n-Pentane carbonylation with CO on sulfated zirconia: an *in situ* solid-state ^{13}C NMR study

Mikhail V. Luzgin, Alexander G. Stepanov,* Vera P. Shmachkova and Nina S. Kotsarenko

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 3832 34 3056; e-mail: a.g.stepanov@catalysis.nsk.su

10.1070/MC2001v011n01ABEH001345

Using ^{13}C CP/MAS NMR, the first evidence has been obtained for *n*-pentane carbonylation with carbon monoxide into C_6 aldehydes, ketones and carboxylic acids on a sulfated zirconia catalyst.

Since the discovery of its strong catalytic activity,[1] sulfated zirconia (SZ) has found potential applications as a catalyst. The strong acidity of SZ opens up new, yet to be studied feasibility of its using as a catalyst, especially for light alkanes conversion.[2] Among the promising applications of SZ is a direct conversion of alkanes into carbonyl-containing compounds, which are of great importance for industrial organic chemistry. It is a common knowledge that alkanes can be carbonylated with carbon monoxide in superacids,[3] in the presence of polyhalomethane-based superelectrophilic systems[4] and in the presence of aluminium chloride as the strong solid Lewis acid.[5] In this paper, using *in situ* solid state ^{13}C NMR spectroscopy,[†] we present the first evidence for *n*-pentane carbonylation with CO on pure SZ as a catalyst.

Figure 1 displays the ^{13}C CP/MAS NMR spectra of the products formed from *n*-pentane and CO on SZ at 70 °C.[‡] If unlabelled *n*-pentane and ^{13}C-labelled carbon monoxide were coadsorbed [Figure 1(*a*)], the most intense signal becomes visible at 231 ppm from the ^{13}C-labelled carbonyl groups of both aldehydes and ketones, strongly interacting with SZ acid sites.[8] In case of using [2-^{13}C]*n*-pentane **1** and unlabelled CO, only ^{13}C-labelled groups were observed in the ^{13}C NMR spectra: both 2-$^{13}CH_2$ group of **1** and carbon atoms in which the 2-$^{13}CH_2$ group is transformed during the reaction. The following spectral features from the reaction products appeared in the spectrum [Figure 1(*b*)]. Besides the signal from the labelled $^{13}CH_2$ group of unreacted **1** at 24.5 ppm,[6,9] two intense signals at 32.2 and 33.8 ppm [Figure 1(*b*)] arise from the product of *n*-pentane isomerization, isopentane **5** with ^{13}C-labels at the CH and CH_2 groups, respectively.[9] Nine signals from the aliphatic fragments of the carbonylation products are also readily identified in this spectrum [Figure 1(*b*),(*c*)] at 22.5–54.3 ppm. Six of them, namely, at 22.5, 29.1, 36.7, 46.3, 50.8 and 54.3 ppm, originate from 2-methylpentanal **6**, 2-ethylbutanal **7**, 2-methylpentan-3-one **9** and 3-methylpentan-2-one **10** (see Scheme 1[§]). We further confirmed the formation of the aldehydes and ketones by high-resolution ^{13}C NMR analysis of the products extracted with Et_2O from SZ.[¶,††]

