

The catalysts were pretreated in D_2 at 673 K for 2 hours. MCH was adsorbed at 423 K over each catalyst. The mass spectra of the recovered samples were taken on a Q 300 C (Atomki, Hungary) quadrupole mass spectrometer and isomerized and D-exchanged products were searched for. The temperature of DMCP adsorption was 298 or 373 K over Pd/CS and 298 or 473 K over Ni/CS. These temperatures were applied as well when the mixture of DMCP and D_2 was adsorbed over the catalysts. After adsorption, the system was evacuated and cooled to 298 K. Spectra were recorded at this temperature.

2.3. Method of infrared measurements

The basic method was as follows: (i) a self-supported wafer prereduced in H_2 was treated with D_2 at 673 K, (ii) reactions (the double-bond isomerization of methylenecyclohexane (MCH), the ring opening of 1,1-dimethylcyclopropane (DMCP), and the ring opening of DMCP in the presence of D_2) were performed over the deuterated catalysts, and (iii) changes in the form and intensity of the OH band (3300–3700 cm^{-1}) and those of the OD band (2500–2750 cm^{-1}) were monitored.

3. Results

3.1. Effect of D_2 treatment on the OH groups of the pure support and the catalysts

The OH content of Cab-O-Sil is generally lower than that of Al_2O_3. Nevertheless, even a fumed silica support contains an appreciable amount of surface OH groups even after evacuation at 673 K. An appreciable amount of OH groups (broad band in the range of 3300–3700 cm^{-1}) could be transformed with D_2 to OD groups (sharp band between 2500 and 2750 cm^{-1}) only at temperature as high as 673 K.

The presence of transition metal on the support facilitated fast and near complete H–D exchange of surface OH groups (denoted as OH–OD exchange in the following) at room temperature. When deuterated catalysts were prepared, 673 K and 79.8 kPa were chosen as standard. Obviously, under these conditions the H–D exchange was complete.

3.2. Adsorption and reactions of MCH

Over acidic catalysts, MCH undergoes double-bond isomerization. However, the Cab-O-Sil support is not acidic enough for isomerization to occur. Neither did H–D exchange in the compound and, thus, OH–OD exchange take place over the pure support.

The results of mass spectrometric analysis revealed that over the Cab-O-Sil supported metals, both double-bond isomerization and H–D exchange in the molecule proceeded. Infrared measurements could verify the latter observation since OH–OD exchange in the hydroxyl groups of the catalyst could be detected. At 423 K, over the D_2-pretreated catalysts the OD band diminished, while the OH band reappeared (see, e.g., Fig. 1). A new band showed up over the
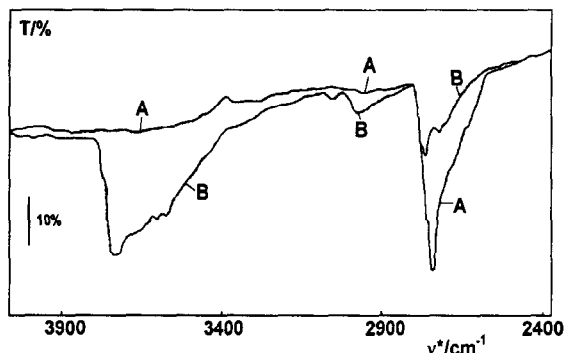
Fig. 1. IR spectra of Ni/CS pretreated with D_2 for 2 hours at 673 K followed by evacuation for 2 hours (A), then contacted with MCH at 423 K for 30 min followed by evacuation for 2 hours (B).

catalysts at around 3000 cm^{-1} during the reaction, and it survived evacuation.

3.3. Interactions of DMCP 'alone' with catalytic surfaces

The support itself proved to be inactive in H–D exchange at 298 K: the OD band did not change measurably even after a 16-hour contact with the cyclopropane.

Decrease in the intensities of the OD bands and concomitant increase in the OH bands were observed over the supported metal catalysts at the temperatures applied (Pd/CS: 298 or 373 K and Ni/CS: 298, 473 K) (see, e.g., Fig. 2).

New bands at 3000 cm^{-1} species could also be recorded over each catalyst. These bands

survived even high-vacuum evacuation. Moderate elevation of temperature did not change or just slightly increased the intensities of these bands over Pd/CS. However, when the contact time became significantly longer (from 0.5 hour to 16 hours) over Pd/CS, they increased appreciably (compare spectra C and D in Fig. 2). Interestingly, the intensity of this band was smaller at 473 K over Ni/CS than at 298 K.

3.4. The behavior of a DMCP + D_2 mixture over the catalysts

3.4.1. Kinetic measurements

At 373 K over Pd/CS and 473 K over Ni/CS, DMCP underwent hydrogenative ring opening in the presence of H_2, giving neopentane (2,3 C–C bond rupture) as major and isopentane as minor products. Hydrogenative ring opening was the predominant (Ni/CS) or the exclusive (Pd/CS) transformation pathway at these temperatures. Hydrogen pressure severely influenced the rate of product formation: the accumulation of both products can be described by maximum curves as the hydrogen pressure rises over both catalysts (Fig. 3 and Fig. 4).