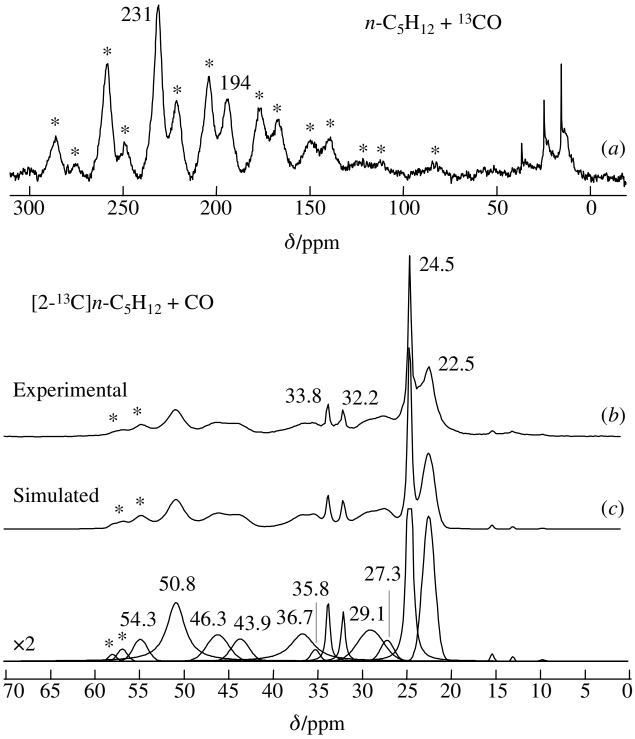


Figure 1 ^{13}C CP/MAS NMR spectra of the products formed from *n*-pentane and CO on sulfated zirconia at 70 °C: (*a*) coadsorption of ^{13}CO and *n*-C_5H_{12}; (*b*) coadsorption of the [2-^{13}C]*n*-C_5H_{12} and CO; (*c*) simulation of experimental spectrum (*b*). Asterisks (*) denote spinning side bands.

The less intense signal at 194 ppm [Figure 1(*a*)], belonging to ^{13}COOH carboxylic groups,[7,11] points to the formation of carboxylic acids in addition to aldehydes and ketones. The

---

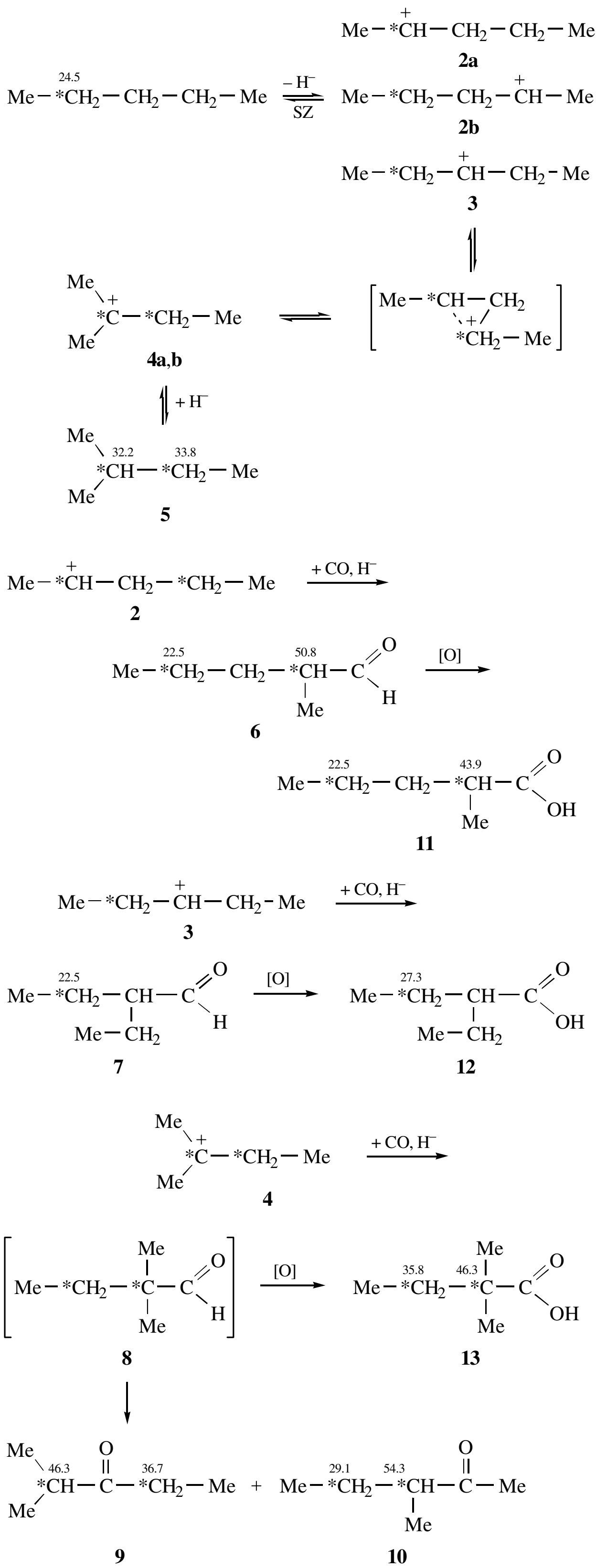
[†] *General experimental details.* A SZ sample of low temperature tetragonal phase with a surface area of 60 m^2 g^{-1} and 9.9 wt.% of SO_3 content was synthesised according to the procedure described earlier.[6] The SZ sample was calcined at 600 °C in air and at 400 °C in a vacuum (10^{-3} Pa) for 2 h. Equal amounts of *n*-pentane and CO (or *n*-pentane, CO and H_2O) (*ca.* 300 μmol g^{-1} of each coadsorbate) were adsorbed on SZ in a vacuum at the temperature of liquid nitrogen. After sealing a glass tube with the SZ sample off from the vacuum system, it was heated at 50–150 °C for 1 h, the initial pressure of CO in the sealed tube could reach 10 atm at 150 °C. The reaction products were analysed *in situ* by ^{13}C CP/MAS NMR in the sealed glass tubes containing the catalyst with adsorbed reaction products and *ex situ* by high-resolution ^{13}C NMR spectroscopy in $CDCl_3$ solution. ^{13}C NMR spectra with cross-polarization and magic angle spinning (^{13}C CP/MAS NMR) and high-resolution ^{13}C NMR spectra in solution were recorded on a Bruker MSL-400 NMR spectrometer at room temperature (~23 °C). The conditions used for CP experiments are described in ref. 7, the spinning rate was 3–4 kHz. A few thousands of scans have been collected for each spectrum. The ^{13}C chemical shifts for carbon nuclei were measured with respect to TMS as an external standard. To facilitate NMR analysis, *n*-pentane labelled with ^{13}C at the second carbon atom, [2-^{13}C]*n*-pentane (82% isotope enrichment), or ^{13}CO (90% isotope enrichment) were used in NMR experiments. [2-^{13}C]*n*-Pentane was prepared from [1-^{13}C]ethanol (82% ^{13}C) *via* a six-step synthesis.

[‡] To follow selectively the transformation of the initial reactants and for the identification of reaction products adsorbed on SZ by ^{13}C NMR, either CO or *n*-pentane labelled with the ^{13}C isotope were used. In this case only signals from ^{13}C-labelled carbon atoms in both reactants and reaction products were preferentially observed in the spectrum.

[§] In Scheme 1, ^{13}C chemical shifts for the carbons in the adsorbed initial [2-^{13}C]*n*-pentane and reaction products are indicated only above the carbons with ^{13}C labels expected in these carbon atoms as the result of the reaction according to Scheme 1.

[¶] The products exhibited the following ^{13}C NMR chemical shifts in $CDCl_3$ solution, δ: **6**, 13.2 (Me), 13.9 (5-Me), 20.2 (4-CH_2), 32.8 (3-CH_2), 46.1 (2-CH), 204.7 (C=O); **7**, 11.3 (Me), 21.5 (CH_2), 55.0 (CH), 204.8 (C=O); **9**, 7.7 (Me), 18.3 [$(Me)_2$], 33.4 (CH_2), 40.6 (CH), 214.5 (C=O); **10**, 11.5 (5-Me), 15.7 (Me), 25.9 (4-CH_2), 27.9 (1-Me), 48.7 (3-CH), 212.0 (2-C=O). The data are in complete accordance with the chemical shifts for these compounds.[10]

[††] The conversion of *n*-pentane was 41% at 70 °C. The selectivity towards the reaction products was as follows: **5**, 35%; **6**, 12%; **7**, 8%; **9**, 18%; **10**, 15%; **11**, 5%; **12**, 2.5%; and **13**, 4%.



Scheme 1

signals from ^{13}C-labelled aliphatic carbons of the acids at 22.5, 27.3, 35.8, 43.9 and 46.3 ppm belong to 2-methylpentanoic **11**, 2-ethylbutanoic **12** and 2,2-dimethylbutanoic **13** acids‡‡ (see Scheme 1§).

When the reaction was carried out in the presence of water, carboxylic acids **11**–**13** were formed as the only products of *n*-pentane carbonylation. No signals from aldehydes and ketones were observed (Figure 2).§§