3.4.2. Infrared measurements

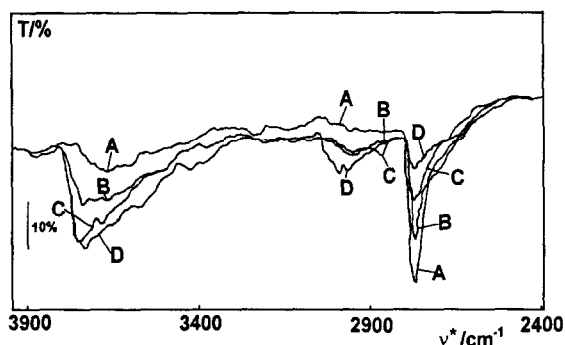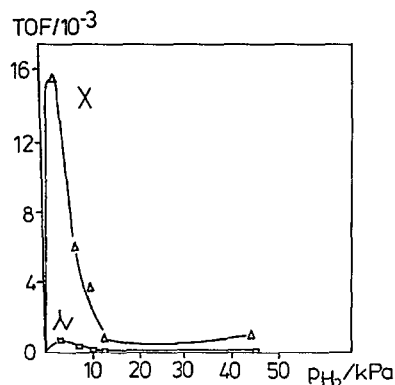When a mixture of D_2 and DMCP was admitted into the IR cell, onto the deuterated

Fig. 2. IR spectra of Pd/CS pretreated with D_2 for 2 hours at 673 K followed by evacuation for 2 hours (A), then contacted with DMCP at 298 K for 30 min (B) or at 373 K for 30 min (C), at 373 K 16 hours (D), each step followed by evacuation for 2 hours.

Fig. 3. Formation of the ring-opening products vs. H_2 pressure for DMCP over Pd/CS at 373 K (TOF: molecule exp. atom^{-1} s^{-1}).
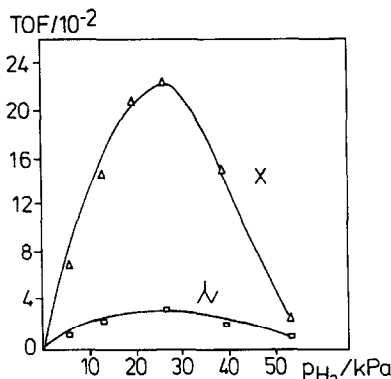
Fig. 4. Formation of the ring-opening productsvs. H_2 pressure for DMCP over Ni/CS at 473 K (TOF: molecule exp. atom^{-1} s^{-1}).

Fig. 6. IR spectra of Pd/CS pretreated with D_2 for 2 hours at 673 K followed by evacuation for 2 hours (A), then contacted with DMCP + D_2 at 298 K for 30 min (B) or for 30 min at 373 K (C) and for 16 hours at 373 K (D), each step followed by evacuation for 2 hours.

catalysts, the OD band remained intact over Pd/CS, but decreased somewhat over Ni/CS. The bands around 3000 cm^{-1}, detected when DMCP was adsorbed without hydrogen, did not show up over Pd/CS. Over Ni/CS, however, it could be registered at 298 K, but not at 473 K (compare spectra B and C in Fig. 5).

Over Pd/CS, the OH band reappeared at 298 K (Fig. 6, spectrum B). The intensity increase could be measured at 373 K after 30 min contact time (Fig. 6, spectrum C). After 16 hours, decrease in OH band intensity was observed (Fig. 6, spectrum D).

Over Ni/CS, a large OH band was registered after a 30 min contact with the reaction mixture at 298 K (Fig. 5, spectrum B). The band re-
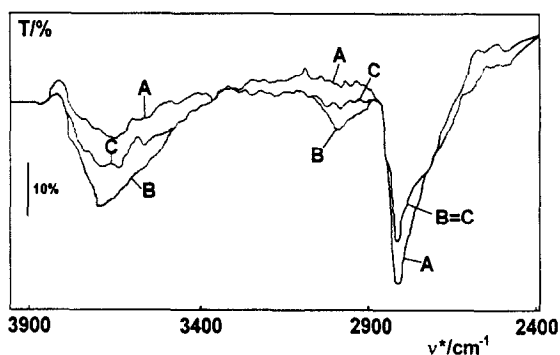
mained measurable at 473 K, but with considerably smaller intensity (Fig. 5, spectrum C).