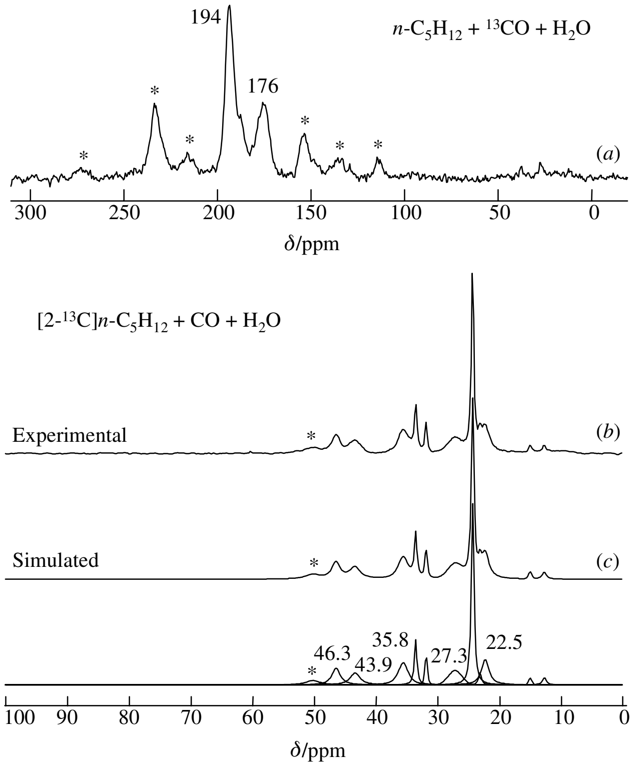


Figure 2 ^{13}C CP/MAS NMR spectra of the products formed from *n*-pentane, CO and water on sulfated zirconia at 150 °C: (*a*) coadsorption of ^{13}C-labelled CO, unlabelled *n*-C_5H_{12} and water; (*b*) coadsorption of [2-^{13}C]*n*-C_5H_{12}, unlabelled CO and water; (*c*) simulation of experimental spectrum (*b*). Asterisks (*) denote spinning side bands.

Thus, the following processes occur in the interaction of *n*-pentane with CO on SZ (see Scheme 1). Two secondary carbenium ions **2** and **3**, which seem to be generated *via* hydride abstraction from *n*-pentane by SZ, react further with CO and the hydride ion to produce **6** and **7**. In addition, *n*-pentyl cation **2** undergoes isomerization giving rise to tertiary isopentyl cation **4**, from which **5** evolves. 2,2-Dimethylbutanal **8**, whose formation from **4** could be expected, was not detected. Instead, two ketones **9** and **10** are generated according to the well-known property of aldehydes with a carbonyl group attached to a quaternary carbon atom to rearrange in liquid acid[3(*b*),13] and in the presence of solid $AlCl_3$[5(*c*),5(*e*),14] by an alkyl shift to form the corresponding ketone.

Acids **11**–**13** seem to be formed by partial oxidation of aldehydes[15] **6**, **7** and **8** with SZ sulfate groups,[16] complete oxidation of aldehydes to acids occurs in the presence of water.[15]

There are two alternative routes for aldehyde formation from *n*-pentane. One of them involves hydride abstraction from the alkane with the formation of carbenium ions **2** and **3**, the subsequent formation of oxocarbenium ions, which are further reduced under acidic hydride-transfer conditions. The other implies direct formylation of the alkane by the formyl cation [H^+CO].[3(*b*)] Evidence for the reaction of *n*-pentane carbonylation by the first route is the formation of **5**, which implies hydride abstraction from **1** to form intermediate cations **2** and **4**. The formation of intermediate formate species on SZ with a signal at 176 ppm from the –HCO fragment[17] [Figure 2(*a*)] is in

---

‡‡ The carboxylic acids extracted with Et_2O from the catalyst reveal the following ^{13}C NMR chemical shifts in $CDCl_3$ solution, δ: **11**, 13.9 (5-Me), 16.8 (Me), 20.5 (4-CH_2), 35.9 (3-CH_2), 39.4 (2-CH), 183.9 (1-COOH); **12**, 11.8 (Me), 24.9 (CH_2), 49.0 (CH), 183.3 (COOH); **13**, 9.2 (Me), 24.5 [$(Me)_2$], 33.3 (CH_2), 42.6 (C), 185.4 (COOH). The data are in complete accordance with the chemical shifts for these compounds.[12]

§§ In the presence of water, the conversion of *n*-pentane was 40% at 150 °C with the following selectivity: **5**, 83%; **11**, 5%; **12**, 5%; and **13**, 7%.

favour of the second route. The formyl cation can be formed from formate as an equilibrated species. To date, we cannot elucidate by which of the two routes the carbonylation occurs. We assume that both routes for aldehyde formation are possible, similarly to the case with isobutane carbonylation on SZ.[18]

In conclusion, this work represents the first example of *n*-pentane carbonylation on a SZ catalyst. This study opens up new possibilities of using SZ catalysts for direct carbonylation of alkanes to produce valuable chemical products (carboxylic acids, aldehydes and ketones).