4. Discussion

Interpretation of results obtained with MCH is relatively straightforward. Double-bond isomerization occurred upon adsorption. The elementary steps include the scission as well as the formation of C–C and C–H bonds (cracking was not observed). OH–OD exchange on the support of the catalysts indicated that the process was not monomolecular. Hydrogen dissociated from the molecule did not undergo 1,3 shift (at least not in significant extent). It became part of the hydrogen pool of relatively strongly adsorbed hydrocarbon-like species and/or simply adsorbed on surface metal atoms, and took part in the exchange of surface OD groups as well. The amount of hydrogen-containing carbonaceous species was appreciable (the band around 3000 cm^{-1} is assigned to hydrocarbon-like species after refs. [11–13]) and they probably participated in H–D exchange reactions with surface OH groups as well. Thus, deuterium observed in the recovered isomerization product should have come directly from surface OD groups and/or indirectly from the hydrocarbon-like layer.

Fig. 5. IR spectra of Ni/CS pretreated with D_2 for 2 hours at 673 K followed by evacuation for 2 hours (A), then contacted with DMCP + D_2 at 298 K for 30 min (B) or for 30 min at 473 K (C), each step followed by evacuation for 2 hours.
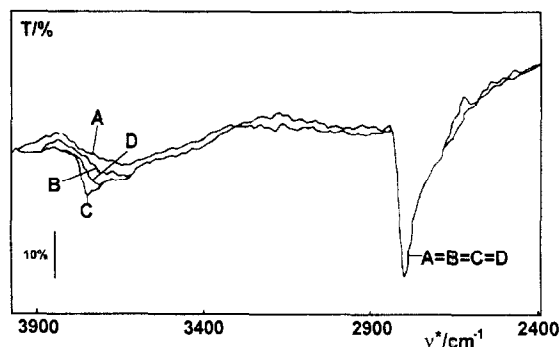
Before entering the discussion of catalysts DMCP 'alone' or catalysts DMCP plus D_2 interactions, results and interpretation of kinetic measurements are summarized briefly.

DMCP 'alone' but even in the presence of H_2 (or D_2) adsorbed irreversibly over these transition metal surfaces. In the absence of H_2 (or D_2) product desorption could not be observed. Hydrogen (or deuterium) facilitated product desorption, which were saturated hydrocarbons over Pd/CS and Ni/CS reduced at high temperature. Product formation rate vs. hydrogen pressure functions yield mechanistic information. On the basis of the curve shapes, dissociative adsorption was proposed for hydrogenative ring opening over Pd/CS at 373 and Ni/CS at 473 K. The observed shape might have been due to a competition between DMCP and hydrogen, in which excess hydrogen sweeps the reactant off the surface. However, cyclopropane and its derivatives are known to be irreversibly adsorbed over these metal surfaces [6], thus, maximum curve reflects the chemistry of the surface reaction.

IR spectroscopic measurements revealed that DMCP 'alone' adsorbed dissociatively over the catalysts. The appearance of the new band at 3000 cm^{-1} was assigned to carbonaceous deposits [11–13], which were strongly bound, relatively hydrogen-rich species. Over Pd/CS they were bound strongly, since they survived evacuation. They were hydrogen-rich because they were not observed when D_2 was also present, i.e., they were ring-opening product precursors and could be hydrogenated off the surface at low temperature. These hydrocarbon-like species could be detected over Ni/CS at 298 K, but their hydrogen content rapidly diminished at 473 K forming coke-like species. These coke deposits were no longer product precursors of the ring opening, i.e., they could not be removed with D_2.

The presence of deuterium altered the surface reactions, occasionally profound changes could be observed. One important change was the lack of the band around 3000 cm^{-1}. It should be noted that in this respect Ni/CS was an exception. At 298 K the band remained detectable even in the presence of D_2. It should also be noted that the OD band intensity decreased at a temperature as low as 298 K, but there was no further decrease at 473 K. The reason for this behavior is not quite clear yet. A possible reason, which is supported by the kinetic measurements, might be that there was no kinetically detectable (i.e., measurable by gas chromatography) ring opening at low temperature. Nevertheless, surface reactions occurred: very intense OH band appeared indicating dissociative adsorption and the carbonaceous deposits still rich in hydrogen at this temperature might have collected more deuterium from the surface OD groups. Perhaps the reverse reaction of OH–OD exchange is also slower at 298 K.

The appearance of the OH band during the reaction of DMCP + D_2 mixture over predeuterated catalysts is clear evidence of dissociative adsorption, since there were no hydrogen atoms in the system other than those of the hydrocarbon. This means that C–H bond rupture occurred over Pd/CS and Ni/CS. These dissociatively adsorbed species could be deadends, however. Nevertheless, when the interpretation deduced from kinetic measurements and IR results coincide as they do over these two metals, one is tempted to state that hydrogenative ring opening of DMCP proceeds through dissociatively adsorbed species.

5. Conclusion

The results of combined kinetic and surface infrared measurements revealed that DMCP and MCH undergo hydrogenative ring opening and double-bond isomerization via dissociatively adsorbed species. It was also found that in the absence of hydrogen (or deuterium) DMCP adsorbs irreversibly and dissociatively as well, however, product desorption only occurs when added hydrogen (or deuterium) is present.

Acknowledgements

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