This research was supported by the Russian Foundation for Basic Research (grant no. 99-03-32454). We are grateful to A. V. Krasnoslobodtsev for his assistance in the extraction experiments and to V. N. Zudin for the synthesis of ^{13}C-labelled *n*-pentane.

References

1 M. Hino, S. Kobayashi and K. Arata, *J. Am. Chem. Soc*., 1979, **101**, 6439.

2 X. Song and A. Sayari, *Catal. Rev. Sci. Eng*., 1996, **38**, 329.

3 (*a*) R. Paatz and G. Weisberger, *Chem. Ber*., 1967, **100**, 984; (*b*) O. Farooq, M. Marcelli, G. K.S. Prakash and G. A. Olah, *J. Am. Chem. Soc*., 1988, **110**, 864; (*c*) S. Delavarenne, M. Simon, M. Fauconet and J. Sommer, *J. Am. Chem. Soc*., 1989, **111**, 383.

4 I. Akhrem, A. Orlinkov, L. Afanas'eva, P. Petrovskii and S. Vitt, *Tetrahedron Lett*., 1999, **40**, 5897.

5 (*a*) H. Hopff, *Ber*., 1931, **64**, 2739; (*b*) H. Hopff, *Ber*., 1932, **65**, 482; (*c*) H. Hopff, C. D. Nenitzescu, D. A. Isacescu and I. P. Cantuniari, *Ber. Dtsch. Chem. Ges. B*, 1936, **69**, 2244; (*d*) H. Pines and V. N. Ipatieff, *US Patent*, 2346701, 1944; (*e*) A. T. Balaban and C. D. Nenitzescu, *Liebigs Ann. Chem*., 1959, **625**, 66.

6 V. M. Mastikhin, A. V. Nosov, S. V. Filimonova, V. V. Terskikh, N. S. Kotsarenko, V. P. Shmachkova and V. I. Kim, *J. Mol. Catal*., 1995, **101**, 81.

7 M. V. Luzgin, A. G. Stepanov, A. Sassi and J. Sommer, *Chem. Eur. J*., 2000, **6**, 2368.

8 D. H. Barich, J. B. Nicholas, T. Xu and J. F. Haw, *J. Am. Chem. Soc*., 1998, **120**, 12342.

9 A. G. Stepanov, V. N. Sidelnikov and K. I. Zamaraev, *Chem. Eur. J*., 1996, **2**, 157.

10 G. E. Hawkes, K. Herwig and J. D. Roberts, *J. Org. Chem*., 1974, **39**, 1017.

11 A. G. Stepanov, M. V. Luzgin, V. N. Romannikov, V. N. Sidelnikov and K. I. Zamaraev, *J. Catal*., 1996, **164**, 411.

12 P. A. Couperus and A. D. Clague, *Org. Magn. Reson*., 1978, **11**, 590.

13 (*a*) S. Danilow and E. Vanus-Danilowa, *Ber. Dtsch. Chem. Ges. B*, 1926, **59**, 377; (*b*) G. A. Olah, D. H. O'Brien and M. Calin, *J. Am. Chem. Soc*., 1967, **89**, 3582.

14 G. A. Olah, A. Burrichter, G. Rasul, G. K. S. Prakash, M. Hachoumy and J. Sommer, *J. Am. Chem. Soc*., 1996, **118**, 10423.

15 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, Allyn & Bacon, Inc., Boston, 1970.

16 T. H. Clingenpeel, T. E. Wessel and A. I. Biaglow, *J. Am. Chem. Soc*., 1997, **119**, 5469.

17 (*a*) T. M. Duncan and R. W. Vaughan, *J. Catal*., 1981, **67**, 49; (*b*) N. D. Lazo, D. K. Murray, M. L. Kieke and J. F. Haw, *J. Am. Chem. Soc*., 1992, **114**, 8552.

18 A. G. Stepanov, M. V. Luzgin, A. V. Krasnoslobodtsev, V. P. Shmachkova and N. S. Kotsarenko, *Angew. Chem., Int. Ed. Engl*., 2000, **39**, 3658.

Received: 22nd June 2000; Com. 00/1671